the material is elastically isotropic. This is surprising because it means that both 180° (electrical) and 109°/71° (mechanical) domain reorientation occurs. To verify this conclusion measurements were made of the compressional and shear stiffnesses through the pressure cycle on unpoled specimens which are necessarily isotropic before and after the transition. These data are shown in Figs. 9 and 10. Following the initial pressure rise it may be seen that Figs. 2, 3, and 9 and Figs. 4, 5, 7, and 10 are identical.

In Figs. 9 and 10 two differences may be noted between the first and subsequent pressure cycles. First, the transition pressure is somewhat higher for the initial pressure rise and second, both the compressional and shear stiffnesses are slightly higher following the first pressure cycle. There is a residual change of about $+4\%$ in c_L and about $+2\%$ in c_S. The increase is thought to be due to incomplete reversion to the FE phase. If the residual AFE volume fraction at zero pressure is assumed to be proportional to the ratio of residual stiffness increase to the total change in stiffness between the FE and AFE phases (extrapolated to zero pressure), Figs. 9 and 10 indicate that about 7% of the volume is AFE following the pressure cycle. The least amount detectable by x ray is thought to be about 5–10%, and in some cases it has been possible to detect some of the AFE phase in this material shortly after exposure to hydrostatic pressures in excess of 40 kpsi. The x-ray results thus lend some support to this explanation.

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An Ionization Process in a Low-Energy Cesium Plasma*

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The mechanisms of ion formation in cesium plasmas at relatively low electron temperatures (3500°K) and pressures of a few Torr are investigated. It is concluded that most of the ions are molecular and that they are formed by collisions between cesium atoms in the first excited state. The excited atoms are predominantly produced by inelastic electron collisions.

The excitation cross section is computed by means of the impact parameter method. It has a maximum value of 100×10^{-16} cm² at 7 eV. The de-excitation cross section is computed and found to be approximately constant at 50×10^{-16} cm². Radiation trapping and diffusion of excited atoms are also studied.

The ionization cross section is calculated by means of statistical thermodynamics from the measured recombination coefficient for the inverse of the ionizing process. It is found to be 1450×10^{-16} cm². The plasma is uniform throughout its volume except in the immediate vicinity of the bounding electrodes.

The proposed mechanism results in performance characteristics for cesium thermionic converters, operating in the "ignited mode," which are in qualitative and quantitative agreement with experimental data.

1. INTRODUCTION

THE purpose of this paper is to investigate theoretically the mechanisms of ion formation in cesium plasmas at relatively low electron temperatures and at pressures of a few Torr.

Performance characteristics of cesium thermionic converters indicate that cesium plasmas at pressures of a few Torr can act as effective ion sources requiring low-voltage inputs. However, the nature of the ions and the dominant ionization processes are not well understood.

It is proposed that most of the ions are molecular and that the dominant ionization mechanism is a two-step process:

$$\mathrm{Cs}+e\rightarrow \mathrm{Cs}^*+e, \qquad \Delta E\simeq 1.4 \text{ eV}, \quad (1)$$

$$\mathrm{Cs}^*+\mathrm{Cs}^*\rightarrow \mathrm{Cs}_2^*\rightarrow \mathrm{Cs}_2^+ +e, \qquad \Delta E\simeq 0. \quad (2)$$

These two reactions are known to occur but the cross sections have not been measured.[1] For the purposes of this paper, the cross sections are calculated theoretically and they are found to be large compared to atomic dimensions. In addition, it is shown that they result in high ionization rates and that they imply thermionic converter performance characteristics which are in agreement with experimental measurements.

In other treatments of volume ionization in high-pressure cesium converters,[2,3] it is postulated that predominantly atomic cesium ions are formed, under the assumption that the ionization cross section is large. However, available experimental data on ionization processes in cesium indicate that the ionization cross section for atomic ions is smaller than the assumed

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values.[4–8] Furthermore, measurements of cross sections for molecular ion formation in general yield values which are large compared to atomic dimensions.[9]

The various aspects of the present plasma analysis are carried out for the same reference plasma conditions; i.e., a thin infinite cesium plasma is considered, bounded by two electrodes 0.05 cm apart, with an atom density of 2×10^{16} cm^{-3}, an atom temperature of 1400°K, and electron temperatures of the order of 3500°K. It is shown that these values can be varied considerably without affecting the major conclusions. They are selected in this range because they are representative of the plasma conditions of cesium thermionic converters with high volume ionization rates.

In the plasma the electron temperature is maintained by a low-voltage discharge. Electrons from the emitter electrodes are accelerated through the emitter sheath into the plasma where they share their energies with the plasma electrons. The atom and ion temperature is determined by the temperature of the electrodes and is not affected by the electrons.

The properties of the plasma can be calculated by a simultaneous solution of numerous equations governing reaction rates, transport effects, and energy transfer, subject to the appropriate boundary conditions. In order to simplify the presentation and to emphasize the physical aspects of the problem, some of the results can be anticipated and incorporated in the analysis. To this end, the analysis begins by considering a uniform plasma with a fractional ionization of 0.25% and an electron temperature of 3500°K. Then it is shown that the plasmas of interest are indeed uniform practically everywhere except in very small regions near the electrodes, that the fractional ionization depends on the electron temperature and that the assumed values are consistent.

The paper is organized as follows. In Secs. 2 and 3 the densities of excited atoms and molecular ions in a uniform cesium plasma are determined from rate balances. In Sec. 4 the effects of the transport of electrons, ions, and excited atoms are investigated and in Sec. 5 the results of the analysis are combined to derive performance characteristics of cesium thermionic converters. The calculated characteristics are compared with some experimental data and good agreement between theory and experiment is established.

2. THE DENSITY OF EXCITED ATOMS

General Remarks

The density of cesium atoms in the first excited state can be determined from a rate balance between the predominant excitation and de-excitation processes

$$R_x=R_{dx}+R_p+R_d, \tag{3}$$

where R_x is the rate (per unit volume) of electron excitation, R_{dx} is the rate of electron de-excitation, R_p is the rate of photon decay, and R_d is the rate of diffusion of excited atoms.

