COLLISIONS OF THE FIRST AND SECOND KIND IN THE POSITIVE COLUMN OF A CÆSIUM DISCHARGE

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ABSTRACT

The power input minus the power lost by recombination at the tube walls measures the number of quanta dissipated by inelastic collisions at the resonance potential, 1.42 volts. For low-pressure low-current conditions this is equal to the number of collisions $C_{1\ 2}$ and the effective area for a collision is

$$q_{1\ 2}=5.4\pm.6\times10^{-15}\ \text{cm}^2$$

At higher pressures and currents collisions of the second kind give energy back to the electrons and the number of quanta dissipated is $C_{1\ 2}-C_{2\ 1}$ where $C_{2\ 1}$ is the number of collisions of the second kind. This gives a basis for computing the number of excited atoms n_2. The value of n_2 can also be measured spectroscopically by analysing light from an incandescent lamp passed through the discharge and finding the lamp temperature T_L at which absorption lines match the background. T_L is nearly the electron temperature, confirming the evidence that collisions of the first and second kind become nearly equal in number.

The measured radiation intensity is equated to the radiation at a temperature T_L over a spectrum range $\Delta\lambda$ to find $\Delta\lambda$. This effective width of the resonance lines ranges from 0.6 to 19 A between 0.006 and 0.35 mm pressure. At constant pressure the radiation is proportional to n_2 and the ratio gives the depth of the layer of vapor from which the radiation comes; 0.003 to 0.001 mm in the above pressure range.

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I. INTRODUCTION

In a recent paper I have reported measurements of power input and power losses in the positive column of a cæsium discharge.[1] The experimental material included radiation measurements and measurements of probe characteristics for a wide range of currents and pressures in tubes 1.8 cm in diameter. The present paper uses these measurements as a basis for a study of the atomic processes involved in the dissipation of power. It was found that in general

[1] F. L. Mohler, Power Input and Dissipation in the Positive Column of a Cæsium Discharge, B. S. Jour. Research, vol. 9 (RP455), p. 25, July, 1932. Referred to as RP455 in the text.

the radiation is an important part of the power loss and that most of the radiation is in the first doublet of the principal series at 8,521 and 8,944 A. The excitation potential is 1.42 volts, and it is known from critical potential experiments[2] that this excitation gives the predominant type of inelastic collision in cæsium. This justifies the approximation that the power input is expended in inelastic collisions at the first resonance potential and in ionization, and that other excitation processes are negligible. This view of the power loss has been proposed and critically examined for the case of the mercury positive column by Killian.[3]

I will assume that the power lost by inelastic collisions at the first resonance potential is equal to the power input minus the power lost by recombination of ions at the walls; $P-W$ per centimeter of the column in the notation of RP455. For low pressure low current conditions this is practically equal to the radiation loss and is entirely justified; but, at the other extreme, my assumption becomes rather arbitrary. If ionization by collision with excited atoms is important, then part of the loss W is at the expense of inelastic collisions. If recombination in free space is important, then W does not account for the full ionization loss. The energy per collision or per quantum is $eV_r=2.26\times10^{-19}$ joules, where V_r is the excitation potential; and the number of quanta dissipated is $(P-W)/2.26\times10^{-19}$ per centimeter of the column per second.

The number of inelastic collisions per centimeter of the column per second, $C_{1\,2}$, can be expressed in terms of the effective collision area $q_{1\,2}$ of an atom for such a collision.

$$C_{1\,2}=q_{1\,2}N_e n_1 v_e f(v)$$

where N_e is the number of electrons per cm of the column, n_1 is the number of atoms per cubic centimeter (accurately the number in the normal state), v_e is the electron velocity and $f(v)$ is the fraction of electron-collisions with kinetic energy greater than eV_r. The electrons have a Maxwell distribution of energy, here expressed in terms of V_0, where

$$eV_0=kT=2/3 \text{ mean energy}$$

Introducing for $f(v)$ the integral over energies between $V_r e$ and infinity

$$C_{1\,2}=q_{1\,2}N_e n_1 v_e\left(\frac{V_R}{V_0}+1\right)\exp\left(-\frac{V_R}{V_0}\right) \tag{1}$$

The probability of an inelastic collision is a function of V which rises abruptly from zero at V_R to a maximum very close to V_R and then decreases less abruptly over a range of several volts.[4] $q_{1\,2}$ is the integrated effect of all electrons of a Maxwell distribution which exceed V_R and so it is a function of V_0 which presumably increases with decreasing V_0.

From the above remarks it seems to follow that the number of collisions is equal to the number of quanta dissipated.

$$C_{1\,2}=(P-W)/2.26\times10^{-19} \tag{2}$$

[2] Foote, Rognley, and Mohler, Phys. Rev., vol. 13, p. 59, 1919.
[3] Killian, Phys. Rev., vol. 35, p. 1238, 1930.
[4] Darrow, Electrical Phenomena in Gases, Williams, Wilkins Co., 1932.

It will be shown that this identity is not justified except for low pressures and currents. Electron energy expended in producing excited atoms may be given back to the electrons by collisions of the second kind so that in general the power dissipated is less than $C_{1\,2}\times 2.26\times 10^{-19}$ watts. In general,

$$C_{1\,2}-C_{2\,1}=(P-W)/2.26\times 10^{-19} \tag{3}$$

where $C_{2\,1}$ is the number of collisions of the second kind per centimeter of the column per second.

II. EXPERIMENTAL PROCEDURE

The type of discharge tube was illustrated in RP455 (fig. 1). It was a termionic discharge in a tube 1.8 cm in diameter. Commonly there were two small probes near the axis and 12 cm apart to measure the voltage gradient, electron energy and electron concentration; and a disk electrode against the wall to measure the flow of ions to the wall. The cæsium was in a side tube, maintained at a lower temperature than the body of the tube. Vapor pressures were computed from the temperature by the relation[5]

$$\log p\ (mm)=-\frac{3{,}966}{T}+7.1650$$

The temperature measured by a thermocouple in contact with the tube wall in the region of the positive column was taken as the gas temperature in computing the number of atoms, n_1.

