Emission of Radiation in the Positive Column of a Mercury Arc

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Intensities, corrected for absorption, of the principal spectral lines of wave-lengths 2259 to 11,289A are given for 4-ampere mercury arcs operated at vapor pressures of 0.03, 20, 450, and 500 mm (Hg). The variation across the arc of the intensity per unit area is given for twenty of these spectral lines. Plots of spectral intensity data were made on two alternative hypotheses: (1) That the concentrations of atoms in excited states are in a Boltzmann equilibrium with one another and that transition probabilities are proportional to $w_{AB}/[\lambda^2(n_A^*+n_B^*)(n_A^*-n_B^*)^2]$, where w_{AB} is the Kronig *a priori* probability, λ is the wave-length of the emitted radiation, and n_A^* and n_B^* are the effective quantum numbers of the upper and lower levels; (2) that all downward transitions are radiative and that the rate of excitation to a given level is proportional to the product of the *a priori* probability of the level and the concentration of electrons with energies which do not differ from the minimum for excitation by more than a constant amount. A Maxwellian distribution of velocities was assumed. The method of plotting is such that, if either hypothesis were correct and if the corrections for absorption were of the proper magnitude, the points on the corresponding plot would all fall on a straight line. Characteristic deviations of the points from a linear relationship are found on each type of plot. Both types of plot indicate that the electron temperature varies little with distance from the axis. This is in disagreement with Elenbaas' theory of the mechanism of a high pressure mercury arc.

ELENBAAS has made an extensive study[1] of the characteristics of mercury arcs operating at pressures ranging from about 10 mm to 760 mm (Hg). He has concluded that many of the characteristics of the discharge can be explained by assuming a Boltzmann-Saha equilibrium between electrons, normal atoms, excited atoms and ions. He assumes that the electrons have a Maxwellian distribution of velocities with an electron temperature approximately the same as the gas temperature. The variation of the gradient with tube diameter, pressure and current computed from this theory agrees well with experimental results. The measured intensities of spectral lines are also in fair agreement with the theory. However, the comparisons with calculated values are limited to three lines, of which only one was actually measured, and no corrections for absorption were made. A more extensive study of the emission of radiation in mercury arcs seemed desirable. Accordingly, a series of measurements on mercury arcs operated at vapor pressures of 0.03, 20, 450, and 500 mm (Hg) was made in this laboratory.

SET-UP AND METHODS

One experimental set-up used in this investigation is shown in Fig. 1. The quartz lens L is set at its principal focal distance from the entrance slit of the monochromator. If the slit height is small compared to the focal length of the lens, this optical system transmits only rays which are approximately parallel to the optical axis when they strike the lens. By manipulating the shutters S, radiation from only tube B, or from both tubes, may be allowed to enter the monochromator. The diaphragm D determines the cross-sectional area of the beam of radiation received from the tubes A and B: to obtain radiation from the entire width of the arc, a diaphragm 2 cm wide and 1.3 cm high was used; to obtain a narrow beam of radiation from some portion of the arc, a diaphragm 2.3 mm wide was used.

The dispersing instrument for the radiation measurements was the quartz double monochromator previously described.[2] This made it possible to measure the weaker lines in the spectrum without appreciable error from stray radiation. The receiver for the intensity measurements was a calibrated photoelectric tube: a "bubble-window" sodium tube for ultraviolet or a caesium tube for visible and infra-red radiation.

The discharge tubes were of Corning No. 972 glass ("high transmission" Corex) and the bubble windows (W) were only 3 to 7 mils thick at the center. The average transmission per window determined on one tube was 0.81 for λ11289,

[1] W. Elenbaas, Physica **1**, 211, 673 (1934); **2**, 155, 169 (1935).

[2] W. E. Forsythe and B. T. Barnes, Rev. Sci. Inst. **4**, 289 (1933).

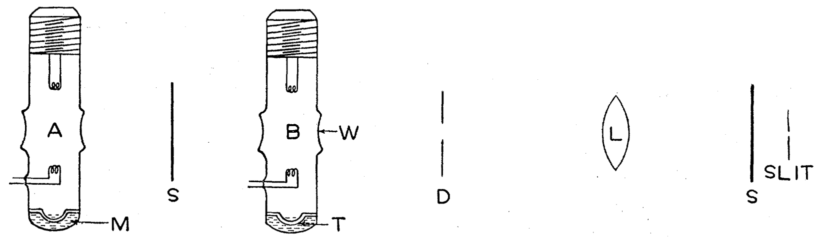

FIG. 1. Diagram of set-up. *A* and *B*, mercury vapor discharge tubes; *W*, thin "bubble" window; *M*, mercury pool; *T*, thermocouple tube; *D*, diaphragm; *L*, lens; *S*, shutter.

0.55 for λ5461, 0.22 for λ2967, and 0.06 for λ2259. The losses at the windows are rather large. They probably are due chiefly to scattering caused by striations and to absorption and scattering by material evaporated or sputtered onto the windows from the electrodes. Another tube had a transmission for λ2259 of 0.54 per window when new and 0.22 after several long runs.

Both electrodes in each tube were oxide-coated tungsten spirals which could be heated by means

TABLE I. *Spectral radiant intensities for positive column of 4-ampere* Hg *arc in tube 36* mm *in diameter. Also spectral transmittance of vapor along radius of tube for radiation from a similar tube.*