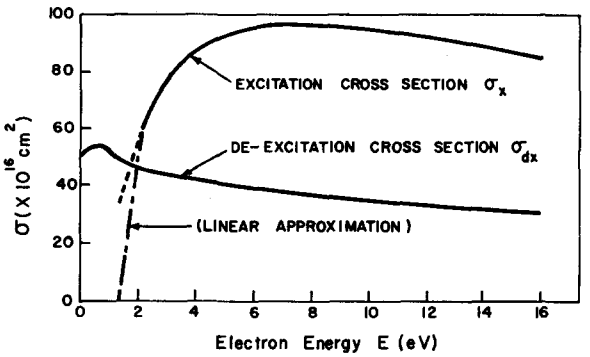

FIG. 1. The $6s$–$6p$ excitation and de-excitation electron collision cross sections of cesium calculated by means of the impact parameter method.

The rate of electron excitation is

$$R_x=N_0n_{e0}\int_{E_x}^{\infty}f_e(E)\sigma_x(E)v_e(E)dE, \tag{4}$$

where N_0 is the density of cesium atoms in the ground state, n_{e0} is the electron density, $f_e(E)$ is the electron energy distribution function, $\sigma_x(E)$ is the excitation cross section, $v_e(E)$ is the electron speed, and E_x is the excitation threshold energy. Similarly,

$$R_{dx}=N_{x0}n_{e0}\int_{0}^{\infty}f_e(E)\sigma_{dx}(E)v_e(E)dE, \tag{5}$$

where N_{x0} is the density of excited atoms and $\sigma_{dx}(E)$ is the de-excitation cross section. If the electron energy distribution is assumed Maxwellian, then integrals (4) and (5) are unique functions of the electron temperature T_e. More specifically,

$$R_x/R_{dx}=(N_0/N_{x0})(\omega_x/\omega_0)\exp(-E_x/kT_e), \tag{6}$$

where ω_x and ω_0 are the statistical weights of excited and ground state atoms, respectively. From what follows, it is seen that, for the plasmas of interest to this paper, $R_x\simeq R_{dx}$. Consequently,

$$N_{x0}/N_0=(\omega_x/\omega_0)\exp(-E_x/kT_e). \tag{7}$$

Inelastic Electron Collision Cross Sections and De-Excitation Rate

Figure 1 shows the calculated cross sections for electron excitation of cesium atoms to the first excited state and for electron de-excitation from the first excited state to the ground state.

The excitation cross section is calculated by means of the semiclassical "impact parameter" method that has

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been developed by Seaton.[10] This method has been previously applied to a very similar case, the electron excitation of sodium to the first excited state, and gave results which are in good agreement with experimental data.[10,11] In the calculation for cesium the oscillator strength is taken as $f=1$. At electron energies near the threshold ($E_x=1.4$ eV) the impact parameter method is not valid. Judged from the data for sodium the calculated cross section for cesium should be fairly accurate down to electron energies of about 2.2 eV. At lower energies the cross section may be approximated by

$$\sigma_x(E)=a(E-1.4), \quad 1.4\leq E\leq 2.2, \tag{8}$$

with $a=75\times10^{-16}$ cm^2/eV as shown in Fig. 1. This approximation is in rather good agreement with the value $a=120\times10^{-16}$ cm^2/eV that Nolan and Phelps[12] derived from their measurement of electron drift velocities in cesium–argon mixtures. Recently, Hansen[13] reported a similar cross section curve calculated by means of Seaton's quantum mechanical method[14] which is within 10% of the impact parameter results except for energies near the threshold.

The de-excitation cross section is calculated from the excitation cross section by means of the principle of detailed balance[15]:

$$\sigma_{dx}(E)=[(\omega_0/\omega_x)(E+E_x)/E]\sigma_x(E+E_x). \tag{9}$$

In the energy range of interest (Fig. 1) the de-excitation cross section is approximately constant ($\bar{\sigma}_{dx}=50\times10^{-16}$ cm^2) so that the rate of de-excitation becomes

$$R_{dx}=N_{x0}n_{e0}\bar{\sigma}_{dx}\bar{v}_e. \tag{10}$$

Radiation Rate

Cesium atoms in the first excited state decay to the ground state by the emission of resonance radiation. This radiation is strongly reabsorbed by atoms in the ground state. Thus the rate of photon decay is

$$R_p=\epsilon G N_{x0}/\tau_n, \tag{11}$$

where ϵ is the spectral emissivity of the electrodes, G is the average photon escape probability, and τ_n is the natural lifetime of the excited atoms.

The average photon escape probability is calculated for a thin infinite plasma slab. A photon of frequency ν emitted at a distance x from one electrode in the direction $\bar{r}$ has the probability $\exp(-N_0\sigma_\nu r)$ not to be absorbed within a distance r, where σ_ν is the radiation absorption cross section at the frequency ν. The photons are emitted with equal probability in all directions so that

$$G=\frac{1}{s}\int_0^s dx\int_x^\infty \frac{x}{r^2}dr\int_0^\infty p_\nu \exp(-N_0\sigma_\nu r)d\nu, \tag{12}$$

where $p_\nu d\nu$ is the probability that the emitted photon has a frequency between ν and $\nu+d\nu$ and s is the plasma thickness.

The absorption and emission spectra are identical when the plasma is in thermodynamic equilibrium.[16] If it is assumed that the spectra are equal even when the electrons and atoms are not at the same temperature then only, say, the absorption spectrum is needed for the evaluation of G.

The shape of the absorption spectrum is affected by pressure, Doppler, and Stark broadening. In the plasma under consideration, the dominant effect is pressure broadening in which collisions between excited and ground-state atoms result in frequency shifts and asymmetry of the spectrum.[17] As it will become evident later, G depends primarily on the shape of the spectrum at the wings. In these regions σ_ν follows closely the Breit–Wigner formula and is given by[18]

$$\sigma_\nu=\frac{e^2 f}{m_e c}\cdot\frac{\Gamma_p/2}{(\Gamma_p/2)^2+(\nu-\nu_0)^2}, \tag{13}$$

where Γ_p is the half-width of the pressure broadened spectrum, f is the oscillator strength, and the other symbols have their standard meaning.