The discharge is characterized by exceptionally low electron speeds and high electron concentration. This makes the precision low, and an added difficulty is the electrical leakage over the cæsiated glass surfaces. The high electron concentration necessitates the use of a small probe surface. The leakage was greatly reduced by avoiding a close fit between the insulator and the probe but this leaves the effective collecting area uncertain. Two sizes of probe were used to cover the range of electron currents obtained; platinum wires 2 mm long and 0.4 mm in diameter, and wires of this diameter cut off flush with the insulator.

Figure 1 (taken from RP455) shows curves of the log of the probe current versus voltage relative to the anode for the two small probes 12 cm apart. The experimental points negative to the space potential (the intersection of the two lines) fall on a straight line showing that the electrons have a Maxwell distribution. The electron energy V_0 is given by the relation

$$V_0=(V_2-V_1)\log e/(\log I_1-\log I_2)$$

The experimental uncertainty is about 0.02 volt and, as V_0 may have values as low as 0.2 volt, the percentage error is high. Recognized sources of error tend to make V_0 too high. The value of V_0 at the tube wall is nearly the same as at the axis.

The random current density at the center of the tube, i_0, is given by the current at the space potential divided by the collecting area.

[5] Rowe, Phil. Mag., vol. 3, p. 534, 1927.

For the 2 mm probes the measured area 0.0257 cm² was used and the effective area of the wire, cut off flush with the insulator, was obtained by comparison with the 2 mm probe. This area 0.002 cm² is greater than the end of the wire because the edge is not completely insulated

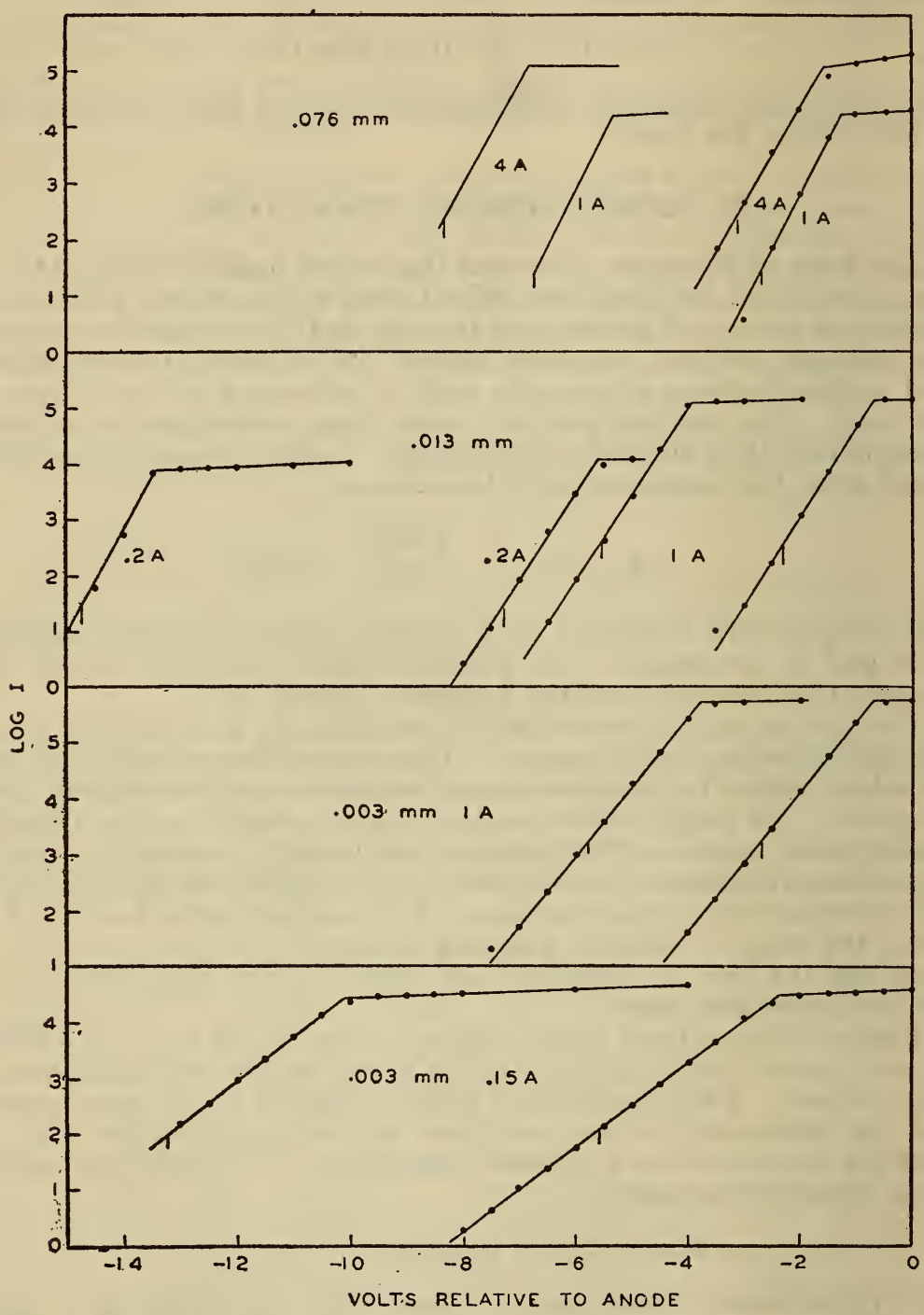

FIGURE 1.—*Probe characteristics for two small probes 12 cm apart at the axis of the positive column*

from the discharge. The number of electrons per cubic centimeter is given by the relation

$$n_0 = 2.51 \times 10^{19} i_0 / v_e$$

The space current decreases from the tube axis to the walls and the variation of current density across the diameter of the tube is roughly parabolic.[6] Two rather inaccurate experiments give a basis for estimating the total number of electrons per unit length of the tube from n_0. Comparison of the currents to a probe at the axis and a fine wire extending the full length of a radius gave the mean current density along the radius as 0.815 i_0. Assuming a parabolic distribution, the mean current density over the cross section is 0.72 i_0. In the second experiment the currents to similar probes at the axis and the walls were compared, and the value 0.325 i_0 for current density at the wall leads to a mean current density across the tube of 0.66 i_0 on the basis of a parabolic distribution. These experiments showed no systematic variation of distribution over a considerable range of pressure and current. The theoretical distribution for the case of low pressure and ionization proportional to the electron concentration gives a mean current density of 0.7 i_0.[7] I will use this value as it is consistent with the experimental values though the conditions do not conform to the postulates of the theory. Since v_e is constant

$$N_e = 0.7\pi r^2 n_0$$

Where r is the tube radius.