Nominal Wave-Length	Lines and Transitions	Argon Press. 5 mm at 25°C — Hg Press (mm) 450, Arc Voltage 51	20, 23	0.030, 10.6	None — 20, 17	500, 49	500, 49 Transmittance
		Milliwatts per Steradian per cm Arc					
11289A	11289 $7^3P_2-7^3S_1$	9.5	0.35	0.3		9.6	0.93
10140	10140 $7^1S_0-6^1P_1$	32.	2.31	1.26	1.96	39.	.90
7087	7092 $8^3P_0-7^3S_1$; 7082 $8^3P_1-7^3S_1$	0.22	.020			.29	.90
6907	6907.5 $8^3P_2-7^3S_1$	.086	0.05		.03	1.03	.90
6716	6716 $8^1P_1-7^1S_0$	0.11	.017			.14	.93
6234	6234 $9^1P_1-7^1S_0$	0.12				.10	.95
5780	5770 $6^3D_2-6^1P_1$; 5790 $6^3D_1-6^1P_1$; 5791 $6^1D_2-6^1P_1$	89.	5.0	0.87	2.38	89.	.81
5461	5461 $7^3S_1-6^3P_2$	133.	22.1	4.3	12.2	133.	.58
4916	4916 $8^1S_0-6^1P_1$	0.56	0.10			1.17	.86
4358	4358 $7^3S_1-6^3P_1$	112.	21.	3.05	10.1	111.	.54
4078	4078 $7^1S_0-6^3P_1$	7.0	0.51		.79	8.8	.70
4047	4047 $7^3S_1-6^3P_0$	67.	12.8	1.78	5.4	73.	.56
3906	3906 $8^1D_2-6^1P_1$; 3902 $8^3D_2-6^1P_1$; 3904 $8^3D_1-6^1P_1$	0.95	0.06			1.35	.82
3654	3650 $6^3D_3-6^3P_2$; 3655 $6^3D_2-6^3P_2$; 3662.9 $6^3D_1-6^3P_2$; 3663.3 $6^1D_2-6^3P_2$	123.	9.5	1.44	3.40	145.	.70
3341	3341 $8^3S_1-6^3P_2$	10.5	0.90	0.07	.29	11.8	.70
3129	3125.7 $6^3D_2-6^3P_1$; 3131.6 $6^3D_1-6^3P_1$; 3131.8 $6^1D_2-6^3P_1$	88.	9.5	1.53	3.79	110.	.61
3022	3021.5 $7^3D_3-6^3P_2$; 3023.5 $7^3D_2-6^3P_2$; 3025.6 $7^3D_1-6^3P_2$; 3027.5 $7^1D_2-6^3P_2$	33.	1.94	0.14	.69	41.5	.71

of step-down transformers with two insulated secondary coils. All of the data for this article were taken on d.c. with only the cathode heated. In some cases external heating of the cathode was used only in starting the arc.

The temperature of the mercury pool in each tube was determined by means of a thermocouple threaded through the tube, T (Fig. 1), which dips into the mercury pool, M, at the bottom of the lamp. A furnace surrounding the lower part of each lamp made it possible to raise the vapor pressure at will. The upper part of each lamp was wrapped with asbestos tape to make it hotter than the mercury pool when the arc was in operation. This kept the windows free of condensed mercury and made the temperature of the mercury pool a reliable measure of the vapor pressure.

Ordinarily both tubes were operated at the same pressure and current. Tube A (Fig. 1) was kept in a fixed position with its axis intersecting the axis of the optical system. Tube B was mounted on a slow-motion screw so that it could be moved sidewise (perpendicular to plane of Fig. 1). Tube A was used as a source for determining the absorption of tube B. These absorption data were used to correct the spectral intensity data taken on tube B for the effect of absorption by the vapor and the thin window. This was done by dividing the measured inten-

TABLE I.—*Continued.*

Nominal Wave-Length	Lines and Transitions	Argon Press. 5 mm at 25°C Hg Press (mm) 450 Arc Voltage 51	20 23	0.030 10.6	None 20 17	500 49	500 49 Transmittance
		Milliwatts per steradian per cm arc					
2967A	2967 $6^3D_1-6^3P_0$	19.5	2.7	0.42	1.07	22.6	0.68
2925	2925 $9^3S_1-6^3P_2$	1.75	.077	.010		1.91	.85
2894	2893.6 $8^3S_1-6^3P_1$	7.5	.52	.07	.225	9.2	.66
2804	2803.5 $8^3D_3-6^3P_2$; 2804.5 $8^3D_2-6^3P_2$; 2805.3 $8^3D_1-6^3P_2$; 2806.7 $8^1D_2-6^3P_2$	11.	.58	.03	.22	15.0	.81
2753	2753 $8^3S_1-6^3P_0$	3.6	.20			4.7	.71
2699	2698.8 $9^3D_3-6^3P_2$; 2699.4 $9^3D_2-6^3P_2$; 2699.8 $9^3D_1-6^3P_2$; 2700.8 $9^1D_2-6^3P_2$	3.8	.18		.11	5.8	.82
2652	2652 $7^3D_2-6^3P_1$; 2654 $7^3D_1-6^3P_1$; 2655 $7^1D_2-6^3P_1$	24.	1.21	.14	.69	35.	.64
2576	2576 $9^3S_1-6^3P_1$	1.25	.10			2.3	.78
2537	2535 $7^3D_1-6^3P_0$; 2536.5 $6^3P_1-6^1S_0$	48.	10.4	15.	7.0	56.	.55
2483	2482.0 $8^3D_2-6^3P_1$; 2482.7 $8^3D_1-6^3P_1$; 2483.8 $8^1D_2-6^3P_1$	7.4	.44		.29	13.8	.70
2464	2464 $9^3S_1-6^3P_0$	.62	.03			1.14	.72
2447	2447 $10^3S_1-6^3P_1$	.57	.03			.82	.75
2399	2399.4 $9^3D_2-6^3P_1$; 2399.7 $9^3D_1-6^3P_1$; 2400.6 $9^1D_2-6^3P_1$	2.8	.19			5.6	.72
2378	2378 $8^3D_1-6^3P_0$	2.6	.17			5.5	.68
2353	2352.4 $10^3D_2-6^3P_1$; 2352.65 $10^3D_1-6^3P_1$; 2353.2 $10^1D_2-6^3P_1$	1.33	.11			2.9	.72
2323	2323.0 $11^3D_2-6^3P_1$; 2323.2 $11^3D_1-6^3P_1$; 2323.6 $11^1D_2-6^3P_1$	.60	.05			1.42	.76
2302	2302 $9^3D_1-6^3P_0$	1.33	.03			3.1	.72
2259	2259 $10^3D_1-6^3P_0$	.53	.04			1.65	.68

TABLE II. *Spectral intensities per unit of projected area (microwatts per steradian per* mm²) *for positive column of 4-ampere* Hg *arc in tube 36* mm *in diameter.*

