ELECTRON CONCENTRATION AND SPECTRAL INTENSITY DISTRIBUTION IN A CESIUM DISCHARGE

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ABSTRACT

The theoretical relation between the transition probabilities for line emission in a given series and the probability of recombination into the final state of the series is derived from the postulate that the line intensity approaches the continuous intensity at the limit in thermal equilibrium. The measured values of A for the subordinate series of cesium lead to a value 1.7×10^{-21} cm^2 for the effective cross section for recombination of a 0.3-volt electron into the 6P limit. Measurements of recombination intensity and electron concentration have led to an identical value at low pressures, but the value apparently increased with pressure. It is concluded that probe measurements are systematically low at higher pressures and the intensity of the continuous spectrum is used as a basis for computing the true values of electron concentration N_e.

It has been shown that at pressures above 60 μ all the higher series lines have the same reversal temperature. One can define a temperature, T_s, by a given value of N_e in Saha's equation and the values so derived are equal to the reversal temperatures of the higher series lines. T_s is always less than the electron temperature but the two approach each other with increasing pressure.

CONTENTS

I. INTRODUCTION

A series [1] of papers has described a systematic study of the columnar discharge in cesium vapor in which various phenomena have been studied as a function of vapor pressure and current in a tube 1.8 cm in diameter. The data include electrical measurements of electron concentration and temperature, measurements of the number of excited atoms in different excited states, and measurements of intensity distribution in the line spectrum and in the continuous recombination spectrum. The purpose of finding general relations between the intensity distribution and the electrical conditions was not fully realized because of an apparent contradiction in the experimental data. In this paper the contradiction is removed by a more or less arbitrary

[1] F. L. Mohler, *Power input and dissipation in the positive column of a caesium discharge*, BS J. Research **9**, 25 (1932) RP455.

Collision of the first and second kind in the positive column of a caesium discharge, BS J. Research **9**, 493 (1932) RP485.

Recombination radiation in the cesium positive column, BS J. Research **10**, 771 (1933) RP565.

Reversal temperature and population of excited states in the cesium discharge, J. Research NBS **16**, 227 (1936) RP869.

Intensity distribution in the line emission spectrum of cesium, J. Research NBS **17**, 45 (1936) RP901.

choice between conflicting results, and a general relation is thereby derived which seems to justify the choice.

The dilemma arose in the measurements of the intensity of the continuous recombination spectrum as a function of the number of electrons per cubic centimeter, N_e. One would expect the intensity to depend only on the number of electrons and ions and on the electron velocity distribution. The experiments indicated that the intensity was from 10 to 40 times as great at a pressure of 300 microns of mercury as at 1 micron for equal values of N_e. This led to the assumption that the probability of recombination with emission of radiation depended on the vapor pressure.[2] The rate of recombination at higher pressures is known to depend on pressure, but the conventional view is that the process is radiationless. An alternative possibility is that the probe wire measurements of N_e are systematically in error at the higher pressures. Studies of the line intensity as a function of discharge conditions and consideration of the theoretical relation between line intensity and continuous intensity support the second alternative.[3]

II. RELATION BETWEEN THE PROBABILITY OF RECOMBINATION AND THE LINE TRANSITION PROBABILITIES

It is a familiar fact that an intense continuous spectrum beyond a series limit is always accompanied by relatively intense higher series lines which gradually merge into the continuum 50 or 100 A on the long wave length side of the theoretical limit and there is no perceptible discontinuity at the limit. The relation between line transition probabilities and the probability of recombination can conveniently be derived from the postulate that in thermal equilibrium the line intensity and the continuous intensity must similarly approach equality at the limit.

