THE ARC SPECTRUM OF BROMINE AND ITS STRUCTURE

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ABSTRACT

The type of spectrum emitted by a Geissler tube containing bromine was found to depend on the pressure of the gas within the tube and the intensity of the exciting discharge. A tube containing the gas at pressures ranging from 10 to 20 mm Hg emits the arc spectrum, characteristic of the neutral atom, when excited by the uncondensed discharge from a high-voltage transformer. The spectrum produced in this manner was photographed from the ultra-violet to beyond 9300 A in the infra-red. More than 300 lines of Br I have been thus recorded and their wave lengths accurately determined. Sixty per cent of these lines, which include practically all the strong ones, together with those observed by Turner in the Schumann region, have been classified as combinations between terms of the doublet and quartet systems. The terms which have been established are, without exception, those required for Br I by Hund's theory, and arise from adding *s*, *p*, and *d* electrons to the basic and metastable terms ^3P, ^1D, and ^1S of Br II. Eleven sets of series-forming terms have been found. From these the distance between $^2P_2$, the basic term of Br I, and $^3P_2$, the basic term of Br II, has been calculated as 95,550 cm^{-1}, which gives an ionization potential of 11.80 volts for the neutral bromine atom.

CONTENTS

		Page
I.	Introduction	667
II.	Experimental procedure	668
III.	Results	671
IV.	Structure of the arc spectrum	678
V.	Conclusion and acknowledgments	690

I. INTRODUCTION

Although the spectra of the halogens have been made the object of many investigations, yet until recent years our knowledge of them has been more or less fragmentary, and only as the result of very recent researches has it been possible to partially characterize them according to the stage of ionization of the radiating atom. The chief cause for this deficiency is to be found in the chemical nature of the halogens themselves; for they vigorously attack and combine with the hot metal electrodes of the discharge tubes, so that most of the sources employed to study them in the elementary state are very short lived or unstable. Recently [1] we described the structure of the arc spectrum of chlorine and the method used in observing it. We here present similar results for the arc spectrum of bromine.

To the list of 88 papers, dealing with the spectra of bromine and cited by Kayser in Volumes V and VII of the Handbuch, must be added the following, which have appeared since that work was issued in 1924: (1) A study of the spectrum in the Schumann region, by

[1] B. S. Jour. Research, 2, p. 1117; 1929.

Turner;[2] (2) an investigation of the fine structure of certain complex lines, by Hori;[3] (3) a description, by L. and E. Bloch,[4] of the arc and spark spectra of Br as emitted in the electrodeless discharge from 6728 A in the red to 2253 A in the violet; (4) an extension, by Vaudet,[5] of the work of the Blochs to include the region from 2246 A to 1302 A; (5) and finally, a brief list of ultra-violet wave lengths obtained by Siracusano [6] in the electrodeless discharge. It should be mentioned here that the preliminary lists of Br spark lines published by the Blochs.[7] are included in their final lists referred to above.

In addition to these papers, all of which contain new wave-length measurements of various portions of the bromine spectra, a few others have appeared which describe the effect on the wave lengths of varying conditions of excitation. Kimura [8] investigated the effects of varying the pressure of the gas within the discharge tube, and of the intensity of the discharge. On the basis of these studies he classified the visible bromine lines as of the arc and spark types, from which he was then able to determine the ionizing effect of a discharge at different points in its path through a bromine atmosphere.[9] He also investigated [10] the fine structure of some of the complex lines and the Zeeman effects of both complex and single lines. In a more recent work Asagoe [11] has repeated Kimura's study of the effect of increasing pressure and current density on the behavior of bromine lines, and, as a result, has been able to distinguish three classes of lines. These he has correctly interpreted as characteristic of the arc and spark spectra of bromine. Lines designated by him as of the arc type appear to be asymmetrically widened when a strong discharge excites the gas at high pressure, causing an apparent red shift in the wave lengths. Very recently his study of the Stark effect [12] of the halogens has shown that for lines of the arc type of Cl, Br, and I, the displacements of the parallel and normal components are toward the red. He, therefore, attributes the asymmetrical broadening mentioned above to Stark effects evoked by the intra-atomic field of ions produced by the large current passing through the vapor.