Partial Pressure of Hg	450 mm			20 mm			0.030 mm	
Nominal Wave-Length	On Arc Axis	5 mm From Arc Axis	8 mm From Arc Axis	On Arc Axis	5 mm From Arc Axis	8 mm From Arc Axis	On Arc Axis	10 mm From Arc Axis
11289	96	15.4	4.6				1.1	0.5
10140	388	71.	17.2	14.2	8.0	3.5	5.9	3.0
5780	780	150.	39.	17.5	11.	5.0	5.3	3.0
5461	1140	336.	97.	91.	50.	29.	23.6	14.2
4358	1090	297.	78.	91.	50.	29.	10.8	7.0
4078	56	11.6	3.8				.8	.47
4047	740	199.	48.	72.	41.	19.	8.3	5.3
3654	1720	315.	81.	74.	45.	20.	4.2	2.9
3341	156	33.7	12.3	5.7	4.0	2.2	.21	.12
3129	1140	231.	64.	69.	46.	22.	4.4	2.95
3022	530	84.	25.3	11.6	7.7	3.7	.39	.34
2967	268	52.	17.3	13.5	9.6	6.1	1.28	.82
2925	20	6.7	3.1				.017	.012
2894	98	21.3	7.2	4.4	2.6	1.3	.196	.115
2804	135	28.4	9.2	4.3	2.6	1.2	.078	.047
2652	372	75.	21.	13.8	7.9	3.9	.32	.18
2537	570	192.	86.				62.	50.
2483	119	24.3	7.2	4.6	2.6	1.0		
2399	62	13.	3.2					
2378	58	11.	2.9					

sities by the square root of the transmission of the entire tube for the beam from tube A. If the thin windows are identical and the absorption in the vapor is small (<10 percent), such a procedure is quite satisfactory.[3] If the absorption in the vapor is fairly high (>20 percent), changes in line contours cause the absorption per unit length to decrease as radiation passes through the vapor. This tends to make the above correction for absorption too small. On the other hand, for a strictly monochromatic portion of a spectral line, the average transmission of the vapor for radiation from an arc centered about the axis of the tube will be greater than the square root of the transmission of the entire width of the tube. Thus these two errors tend to counterbalance each other. Re-radiation of part of the absorbed energy at the same wave-length would tend to make the correction for absorption too large.

Spectral Intensity Data

Table I gives the intensities, corrected for absorption,[4] of the line radiation from the positive column of 4-ampere mercury arcs. The measured radiation came from a region midway between the electrodes. Each tube had an arc gap of 7 cm and an internal diameter of about 36 mm. The last three columns of this table give data on a tube containing only mercury vapor; the preceding three columns give data on tubes with 5 mm argon pressure (measured at 25°C with arc not running). The partial pressure of mercury vapor and the arc voltage are given at the top of each column. The arc voltage includes an electrode drop which is estimated to be between 6 and 20 volts. The data for 450 mm pressure are averages of intensities for two tubes; the values for 20 mm mercury pressure in a tube containing argon were obtained on only one of these tubes and those for 0.030 mm on the other one. For the weaker lines, approximate correc-

[3] Provided that relatively few of the downward transitions are radiative. If all downward transitions were radiative, there would be little or no correction for absorption in the vapor.

[4] Of both thin window and vapor, except for data for weak lines. In these cases, correction made only for absorption of thin window (measured with tube at room temperature). The absorption in the vapor for the weak lines is relatively small. This is shown by the last column of Table I which gives a rough approximation to the transmission, for radiation from a similar arc, of the vapor along a radius of the tube. These are data obtained on the tube without argon when it was operated at 4 amperes and 500 mm pressure. The values for the shorter wave-lengths are too low because the over-all transmission was divided by the transmission of the window at room temperature, instead of its transmission at operating temperature. The transmissions for all the lines of wave-lengths less than 2482A, except perhaps for λ2378, probably should be between 0.90 and 1.00.

tions for continuous radiation included in the measurements were made by subtracting from the deflection at the line setting the average of the deflections given by the continuous radiation and weak lines on the two sides of the line setting. These corrections were 70 to 85 percent of the original deflection for λ's 2576, 6234, 6716 and 7087, about 55 percent for λ2259 and less than 50 percent for all other lines.

In many cases several lines were included in a single measurement. Table I lists these lines, together with the corresponding transitions. The designations for the levels are those used by Bacher and Goudsmit.[5] The order of listing the terms corresponds to designation of term values as positive with respect to the ground state, as recommended by Condon and Shortley.[6]

The values in Table I represent radiation from the full width of the arc. Table II gives the intensity per unit area, treating the arc as if it were a flat emitting surface, for points at different distances from the axial plane of the arc which is parallel to the axis of the optical system. These data were obtained on the tubes containing argon and were corrected for absorption of the tube wall and of the vapor in the same manner as the data of Table I. They represent the summation of the radiation emitted along a diameter or some other chord of the tube.

Discussion

Table II shows the variation in intensity across a projected image of the positive column. However, this variation is roughly the same[7] as the variation along a radius of the amount of radiation emitted per unit of volume. To this degree of approximation, the data of Table II will represent the relative intensity of emission per unit volume at the axis of the arc and at different distances from the axis. If the laws governing the excitation of mercury atoms and the subsequent emission of radiation were known, the spectral distribution of the emitted radiation would indicate the distribution of electron velocities at these same points. If these velocity distributions are Maxwellian, they may be described completely by assigning an electron temperature to each of them.

If there is "natural excitation," i.e., if the concentrations of atoms in all the states[8] of a given level are equal, the emitted radiation is isotropic. If, in addition, the population of the lower level for a given line is so low that self-absorption may be neglected, the intensity (per steradian) of the line due to all transitions from level A to level B is given by

$$J_{AB}=(16\pi^3c/3\lambda^4)N_AS_{AB} \tag{1}$$

in which N_A = concentration of atoms in each state of the upper level, c = velocity of light, λ = wave-length of emitted radiation, S = strength of line, as defined by Condon and Shortley (reference 6, p. 98).

The intensity (per steradian) of a spectral line, expressed in terms of the oscillator strength f used in dispersion theory, is[9]

$$J_{AB}=(2\pi he^2/\mu\lambda^3)(2j_A+1)N_Af_{AB} \tag{2}$$

where h = Planck's constant, e = electronic charge, μ = mass of electron, j = inner quantum number.