The absorption cross section in the wings of the pressure broadened cesium $6s$–$6p$ line has been measured by Gregory.[19] His data agree with the theoretical results of Furssow and Wlassow[20] who calculate the half-width to be

$$\Gamma_p=2e^2N_0 f/3\pi m_e\nu_0. \tag{14}$$

Thus the emission probability density is

$$p_\nu=\frac{1}{\pi}\frac{\Gamma_p/2}{(\Gamma_p/2)^2+(\nu-\nu_0)^2}; \quad \int_0^\infty p_\nu d\nu=1. \tag{15}$$

The combination of Eqs. (12)–(15) yields the average photon escape probability in terms of a complicated integral. A first approximation to this integral is found by neglecting $(\Gamma_p/2)^2$ in comparison with $(\nu-\nu_0)^2$:

$$G=(4/3\pi)(\lambda_0/3s)^{\frac{1}{2}}, \tag{16}$$

where λ_0 is the wavelength at the resonance frequency ν_0. This approximation neglects the contributions to G from photons with frequencies near the resonance.

A second approximation to G is obtained by separating the integral into two parts, for small and large values of

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[17] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1961), p. 158.
[18] See Ref. 17, pp. 96, 185.
[19] C. Gregory, Phys. Rev. **61**, 465 (1942).
[20] W. Furssow and A. Wlassow, Physik. Z. Sowjetunion **10**, 378 (1936).

r. Thus

$$G=(4/3\pi)(\lambda_0/3s)^{\frac{1}{2}}(1-0.9(\lambda_0/3s)^{\frac{1}{2}}). \quad (17)$$

Since $\lambda_0 \ll s$ the correction introduced by the second approximation is negligible. Equation (16) gives G with sufficient accuracy and justifies the assumption that the shape of the spectrum near the resonance is not important. Therefore, the rate of photon decay is

$$R_p=(4/3\pi)(\lambda_0/3s)^{\frac{1}{2}}(\epsilon N_{x0}/\tau_n). \quad (18)$$

It is interesting to note that the average photon escape probability G is independent of the cesium atom density. This is only true as long as collisions with cesium atoms are the dominant source of spectrum broadening. The equation for G agrees with the formula derived by Holstein[21] for pressure broadened spectra in a cylindrical geometry.

The present treatment of resonance radiation trapping applies to the two members of the first resonance lines ($6s$–$6p_{\frac{1}{2}}$ and $6s$–$6p_{\frac{3}{2}}$) separately. Since the wavelengths of the two lines are close together (8521 and 8943 Å), the two members have essentially the same escape probability and are treated as one.

Diffusion Rate

The rate at which excited atoms diffuse to the walls containing the plasma depends on the density distribution of excited atoms near the walls and is treated in detail in Sec. 4. An upper limit to the diffusion rate can be derived by assuming that the density of excited atoms is uniform right up to the walls. Then the diffusion current is $N_{x0}\bar{v}_x/4$, where $\bar{v}_x$ is the average velocity of the excited atoms. Excited atoms diffuse to both walls of the plasma, so that the average diffusion rate is

$$R_d=N_{x0}\bar{v}_x/2s. \quad (19)$$

Density of Excited States

For the reference plasma under consideration $\lambda_0=8700$ Å, $s=0.05$ cm, $\epsilon=0.4$, $\tau_n=3.5\times10^{-8}$ sec,[22] $n_{e0}=5\times10^{13}$ cm^{-3}, $\bar{\sigma}_{dx}=50\times10^{-16}$ cm^2, $\bar{v}_e=3.5\times10^7$ cm-sec^{-1}, and $\bar{v}_x=4.7\times10^4$ cm-sec^{-1}. Thus, comparison of Eqs. (18) and (19) with Eq. (10) yields

$$R_p/R_{dx}=(4/3\pi)(\lambda_0/3s)^{\frac{1}{2}}(\epsilon/\tau_n n_{e0}\bar{\sigma}_{dx}\bar{v}_e)=0.013, \quad (20)$$

$$R_d/R_{dx}=\bar{v}_x/2sn_{e0}\bar{\sigma}_{dx}\bar{v}_e=0.054. \quad (21)$$

Since R_d is an estimated upper limit it is concluded that $R_x \simeq R_{dx}$ [Eq. (3)] and that the density of excited states is given by Eq. (7).

3. THE PLASMA DENSITY

General Remarks

The plasma density can be calculated from a balance between the rates of ionization and recombination. It is assumed that all the ions are molecular, that they are produced by collisions between excited atoms and that recombination occurs only by the reverse ionization process. It is shown that these reactions occur at high rates so that other ionization and recombination mechanisms can be expected to have only a small effect on the plasma density. Diffusion losses that occur near the boundaries of the plasma are examined in Sec. 4.

Recombination Rate

The rate at which molecular cesium ions recombine with electrons is

$$R_r=\alpha_r n_{i0}n_{e0}, \quad (22)$$

where α_r is the recombination coefficient for the reverse ionization process [Eq. (2)], and n_{i0} is the density of molecular ions.

The only measurements of the molecular ion–electron recombination coefficient in cesium are those of Dandurand and Holt.[23] These authors deduced from their measurements a value of 2×10^{-6} cm^3 sec^{-1} at electron temperatures of about 1400°K. The recombination coefficient varies approximately with the minus three halves power of the electron temperature[24] so that

$$\alpha_r=2\times10^{-6}(1400/T_e)^{\frac{3}{2}} \text{ cm}^3 \text{ sec}^{-1}. \quad (23)$$

This coefficient is very large. The only mechanism that can yield such high values is dissociative recombination[25] which can be thought of as occurring in two steps. The first step results in a highly excited cesium molecule

$$Cs_2^+ + e \rightarrow Cs_2^*. \quad (24)$$

In the second step the excited molecule dissociates in two neutral atoms, one or both of which may be in an excited state. The lifetime of this process may be extremely short,[24] of the order of 10^{-13} sec. According to the Franck–Condon principle[26] the probability of a transition is high if the potential energy curves for the initial and final states are close together when plotted against internuclear distance. While these curves are not known for cesium, it is likely that there will be a high probability of transition to two excited cesium atoms because the heat of reaction for this process is very small. Accordingly, it is assumed that the molecular recombination coefficient measured by Dandurand and Holt is appropriate for the reverse ionization mechanism [Eq. (2)]. This interpretation is contrary to that offered by Dandurand and Holt who observed almost a purely molecular spectrum in the afterglow of their discharge and concluded that recombination leads to the ground state of the cesium molecule. However, their observa-

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[25] L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Los Angeles, California, 1955), p. 591.
[26] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1950), p. 420.