II. EXPERIMENTAL PROCEDURE

The program of spectroscopic research in progress at the Bureau of Standards for more than 15 years has had as one of its objects the exploration of the hitherto unknown red and infra-red regions of the spectra of the different elements as far as present photographic methods will permit. Work on the spectrum of bromine was started in January, 1922, on receipt from Prof. J. M. Eder, of Vienna, of several Geissler tubes containing Br at pressures of 10, 20, 30, and 45 mm Hg. The experiments with these tubes revealed a spectrum extending at least to 8272 A. The lines, however, were not sharp, owing to the fact that with the transformer then available the tubes could be operated only with highly condensed discharges.

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[2] Phys. Rev., **27**, p. 397; 1926.
[3] Mem. College Sci. Kyoto Imperial Univ., **9**, p. 307; 1926.
[4] Ann. de Physique, **7**, p. 205; 1927.
[5] Compt. rend., **185**, p. 1272; 1927.
[6] Atti Accad. Lincei, VI, **7**, p. 835; 1928.
[7] Compt. rend., **184**, p. 193; 1927.
[8] Mem. College Sci. Kyoto Imperial Univ., **4**, p. 127; 1920.
[9] Mem. College Sci. Kyoto Imperial Univ., **4**, p. 151; 1920.
[10] Mem. College Sci. Kyoto Imperial Univ., **4**, p. 139; 1920.
[11] Japanese J. Physics, **4**, p. 85; 1927.
[12] Sci. Papers, Inst. Phys. Chem. Research (Japan), **11**, p. 243; 1929.

When recently, however, new experiments on the spectrum of chlorine were initiated, the work on bromine also was resumed. The same type of tube as used for chlorine [13] was used in the experiments with bromine. The essential feature of this discharge tube is that it has attached to it a reservoir containing the gas at a pressure in excess of that required for the experiments. The pressure within the tube may, therefore, be adjusted from time to time to compensate for the loss of gas through combination with the hot metal of the Pt electrodes. As in the experiments with chlorine, it was found that the rate of combination of the bromine with the platinum electrodes decreased after the tube had been in operation for several hours. Finally a stage approaching saturation was reached after which a tube could be operated for more than 100 hours before the admission of fresh bromine would be required.

The bromine used in these experiments was specially purified to insure its freedom from the other halogens. To our colleague, Dr. B. H. Carroll, we wish to express our appreciation for his interest in supplying us with this material, and for furnishing the following statement of its preparation:

A good grade of CP potassium bromide, containing not more than 0.5 per cent chloride, and giving a negative test for iodide, was used as the source of bromine. This was recrystallized once from distilled water leaving about one-third of the material in the mother liquor. A concentrated solution of the recrystallized salt was then treated successively with three small portions of CP sulphuric acid and recrystallized CP potassium permanganate, each portion being sufficient to oxidize about 2 per cent of the bromide. The bromine oxidized by each portion was evaporated off before adding the next portion; as iodide is oxidized more readily than bromide, three treatments of this type should remove all iodide present. Following this, permanganate and acid sufficient to oxidize about 90 per cent of the remaining bromide were added to the solution and the bromine was distilled off into all-glass apparatus. Oxidation, distillation, and condensation were made incomplete, deliberately, to reduce the amount of chlorine carried over with the bromine. The bromine was separated from the aqueous layer of the distillate and washed three times with distilled water to remove hydrobromic acid. It was then allowed to stand overnight in contact with phosphorous pentoxide. The only contact of the bromine with organic matter was in the stopcock of the separatory funnel.