We shall introduce the quantity

$$\varphi_{AB}\equiv(2j_A+1)f_{AB}.$$

Then
$$J_{AB}=(2\pi he^2/\mu\lambda^3)N_A\varphi_{AB}. \tag{3}$$

It is customary to assume that, within a multiplet, the "line strengths" S are proportional to the *a priori* probabilities of Kronig[10] for the corresponding transitions. In the article immediately following this one, reasons are given for assuming that φ_{AB} is proportional to the Kronig factors divided by some function of

Table III. *Relative a priori probabilities of transition in a two-electron atom.*

	$^1S_0$	$^1D_2$		
$^1P_1$	12	120		
	$^3S_1$	$^3D_1$	$^3D_2$	$^3D_3$
$^3P_0$	4	40		
$^3P_1$	12	30	90	
$^3P_2$	20	2	30	168

[5] *Atomic Energy States* (McGraw-Hill Co., New York, 1932).

[6] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 5.

[7] See article immediately following this one. Also, W. Elenbaas, Physica **1**, 680 (1934).

[8] The nomenclature is that used by Condon and Shortley; see reference 6, page 97–8.

[9] See reference 6, page 108.

[10] Kronig, Zeits. f. Physik **33**, 261 (1925). See Table III of the present article for the Kronig probabilities for Hg.

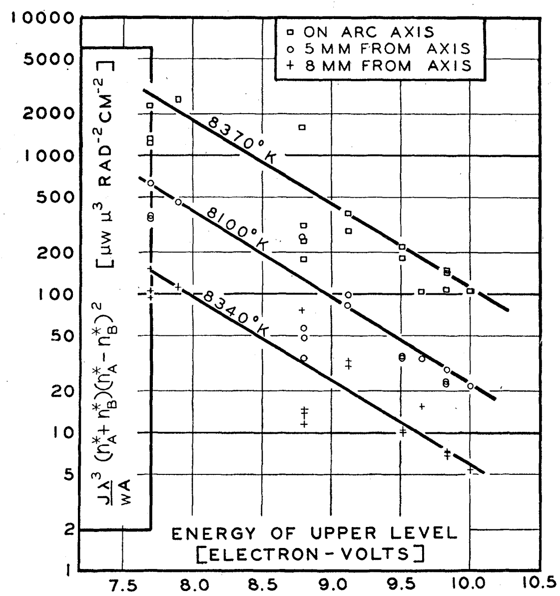

FIG. 2. Boltzmann plots of radiant intensity per unit of projected area at three different distances from arc axis for tubes containing argon. Each point represents a spectral line. (See Table IV.) Arc current 4.0 amperes; vapor pressure 450 mm. Ordinate is microwatts per steradian per cm² multiplied by cube of wave-length in microns and by indicated function of effective quantum numbers, and divided by *a priori* probability of transition as given by Kronig. Abscissa is energy, with respect to 6^1S_0, of upper level for corresponding transition. The computed electron temperature is written above each straight line.

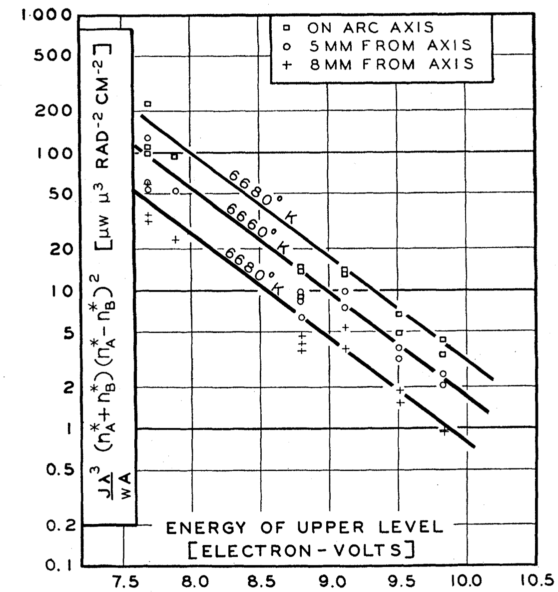

FIG. 3. Boltzmann plots of radiant intensity per unit of projected area at three different distances from arc axis for tubes containing argon. Arc current 4.0 amperes; vapor pressure 20 mm. Coordinates as in Fig. 2.

the effective quantum numbers of the upper and lower levels.

In case there is a Boltzmann equilibrium between electronic and atomic energies in an element of volume, then the concentration of atoms excited to state A would be

$$N_A = N_0 e^{-\epsilon V_A/kT} \tag{4}$$

in which N_0 = concentration of atoms in ground state, ϵV_A = energy of excited state A with respect to ground level, k = Boltzmann constant, T = electron temperature. Since each level of the atom is composed of $2j+1$ states, the total population in the level is $(2j+1)N$.

Equations (3) and (4) give, for the case of a Boltzmann equilibrium and negligible self-absorption, $J\lambda^3 \propto \varphi e^{-\epsilon V/kT}$ or

$$\ln (J\lambda^3/\varphi) = \text{const.} - \epsilon V/kT. \tag{5}$$

in this case, if $\log (J\lambda^3/\varphi)$ be plotted against ϵV, the points lie on a straight line, whose slopes is a measure of the electron temperature.

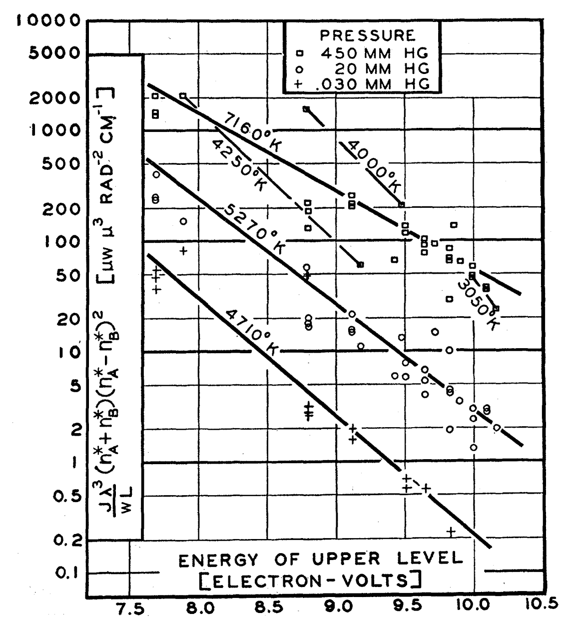

FIG. 4. Boltzmann plots of radiant intensity per unit length of arc for three different vapor pressures for tubes containing argon. Arc current 4.0 amperes. Ordinate is microwatts per steradian per cm of arc multiplied by cube of wave-length in microns and by indicated function of effective quantum numbers, and divided by *a priori* probability of transition as given by Kronig.