III. COLLISIONS OF THE FIRST AND SECOND KIND

Assuming that the number of inelastic collisions is equal to the number of quanta dissipated, neglecting collisions of the second kind, equations 1 and 2 give

$$q_{1\,2} = (P-W)/\left[2.26\times10^{-19}N_e n_1 v_e\left(\frac{1.42}{V_0}+1\right)\exp\left(-\frac{1.42}{V_0}\right)\right] \qquad (4)$$

Values of $q_{1\,2}$, computed on this basis from measurements at low pressures, are plotted in Figure 2 as a function of the discharge current. For pressures 0.003 and 0.0016 mm, there is a range of current, 0.5 amp and less, in which the value does not seem to depend on the current. There were 12 measurements in this range (some points in fig. 2 represent means of several measurements) which give a mean value

$$q_{1\,2} = 5.4 \pm .6 \times 10^{-15}\text{cm}^2$$

Any dependence of $q_{1\,2}$ on V_0 was concealed by the large experimental error; but, in view of the comparatively small range of values of V_0, this value can be used to give at least a rough estimate of the number of inelastic collisions under all conditions.

Brode's [8] measurements of the scattering of electrons by cæsium atoms give a value for the effective scattering area for 1.42-volt electrons of $56\times10^{-15}\text{cm}^2$. There are no direct measurements of $q_{1\,2}$. Loveridge [9] has obtained values for sodium and potassium based on absolute measurements of the radiation excited by a beam of electrons of uniform speed. His maximum value is about 1 per cent of

[6] Killian, Phys. Rev., vol. 35, p. 1238, 1930.
[7] Tonks and Langmuir, Phys. Rev., vol. 34, p. 876, 1929.
[8] R. Brode, Phys. Rev., vol. 34 p. 673, 1929.
[9] Loveridge, Univ. of Cal., Thesis, 1931.

the scattering area found by Brode. The experiment is extremely difficult and the uncertainty even greater than for the method used here. My value for cæsium is 10 per cent of the scattering area and this is an average value and not a maximum.

An examination of equation (4) shows the correlation between the curves of Figure 2 and other variables. At constant pressure the important variables are N_e and the exponential factor involving V_0. A curve of V_0 as a function of current is included in Figure 4. N_e increases roughly as the square of the current and up to 0.5 amp at 0.003 mm the decrease in V_0 compensates for the increase in N_e to keep the value of $q_{1\,2}$ constant. With higher currents, V_0 is constant and the increase in N_e gives a decrease in $q_{1\,2}$ that is entirely incompatible with the assumption that it measures a collision area. This is the case at all currents for higher pressures.

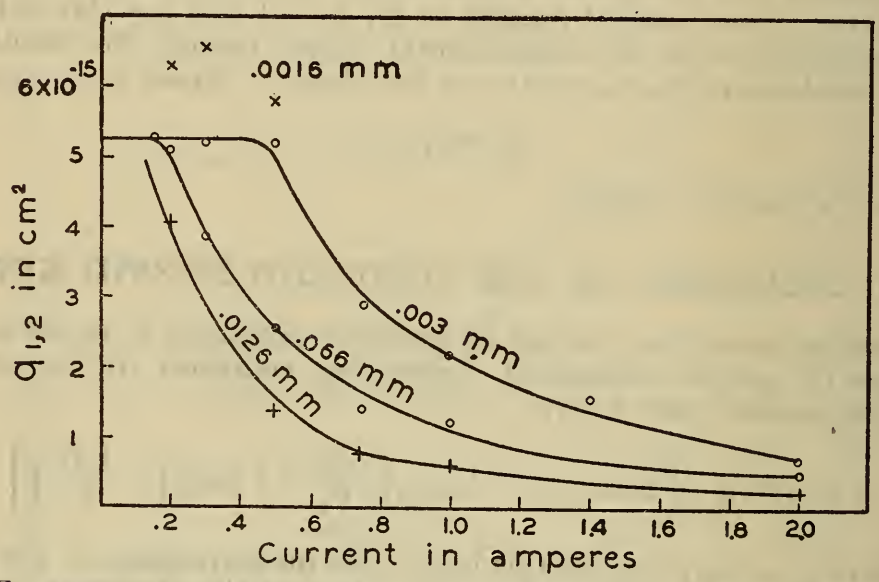

FIGURE 2.—*Values of $q_{1\,2}$ computed by equation (1) assuming that $C_{1\,2}$ is the number of quanta dissipated*

The difficulty is removed by the recognition that collisions of the second kind become increasingly important at higher currents. Figure 3 shows the data at 0.003 mm presented in accord with this idea. $C_{1\,2}$ is the number of collisions of the first kind as given by equation 1, and $C_{1\,2}-C_{2\,1}$ gives the number of quanta dissipated as given by equation 3. The two curves are nearly coincident up to 0.5 amp and above this point rapidly diverge with $C_{1\,2}$ nearly proportional to N_e. At high pressure it increases somewhat faster than N_e over the entire range of current. The number of collisions of the second kind, $C_{2\,1}$, is given by the difference between the two curves and it rises from a negligible quantity at 0.5 amp to 0.6 $C_{1\,2}$ at 1 amp, 0.8 $C_{1\,2}$ at 2 amps and 0.9 $C_{1\,2}$ at 3 amps. The predominant process at high currents is a reversible interchange of energy between the atoms and the electrons without dissipation of power.