The intensity in ergs per cubic centimeter of radiation from a transition from the nth state of a series into a common final state is

$$J_n = N_n A_n h\nu, \tag{1}$$

where A_n is the transition probability and N_n is the population of the nth state. At a temperature, T,

$$N_n = N_1 \frac{g_n}{g_1} \exp. (-E_n/kT), \tag{2}$$

where E_n is the energy of the nth state relative to the normal state, N_1 is the population of the normal state, and g_n and g_1 are the weights of the two states. The average frequency interval between two successive lines of a hydrogen series, or any series if n is large, is

$$\delta\nu = 2R/n^3, \tag{3}$$

where R is the Rydberg frequency. In a finite interval, $\Delta\nu$, near the limit there are then $\Delta\nu n^3/2R$ lines and the integrated intensity is

$$\int_{\Delta\nu} \frac{J_n}{h\nu} d\nu = N_1 \frac{g_n}{g_1} \exp. (-E_n/kT) \int_{\Delta\nu} \frac{A_n n^3}{2R} d\nu,$$

2 BS J. Research 10, 771 (1933) RP565.
3 J. Research NBS 17, 45 (1936) RP901.

where E_n is an average value. Since $A_n n^3$ is a constant for large values of n

$$\int_{\Delta\nu} \frac{J_n}{h\nu} d\nu = N_1 \frac{g_n}{g_1} \exp. \; (-E_n/kT) \frac{A_n n^3}{2R} \Delta\nu. \tag{4}$$

The continuous spectrum arises from electrons with a continuous range of kinetic energy, E, falling into a level of limiting frequency, ν_i, with emission of radiation of frequency, ν, where

$$h\nu = h\nu_i + E. \tag{5}$$

The probability of capture into this level can be expressed in terms of the effective collision area, q. The number of effective collisions of electrons in an energy range, ΔE, with ions equals the number of quanta in the corresponding frequency range, $\Delta\nu$. In equilibrium the fraction of collisions in the energy range, ΔE, is given by kinetic theory, the number of ions and electrons is equal, and

$$\frac{J(\nu)\Delta\nu}{h\nu} = \frac{4\pi^{-1/2}h}{\sqrt{2m}} \frac{N_e^2}{(kT)^{3/2}} \exp. \; (-E/kT) Eq\Delta\nu. \tag{6}$$

Saha's equation gives for the value of N_e^2

$$N_e^2 = \frac{(2\pi m)^{3/2}}{h^3} (kT)^{3/2} \frac{2g^+}{g_1} N_1 \exp. \; (-E_i/kT), \tag{7}$$

where g^+ is the weight of the ionized state and E_i the ionization energy. Putting this value of N_e^2 in equation 6,

$$\frac{J(\nu)\Delta\nu}{h\nu} = \frac{16\pi m}{h^2} \frac{g^+}{g_1} N_1 \exp. \left(-\frac{E_i + E}{kT}\right) Eq\Delta\nu. \tag{8}$$

As E approaches zero, Eq remains finite [4] and the exponent approaches E_i/kT. In equation 4 the exponent has the same limiting value, and the condition that line and continuous spectra have equal intensities at the limit reduces to

$$Eq = \frac{h^2}{32\pi mR} \frac{g_n}{g^+} A_n n^3 = 1.45 \times 10^{-43} \frac{g_n}{g^+} A_n n^3. \tag{9}$$

This is not a new relation but could be derived from the law that the line absorption equals the continuous absorption at the limit.[5] The two products, Eq and An^3, are both roughly proportional to λ, and this approximation will be used in deriving values at the limit from observed values.

III. PROBABILITY OF RECOMBINATION INTO 6P OF CESIUM

Equation 9 will be used to compare experimental values of A_n for the subordinate series of cesium and q for the continuous spectrum beyond the 6P series limit. This is a doublet system with limits $\lambda_0 = 5080$ and 4944, the first being the more intense. For simplicity this will be treated as a single limit at $\lambda_0 = 5080$.

[4] Mohler and Boeckner, BS J. Research **2**, 489 (1929) RP46.
[5] Sugiura, J. Phys. **8**, 113 (1927).