It is obviously impossible to isolate the radiation from an element of volume over which N_0

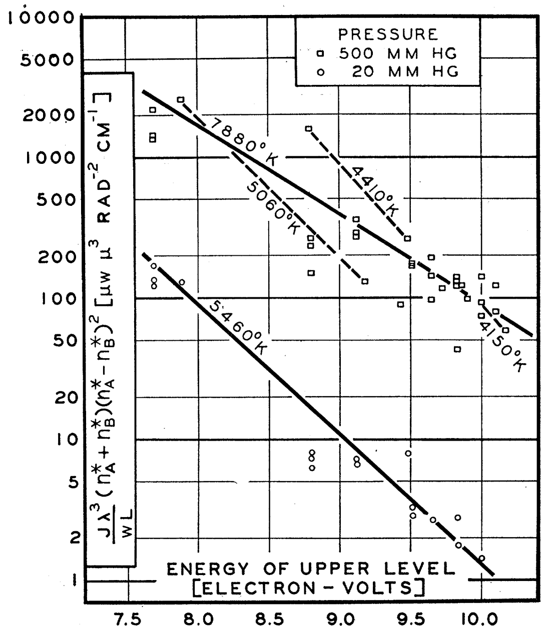

FIG. 5. Boltzmann plots of radiant intensity per unit length of arc at two different vapor pressures for tube without argon. Arc current 4.0 amperes. Ordinates as in Fig. 4.

and T are certainly constant. However, if there were a Boltzmann equilibrium at each point in the arc and if the values of φ were known for all the lines, the data of Table II would serve to give values of T which would not be much less than the maxima for the portions of the discharge concerned. This is true because the intensity of the radiation of a given wave-length would vary with T as

$$e^{-\epsilon V/kT}/N_0.$$

(N_0 probably would not vary much faster than the reciprocal of T. Hence the effect of the exponential would predominate and most of the radiation would come from portions of the discharge for which T is near its maximum value.)

Since the "transition strength" φ is not known for any mercury line except λ2537 and λ1849, Eq. (5) cannot be used to test for the existence of a Boltzmann equilibrium in a mercury arc. However, one may take plausible values for φ and see whether a semi-logarithmic plot corresponding to (5) gives a linear arrangement of points and a reasonable value of electron temperature. We shall asume that

$$\varphi_{AB} \propto w_{AB}/[(n_A^*+n_B^*)(n_A^*-n_B^*)^2],$$

where w_{AB} is the Kronig *a priori* probability of transition from level A to level B, as given in Table III; n_A^* and n_B^* are the effective quantum numbers of A and B, respectively. Figs. 2 and 3 give the plots, on this basis, of the data of Table II for 450 and 20 mm mercury vapor pressure, respectively. A straight line has been drawn among each set of points on Figs. 2 and 3. The electron temperature corresponding to the slope is given above each of these lines.

Figs. 2 and 3 show that the spectral distributions of the radiation from different portions of the arc are approximately the same. Since this is the case, there is theoretical justification for making a similar plot for the radiation from the entire width of the arc. Fig. 4 is a plot of the data of Table I for the tubes containing argon. This table is more accurate and includes more lines than Table II. The data for a mercury vapor pressure of 0.030 mm are included in Fig. 4 although a Boltzmann equilibrium is not ex-

TABLE IV. *Lines due to downward transitions from a given level of the mercury atom. Lines in parentheses not measured. Lines in brackets not included in Boltzmann plots.*

Upper Level	7^3S_1	7^1S_0	7^3P_2	6^3D	8^3S_1	8^1S_0	8^3P_{01}	8^3P_2	7^3D*
Energy (Electron-Volts)	7.69	7.89	8.78	8.80	9.12	9.18	9.43	9.48	9.51
Lines	4047	10140	11289	3650–63	2753	4916	7082–92	6907	3021–28
Lines	5461	[4078]		3125–32	3341				2652–55
Lines	4358			2967	2894				(2535)
Lines				[5770–91]					
Upper Level	9^3S_1	8^1P_1	$8D$	9^1P_1	10^3S_1	9^3D*	10^3D*	11^3D*	
Energy (Electron-Volts)	9.65	9.72	9.83	9.86	9.90	10.0	10.1	10.17	
Lines	2464	6716	2378	6234	2447	2302	2259	2323–24	
Lines	2576		2482–84			2399–2401	2352–53		
Lines	2925		2803–07			2699–2701	(2640)		
Lines			3906						

* Intercombination line from corresponding $^1D_2$ level included.

pected at this pressure. However, the average deviation of the points from a straight line is hardly as great as that of the corresponding points for either 450 mm or 20 mm pressure.

The electron temperatures indicated by the solid lines drawn among the points in the upper two plots on Fig. 4 should be approximately equal to the weighted mean of the electron temperatures indicated by the straight lines on Figs. 2 and 3, respectively. This is not the case. The discrepancies are too large to ascribe to differences between discharge conditions on successive runs. A detailed examination indicated that unintentional differences in the procedures used for correcting for absorption, for taking a weighted mean of the data for the two tubes used for the high pressure runs, and for drawing representative straight lines among the widely divergent points might account for much of the discrepancy.

The solid lines were drawn among the points on Fig. 4 in the same manner as on Figs. 2 and 3. The dashed lines connect points corresponding to transitions having the same lower level and having upper levels differing only in total quantum number. The significance of the electron temperatures indicated by these dashed lines is discussed in the article immediately following this one.

Figure 5 is a plot, on the same basis as Fig. 4, of the data in Table I for the tube without argon. The solid and dashed lines were drawn as on Fig. 4. The points on this plot for a pressure of 500 mm may be identified by means of Table IV. The lines in each multiplet are listed in the order in which they appear on the graph, the uppermost point on the graph corresponding to the line listed first in the table. Table IV does not serve to identify points on the other plots, except for the cases where only one line is listed for each upper level.