The number of collisions of the second kind is expressed by an equation analogous to equation 1

$$C_{2\,1}=q_{2\,1}N_e n_2 v_e \tag{5}$$

where $q_{2\,1}$ is the effective area of the excited atoms and n_2 is the number of atoms per cubic centimeter in the excited state. $q_{2\,1}$ can be computed from $q_{1\,2}$ by the principle of detailed balance which states that in thermal equilibrium between cæsium atoms and electrons $C_{2\,1}$ must equal $C_{1\,2}$. Equations (1) and (5) are applicable to the equilibrium state at a temperature $T = V_0/11{,}600$. In equilibrium n_2 is given by Boltzmann's equation

$$n_2 = \frac{g_2}{g_1} n_1 \exp\left(-V_R/V_0\right) = 3n_1 \exp\left(-1.42/V_0\right) \tag{6}$$

where g_2 and g_1 are the weights of the $2P_{1\,2}$ and $1S_1$ states, respectively. Equating (1) and (5) and eliminating n_2 by equation (6) gives

$$q_{2\,1} = \frac{g_1}{g_2} q_{1\,2} \left(\frac{V_R}{V_0} + 1\right) \tag{7}$$

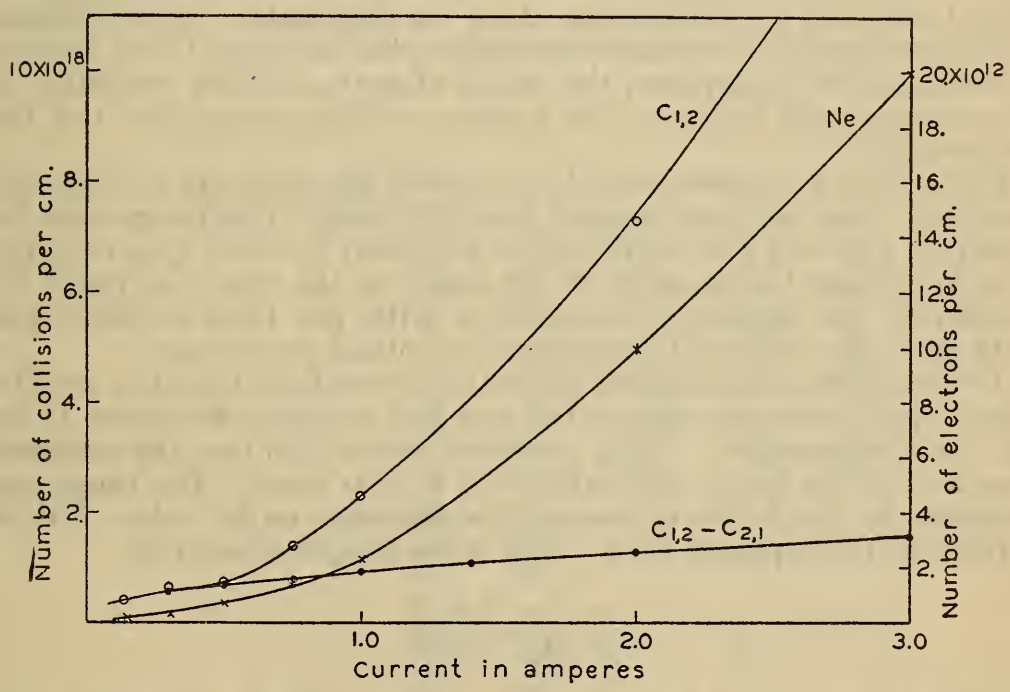

FIGURE 3.—*The number of collisions of the first kind and the number dissipated per cm of the column (left scale); the number of electrons per cm (right scale); from measurements at 0.003 mm pressure*

This is not the usual form of the Klein and Rosseland relation.[10] It is the equation applicable to all electrons of the Maxwell distribution and not to the particular speeds corresponding to V_0 and $V_R + V_0$.

Equation (5) now becomes

$$C_{2\,1} = \frac{1}{3} q_{1\,2} \left(\frac{V_R}{V_0} + 1\right) N_e n_2 v_e \tag{8}$$

This equation and equation (1) can be used to evaluate n_2 from the measured value of $C_{1\,2} - C_{2\,1}$. I will first give some direct experimental evidence as to the concentration of excited atoms.

[10] Klein and Rosseland, Zeits. für Phys., vol. 4, p. 46, 1921.

IV. THE NUMBER OF EXCITED ATOMS

A direct measure of the number of excited atoms can be obtained by a spectroscopic method which has been applied to measure flame temperatures. Light from an incandescent lamp is passed through the discharge and analyzed by a spectrograph. The resulting spectrum will show the cæsium absorption lines either as dark or bright lines, depending on whether the lamp temperature is above or below a critical temperature T_L, here called the reversal temperature. Hedwig Kohn [11] has shown that T_L, for a line emitted in a transition between states 2 and 1, differing in energy by $E_{2\,1}$, is related to the relative number of atoms in the two states by an equation identical in form to Boltzmann's equation

$$n_2/n_1 = (g_2/g_1) \exp\,(-E_{2\,1}/kT_L) \tag{9}$$

where the g's are the weights of the two states. The only assumption is that n_2/n_1 has a definite value along the light path. In equilibrium all lines reverse at the same temperature, but in general they do not. The strength of absorption, the length of path, and the resolution of the spectrograph influence the accuracy of the setting but not the value of T_L.

Light from a tungsten strip lamp passed diametrically through the discharge tube and was focused near the axis. The image was focused by a second lens on the slit of a 3-prism Steinheil spectrograph. The brightness temperature of the image in the tube was found by measuring the apparent temperature with the tube in place and with the tube removed by means of an optical pyrometer.

Photographs of the spectra show the reversals of the $2P_{1\,2}$ doublet clearly with pressures above 0.01 mm and at higher pressures T_L for $3P_{1\,2}$ was measurable. With pressures above 0.08 mm the temperature falls in the range attainable with a strip lamp. The range was extended by the device of keeping the discharge on for only a fifth or a tenth of the exposure time. If S is the lamp temperature

$$\frac{1}{S} - \frac{1}{T_L} = \frac{\log R}{7{,}320}$$

where R is the ratio of total exposure to the time the discharge is on. The method was checked in the range where T_L could be obtained by the lamp, but theoretically it is open to objection. The discharge lowers the vapor density so that n_1 is not the same as with the discharge off.

At the higher pressures the line at 8,521 A showed a sharp self-reversal which did not disappear at T_L. The resolution of 8,944 was less and it disappeared over a range of temperature of 50° or 100°. The failure of the method with high resolution and the range of uncertainty with low resolution comes from the variation of n_2/n_1 across a diameter.