The tubes, which were made either of pyrex glass or fused quartz, were excited by current from a transformer which stepped up 100 volts, a. c. to 40,000 volts. Preliminary observations made visually with a direct-vision spectroscope, verified the results of the previous observers as to the effects of increasing pressure and type of discharge on the nature of the spectrum. With only a few millimeters of gas in the tube, excited by an uncondensed discharge, the capillary of the tube appeared orange yellow, the spectrum consisting of bands, hardly resolved with the direct-vision prism used to view it. With increasing pressure, up to 10 or 12 mm, the color of the capillary changed to a light red, and through the prism, it was seen that the band spectrum had almost disappeared, and superposed on it was a spectrum of bright lines among which those at 6148 A and 6350 A were most conspicuous. It is these lines which impart the characteristic red color to low pressure bromine excited by uncondensed discharges. They are prominent members of the spectrum emitted by the neutral atom; and the conditions under which they appear with maximum brilliancy seem to be best for obtaining the arc spec-

[13] B. S. Jour. Research, 2, p. 1119; 1929.

trum. As the gas pressure increased, up to 50 mm, or more, new lines appeared in the green and blue; the arc lines diminished in intensity and the characteristic color of the capillary became grayish blue. If at this stage capacity of 0.006 μf was introduced into the circuit, the arc lines became asymmetrically diffuse, sharp on the violet edge and shaded toward the red, and scarcely distinguishable from the faint background of apparently continuous spectrum; the green and blue lines, characteristic of singly ionized atoms, were symmetrically broadened, and an entirely new class of lines appeared which were sharp and bright, no doubt emitted by doubly ionized atoms. The phenomena here observed for bromine are very similar to those reported for chlorine, and were the evidence used by Kimura and by Asagoe to disinguish lines belonging to the arc spectrum from those of the spark spectrum.

These facts are clearly exhibited in Figure 1 which illustrates the violet and blue regions of the spectrum. The upper strip (*b*) represents the spectrum when the conditions for the appearance of the arc lines are most favorable; the lower strip (*c*) represents the spectrum which is obtained when the gas at high pressure is excited by a strongly condensed discharge. Figures 2 and 3 illustrate the arc spectrum from the blue to the limit reached in the infra-red. The half-length lines seen in the upper portions of Figure 3 are the overlapping second-order lines in the violet and blue. Except for the lines observed by Turner, the figures show the entire arc spectrum described in this paper.

Most of the bromine spectrograms were obtained with the concave grating ruled with 7,500 lines per inch. A few, however, were secured with the 20,000 lines-per-inch grating. The spectrographs in which these gratings are mounted have been adequately described in previous papers.[14] Each exposure to the bromine source was accompanied by exposures to the iron arc which furnished the reference standards in the wave-length determinations. The spectrograms were made on thin-glass plates, coated with Eastman 36 emulsion, which could be bent to the focal curve of the spectrograph; and, when necessary, were appropriately sensitized to record the green, yellow, red, and infra-red spectral regions according to our usual practice.[15] When the spectrograph was adjusted to record the red and infra-red portions of the spectrum, between 6,000 A and 10,000 A, the filter which was used to transmit these waves, usually covered only half of the slit, so that the spectrogram thus obtained recorded the overlapping second order in addition to the first-order spectrum. The exposure times required to record the bromine spectra ranged from a few minutes for the strong spark lines in the blue and violet to 24 hours for the infra-red arc lines.

To verify the observations of Kimura and of Hori as to the complex nature of some of the bromine lines a few observations of the spectrum were made with a Fabry-Perot interferometer. Not only were most of the lines mentioned by them found to be complex, but also a number of the new infra-red ones as well. The results obtained from the measurement of these and of additional plates to be obtained with higher orders of resolution, will be reported at another time. Hori's statement, however, that most of the "complex lines seem to

[14] B. S. Sci. Papers No. 441, 18, p. 191; 1922.
[15] B. S. Sci. Papers No. 422, 17, p. 353; 1921.