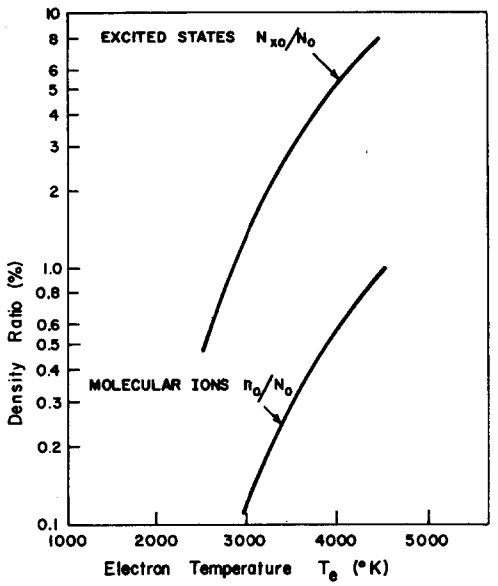

FIG. 2. Fractional excitation N_{x0}/N_0 and fractional ionization n_0/N_0 as functions of electron temperature.

tion was more likely due to resonance absorption of atomic lines as pointed out by Loeb.[25]

Ionization Rate

The cross section for ionization by collisions between excited cesium atoms is calculated from the recombination coefficient by applying the principle of detailed balance to a plasma at thermodynamic equilibrium. The calculated cross section is then used to determine the rate of ion formation in the nonequilibrium reference plasma.

In a plasma at equilibrium temperature T, the ionization rate by collisions between excited atoms [Eq. (2)] is[27]

$$R_i=(1/2)^{\frac{1}{2}}N_{x0}^2\bar{\sigma}_i\bar{v}_x(T), \tag{25}$$

where $\bar{\sigma}_i$ is the average ionization cross section and $\bar{v}_x(T)$ is the average speed of the cesium atoms. This rate is equal to the recombination rate[28] $R_r=\alpha_r(T)n_{i0}n_{e0}$ and therefore:

$$\bar{\sigma}_i=(2)^{\frac{1}{2}}\left(\frac{\alpha_r(T)}{\bar{v}_x(T)}\right)\left(\frac{n_{e0}n_{i0}}{N_{x0}^2}\right)=(2)^{\frac{1}{2}}\left(\frac{\alpha_r(T)}{\bar{v}_x(T)}\right)K(T). \tag{26}$$

The equilibrium constant $K(T)$ is determined from statistical thermodynamics[29,30]:

$$K(T)=(\omega_e\omega_i/\omega_x^2)(m_em_i/m_a^2)^{\frac{3}{2}}\times(4\pi^2AkT/h^2)(kT/h\nu_1). \tag{27}$$

The moment of inertia A and the lowest vibration frequency ν_1 for cesium molecular ions are not known. They may be approximated by the corresponding known values for cesium molecules since most of the measured values of A and ν_1 for molecules and molecular ions of a species are nearly equal.[31] For the cesium molecule $A=2.3\times10^{-37}$ g-cm^2,[32] $\nu_1=1.26\times10^{12}$ sec^{-1}.[31] The statistical weights are: for electrons $\omega_e=2$; for cesium atoms $\omega_x=6$; for molecular ions $\omega_i=2$. Thus the equilibrium constant is $K(T)=1.2\times10^{-9}T^2$, where T is expressed in °K. This result is close to the one obtained by Clifton.[33]

The combination of Eqs. (23) and (26) and (27) leads to

$$\bar{\sigma}_i=1450\times10^{-16}\text{ cm}^2. \tag{28}$$

This cross section is independent of temperature and it is large. Its magnitude could have been expected since the reaction involves two cesium atoms at thermal velocities in a radiationless transition.

The significance of the large ionization cross section can be best demonstrated by calculating the total ion current I_{it} that is produced in a plasma of thickness $s=0.05$ cm. For the nonequilibrium reference plasma conditions $N_{x0}=0.03N_0$, $I_{it}=R_ies=14$ A-cm^{-2}. This current is very large compared to the ion diffusion current leaving the plasma at the boundaries. As it is shown in Sec. 4, the diffusion current is of the order of 0.3 A-cm^{-2} for the same reference plasma conditions.

The Plasma Density

For the reference plasma that consists of electrons at temperature T_e and molecular ions at the atom temperature T_a, the rate of ionization is

$$R_i=(\tfrac{1}{2})^{\frac{1}{2}}N_{x0}^2\bar{\sigma}_i\bar{v}_x(T_a), \tag{29}$$

and the rate of recombination is

$$R_r=n_{i0}n_{e0}\alpha_r(T_a)(T_a/T_e)^{\frac{3}{2}}. \tag{30}$$

The plasma is electrically neutral, $n_{e0}=n_{i0}=n_0$, and the rates of ionization and recombination are equal. Therefore:

$$n_0=1.06\times10^{-4}N_0T_e^{\frac{3}{2}}T_a^{\frac{1}{2}}\exp(-E_x/kT_e). \tag{31}$$

Note that the fractional ionization (n_0/N_0) is independent of the cesium density and that it is only a weak function of the atom temperature $(T_a^{\frac{1}{2}})$. This weak dependence shows that only a small error is introduced by replacing the atom temperature profile across the plasma by an average temperature. It also shows that in the absence of atomic ions only a small correction is necessary to account for the fact that the electron and atom temperatures are not equal. It is also worth noting

[27] J. Jeans, *The Dynamical Theory of Gases* (Dover Publications, Inc., New York, 1954), p. 37.
[28] S. R. DeGroot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951), p. 169.
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[32] H. O. Jenkins, Trans. Faraday Soc. 51, 1942 (1955).
[33] D. G. Clifton, Los Alamos Report No. LA-2419 (1960).

that the absolute values of α_r and $\bar{\sigma}_i$ do not appear in Eq. (31). Nevertheless they are necessary to establish the importance of the proposed ionization mechanism.

The fractional ionization n_0/N_0 and the fractional excitation N_{x0}/N_0 are plotted in Fig. 2 as functions of the electron temperature. At the reference electron temperature of 3500°K the fractional ionization is approximately 0.25%, consistent with the value assumed in Sec. 2.