In Table 1 and Figure 4 reversal temperatures are expressed in terms of electron volts ($V_L = T_L/11{,}600$) for comparison with values of V_0 measured electrically. The experimental error in V_0 is considerably larger than the inherent uncertainty in V_L. In equilibrium $V_L = V_0$

[11] Kohn, Phys. Zeits., vol. 29, p. 49, 1928.

and under actual discharge conditions V_L must be somewhat less than V_0 and the difference should decrease with increasing current and pressure. The observed differences are in the right direction, but the variation with current and pressure is not systematic. All differences fall within the range of the estimated error in V_0 so there is little basis for computing the departure from equilibrium. Reversals could not be measured at the lowest pressures where a large difference is to be expected. The small difference between values of T_L for 2P and 3P is real and shows that the number of atoms in the 3P state is further from the equilibrium value than the 2P state.

The results confirm the prediction that at moderate pressures and currents there is nearly an equilibrium between the electrons and the atoms in the first excited state. Or accepting this view they give a desirable check on the electrical method of measuring electron temperatures. Values from curves of Figure 4 (the upper one where there are two) will be taken for V_0 in the following computations.

TABLE 1.—*Electron temperature and reversal temperature in electron volts and the number of excited atoms*

Pressure	Current	V_0	V_L (2P)	V_L (3P)	$\frac{n_2}{n'_2}$ (2P)	$\frac{n_3}{n'_3}$ (3P)
mm	*Amp.*	*Volts*				
0.35	0.5	0.185	0.168	0.161	0.73	0.27
	1	.200	.180	.174	.91	.50
	2	.217	.195	.186	.96	.45
.16	.2	.175	.179	.163	----------	----------
	.5	.183	.184	.171	.79	.22
	1.0	.205	.192	.180	.93	.33
	2	.220	.206	.192	.97	.37
.076	.2	.200	.189	.174	----------	----------
	.5	.205	.195	.180	.81	.20
	1.0	.218	.202	.186	.93	.27
	2	.228	.211	.199	.97	.45
.032	.5	.232	.216	----------	.76	----------
	1	.232	.218	----------	.92	----------
	2	.238	.224	----------	.96	----------
	4	.266	.236	----------	.97	----------
.0126	.2	.257	.228	----------	----------	----------
	.5	.257	.246	----------	.61	----------
	1	.257	.249	----------	.87	----------
	2	.257	.251	----------	.95	----------
	4	.291	.263	----------	.96	----------
.0056	.2	.298	.270	----------	----------	----------
	.5	.283	.276	----------	----------	----------
	1.0	.283	.288	----------	.72	----------
	2	.283	.283	----------	.91	----------

The actual values for the number of excited atoms can best be computed from the value of $C_{12}-C_{21}$ with C_{12} and C_{21} as given by equations 1 and 8.

$$C_{12}-C_{21}=q_{12}N_e v_e\left(\frac{V_R}{V_0}+1\right)\left[n_1\exp\left(-\frac{V_R}{V_0}\right)-\frac{1}{3}n_2\right]$$

$$n_2=n'_2-3(C_{12}-C_{21})/\left[q_{12}N_e v_e\left(\frac{V_R}{V_0}+1\right)\right] \qquad (10)$$

where

$$n'_2=3n_1\exp\left(-\frac{V_R}{V_0}\right)$$

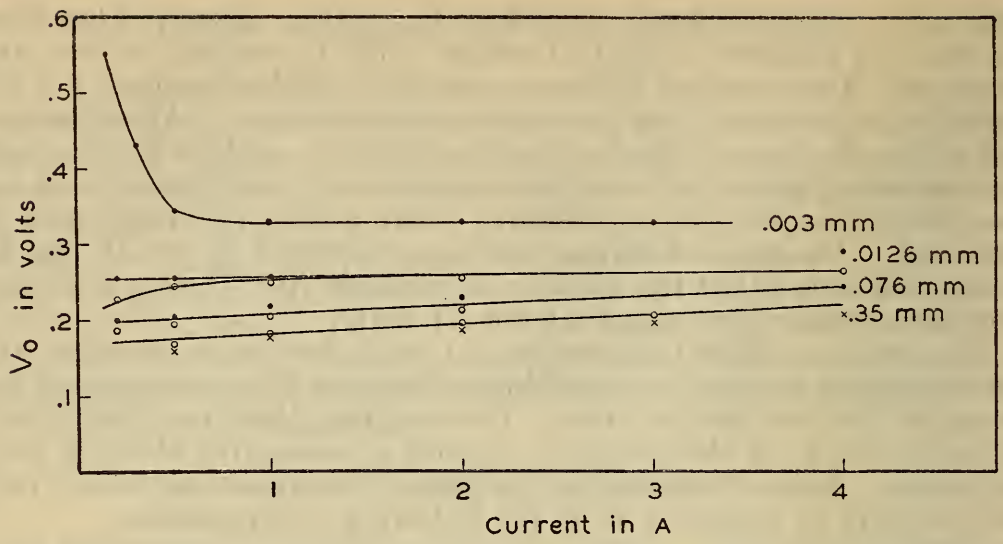

FIGURE 4.—*Measurements of electron energy V_0 shown by dots, V_L from reversal temperature of $1S-2P_{12}$ shown by circles, V_L from reversal temperature of $1S-3\ P_{12}$ shown by crosses*

Equation 10 gives the number of excited atoms in terms of the number that would exist in equilibrium at the electron temperature minus a term that becomes very small for high pressures and currents. Thus the fact that experimental uncertainties in the term on the