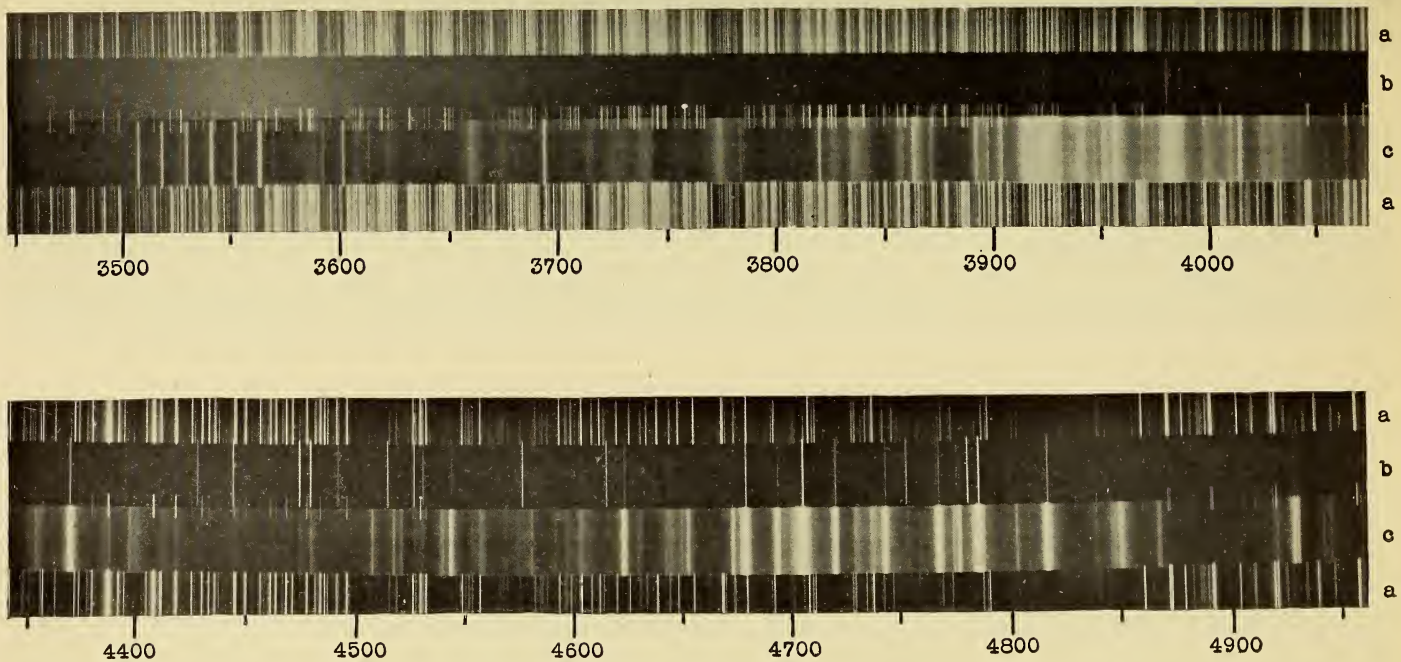

FIGURE 1.—*Arc and spark spectra of bromine in the violet and blue*

a, Fe arc spectrum; *b*, Br arc spectrum; *c*, Br spark spectrum.

