THE INTENSITIES OF THE LINES IN THE SPECTRUM OF MERCURY

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Abstract

Number of quanta emitted per atom.—The total radiation, measured with a thermocouple, in the spectral region 6000 to 2300A from a small quartz mercury lamp of known size filled with mercury vapor at a known pressure was 1.85×10^{-10} ergs per atom per sec. From this and the intensities of the lines it came out that each atom on the average emitted each second 11.4, 8.9, 5.0, 2.3, etc., quanta of yellow, green, blue, violet, etc., light, respectively.

The intensities of the lines.—The intensities of twenty-four lines of the spectrum were measured with a quartz spectrograph, a thermocouple and a photoelectric cell, all calibrated, and in some cases with a photographic densitometer. Plotting the logarithm of the intensity against the frequency for the lines of a series gave roughly straight lines of about the same slope for the sharp series ($2^3P_n - m^3S_1$) and for the diffuse series ($2^3P_n - m^3D_{123}$). The temperatures of the excited atoms derived from the slopes were 3900° and 2600° Kelvin for the sharp and diffuse series, respectively.

THE intensities of twenty-four lines of the mercury spectrum in the region λ6000 to 2300A have been measured in order to find the intensity relationship among the lines of a series. Earlier measurements[1] were not sufficiently extensive for this purpose. The present experiments have led to the conclusion that the distribution of energy among the lines was as if the temperatures of the excited atoms were several thousand degrees.

A quartz mercury lamp, Fig. 1, was filled with mercury and maintained at a pressure of 1.3 atmospheres. Current was introduced by means of the electrodes A and D. The section BC, 4.5 cm in length and of internal diameter 0.4 cm was heated by a flame or a hot wire until the mercury vaporized and

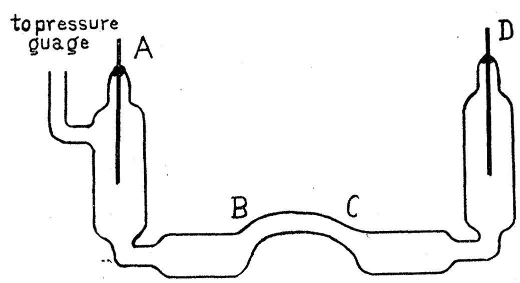

Fig. 1. Quartz mercury lamp.

the arc started. Once started, the heating element was removed and the arc burned steadily and brightly. With 5 amperes direct current and 130 volts in the lamp the surface brightness was 500 times or more that of the "Lab Arc."

[1] See Harrison and Forbes, Journn. Opt. Soc. of Amer. **10**, 1 (1925), and references *infra*.

The number of quanta emitted per atom. The energy radiated from the mercury lamp was measured with a thermopile and galvanometer which had been calibrated with a tungsten lamp in a manner described in a former paper.[2] A galvanometer deflection of 1 mm meant an energy flux of 9.7 erg cm^{-2} falling on the thermopile. By means of a diaphragm with a hole in it the radiation from a section of the mercury arc 4 mm in length was allowed to fall upon the thermopile, which was 240 cm away and in a box with a quartz window to protect it from air currents. The galvanometer deflection was 80 mm when the pressure in the arc was 1.3 atmospheres and the power was 650 watts (5 amperes and 130 volts). By the use of calibrated absorbing screens it was found that 0.275 of the energy radiated from the arc and received by the thermopile with the quartz window was in the spectral region 2300 to 6500A. Assuming that the 4 mm section of the mercury lamp was a point source the total energy in this spectral region radiated in all directions from the section of the lamp was

$$4\pi \times 240^2 \times 80 \times 9.7 \times 0.275 = 1.54 \times 10^8 \text{ erg sec}^{-1}.$$

Taking the temperature of the mercury vapor to be 546° Kelvin the number of atoms in the lamp section was 8.33×10^{17}. Therefore the energy in the spectral region 2300 to 6500A radiated per atom per second was $1.54 \times 10^8 \div 8.33 \times 10^{17} = 1.85 \times 10^{-10}$ erg. When the pressure was increased to 2, 2.5 and 3.5 atmospheres, maintaining the power always at the constant value 650 watts, the ergs radiated per atom per sec. were 1.8, 1.6 and 1.3×10^{-10}, respectively (assuming the temperature to be 546° Kelvin at all times). Thus the energy radiated per atom was roughly constant as the pressure was increased over a small range, other factors remaining constant, and the energy radiated from the section of the lamp increased linearly with the pressure.