In each plot on Figs. 2 to 5, the points for the lines in a multiplet have a much greater spread than is to be expected from errors in intensity measurements. (The deviation caused by 5 percent error would be barely perceptible.) Consequently, either the assumptions concerning transition strengths are incorrect or the proper correction for absorption was not made. Since the highest point for a multiplet is generally that

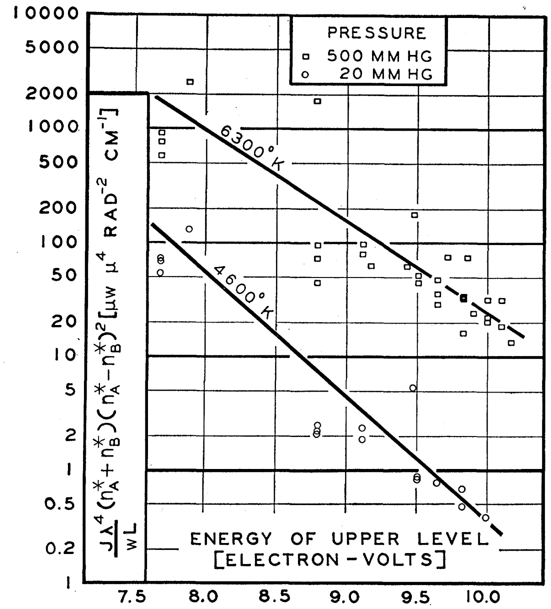

FIG. 6. Plots as in Fig. 5 except that intensities are multiplied by λ^4 instead of λ^3.

for the component with the least self-absorption, the correction for absorption may have been too small. To allow for this possibility, the straight lines on Figs. 2 to 5 were drawn somewhat above the points for strongly absorbed triplets.

The large deviation of points for certain transitions from the corresponding straight lines in Figs. 2 to 5 suggests that either a Boltzmann equilibrium does not exist or the transition strengths are not proportional to $w/[(n_A^*+n_B^*)\cdot(n_A^*-n_B^*)^2]$. Two other formulas for transition strength were tested out. For the data plotted in the upper part of Fig. 5, the expression $\varphi=w/(n_A^*-n_B^*)^3$ gave a plot with about the same spread of points as Fig. 5. The point for λ11289 came much nearer to the straight line drawn among the other points, but the points for λ's 7087, 4916, and 3906 were further from the straight line than in Fig. 5. The straight line drawn on this plot indicated an electron temperature of 14,500°K. Since an electron temperature of the order of 6000°K is sufficient to account for measured line breadths[11] and for the electrical characteristics of the arc, a temperature of nearly 15,000°K appears improbable.

[11] See article immediately following this one.

For the data plotted in Fig. 4, the formula $\varphi = w$ gave plots with a greater spread of points than those in Fig. 4. The electron temperature indicated by a representative straight line drawn among the points on the plot for 450 mm pressure would be less than 3800°K. This is too low to account for measured line breadths or for the electrical characteristics of the arc.

Although we believe that it is incorrect to identify the "line strength" S with the *a priori* probability of transition, we have made some Boltzmann plots on this basis. From Eq. (1)

$$\log (J\lambda^4/S) = \text{const.} - \epsilon V/kT. \quad (6)$$

Fig. 6 is a plot of the data in Table I for 500 mm Hg pressure, in which Eq. (6) is used and it is assumed that $S = w/[(n_A^* + n_B^*)(n_A^* - n_B^*)^2]$. The only difference between Figs. 6 and 5 is that intensities are multiplied by λ^4 in the one case and λ^3 in the other. Since the points of wavelengths less than 2967A are all on the right hand side of the plot, multiplication of intensities by λ^4 instead of λ^3 reduces the electron temperature indicated by a straight line drawn among the points. It also makes the points for λ10140 and λ11289 come considerably above the general level of the other points. Otherwise, the spread of the points is much the same on the two plots.

Plots based on Eq. (6), using for the line strength S the formulas $w/[n_A^* n_B^* (n_A^* - n_B^*)^2]$, $w/(n_A^* n_B^*)^3$, w/n_A^{*3} and w alone, all showed greater spreads of points than Fig. 6. The same was true of plots using w/n_A^3 and $w/(n_A n_B)^3$, where n_A and n_B are the total quantum numbers of the upper and lower states, respectively. The electron temperatures given by straight lines drawn on these plots among the points for 500 mm pressure ranged from about 6500°K for the plot using $S = w/[n_A^* n_B^* (n_A^* - n_B^*)^2]$ to approximately 3000°K for the plot using $S = w$. Since the criteria used in drawing these straight lines (assumption that λ10140 and λ11289 points are too high and points for strongly absorbed lines are too low) are questionable, the electron temperatures obtained from their slopes are of no value except for rough comparisons.

Since certain points on each Boltzmann plot deviated from the straight lines by amounts equal to many times the errors in intensity measurements, we conclude that either (1) a Boltzmann equilibrium does not exist, or (2) none of the formulas used for transition probability are even approximately correct, or (3) the absorption losses for the strongest lines range from 90 to 95 percent instead of the experimental values of 30 to 50 percent. Although alternative (2) or (3) may be true, it seems proper to inquire whether a Boltzmann equilibrium should exist in a four-ampere mercury arc, even with a pressure as high as 500 mm. A Boltzmann equilibrium cannot be set up between the excited levels of an atom unless the total rate of downward transitions from each level is many times the total rate of radiation of quanta in the spectral lines corresponding to these transitions. Consequently, the probability of excitation to the level must far exceed the probability of radiative transition from it. This can be true only if there is a high concentration of electrons of sufficient velocity for exciting to the level or if there is no "permitted" radiative transition from the level. The latter case need not be considered here because the populations in levels above 6^3P_2 are our chief concern. The question as to the sufficiency of the supply of electrons cannot be answered without a knowledge of the electron temperature and the transition probabilities for all the processes under consideration. However, a study of other discharges in which a Boltzmann equilibrium seems to exist may indicate whether such an equilibrium in a mercury discharge is equally probable.