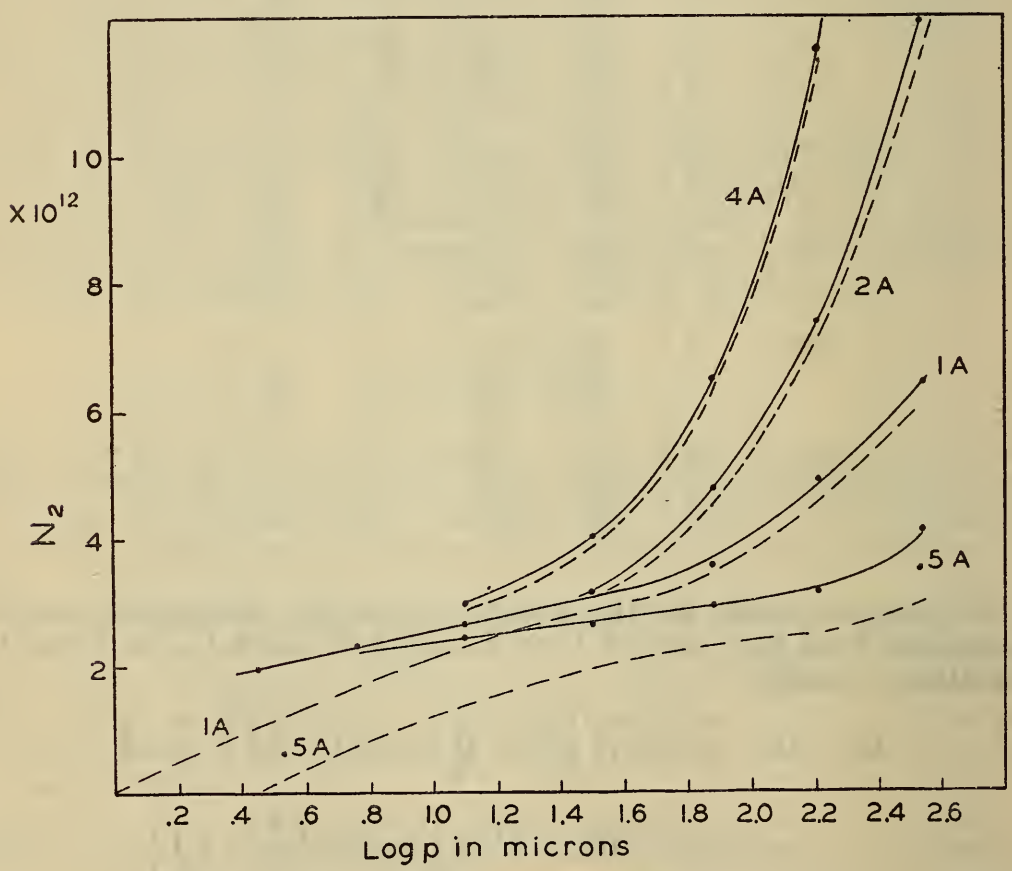

FIGURE 5.—*The number of excited atoms in the $2P_{12}$ states*

Full lines are the number that would exist in equilibrium at the electron temperature; broken lines give the actual number as estimated by equation 10.

right may become large under these conditions does not seriously affect the conclusions.

In Figure 5 the solid lines are values of n'_2 computed from V_0 as given in Figure 4. The broken lines are values of n_2 as given by equation 10. The values of n'_2 increase slowly with pressure, the equilibrium concentration n'_2/n_1 decreases. For 0.5 amp it ranges from 3.4×10^{-2} at 0.003 mm to 7×10^{-4} at 0.35 mm. Table 1 includes values of the ratio n_2/n'_2 which is a measure of the approach to equilibrium and Figure 6 shows this ratio as a function of the current. Dots are computed by equation 10 and are fairly accu-

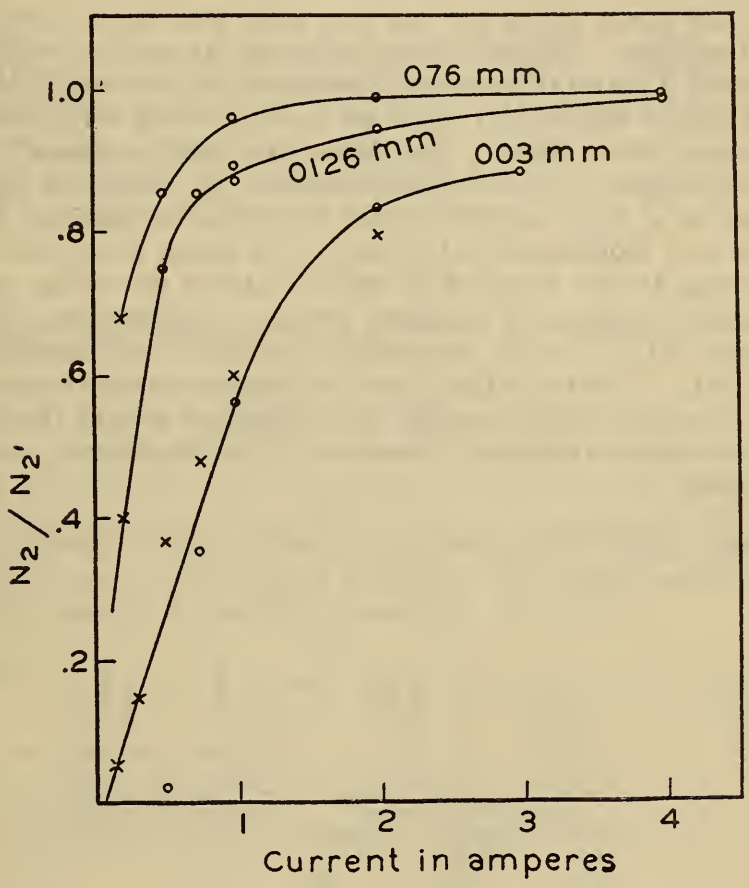

FIGURE 6.—*The ratio of the number of excited atoms to the equilibrium number measuring the approach to equilibrium as a function of current*

Dots are based on equation 10 while crosses are computed from the assumption that n_2 is proportional to the radiation intensity.

rate as the ratio approaches 1. The values become indeterminate at low current because of arbitrary assumptions in the derivation of 10. It will be shown in the following section that n_2 is roughly proportional to the intensity of the radiation, and the crosses in Figure 6 have been computed on this basis from a single high-current value of n_2 as given by equation 10. The rapid decrease in the ratio at low current comes in large part from the increase in n'_2 Table 1 includes some values of the ratio n_3/n'_3 for the $3P_{1\,2}$ state. This is derived from the tabulated values of n_2/n'_2 and the difference in T_L for the two doublets.

V. RADIATION INTENSITY AND REVERSAL TEMPERATURE

The luminous cæsium vapor is transparent except at the absorption lines and over the width of the lines it is completely opaque. The cæsium radiation may be considered as the radiation of an incandescent body at the temperature T_L which has zero emissivity except at the resonance lines. (The contribution of other lines is negligible.) The radiation per cm² can be expressed in the form of Wien's law:

$$J = C_1 \lambda^{-5} \exp\ (-V_R/V_L)\ \Delta\lambda$$

where λ is the mean value for the two lines and $\Delta\lambda$ is the sum of the widths of the lines. Table 2 gives values of $\Delta\lambda$ computed from measured values of T_L and of the total radiation as given in RP455. This effective width is about the same as the apparent width of the lines on the spectrograms though the dispersion was too small for an accurate comparison. It is nearly constant at constant pressure, so the increase in J with current comes from the increase in T_L. Since Wien's law and Boltzmann's law have the same form, the radiation is proportional to the number of excited atoms per cubic centimeter.