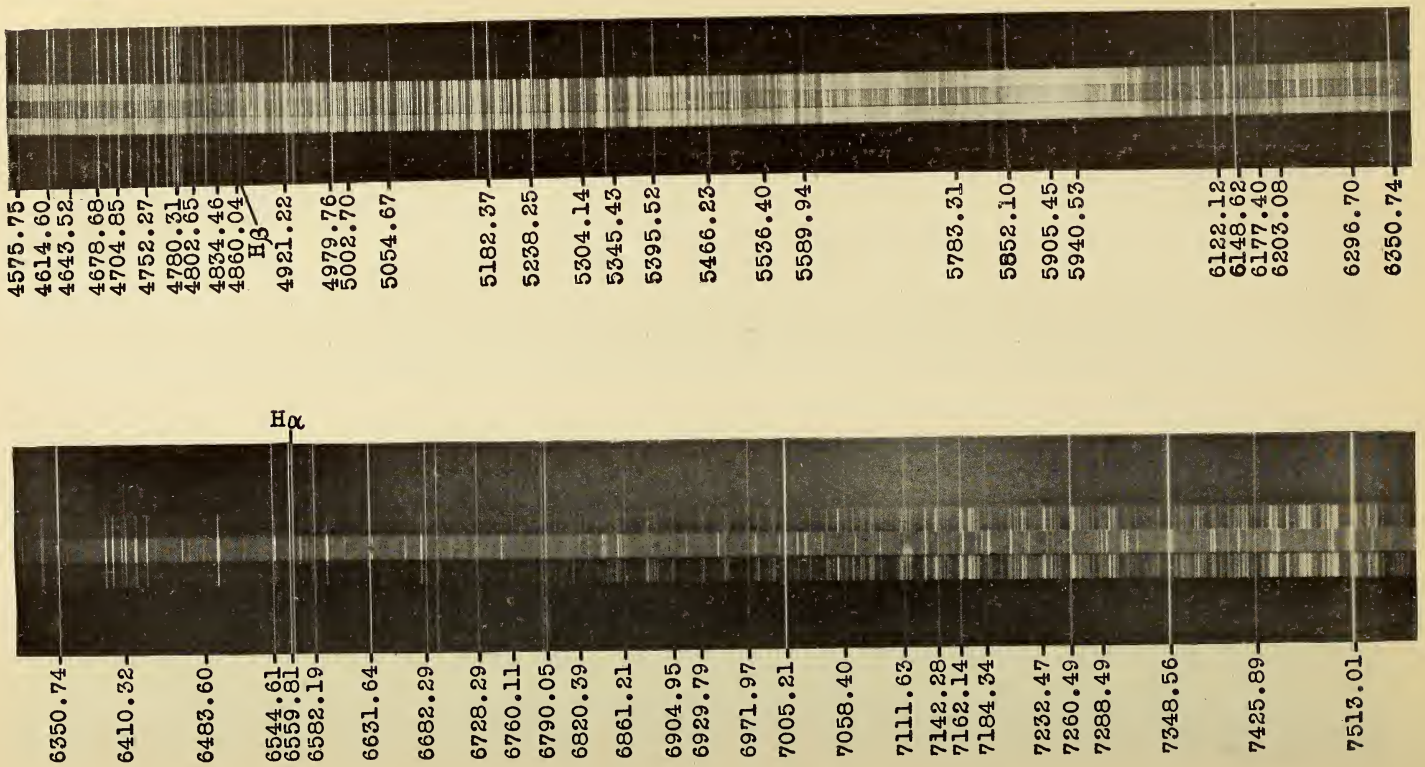

FIGURE 2.—*Arc spectrum of bromine in the visible region*

Fe arc comparison spectrum.