Populations in excited states corresponding approximately to a Boltzmann equilibrium have been reported[12] for a neon discharge. Here the energy required to excite an atom from the ground level directly to the highest level under consideration was only 14 percent greater than that for the lowest excited level. In the mercury atom, the energy required for direct excitation to the 7^3S_1 level is 65 percent greater than that for excitation to the 6^3P_0 level; the energy for direct excitation to the $8D$ levels is 2.11 times that for the 6^3P_0 level. This relatively greater spacing of the excited levels in Hg may make establishment of a Boltzmann equilibrium relatively more difficult than in a similar Ne discharge. Furthermore, the electron temperature

[12] H. Kopfermann and R. Ladenburg, Naturwiss. **19**, 513 (1931).

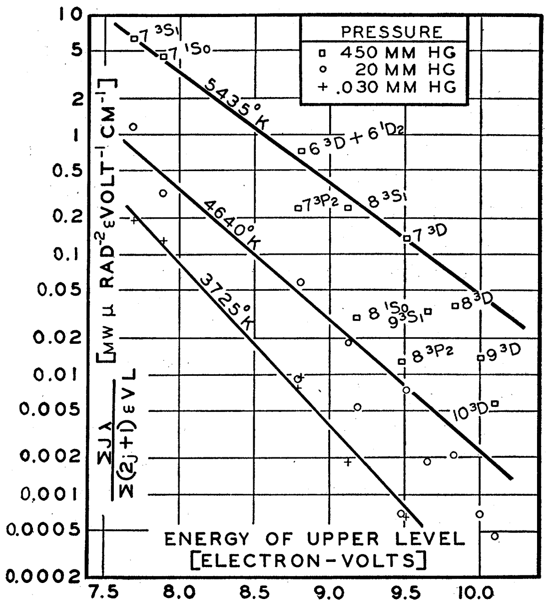

FIG. 7. "Excitation" plots of radiant intensity per unit length of arc for three different vapor pressures for tubes containing argon. Arc current 4.0 amperes. Ordinate is sum, for all downward transitions from a level or group of levels, of the milliwatts per steradian per cm of arc times wavelength in microns, divided by energy in electron-volts and by *a priori* probability of level or group. Designation of level or group of levels is given for upper set of points.

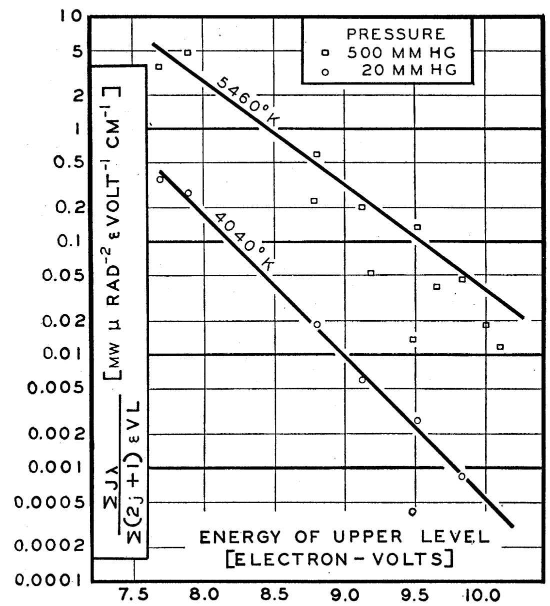

FIG. 8. "Excitation" plot of radiant intensity per unit length of arc at two different vapor pressures for tube without argon. Arc current 4.0 amperes. Ordinates as in Fig. 7.

values (18,000–20,000°K) obtained by Kopfermann and Ladenburg[12] for a neon discharge at 0.7 amp. and 1 mm pressure are much higher than that indicated by Fig. 5 for a 4 amp. Hg arc at 500 mm pressure. This partially offsets the higher excitation energies required for neon atoms. On the other hand, the higher pressure and current density favor the establishment of a Boltzmann equilibrium in the mercury arc mentioned above.

In the case of a carbon arc burning in air the spectral distribution within the CN band at 3883A indicates a Boltzmann equilibrium among the corresponding upper levels. It is possible that this equilibrium exists only between these closely spaced levels, not between all the levels of the CN molecule. This would probably be true if the mechanism for establishing equilibrium is most effective when the amounts of energy to be transferred are small.

Since spectral intensity data for a mercury discharge do not fit well on any of the Boltzmann plots that we have made, it seems proper to inquire whether some other type of plot would be more suitable. If radiation is the major factor in dissipating the energy of excited states, line intensities may be quite different from those obtaining in a Boltzmann equilibrium. For example, if all downward transitions were radiative, transition probabilities would determine only the relative intensities of different lines from the same upper level; line intensities would be determined primarily by the rate of excitation to the upper level concerned. If this rate is proportional[13] to $(2j+1)$ times the number of collisions between unexcited atoms and electrons with energies which do not differ by more than a certain amount from the energy required for excitation, and if the distribution of electron velocities is Maxwellian,[14] then the total rate of transitions from a given upper level will be

[13] This is a reasonable assumption provided that the supply of electrons of the proper velocities is not unduly diminished by the excitation which takes place. Subsequent collisions of the second kind which transfer the excitation to another level with approximately the same energy (within 0.01 electron-volt) need not concern us because, in the following discussion, the rates of transition from such levels are all added together before any plot of the data is made.

[14] A Maxwellian distribution of electron velocities usually exists in the positive column of an arc. See I. Langmuir and K. T. Compton, Rev. Mod. Phys. 2, 222 (1930).

proportional to $(2j+1)\epsilon V e^{-\epsilon V/kT}$. The factor $(2j+1)$ takes account of the $2j+1$ states in each level.

$$\text{Then}\quad \log_{10}\sum J\lambda/[(2j+1)\epsilon V]=C-(5040/T)\,\epsilon V,$$

where λ is the wave-length and J the intensity of a given line. The summation is made for all the transitions from a given upper level. C is a constant for a given set of discharge conditions and ϵV is the energy of the upper level with respect to the ground level (or any other level, if C is changed to correspond). Thus, a semi-logarithmic plot of $\Sigma J\lambda/[(2j+1)\epsilon V]$ against ϵV would give a straight line whose slope would be a measure of the electron temperature, T. For brevity, such plots will be called "excitation" plots.