At constant current J remains nearly independent of pressure. The decrease in T_L with increasing pressure compensates for the increase in $\Delta\lambda$. The radiation does not remain proportional to n_2 for, because of the increasing opacity, the radiation comes from a smaller depth of the vapor at higher pressure. This depth can be estimated as given below.

TABLE 2.—*Effective line width and effective depth of radiating vapor*

	0.35 mm	0.16 mm	0.076 mm	0.0126 mm	0.0056 mm
0.2 ampere	----------	8.5 A	5.6 A	1.25 A	0.55 A
0.5 ampere	20 A	9.35 A	5.64 A	1.48 A	.603 A
1.0 ampere	18.6 A	9.45 A	5.5 A	1.37 A	.625 A
2.0 amperes	17.8 A	9.0 A	5.86 A	1.52 A	.725 A
$\Delta\lambda$ mean	18.8	9.05 A	5.65 A	1.40 A	.626
Δr in cm	1.22×10^{-3}	1.42×10^{-3}	1.62×10^{-3}	2.28×10^{-3}	3.1×10^{-3}
$\frac{\Delta\lambda\times10^{-12}}{\Delta r\times n_1}$	2.6	2.3	2.5	2.8	1.9

The rate of radiation of atoms in the $2P_{1\ 2}$ states is very closely that of a classical oscillator of the frequency of the cæsium lines[12]

$$A = \frac{8\pi^2 e^2}{3\ c\ m\lambda^2} = 2.8\times10^7 \text{ per second}$$

The radiation from n_2 atoms is then $2.8\times10^7\ n_2$ quanta per second. The measured radiation per square centimeter, divided by this number, gives the volume or the depth from which the radiation comes. Values of this effective depth, Δr, are included in Table 2 and range from 1 to 3×10^{-3} cm. The ratio $\Delta\lambda/\Delta r$ should be proportional to the number of atoms per cubic centimeter. The last row of the table shows that this proportionality holds except perhaps for the lowest pressure.

[12] Handbuch der Phys., vol. 20.

VI. DURATION OF EXCITED STATES

While the radiation life of an excited atom is $1/A = 3.56 \times 10^{-8}$ seconds, the duration of excitation within the discharge tube may be much longer than this. The radiation will be absorbed and reemitted in a distance comparable with Δr computed in the preceding section. If this experimental quantity is taken as the mean free path of a quantum of resonance radiation, then the time of diffusion of resonance radiation out of the cylindrical tube will be—

$$\tau_r = 0.75\ (r/\Delta r)^2 \times 3.56 \times 10^{-8} = 0.015 \text{ to } 0.0025 \text{ second} \qquad (11)$$

using extreme values of Δr. This can only be right in order of magnitude because of the approximations used in the derivation of Δr.

The actual duration of the excited state in the discharge, τ, will be shorter than this because of collisions of the second kind. This time can be computed by equating the number of excited atoms to the rate of production times the duration—

$$n_2 = C_{12}\ \tau/\text{vol} \qquad (12)$$

The time between collisions τ_{21} is given by the relation—

$$1/\tau_{21} = q_{21}\ N_e v_e/\text{vol} \qquad (13)$$

Some values are given in Table 3 and it is seen that except at low currents and pressures τ and τ_{21} are nearly equal and by equation 13 inversely proportional to N_e which has a large range of values. The extreme value of $\tau = 3.8 \times 10^{-8}$ is nearly equal to the radiation life which means that in the 4 amp discharge the duration of an excited state is reduced to half its normal value.

TABLE 3.—*The duration of excited states and the time between collisions*

Pressure	Current	τ	τ_{21}	τ_0
mm	*Amperes*			
0.003	2	0.58×10^{-6}	0.70×10^{-6}	3.3×10^{-6}
	1	1.54	2.65	3.7
	.5	3.24	12	4.4
	.15	4.95	90	5.2
.0126	2	.25	.264	5.0
	1	.77	.88	5.9
	.5	1.90	3.0	5.9
.076	4	.038	----------	----------
	2	.098	.101	3.3
	1	.28	.30	4.0
.35	2	.094	.098	2.5
	1	.24	.26	2.9

The duration of an excited state in the absence of collisions of the second kind τ_0 is given by—

$$\frac{1}{\tau_0} = \frac{1}{\tau} - \frac{1}{\tau_{21}} \qquad (14)$$

It can be shown that $\tau_{21}/\tau = n'_2/n_2$ so that the small quantity $1/\tau_0$ can be evaluated by equation (14) in spite of experimental errors in τ

and τ_{21}. The values τ_0 which remain of the magnitude 5×10^{-6} seconds for all conditions are much smaller than the diffusion times as given by equation 11. Possibly collisions of the first kind with excited atoms are a more important factor than diffusion. However, the diffusion time and τ_0 are quantities of secondary importance in the discharge and, as the theory has been limited to first-order approximations, conclusions as to second-order effects are scarcely legitimate.

VII. KILLIAN'S MEASUREMENTS ON THE MERCURY POSITIVE COLUMN [13]

Killian has published a detaile dstudy of electrical conditions in a mercury discharge in a tube 6.2 cm in diameter with a constant current of 5 amps at three pressures. The precision is presumably much higher than that obtained with cæsium. The dissipation of power apart from recombination is ascribed by Killian to inelastic collisions at 4.9 volts. In Table 4 I present the essential data and the results of computations such as have been made for cæsium. The effective collision area q_{12}, computed by equation 1, is far from constant and I assume that the low-pressure value is correct and that collisions of the second kind are important at the higher pressures. In mercury there are three low-excitation potentials at 4.66, 4.86, and 5.43 volts, giving the states 2^3P_0, 2^3P_1, and 2^3P_2 of weights 1, 3, and 5. The assumption that the three states are in their equilibrium ratio leads to values of the number of excited atoms which seem unreasonably high and there are other good reasons to doubt that 2^3P_2 is populated in proportion to its weight. If most of the atoms are in 2 P_0 and 2 P_1, populated in the ratio of 1 to 3—