Since the relative intensities of the lines in the spectrum from 2500 to 6500A were known (as described in later paragraphs) the energy 1.85×10^{-10} erg sec^{-1} $atom^{-1}$ may be divided among the various spectrum lines according to their intensities in order to determine the number of quanta emitted per atom per second. It came out that on the average each atom emitted each second 11.4 quanta of yellow light (5790 and 5770A), 8.9 quanta of green light (5461A), 5.0 quanta of blue light (4358A), 2.3 quanta of violet light (4077 and 4047A), 6.8 quanta in the group of ultra-violet line at 3660A, etc. It may be recalled that the number of quanta per atom per second emitted in the stronger Balmer lines of hydrogen was found to be of unit order.[2] It is perhaps not at all surprising that the numbers of quanta of the more intense mercury lines were again roughly of unit order, because the densities of the atoms in the mercury discharge were an order of magnitude or so greater than in the hydrogen discharge and spectroscopic experience showed that the prominent mercury lines were somewhat more intense than the prominent hydrogen lines.

The intensities of the lines. Spectrograms of the mercury arc are given in Fig. 2. The diffuse series lines were broadened by the high pressure and

[2] Crew and Hulburt, Phys. Rev. **29**, 843 (1927).

current conditions in the mercury vapor, and a fairly strong continuous spectrum appeared in the region 2800 to 2500A. The exposure in the second strip of Fig. 2 was not long enough to show the continuous background

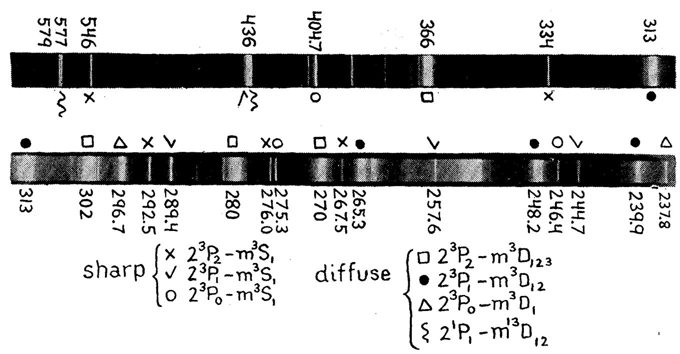

Fig. 2. Spectra of quartz mercury arc.

clearly. The light of the mercury arc was focussed by a concave mirror, of platinum cathodically deposited on glass, on to the slit of a quartz spectrograph (Hilger, Type D33). The spectral energy curve, given in Fig. 3, was measured with a thermocouple and galvanometer, the thermocouple being placed behind the second slit of the spectrograph. The curve of Fig. 3, which gives the true spectral energy distribution, was obtained by correcting the galvanometer deflections for the reflecting power of platinum and the calculated transmission of the spectrograph at each wave-length. The

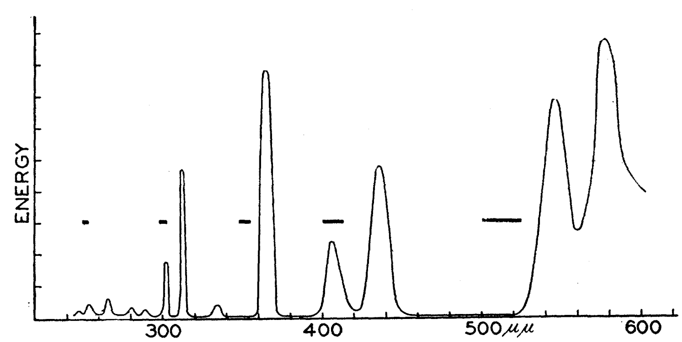

Fig. 3. The true distribution of energy in the mercury spectrum determined with the thermopile. The black marks give the spectral impurity due to the finite width of the slits of the spectrograph.

impurity of the spectrum, obtained by adding together the widths of the two slits in angstrom units, for various wave-lengths is shown by the heavy black marks in Fig. 3. It is seen that the curves of the mercury lines, or line groups, are as wide as these black marks. This is as it should be for slits which are wider than the lines, and hence no slit-width correction was necessary.