If all downward transitions are radiative and if radiative transitions from an excited level are much more probable than excitation to a still higher level, absorption of radiation in the vapor will have little net effect on the number of emitted quanta due to transitions from a given level. Consequently no correction should be made for absorption in the vapor. Elimination of the correction for the absorption of the vapor from all the data of Tables I and II was not possible. However, data on the transmission of the thin window when cold were available in most cases. These were used to correct the measured intensities, although the correction was doubtless too small in the far ultraviolet because hot glass has a greater absorption than cold. A plot of the energy per centimeter of arc, received from the entire width of the arc, is given in Fig. 7 for the tubes containing argon, and in Fig. 8 for the tube without argon.

The points on the graphs and the lines used for obtaining the plotted values may be identified by referring to Table IV. The designation of the upper level for each group of radiative transitions is indicated on Fig. 7 opposite the points for the highest pressure. In cases where lines due to transitions from several neighboring levels are included in one intensity measurement, the sum of the $J\lambda$'s for all the lines due to transitions from the group of levels is divided by $\Sigma(2j+1)$. When one of the lines of a triplet was not measured or not separated from a much stronger line (for example, λ2535), the summation was completed by assuming the relative intensities within the triplet to be proportional to $w/[\lambda^3(n_A^*+n_B^*)\cdot(n_A^*-n_B^*)^2]$, where w is the *a priori* probability of a transition as given by Table III.

The points for some of the weaker lines are further from the straight lines in Figs. 7 and 8 than in Figs. 4 and 5. On the other hand, the points for λ11289 lie nearer to the corresponding straight lines in Figs. 7 and 8 than in Figs. 4 and 5. Except for the data for λ11289, the points for the principal transitions from levels less than 9.8 electron volts above the ground level lie fairly near to the straight lines in Figs. 7 and 8. The deviations of the points representing transitions from the 8^1S_0, 8^3P_2, 9^3S_1 and the 8^3D to 10^3D levels are discussed in the article immediately following this one.

Conclusions

1. The electron temperature in a mercury arc varies little with distance from the arc axis. This is in disagreement with Elenbaas' theory of the mechanism of a high pressure mercury arc.

2. A decrease of electron temperature with decreasing mercury vapor pressure appears to be well established, regardless of the theoretical basis for plotting the intensity data.

3. The existence of a Boltzmann equilibrium in a high pressure mercury arc cannot be proved or disproved at present because the probability of a radiative transition from one level to another is not known as yet.

4. Various arbitrary but more or less plausible formulas for transition probability were tried out. None of them made the points on a Boltzmann plot lie on a straight line.

5. On Boltzmann plots, the points for strongly absorbed lines generally fall below a straight line drawn among the points for weakly absorbed lines. While this may be due to incorrect formulas for transition probabilities, it may indicate that the correction for absorption was too low. This is to be expected whenever a line is reversed in the arc used as a source for absorption measurements.

6. "Excitation" plots, based on the assumption that nearly all downward transitions are radiative, showed deviations of the points from

representative straight lines. These deviations were of the same order of magnitude as those on the best Boltzmann plots. The latter plots are based on the assumption that relatively few downward transitions are radiative and that the probabilities of radiative transition are proportional to $w_{AB}/[\lambda^2(n_A^*+n_B^*)(n_A^*-n_B^*)^2]$ where w_{AB} is the Kronig *a priori* probability, n_A^* and n_B^* are the effective quantum numbers of the upper and lower levels, and λ is the wave-length of the emitted radiation.

7. Representative straight lines drawn among the points on the Boltzmann plots described above gave electron temperatures of 7160 and 7880°K for mercury vapor pressures of 450 and 500 mm, respectively. Similar lines on the corresponding "excitation" plots gave electron temperatures of 5435 and 5460°K, respectively. Line breadth measurements and theoretical calculations set forth in the paper immediately following this one indicate that the electron temperature is at least 6000°K at these two pressures. The electron temperatures indicated by the "excitation" plots agree with this computed minimum value within the limits of uncertainty set by the scatter of the points on these plots. The electron temperatures indicated by the Boltzmann plots are not impossible, but are much higher than is required by the measured line breadths and the electrical characteristics of the arc. This conclusion is contingent on the formula chosen for transition probabilities.

8. Since neither excitation probabilities nor the probabilities of downward transitions are known, no quantitative basis is available for choosing between the hypothesis of a Boltzmann equilibrium and the hypothesis of an excitation-radiation balance.

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The Mechanism of the Positive Column in Mercury Vapor at Intermediate Pressures

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Calculations based on the radiant intensity for the principal spectral lines of 4-ampere mercury arcs at 450 mm and 500 mm (Hg) pressure, indicate for low quantum states a dynamic equilibrium with electrons at approximately 6000°K, the temperature indicated by the absolute spectral intensity for three reversed lines. For high quantum states differing only in total quantum number, there appears to be a tendency toward Boltzmann equilibrium due to collision with normal atoms at approximately the temperature (2500°K) calculated from the heat balance by Langmuir's theory of conduction and convection in gases. This agrees with predictions from the principle of *spectroscopic stability*.

THE electric discharge[1] in the inert gases or in mercury vapor offers the advantage of a relatively simple system: a single molecular species[2] with no rotational energy, and incapable of any other dissociation than that into electrons and positive ions. Yet even this simple system is effectively a system of three components, atoms, ions, and electrons, present in different concentrations, and obeying different laws of motion.

The fact that some of the atoms are excited will have no material influence on the mechanical behavior of the gas, since the mass of the atom is not altered appreciably, and since collision of the second kind, whether between atoms or between an atom and a positive ion, will rarely have any other effect than an exchange of roles.[3] Collisions

[1] The discharge in mercury at atmospheric pressure is customarily referred to as a mercury arc. By Ornstein and Brinkman's definition (Physica **1**, 797 (1934)) it is a high pressure glow discharge, if, as we now believe, the electron temperature is significantly higher than the gas temperature.

[2] Mercury molecules and molecule ions are present in the discharge and may play an essential role, but in concentrations which will not affect significantly the mechanical and thermal properties of the vapor. Energy of electron excitation or spin is not ordinarily called "rotational energy."

[3] See, however, section on "Collision with Normal Atoms."