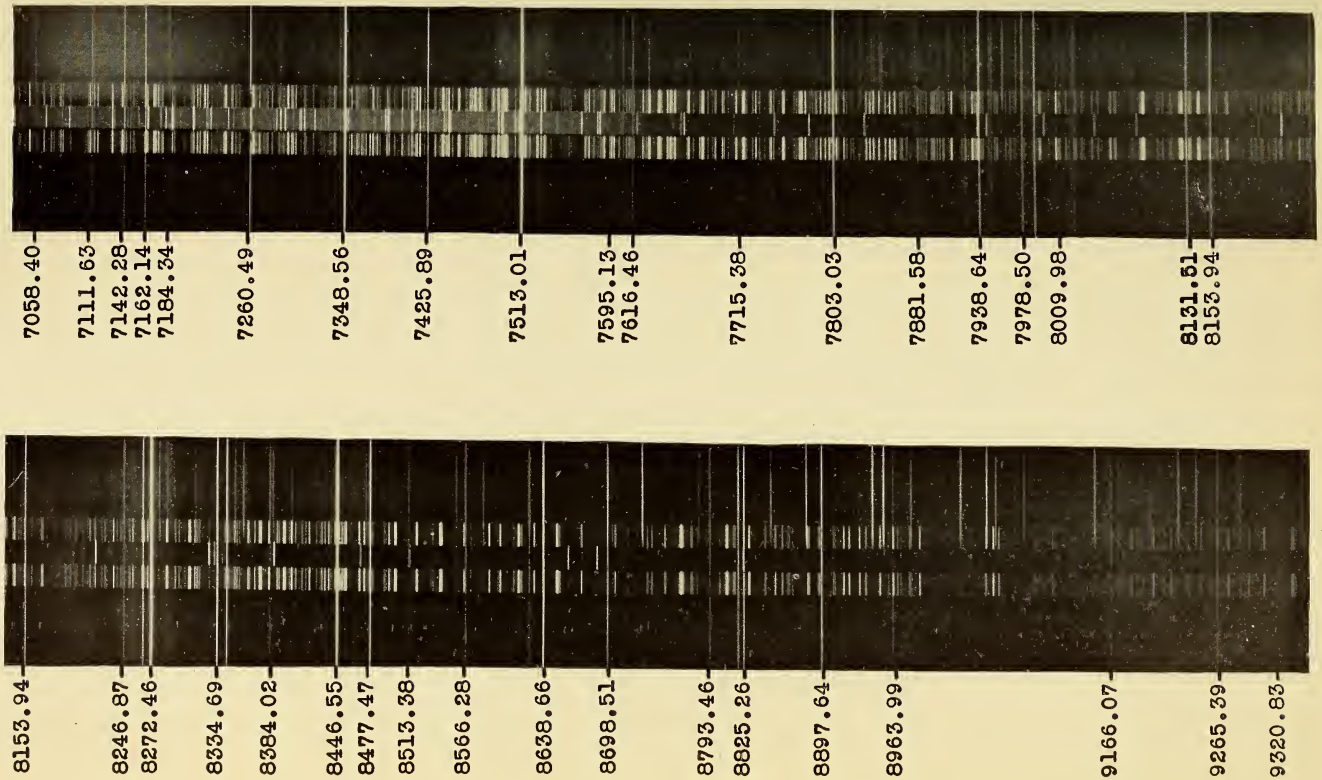

FIGURE 3.—*Arc spectrum of bromine in the red and infra-red*

First and second order Fe arc comparison spectrum.

be of the 'arc' type" is not verified. Of his list of nearly 60 lines with fine structure, only 14 find a place in the arc spectrum according to our analysis of its structure.

III. RESULTS

In Table 1 are entered more than 300 wave lengths derived from measurement of the spectrograms. These results are, in general, the means obtained from three to nine individual determinations, their accuracies being indicated by the letters in the third column, which have the following significance:

A=error less than 0.01 A.
B=error between 0.01 A and 0.02 A.
C=error between 0.02 A and 0.03 A.
D=error greater than 0.03 A.
E=only one determination.

Lines marked E have been corrected by an amount necessary to reduce the other wave lengths of the same spectrogram to the mean of all the measurements. In column 2, the letters *c* and *l*, following the intensity estimates, indicate, respectively, that the line is complex, and that it is diffuse and shaded toward the red when excited by a condensed discharge in the gas at high pressure.

The lines presented in Table 1 are believed to be characteristic of the arc spectrum of bromine. No lines belonging to the other halogens were encountered. The only impurity lines measured were due to hydrogen. The first three Balmer lines appeared on many of the plates. On a few spectrograms, secured near the close of the observations, many faint lines appeared which were found to belong to the secondary or many-lined spectrum of hydrogen. The presence of hydrogen in the tube may be attributed to the formation of HBr resulting from the destruction of the stopcock grease used at the inlet from the bromine reservoir to the discharge tube. No lines, attributable to the metal of the electrodes or lead-in wires, were found.