4. TRANSPORT EFFECTS

General Remarks

In the vicinity of a flat electrode, which constitutes a plasma boundary, the plasma consists of three distinct regions as shown in Fig. 3. In the main plasma region the densities of excited and charged particles are uniform (and they are calculated in Secs. 2 and 3) and the flow of an electron current I results in a constant potential gradient. The resistivity, ρ_0, of this region is

$$\rho_0=\frac{m_e}{e^2}\cdot\frac{\sigma_m\bar{v}_e}{n_0/N_0}+\frac{\pi^{\frac{3}{2}}m_e^{\frac{1}{2}}e^2c^2}{1.164(2kT_e)^{\frac{3}{2}}}\times\ln\{(3/2e^2)(k^3T_e^3/\pi n_0)^{\frac{1}{2}}\},\quad(32)$$

where σ_m is the effective momentum transfer collision cross section approximately equal to 200×10^{-16} cm^2.[34–37] The first term on the right-hand side of Eq. (32) is due to electron atom scattering[38] and the second to electron–ion scattering.[39]

In the transition region a positive space charge develops and the particle densities are not uniform because of ambipolar diffusion. In the sheath region, which extends over a distance comparable to a Debye length, the transport of charged particles is determined by the electric field and collisions can be neglected.

What follows is an analysis of the transition region considering the main plasma and the sheath as boundary conditions. The purpose of this analysis is to verify that the plasma is uniform in a major fraction of its volume and to derive formulas for the remaining effects of the transport of electrons, ions, and excited atoms throughout the plasma.

Basic Differential Equations for the Transition Region

The density of excited atoms N_x in the transition region can be determined from the rate balance

$$R_x=R_{dx}+R_d.\quad(33)$$

The rate of photon decay is neglected from Eq. (33)

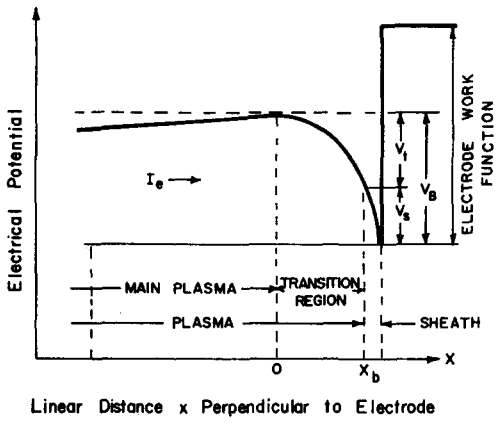

FIG. 3. Plasma potential distribution near an electrode.

because it is shown in Sec. 2 that $R_p\ll R_{dx}$. To a first approximation the net diffusion rate is

$$R_d=-D_x d^2N_x/dx^2,\quad(34)$$

where D_x is the diffusion coefficient for excited cesium atoms in a cesium vapor. Replacing Eqs. (6), (7), (10), (34) in Eq. (33) yields

$$d^2(N_x/N_{x0})/dx^2=-(1/\alpha^2)(n/n_0)(1-N_x/N_{x0}),\quad(35)$$

where $\alpha^2=D_x/\bar{\sigma}_{dx}\bar{v}_e n_0$ and $n=n_e$ is the electron density in the transition region. This density is almost equal to the ion density n_i.

The ion density can be determined from a balance between the rates of ionization, recombination, and ambipolar diffusion:

$$R_i=R_r+R_a.\quad(36)$$

The ambipolar diffusion rate R_a is

$$R_a=-D_a d^2n_i/dx^2,\quad(37)$$

where D_a is the ambipolar diffusion coefficient.[40] Replacing Eqs. (29), (30), and (37) in Eq. (36) and assuming $n_i\simeq n_e=n$ yields

$$d^2(n/n_0)/dx^2=-(1/2\beta^2)[(N_x/N_{x0})^2-(n/n_0)^2],\quad(38)$$

where $\beta^2=D_a/2\alpha_r(T_e)n_0$.

The characteristic lengths α and β are indicative of the size of the transition region. The length α depends on D_x which in turn for spherically symmetric, monatomic gases is calculated to be[41]

$$D_x=(3/8N_0\bar{\sigma}_D)(\pi kT_a/m_a)^{\frac{1}{2}}.\quad(39)$$

The average diffusion cross section $\bar{\sigma}_D$ for collisions between excited and ground-state cesium atoms is not known. It is expected to be much larger than the diffusion cross section between ground state atoms

[34] R. B. Brode, Phys. Rev. **34**, 673 (1929).
[35] D. Roehling, Advan. Energy Conversion **3**, 69 (1963).
[36] R. K. Flavin and R. G. Meyerand, Jr., Advan. Energy Conversion **3**, 3 (1963).
[37] L. P. Harris, J. Appl. Phys. **34**, 2958 (1963).
[38] H. W. Lewis and J. R. Reitz, J. Appl. Phys. **30**, 1439 (1959).
[39] L. Spitzer, *Physics of Fully Ionized Gases* (Interscience Publishers, Inc., New York, 1962), p. 139.
[40] D. J. Rose and M. Clark, *Plasmas and Controlled Fusion* (Technology Press, Cambridge, Massachusetts, 1961), pp. 75–77.
[41] A. Dalgarno, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 16, p. 644.

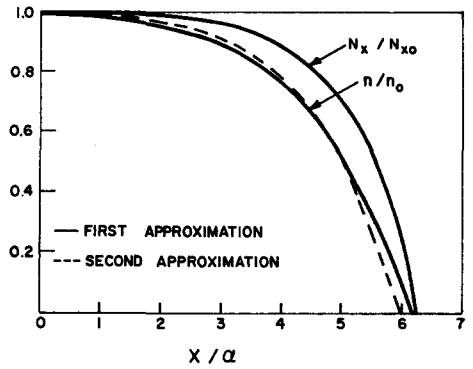

FIG. 4. Approximate plasma (n) and excited atom (N_x) densities in the transition region.

because of excitation transfer, a process that has a strong effect in the present case of an optically allowed transition.[42] Therefore, $\bar{\sigma}_D$ is approximated by the total cross section of 2350×10^{-16} cm^2 [43] for cesium atoms in the ground state. For the reference plasma conditions, it is found that $D_x=4.2$ cm^2 sec^{-1} and $\alpha=0.7\times10^{-3}$ cm.