A sodium hydride quartz photoelectric cell, connected to a quadrant electrometer, was placed behind the second slit of the spectrograph. Either the cell or the thermocouple could be moved into position behind the slit. Readings with the cell and the thermocouple in turn for the strong mercury lines gave the sensitivity curve of the photoelectric cell, Fig. 4: again, as in Fig. 3, the heavy black marks in Fig. 4 give the spectrum impurity due to the finite width of the slits. This curve was used thenceforth in reducing the electrometer readings to relative energy values. Because of the relatively low values of the sensitivity of the cell and of the intensities of the mercury lines in the wave-length region below 3000A there was an appreciable effect of scattered light in this region. This was carefully determined by observations with a glass absorbing screen which was opaque to wave-lengths below 3000A.

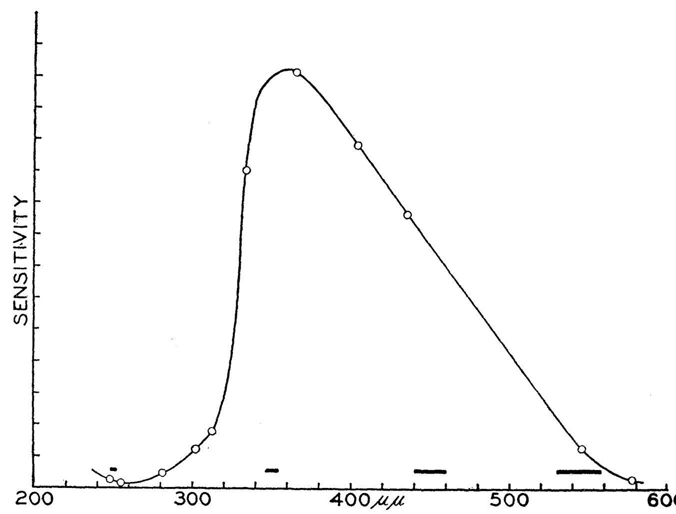

Fig. 4. The sensitivity curve of the sodium hydride quartz photoelectric cell.

In Fig. 5 is given the true energy spectrum of the mercury light for the shorter wave-lengths obtained with the photoelectric cell. The portion of the energy due to scattered light is in the area below the straight dotted line. The curved dotted line which is drawn touching the valleys of the energy curve was taken to represent the energy of the continuous spectrum. The energy in each line was obtained from the area of each peak above the continuous spectrum curve. The two black marks give the impurity of the spectrum. The lines were for the most part narrower than the spectral impurity due to the width of the slits, and no slit-width correction was made. For the lines varied greatly in their characteristics, being narrow, diffuse, complex, etc., as seen in Fig. 2, and it was thought that a slit correction might perhaps have introduced as many errors as it eliminated. As a matter of fact the valleys between the peaks should perhaps be deeper, they are too shallow because of the effect of the slit width. Therefore too much energy has been ascribed to the continuous spectrum and not enough to the peaks. This systematic error is probably, compensated, partially at leaste by the method of using the area under the peak to give th relative intensity of the line, a method which becomes erroneous in the case for which the line is narrower than the slits.

In Table I are given the intensities in ergs emitted per atom per second of twenty-four lines or line groups. Seventeen of these came directly from Figs. 3 and 5, the seven others required special treatment. The line 4046 was resolved from its neighbor 4077 by means of the photoelectric cell and spectrograph with narrowed slits. The intensities of the lines 2752, 2759, 2464, 2446 and 2675 were determined by means of calibrated recording densitometer curves of photographic spectrograms. The combined