Values [6] of A_n obtained in a limited range of discharge conditions (pressure greater than 60 μ) in which both N_n and J could be evaluated gave

$$A_n n^3 = 5.8 \times 10^8 \text{ at } \lambda 5080$$

for the sum of the doublet components. The integral on the left side of equation 4 must include all series with the common limit. For the S series, $g_n A_n$ is 0.1 times the value for the D series and for both

$$\frac{g_n}{g^+} A_n n^3 = 6.4 \times 10^9.$$

From equation 9, $Eq = 9.3 \times 10^{34}$ at $\lambda = 5080$. For comparison with the recombination spectrum, q will be evaluated at $E = 0.48 \times 10^{-12}$ erg or 0.3 electron volt, corresponding to 4520 A.

$$Eq = 8.3 \times 10^{-34}. \quad q = 1.72 \times 10^{-21} \text{ cm}^2.$$

The experimental value of q based on recombination measurements at low pressures is almost exactly this, viz., $q = 1.7 \times 10^{-21}$. The exact agreement is certainly accidental but the precision is sufficient to show that the values of A measured at high pressure are consistent with the low-pressure values of q and not with the high-pressure values which are over 10 times as great. The value 1.7×10^{-21} cm^2 is of the same magnitude as the theoretical value for recombination of a 0.3-volt electron into the 2_2 level of hydrogen, viz., 3.66×10^{-21} cm^2.[7]

These considerations strongly support the conclusion that there is a systematic error in the probe measurements of N_e used in computing values of q from the observed intensity of the recombination spectrum. A possible explanation of the error is that the current to the probe lowers the concentration of the electrons in the plasma near the probe. Such an effect would increase with pressure and the magnitude of the effect seems sufficient to account for the discrepancy. The theory of probe measurements is rigorous only at low pressures and the best experimental checks on the theory have been made at low pressures.[8] There are many possible complications at higher pressures [9] and no assurance that the electron diffusion effect is predominant.

IV. ELECTRON CONCENTRATION FROM INTENSITY MEASUREMENTS

There is no reason to doubt the constancy of atomic transition probabilities, and the intensity of the recombination spectrum can be used to compute values of N_e. The author has published intensity measurements as a function of apparent values of N_e for pressures ranging from 0.78 to 290 μ.[10] There is roughly a twofold change in electron temperature in this range and equation 6 shows that the intensity at the limit varies inversely as $T^{3/2}$. Figure 1 gives a

6 J. Research NBS 17, 45 (1936) RP901.
7 Stueckelberg and Morse, Phys. Rev. 36, 16, (1930).
8 Langmuir and Mott-Smith, Gen. Elec. Rev. 27, 449, 538, 616, 762, 810 (1924).
9 Seeliger and Hirchert, Ann. Phys. 5-11, 817 (1931).
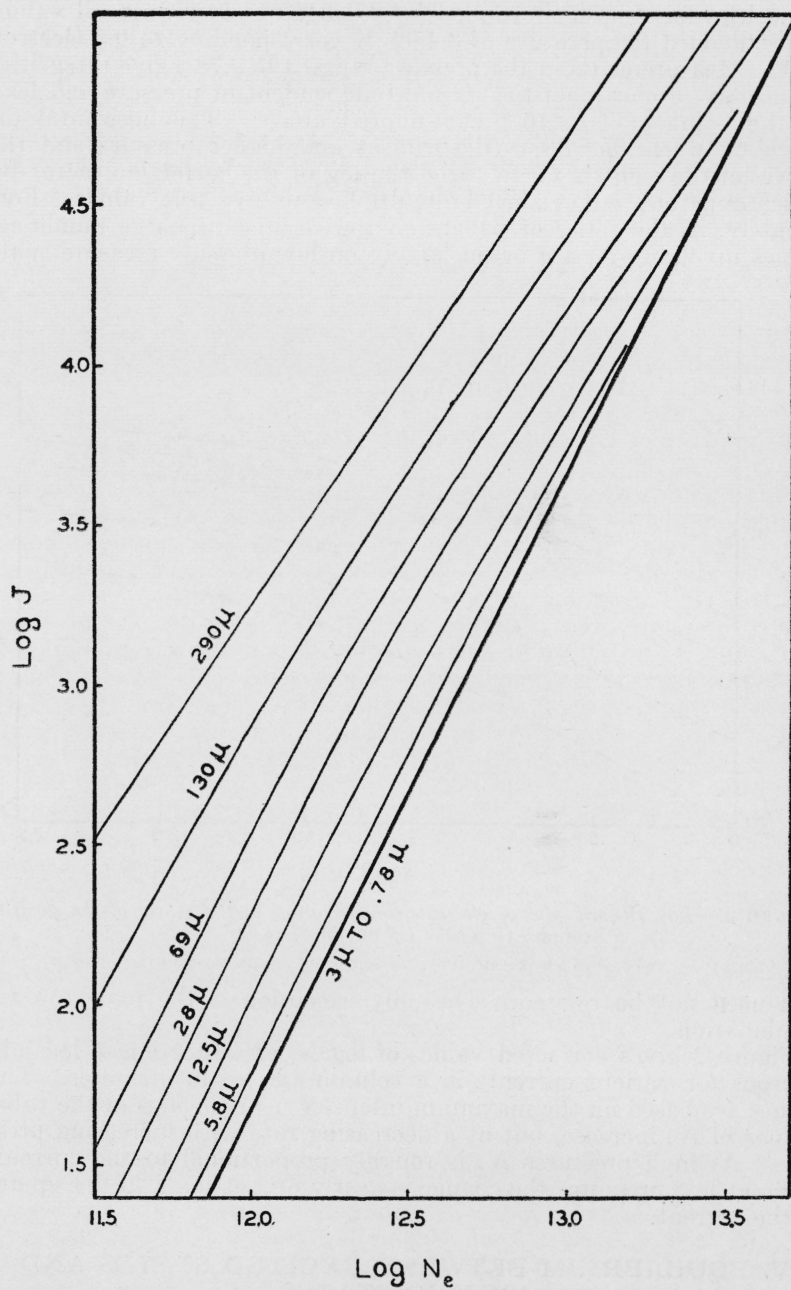10 BS J. Research 10, 771 (1933) RP565.