$$q_{21}=\frac{1}{4}\,q_{12}\left(\frac{4.9}{V_0}+1\right) \tag{15}$$

TABLE 4.—*Collisions of the first and second kind in mercury*

	0.0002 mm	0.001 mm	0.0053 mm
Atoms/cm³	0.61×10^{13}	3.1×10^{13}	16.1×10^{13}.
N_e	1.11×10^{12}	2.18×10^{12}	4.57×10^{12}.
V_0	3.27 volts	2.37 volts	1.71 volts.
$C_{12}-C_{21}$	0.31×10^{18}	0.96×10^{18}	1.71×10^{18}.
q_{12}	0.68×10^{-15} cm²	(0.355×10^{-15})	(0.12×10^{-15}).
q_{21}		0.52×10^{-15} cm²	0.66×10^{-15} cm².
Excited atoms per cm³, n_2		0.50×10^{13}	2.46×10^{13}.
Normal atoms, n_1		2.6×10^{13}	13.6×10^{13}.
Duration, τ		0.97×10^{-4} seconds	0.905×10^{-4} seconds.
Time between collisions, τ_{21}		2.56×10^{-4}	1.14×10^{-4}.
Duration, τ_0		1.56×10^{-4}	4.35×10^{-4}.

(Inclusion of 2^3P_2 changes ¼ to ⅑.) With this rather arbitrary assumption, the tabulated values for the number and duration of excited atoms are derived. n_2/n_1 is so high that n_1 is appreciably less than the total number of atoms. At the highest pressure the duration of excited states is nearly equal to the time between collisions of the second kind and the concentration n_2 has reached nearly its equilibrium value.

[13] Killian, Phys. Rev., vol. 35, p. 1238, 1930.

The computed value of τ_0, the duration in the absence of collisions, can be compared with direct measurements of the duration of 2^3P_0 and 2^3P_1 atoms. Couilette [14] has measured the diffusion time of 2^3P_0 atoms between concentric spheres 3.17 cm apart and finds the time 2.5×10^{-4} seconds at 0.0013 mm and 5×10^{-4} seconds at 0.0051 mm. The conditions are roughly comparable with Killian's conditions and the diffusion times are seen to be almost equal to the two values of τ_0. Measurements of the diffusion time of resonance radiation which give the duration of 2^3P_1 lead to values of the order of one-twentieth of this.[15]

The agreement between the computed values of τ_0 and the observed diffusion time of 2^3P_0 atoms implies a predominance of 2^3P_0 atoms in contradiction to my assumptions. Actually the number of atoms in 2^3P_0 must be more than a third of n_2 and the values for n_2, τ and τ_0 will be somewhat less than in Table 4. Apart from this minor complication, the results are consistent with the view that collisions of the second kind play an important part in the mercury discharge, even with low pressures and current densities.[16]

VIII. MEASUREMENTS OF KOPFERMANN AND LADENBURG ON THE NEON POSITIVE COLUMN [17]

Studies of the anomalous dispersion of excited neon give detailed information as to the concentration of different excited states under a wide range of conditions. Measurements were made on the transitions between the lower states s_3, s_4, s_5, and the various p states (Paschen notation). The lower states are analogous to the 2^3P states of mercury but in inverted order. The concentrations of these states approach constant values in the equilibrium ratios with a current density of about 0.1 amp/cm^2 for a pressure of 1 mm. Only at very low currents is there a marked preponderance of the metastable states as compared with the radiating state. With increasing pressure up to 9 mm the equilibrium is attained at lower currents in accord with the results with cæsium, but unlike cæsium the number of excited atoms decreases with increasing pressure. Only with the highest current density, 1.4 amp/cm^2, is the number of atoms in the higher states near the equilibrium value. The equilibrium value for the p states at 1 mm pressure corresponds to an electron energy $V_0=2$ volts while the s states correspond to values between 1.6 and 1.85 volts. Measurements of electron energies in the neon positive column[18] give values within this range for comparable conditions of pressure and current.

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[14] Coulliette, Phys. Rev., vol. 32, p. 636, 1928.

[15] Webb and Messenger, Phys. Rev., vol. 33, p. 319, 1929.

[16] Latysceff and Leipunksy, Zeits. f. Phys., vol. 65, p. 111, 1930, give direct measurements of collisions of the second kind in mercury. The demonstration of the effect is very convincing, but their estimate of the absolute value of the probability is based on an assumed value of the number of excited atoms which is certainly far too high. Their value of the probability is much lower than that deduced from Killian's measurements. Published estimates of $q_{1,2}$ cover a very wide range of values and are, in general, much less than I deduce. Killian's experimental data can not be wrong in order of magnitude and the assumptions I have used tend to give a value of $q_{1\,2}$; that is, too low rather than too high.

[17] Kopfermann and Ladenburg, Zeits. f. Phys., vol. 48, pp. 15, 26, 51, and 192, 1928. Zeits. f. Phys., vol. 65, p. 167, 1930.

[18] Seeliger and Hichert, Ann. der Phys., vols. 5–11, p. 817, 1931.

IX. CONCLUSIONS

In a cæsium positive column with pressures above 0.006 mm there are simple relations between the electron temperature T_e, the number of excited atoms, n_2, and the radiation intensity. The number of excited atoms in the first excited state is nearly equal to the number which would exist in equilibrium at a temperature T_e. With increasing current T_e and n_2 slowly increase and the radiation intensity remains proportional to n_2. The electron concentration and the number of collisions of the first kind increase greatly, but the number of collisions of the second kind increase at an equal rate and the only primary effect is to reduce the life of the excited states. With increasing pressure, T_e and the concentration of excited atoms decrease while n_2 gradually increases. The radiation remains nearly constant.

The studies of Kopfermann and Ladenburg of anomalous dispersion in the neon positive column and my deductions from Killian's electrical measurements in the mercury positive column indicate that the relation between the number of excited atoms and T_e are qualitatively similar for neon, mercury, and cæsium. These atoms are extremely different in structure and one can conclude that the relation is quite general. While the approach to equilibrium concentration occurs at low current for the first excited state (or close group of states) it requires high currents to approach equilibrium in the second states. Thus there is no reason to expect a distribution of intensity in the line spectrum (in a series of lines, for instance) that is simply related to the electron temperature.

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