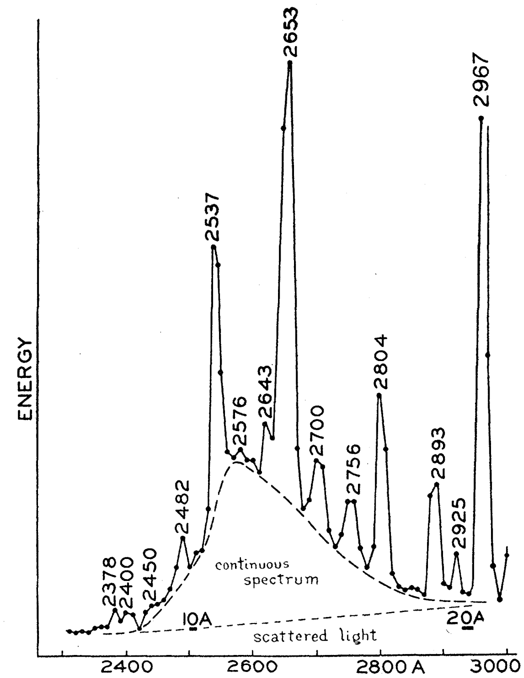

Fig. 5. The true distribution of energy in the shorter wave-length region of the mercury spectrum determined with the photoelectric cell.

TABLE I. *Intensities of mercury lines.*

Series	m	Wave-length (ang-stroms)	Energy (ergs atom^{-1} sec^{-1})	Series	m	Wave-length (ang-stroms)	Energy (ergs atom^{-1} sec^{-1})
					3,4	5790	40.9
	2	4046	9.80×10^{-12}	$2^1P_1-m^1D_1$		5770	
$2^3P_0-m^3S_1$	3	2752	0.146		4,5	4347	
	4	2464	0.024	$2^1P_1-m^3D_2$		4339	2.0
	2	4358	20.3				
$2^3P_1-m^3S_1$	3	2893	0.244		3	2967	2.1
	4	2576	0.023	$2^3P_0-m^3D_1$	4	2534	—
	5	2446	0.016		5	2378	0.032
	2	5460	32.2				
	3	3341	1.86		3	3131	22.0
$2^3P_2-m^3S_1$	4	2925	0.68	$2^3P_1-m^3D_{12}$	4	2653	1.16
	5	2759	0.056		5	2482	0.086
	6	2675	0.007		6	2399	0.054
					3	3663	36.4
				$2^3P_2-m^3D_{1,2,3}$	4	3025	6.3
					5	2805	0.45
					6	2699	0.20

intensity of the two yellow lines is given in the table, their separate intensities were not determined (they seemed to be of about equal intensity). The combined intensity of the second members (4347 and 4339) of their respective series was determined with the recording densitometer; the two lines were much weaker than their companion 4358. The values, given in Table I as ergs emitted per atom per second, were obtained by dividing up the total emitted energy 1.85×10^{-10} erg atom^{-1} sec^{-1} among the lines and the continuous spectrum according to their relative energies.

Temperatures of the excited atoms. If there is a sort of temperature equilibrium in the mercury arc the number of atoms excited from an energy E_0 to an energy E will be proportional to the Boltzmann factor $\epsilon^{-(E-E_0)/KT}$, where K is the molecular gas constant and T is the temperature of the excited atoms. Writing $hc\nu$ for $E-E_0$, the intensity i of radiation of wave-number ν (frequency $c\nu$) is

$$i=a\epsilon^{-hc\nu/KT}, \tag{1}$$

where a represents the various probabilities of state and of transition. If a is a constant for the lines of a series the logarithm of the intensity of a line plotted against the wave-number should be a straight line for the series.

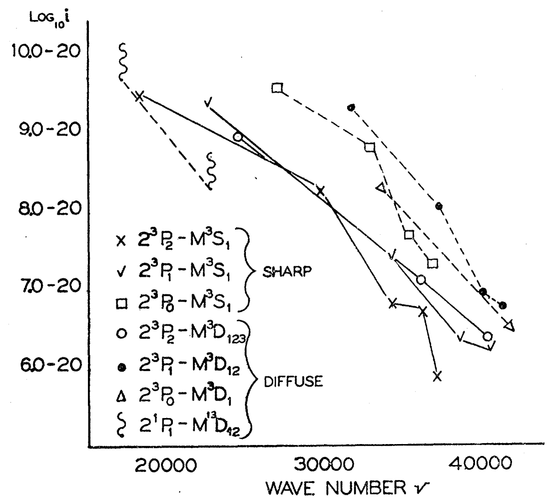

Fig. 6. The logarithm to the base 10 of the line intensity i plotted against the wave-number ν for the lines of the various series of the mercury spectrum.