FIGURE 1.—*Logarithmic plot of intensity of the continuous spectrum near the 6P limit versus the observed electron concentration.*

Observed values of J are reduced to a standard electron temperature of 3,480° K

logarithmic plot of intensity versus measured values of N_e. Observed intensities have been multiplied by $(T_e/3480)^{3/2}$ to reduce all values to a standard temperature of 3,480° K corresponding to 0.3 electron volt. Measurements in the pressure range 3 to 0.78 μ give intensities accurately proportional to N^2_e and independent of pressure and lead to the value $q=1.7\times10^{-21}$ cm² quoted above. The horizontal interval between the observed curve at any higher pressure and the curve on the right is taken to be the log of the correction factor by which apparent values must be multiplied to give true values. Fortunately, in the series of papers on the cesium discharge numerical values involving N_e are based largely on low-pressure measurements
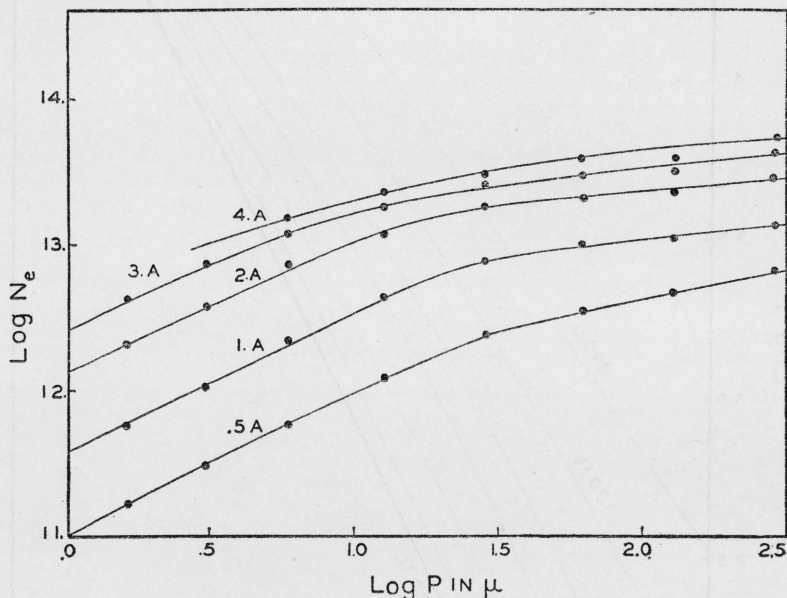

FIGURE 2.—*Logarithmic plot of electron concentration at the center of the positive column in a tube 1.8 cm in diameter.*

Values of N_e are based on low-pressure probe measurements and the recombination intensity.

and need not be revised. The only exception is the paper on recombination.