The value of β depends on the ambipolar diffusion coefficient[40]

$$D_a=(D_e\mu_i+D_i\mu_e)/(\mu_i+\mu_e)\simeq\mu_i(kT_e+kT_a), \quad (40)$$

where D_j, μ_j are the diffusion coefficient and mobility of particle j, respectively. The mobility of molecular cesium ions is not known. If it is approximated by the mobility of atomic cesium ions then[23,44]

$$\mu_i=50N_{st}/N_0 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}, \quad (41)$$

where N_{st} is the density of a perfect gas at 1 Torr and 0°C. Thus, for the reference plasma conditions $D_a=37$ cm^2 sec^{-1} and $\beta=0.85\times10^{-3}$ cm. Note that both lengths α and β are very small compared to the thickness $s=50\times10^{-3}$ cm of the reference plasma. In addition, the values of α and β are nearly equal. For simplicity, in the subsequent analyses α will be assumed equal to β, for all plasma conditions of interest. Since the ratio α/β is independent of any particle densities and depends only on T_e this simplification does not introduce appreciable errors in the temperature range of interest ($T_e=3000°$–$5000°$K).

Density Distributions

Equations (35) and (38) are difficult to solve explicitly. Approximate solutions, however, can be obtained by considering limited ranges of values of the normalized variables.

Consider the region $N_x/N_{x0}\simeq1$, $n/n_0\simeq1$. With $\alpha=\beta$ and the boundary conditions $dN_x/dx=dn/dx=0$ at $x=0$ and $N_x=N_{xb}$, $n=n_b$ at $x=x_b$, the solution is

$$N_x/N_{x0}=1-(1-N_{xb}/N_{x0})\exp[-(x_b-x)/\alpha], \quad (42)$$

$$n/n_0=1-[(1-n_b/n_0)+(1-N_{xb}/N_{x0})(x_b-x)/2\alpha]\times\exp[-(x_b-x)/\alpha]. \quad (43)$$

Equations (42) and (43) are useful only for densities that are close to those in the main plasma. As a first approximation, however, they are plotted in Fig. 4 for all values of n/n_0, N_x/N_{x0}.

As a second approximation, consider the region $(N_x/N_{x0})-(n/n_0)\ll1$. Under the same boundary conditions as before it is found that

$$(x_b-x)/2\alpha=\tanh^{-1}[(1+2N_x/N_{x0})/3]^{\frac{1}{2}}-\tanh^{-1}[(1+2N_{xb}/N_{x0})/3]^{\frac{1}{2}}. \quad (44)$$

This solution is very close to that given by Eq. (42) as shown by the dotted line in Fig. 4.

These two approximate solutions show that diffusion losses lower the densities of charged and excited particles only over a distance of a few characteristic lengths from the boundaries. This confirms the previously made assumption that most of the plasma is uniform.

The boundary between the transition region and the sheath is somewhat arbitrary. If it is defined as the point at which an electron receives from the electric field an amount of energy comparable to the thermal energy over a distance of one mean free path,[45] then:

$$\mathcal{E}(x_b)/\sigma_mN_0=kT_e, \quad (45)$$

where the electric field $\mathcal{E}(x)$ is given by[40]

$$\mathcal{E}(x)=I_e/e\mu_en_e+(kT_e/n_e)dn_e/dx. \quad (46)$$

For the electron currents of interest, it is found that the plasma density in the transition region drops by less than 50% before the electric field becomes so large that ambipolar diffusion is no longer applicable. Consequently, it is not necessary to have more accurate solutions for the density distributions than those given by Eqs. (42) and (43) or (44).

Potential Drops

The potential drop across the main plasma can be readily calculated from the resistivity ρ_0.

The potential drop V_t across the transition region can

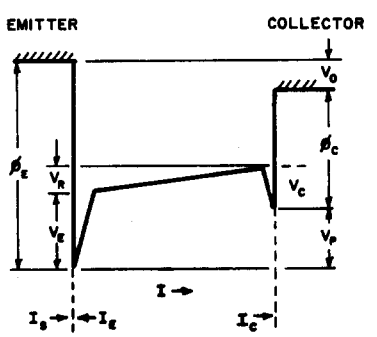

FIG. 5. Schematic of the potential distribution in a thermionic converter.

[42] See Ref. 41, p. 650.
[43] I. Estermann, S. N. Foner, and O. Stern, Phys. Rev. **71**, 250 (1947).
[44] J. W. Sheldon, J. Appl. Phys. **34**, 444 (1963).
[45] E. O. Johnson, RCA Rev. **16**, 510 (1955).

be found by integrating the electric field [Eq. (46)]:

$$V_t=\int_0^{x_b}\mathcal{E}(x)dx, \tag{47}$$

assuming that the thickness of the transition region is x_b. Since the flow of ions is small, the electron current is practically constant and thus

$$V_t=I_e x_b/en_0\mu_e+kT_e\ln(n_b/n_0)$$
$$=I_e x_b\rho_0+kT_e\ln(n_b/n_0). \tag{48}$$

Current and Particle Losses

The electron losses to an electrode are given by

$$I_e=I_{er}\exp[-(V_t+V_s)/kT_e]$$
$$=I_{er}\exp(-V_B/kT_e), \tag{49}$$

where I_{er} is the random electron current in the main plasma region and V_s is the sheath potential.

The ion current losses are

$$I_i=-eD_a dn/dx|_{x=x_b}. \tag{50}$$

An estimate of this current is found by taking the density gradient from Eq. (46), neglecting the electron current, and replacing $n(x_b)$ by n_0. Thus

$$I_i=0.63(1+T_e/T_a)I_{ir}. \tag{51}$$

Note that the ion losses are greater than the random ion current, I_{ir}. This is due to the electric field in the transition region. For the reference plasma conditions $I_i=0.15$ A-cm^{-2}, which is much smaller than the electron current necessary for the maintenance of the plasma.

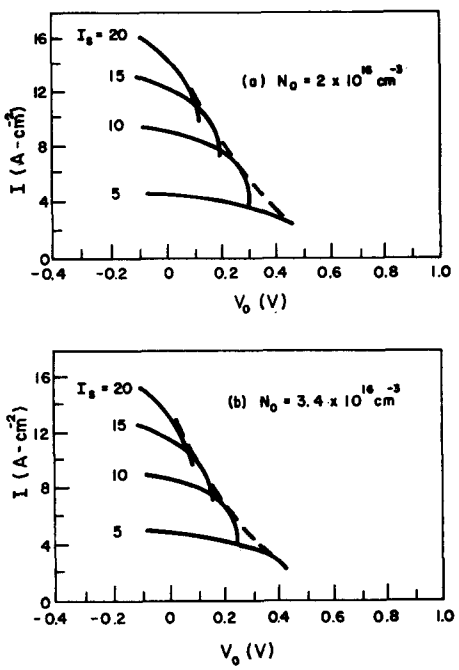

FIG. 6. Calculated thermionic converter performance characteristics for $T_E=1608$°K, $s=0.025$ cm, and $\phi_c=1.6$ V.