This is done in Fig. 6, using the intensities of Table I, and it is seen that the points lie roughly on straight lines. This indicates that the Boltzmann term was the important one and that the variation in the probability function a with the march of the series was relatively small; although it is possible, of course, that a is not constant but varies with ν in some regular manner.

The slopes of the lines of Fig. 6 were approximately the same for the three sharp series and for the four diffuse series. From the slopes the temperatures of the excited atoms of the sharp and diffuse series were calculated to be

3900 and 2600° Kelvin, respectively. These values seem to be in accord with general notions of the effects in an electric discharge. The average temperatures of the gas molecules are probably lower. It may be recalled that measurements of the widths of spectrum lines of discharges at pressures below 1 mm of mercury gave, on the theory of Doppler broadening,[3] temperatures for the emitting particles sometimes of several hundred and sometimes of several thousand degrees.

If instead of comparing the intensities of the lines of a series, we examine lines which arise from transitions from the same upper level to differing lower levels, things are not so simple. For example the three lines 5460, 4358 and 4045A have the upper level 2^3S_1 in common and their respective lower levels are 2^3P_2, 2^3P_1 and 2^3P_0. Their relative intensities are 32.2, 20.3 and 9.8 and the log i,ν curve is not at all a straight line. Similarly for the diffuse levels. In this case, therefore, the intensities depend upon other probabilities in addition to the Boltzmann term. Assigning weights in accordance with the numbers of Zeeman sub-levels gave no better agreement. Apparently theory is hardly able yet to describe completely the complicated actions in a mercury arc at atmospheric pressure. Slack[4] found similar discrepancies between the calculated and the observed intensities of the Balmer lines of hydrogen.

Brief discussion of the measurement of the intensity of spectrum lines. An extended investigation of the intensities of spectral lines over wide ranges of wave-length is a step-by-step process at the present time. The energies in large blocks of the spectrum must first be determined by absorption screen methods. Detailed mapping of the lines in each block may then be carried out with a spectrograph and suitable measuring devices, such as the thermocouple and the photoelectric cell. These devices may be supplemented by photographic methods, such as the densitometer and the neutral wedge. The photographic methods give high resolution but require independent calibration; the spectra of Fig. 2 and the data of Table I could be used conveniently for calibration purposes. The neutral wedge method, due to Merton,[5] is very elegant, but a wedge which is accurately neutral over wide intervals of the spectrum is difficult to find. It might be possible to make by photographic methods an optical wedge, so adjusted for use with a particular photographic plate, that the intensities of all the lines could be read directly from the spectrogram.

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[3] Merton, Proc. Roy. Soc. **A91,** 421 (1915): Schönrock Ann. d. Physik **20,** 995 (1906).
[4] Slack, Phys. Rev. **31,** 527 (1928).
[5] Merton, Proc. Roy. Soc. **92,** 322 (1915).

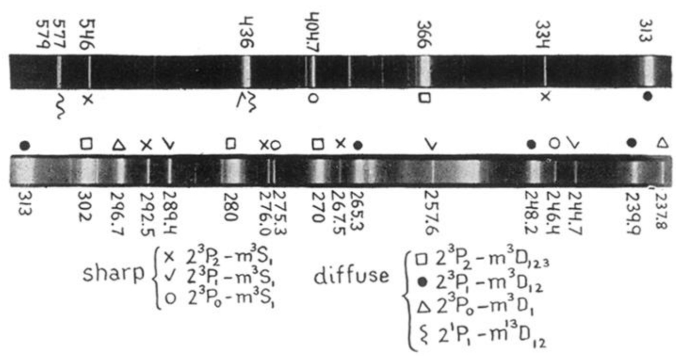

Fig. 2. Spectra of quartz mercury arc.