Figure 2 gives corrected values of log N_e as a function of log p in microns for various currents in a column 1.8 cm in diameter. The values are based on the maximum intensity near the axis of the tube. Values of N_e increase, but at a decreasing rate with increasing pressure. At high pressures N_e is roughly proportional to the current, while at low pressures the change is nearly proportional to the square of the current.

V. EQUILIBRIUM BETWEEN EXCITED STATES AND IONIZED STATES

Direct measurements of the reversal temperature of the higher series lines of the principal series [11] and intensity measurements in S, D, and F series indicate that at pressures of the order of 100 μ all

[11] J. Research NBS 16, 227 (1936) RP869; 17, 45 (1936) RP901.

states beyond the third in each series have the same reversal temperature. The number of atoms in a given state, N_n, is related to the reversal temperature, T_n, by an equation of the Boltzman form.

$$N_n = N_1 \frac{g_n}{g_1} \exp. \ (-E_n/kT_n). \tag{10}$$

There is then a temperature distribution of excitation among the higher states and the theoretical considerations of the first section suggest that this common value of T_n must be related to the electron concentration, N_e. By equation 10 a value of T_n is defined by a given value, N_n, without any assumption as to equilibrium, and in the same way one can define a temperature, T_s, by the use of Saha's equation and a given value of N_e,

$$N_e^2 = 2.43 \times 10^{15} \frac{g^+}{g_1} N_1 T_s^{3/2} \exp. \ (-E_i/kT_s) \tag{11}$$
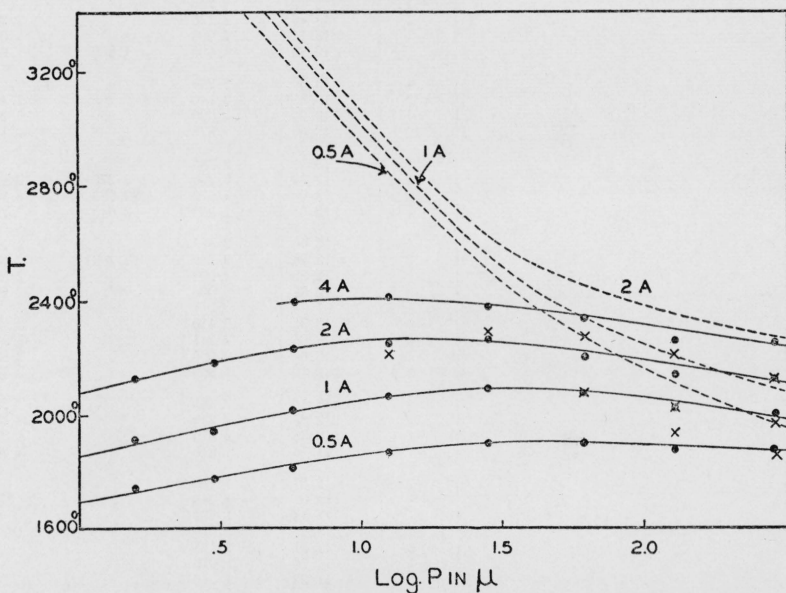

FIGURE 3.—*Full lines and dots give T_s based on values of N_e from figure 2 and Saha's equation; crosses give reversal temperatures of higher series lines and broken lines give the reversal temperatures of the resonance doublet which is nearly equal to T_e.*

It can be seen from the derivation of equation 9 that if the line intensity approaches the continuous intensity at the limit then T_n must approach T_s.

Values of N_e from figure 2 have been used to compute values of T_s, and table 1 and figure 3 show that there is a fairly satisfactory agreement between T_n and T_s in the range in which T_n can be evaluated. This consistency of the results justifies the method of basing values of N_e on intensity measurements, for the correction brings a wide range of experimental data into fair agreement.