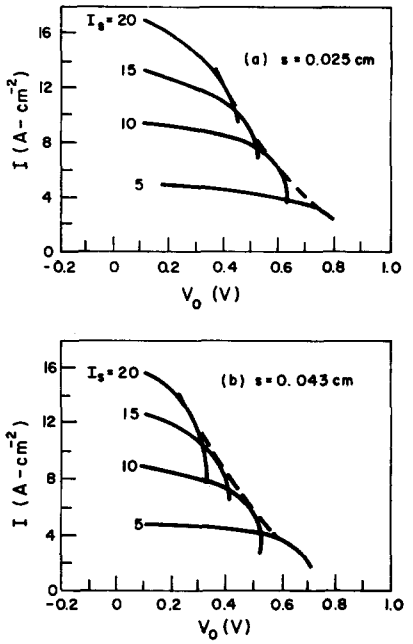

FIG. 7. Calculated thermionic converter performance characteristics for $T_E=1785$°K, $N_0=2\times10^{16}$ cm^{-3}, and $\phi_c=1.6$ V.

The excited atom current loss is given by

$$J_x=-D_x dN_x/dx|_{x=x_b}. \tag{52}$$

An estimate of this current is derived by considering the maximum gradient given by Eq. (44). Thus

$$J_x=5(n_0/N_0)^{\frac{1}{2}}(T_e/T_a)^{\frac{1}{2}}J_{xr}, \tag{53}$$

where J_{xr} the random current of excited atoms in the main plasma. For the reference plasma conditions $J_x=0.34\,J_{xr}$.

5. APPLICATIONS

General Remarks

The purpose of this section is to examine whether the proposed ionization mechanism can account for observed performance characteristics of cesium thermionic converters.

It is observed experimentally that cesium thermionic converters, operated at emitter temperatures of about 1600°K and cesium pressures of a few Torr,[46] produce high output currents. These currents can be justified only if there is a high rate of ion formation in the volume of the cesium plasma. Therefore, a valid test of the proposed dominant ionization mechanism is achieved by neglecting all other ionization mechanisms, by calculating current–voltage characteristics on the basis of the results of Secs. 2–4, and by comparing these characteristics with available experimental data.

Computation of Cesium Thermionic Converters Performance Characteristics

Performance characteristics for cesium thermionic converters, operated in the ignited mode, can be derived

[46] This is called the ignited mode of operation (see Ref. 47).

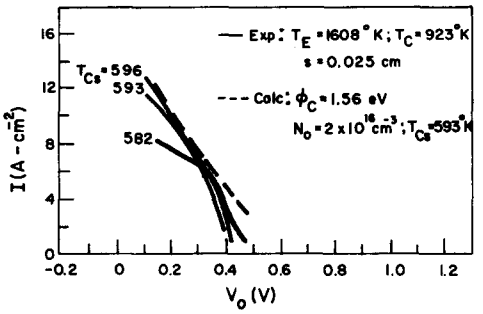

FIG. 8. Comparison of experimental performance characteristics with calculated envelope of optimum performance for a Ta–Mo thermionic converter.

from the voltage, current, and power balance equations. Such equations have been used by many other authors[47] but are repeated here for convenience.

The voltage balance is based on the potential distribution across the converter, shown schematically in Fig. 5. The output voltage is

$$V_0=\phi_E-\phi_C-V_P, \tag{54}$$

where ϕ_E and ϕ_C are the emitter and collector work functions, respectively, and V_P is the plasma potential drop

$$V_P=V_E-V_C+V_R. \tag{55}$$

The voltages V_E and V_C are the potential drops in the emitter and collector transition plus sheath regions and $V_R=\rho_0 sI$ is the plasma resistance drop, where s is the converter spacing, I is the converter output current, and ρ_0 the plasma resistivity [Eq. (32)].

The current balance is

$$I=I_s-I_E=I_C, \tag{56}$$

where $I_s=120T_E^2\exp(-\phi_E/kT_E)$ is the emitter saturation current at temperature T_E, $I_E=I_{er}\exp(-V_E/kT_e)$ is the electron current returned by the plasma to the emitter, and $I_C=I_{er}\exp(-V_C/kT_e)$ is the current that reaches the collector. The main plasma random current $I_{er}=en_0\bar{v}_e/4$ is calculated from the plasma density n_0 [Eq. (31)].

The electron power balance is

$$2kT_EI_s+IV_P=2kT_e(I_E+I)+P_c, \tag{57}$$

where P_c is the power lost by collisions in the plasma. Most of the collisional power loss is caused by inelastic electron collisions that raise cesium atoms to the first excited state. Therefore, P_c can be approximated by the rate at which the excitation energy is lost to the electrodes by photons and diffusion of ions and excited atoms,

$$P_c=P_p+P_x+P_i. \tag{58}$$

The photon power loss is

$$P_p=seE_xR_p=(4/\pi\tau_n)(\lambda_0 s/3)^{\frac{1}{2}}\epsilon eE_xN_0 \times\exp(-E_x/kT_e). \tag{59}$$

The excited atom diffusion power loss is

$$P_x=2eE_xJ_x=7.5(n_0/N_0)^{\frac{1}{2}}(T_e/T_a)^{\frac{1}{2}}e\bar{v}_xN_0E_x \times\exp(-E_x/kT_e). \tag{60}$$

Similarly, the ion diffusion power loss is

$$P_i=2(2E_x)I_i=0.63(1+T_e/T_a)e\bar{v}_in_0E_x. \tag{61}$$

Combination of Eqs. (54)–(61) yields the current–voltage characteristics that are desired for different values of the input parameters N_0, s, T_E, ϕ_E, and ϕ_C. The emitter temperature is selected smaller than 1800°K so that surface ionization is negligible. Typical calculated current–voltage characteristics are shown in Figs. 6 and 7. These characteristics have the expected shape. The current approaches saturation for negative output voltages. At low currents the curves fold under, i.e., the output voltage decreases with decreasing current because electrical energy input is required to maintain the discharge [Eq. (57)]. This effect has been observed experimentally.[48] It should be pointed out that experimental thermionic converter current–voltage characteristics do not usually represent constant values of I_s and may therefore differ from the curves of Figs. 6 and 7.