TABLE 1.—*Wave lengths in the arc spectrum of bromine*

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
9320. 83	4	B	10725. 72	$5s^2P_1-5p^2D_2$
9265. 39	8	B	10789. 90	$5s^4P_2-5p^4D_3$
9178. 16	4	C	10892. 44	$5s^2P_2-5p^4D_1$
9173. 59	4	C	10897. 87	$5s^2P_1-5p^2S_1$
9166. 07	7	B	10906. 81	$5s^4P_2-5p^4P_1$
9078. 79	0	E	11011. 90	$5p^4D_2-7s^2P_2$
8963. 99	5	C	11152. 69	$5s^2D_3-5p^2P_2$, (^{1}D)
8949. 31	2	C	11170. 98	$5s^2D_2-5p^2P_2$, (^{1}D)
8932. 39	3	C	11192. 14	$5s^4P_1-5p^4D_1$
8897. 64	15	B	11235. 86	$5s^4P_3-5p^4P_3$
8888. 83	2	D	11246. 99	$5s^2D_2-5p^2P_1$, (^{1}D)
8833. 23	0	E	11317. 97	
8825. 26	15	B	11328. 00	$5s^2P_2-5p^2D_3$
8819. 95	10	B	11334. 82	$5s^2D_3-5p^2F_4$, (^{1}D)
8808. 91	1	E	11349. 78	$5s^2S_1-6p^2P_2$, ($^1S^3P$)?

TABLE 1.—*Wave lengths in the arc spectrum of bromine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
8807. 52	2	D	11350. 82	$5s^2D_3-5p^2F_3$, (^1D)
8793. 46	6	C	11368. 97	$5s^2D_2-5p^2F_3$, (^1D)
8764. 08	0	E	11407. 08	
8760. 26	0	E	11412. 25	
8725. 28	1	C	11457. 81	
8709. 00	1	E	11479. 22	
8698. 51	10	B	11493. 07	$5s^2P_2-5p^4S_2$
8668. 94	1	D	11532. 27	$5p^4D_2-7s^4P_2$
8638. 66	25	B	11572. 69	$5s^4P_3-5p^4P_2$
8628. 85	0	E	11585. 85	
8625. 40	6	C	11590. 48	$5s^2S_1-6p^2P_1$, ($^1S^3P$)
8612. 13	0	E	11608. 55	
8592. 53	0	E	11635. 02	
8578. 88	0	E	11653. 33	$5p^4D_1-4d^4D_1$
8566. 28	6	B	11670. 48	
8560. 58	1	C	11678. 25	$5p^4S_2-4d^4F_3$
8557. 73	5	C	11682. 14	$5s^2P_2-5p^2P_1$
8513. 38	5	C	11742. 99	$5p^2D_2-4d^2F_3$
8503. 82	1	D	11756. 20	$5p^2D_3-4d^4F_4$
8477. 47	20	B	11792. 74	$5s^4P_1-5p^4S_2$
8471. 58	3	C	11800. 94	
8467. 26	0	E	11806. 95	
8446. 55	50	A	11835. 90	$5s^4P_2-5p^4D_2$
8408. 66	1	E	11889. 24	
8389. 76	1	D	11916. 02	$5p^2D_3-4d^4F_2$
8384. 02	5	B	11924. 18	$5p^2S_1-4d^2P_1$
8361. 70	1	E	11956. 01	
8360. 56	1	E	11957. 63	$5p^2D_2-4d^2D_3$
8356. 51	0	E	11963. 44	
8343. 70	20	A	11981. 80	$5s^4P_1-5p^2P_1$
8334. 69	20 *c*	A	11994. 75	$5s^2P_2-5p^2P_2$
8294. 45	0	D	12052. 95	
8291. 07	1	C	12057. 86	$5p^4D_3-7s^2P_2$
8272. 46	75 *l*	A	12084. 98	$5s^4P_3-5p^4D_4$
8264. 95	10	A	12095. 98	$5p^2D_2-4d^2P_1$
8250. 32	1	C	12117. 42	$5p^4D_1-4d^4P_1$
8248. 45	0	E	12120. 16	
8246. 87	5	B	12122. 48	$5p^2D_2-4d^2D_2$
8238. 03	1	E	12135. 49	
8215. 05	0	E	12169. 44	
8184. 16	0	E	12215. 37	
8183. 47	0	E	12216. 40	$5p^4D_1-7s^4P_1$
8153. 94	12 *c*	A	12260. 65	$5s^4P_3-5p^4D_3$
8152. 71	2	C	12262. 49	
8131. 51	12	A	12294. 46	$5s^4P_1-5p^2P_2$
8073. 04	0	E	12383. 50	
8028. 55	0	E	12452. 13	$5s^2D_2-5p^2P_1$ ($^1D^1S$)
8026. 35	6	B	12455. 54	$5s^2D_3-7p^4P_2$, ($^1D^3P$)
8023. 93	2	B	12459. 30	
8022. 62	1	B	12461. 34	$5p^4P_1-7s^4P_2$