The common value of T_n and T_s is much less than the electron temperature, while the reversal temperature of the first doublet of the principal series, T (2P), is nearly equal to the electron temperature

except at very low pressures.[12] Values of T (2P) have been included in figure 3 and table 1. The two temperatures, T_e and T_s, define the electrical conditions in the plasma. The one gives the velocity distribution of the electrons and the other the number of electrons and ions per cubic centimeter for a given value of N_a. At high pressures where electrical methods fail, both can be measured by optical methods. The intensity of the continuum near a series limit gives T_s, and the intensity distribution depends on T_e.[13]

TABLE 1.—*Electron concentration, T_s, and reversal temperatures for a positive column in cesium vapor*

P	Current	Log N_e corrected	T_s	T_n higher lines	T (6P)
μ	amp		°K		
290	4	13. 73	2, 250		
	2	13. 46	2, 125	2, 115	2, 260
	1	13. 14	2, 000	1, 970	2, 090
	. 5	12. 82	1, 880	1, 860	1, 950
130	4	13. 59	2, 260		
	2	13. 35	2, 140	2, 205	2, 400
	1	13. 04	2, 020	2, 030	2, 230
	. 5	12. 66	1, 875	1, 938	2, 140
69	4	13. 58	2, 335		
	2	13. 32	2, 200	2, 270	2, 450
	1	13. 00	2, 070	2, 080	2, 340
	. 5	12. 55	1, 900	2, 045	2, 260
28	4	13. 46	2, 375		2, 740
	2	13. 26	2, 260	(2, 290)	2, 600
	1	12. 88	2, 090		2, 530
	. 5	12. 38	1, 900		2, 500
12.5	4	13. 36	2, 410		3, 050
	2	13. 05	2, 245	(2, 210)	2, 920
	1	12. 64	2, 060		2, 890
	. 5	12. 10	1, 860		2, 860
5.8	4	13. 15	2, 385		
	2	12. 85	2, 230		3, 280
	1	12. 33	2, 010		3, 280
	. 5	11. 76	1, 810		3, 200
3	2	12. 57	2, 180		
	1	12. 02	1, 940		
	. 5	11. 48	1, 775		
1.6	2	12. 31	2, 125		
	1	11. 76	1, 910		
	. 5	11. 22	1, 740		

The elementary interactions between electrons, atoms, and radiation in a discharge become very complicated with increasing pressure, but these processes gradually approach equilibrium with each other so that statistically the discharge conditions become simpler as pressure and current increase. At extremely low pressures the plasma electrons take up a temperature distribution of velocity. (The mechanism is not entirely clear.) Above a pressure of 10 μ collisions of the first and second kind keep the number of atoms in the first excited state nearly in equilibrium with the electron temperature. Ionization of highly excited states and recombination into these states bring the number of ions and of excited states to equilibrium near 60 μ. Above this pressure the intensity of the higher series lines and of the continuum near the limit is characteristic of the temperature, T_s, but the population of the first excited state and the intensity distri-

[12] BS J. Research 9, 493 (1932) RP485.
[13] Mohler and Boeckner, BS J. Research 3, 303 (1929) RP96.

bution in the continuum depend on T_e. It is seen from figure 3 that these two temperatures approach each other with increasing pressure. Presumably recombination on the tube walls keeps T_s below T_e, and they will approach equality when spacere combination becomes predominant. Then one temperature will define electrical conditions and spectral intensity distribution for a given value of N_a. The gas temperature has been assumed to be the wall temperature, but is probably appreciably above this at the higher pressures, and the value of N_a becomes uncertain.

Studies of arcs at atmospheric pressure [14] indicate that the gas temperature in the core of the discharge is nearly equal to the electron temperature. This last stage in the approach to equilibrium is probably not approached in the range of pressure studied here.

I am indebted to Dr. C. Boeckner for pointing out the possibility that probe measurements of electron concentration may be systematically low at higher pressures.

WASHINGTON, October 16, 1936.

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[14] Mannkopff, Z. Phys. **86**, 161 (1933).