The dotted lines shown in Figs. 6 and 7 are the loci of optimum performance at given values of N_0, s, and T_E. They constitute envelopes of the calculated performance curves. The envelopes are useful for comparisons with experimental data as discussed in the next paragraph.

Comparison with Experimental Results

A direct comparison between calculated and experimental characteristics is not possible because the effective emitter work function of converters operating in

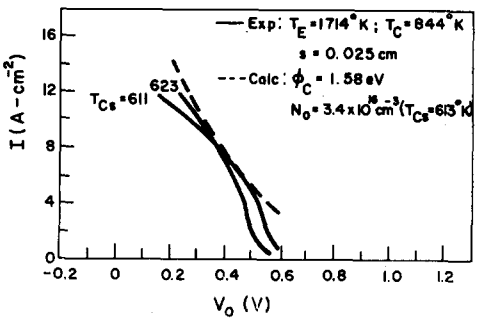

FIG. 9. Comparison of experimental performance characteristics with calculated envelope of optimum performance for a Ta–Mo thermionic converter.

[47] J. M. Houston and H. F. Webster, *Advances in Electronics and Electron Physics* (Academic Press Inc., New York, 1962), Vol. 17, pp. 125–206.

[48] S. S. Kitrilakis, M. E. Meeker, and N. S. Rasor, Thermo Electron Engineering Corporation, Report No. 2–63, Vol. I, p. 65 (1963).

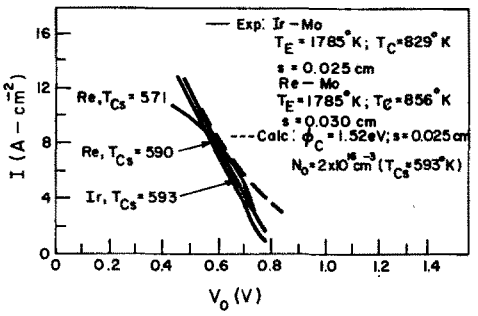

FIG. 10. Comparison of experimental thermionic converter performance characteristics with calculated envelope of optimum performance.

the ignited mode cannot be accurately measured. For this reason, experimental envelopes of optimum performance are compared with similar envelopes derived theoretically. The input data are the emitter temperature, T_E, the converter spacing, s, and the collector work function, ϕ_C, which can be measured and the density N_0 which is inferred from the cesium bath temperature T_{Cs} by assuming that the cesium vapor is a perfect gas, at an average temperature $T_a = 1400°K$ and calculating the pressure from the empirical equation[2]:

$$p_{Cs} = 2.45 \times 10^8 T_{Cs}^{-\frac{1}{2}} \exp(-8910/T_{Cs}) \text{ Torr.} \quad (62)$$

The experimental data are from Refs. 49 and 50. These data were taken with the same apparatus and procedures with tantalum, rhenium and iridium emitters and molybdenum collectors. Experimental current–voltage characteristics and the corresponding theoretical envelopes of optimum performance are shown in Figs. 8–10. The agreement between theory and experiment is quite good.

Experimental performance characteristics are also available at much lower converter spacings and/or cesium densities where the thickness of the plasma boundary regions is of the same order of magnitude as the converter spacing. Under these conditions the results of the preceding plasma analysis are not directly applicable because the densities of ions, electrons and excited atoms are no longer uniform over most of the plasma volume.

For completeness, a summary of the computed plasma parameters T_e, V_P, V_E, V_C, V_R is included as Table I for the curves of Fig. 6(a). The numerical values apply

[49] See Ref. 48, Vol. II.

[50] S. S. Kitrilakis, N. S. Rasor, and L. vanSomeren, Thermo Electron Engineering Corporation, Report No. 20-63 (1963).

TABLE I. Plasma conditions in a converter operating at $T_E = 1608°K$, $s = 0.025$ cm, $N_0 = 2 \times 10^{16}$ cm^{-3}, and $\phi_C = 1.6$ eV.

I_s (A-cm^{-2})	ϕ_E (eV)	T_e (°K)	I (A-cm^{-2})	V_0 (V)	V_P (V)	V_C (V)	V_E (V)	V_R (V)
20	2.29	4000	16.72	−0.14	0.83	0.81	1.37	0.27
		3500	13.80	0.04	0.65	0.54	0.81	0.38
		3000	10.03	0.12	0.57	0.30	0.30	0.57
15	2.33	4000	13.12	−0.17	0.90	0.89	1.58	0.21
		3500	11.30	0.08	0.65	0.60	0.94	0.31
		3000	8.40	0.19	0.54	0.34	0.41	0.47
10	2.39	4000	9.40	−0.25	1.04	1.05	1.94	0.15
		3500	8.22	0.09	0.70	0.69	1.17	0.22
		3000	6.42	0.27	0.52	0.41	0.57	0.36
		2500	3.70	0.30	0.49	0.18	0.05	0.62
5	2.49	3500	4.69	0.01	0.88	0.86	0.61	0.13
		3000	3.88	0.33	0.56	0.54	0.88	0.22
		2500	2.50	0.47	0.46	0.27	0.31	0.42

to the particular conditions $T_E = 1608°K$, $s = 0.025$ cm, $N_0 = 2 \times 10^{16}$ cm^{-3} but they are typical of the values that are calculated for the other characteristics as well. Table I shows that the plasma electron temperature varies between 2500° and 4000°K with the optimum performance near 3500°K.

6. CONCLUSIONS

A mechanism of ion formation in a low-energy cesium plasma at pressures of a few Torr has been investigated. It is concluded that most of the ions are molecular and that they are formed by collisions between cesium atoms in the first excited state. This conclusion is based on the following evidence:

(a) The density of excited atoms in the plasma is found to be a few percent of the cesium atom density. This high density is due to the large cross section for electron excitation and to the strong trapping by the plasma of the resonance radiation emitted through the decay of excited atoms.

(b) The rate of molecular ion formation by collisions of excited atoms is high because of the high ionization cross section that is obtained from the measured recombination coefficient.

(c) A plasma analysis, in which only cesium molecular ions formed by collisions between excited atoms are assumed, yields results that are in qualitative and quantitative agreement with experimental data on performance characteristics of cesium thermionic converters with high plasma ionization rates.

It is hoped that this study will stimulate further experimental investigations of low-energy cesium plasmas and particularly of the role that molecular ions play in them.