TABLE 1.—*Wave lengths in the arc spectrum of bromine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
8021. 61	1	E	12462. 91	$5s^2D_3-5p^2D_3$, (^1D)
8014. 72	2	B	12473. 61	$5s^2D_2-7p^4P_2$, ($^1D^3P$)
8009. 98	4	B	12481. 00	$5s^2D_2-5p^2D_3$, (^1D)
7989. 94	12	A	12512. 31	$5s^2P_2-5p^2D_2$
7978. 50	10	A	12530. 24	$5s^2D_3-5p^2D_2$, (^1D)
7966. 95	2	B	12548. 40	$5s^2D_2-5p^2D_2$, (^1D)
7950. 19	5	B	12574. 86	$\left\{ \begin{array}{l} 5s^2D_3-5p^2P_2, (^1D^1S) \\ 5s^2S_1-5p^2P_2, (^1S^1D) \end{array} \right\}$
7947. 95	4	C	12578. 41	$5p^4D_3-7s^4P_2$
7938. 64	12 c *l*	A	12593. 15	$5s^2D_2-5p^2P_2$, ($^1D^1S$)
7929. 71	0	E	12607. 34	
7925. 88	4	C	12613. 43	$\left\{ \begin{array}{l} 5p^4D_4-7s^4P_3 \\ 5p^2P_2-4d^2P_1 \end{array} \right\}$
7889. 96	0	E	12670. 85	
7881. 58	2	C	12684. 33	$5s^2P_2-5p^2S_1$
7843. 60	1	E	12745. 74	$5p^4P_2-7s^2P_2$
7827. 24	1	D	12772. 39	
7807. 72	1	D	12804. 32	
7803. 03	15 *l*	A	12812. 01	$5s^4P_1-5p^2D_2$
7733. 64	2	E	12926. 97	$5p^2D_3-4d^2F_3$
7726. 15	1	E	12939. 50	$5s^2S_1-6p^2D_2$, ($^1S^3P$)
7715. 38	4	C	12957. 56	$5p^2D_3-4d^2F_4$
7688. 11	0	C	13003. 53	
7684. 97	0	E	13008. 84	
7663. 40	0	E	13045. 45	$5s^2S_1-6p^4S_2$, ($^1S^3P$)
7652. 83	1	E	13063. 47	$5p^4S_2-5d^4D_1$
7647. 54	0	E	13072. 51	
7642. 99	0	E	13080. 29	
7641. 62	2	E	13082. 64	$5p^4P_3-7s^2P_2$
7616. 46	6	B	13125. 85	$5p^4P_2-7s^4P_3$
7607. 40	4	C	13141. 48	$5p^2D_3-4d^2D_3$
7595. 13	3	B	13162. 71	
7593. 13	0	E	13166. 18	
7591. 59	2	C	13168. 85	$5s^4P_2-5p^4D_1$
7570. 87	2	C	13204. 89	$5p^4D_2-4d^4D_3$
7569. 16	2	D	13207. 87	
7551. 59	3	D	13238. 61	$5s^2S_1-6p^2S_1$, ($^1S^3P$)
7535. 81	3	D	13266. 33	$5p^4P_2-7s^4P_2$
7513. 01	50 *l*	A	13306. 58	$5s^4P_3-5p^4D_2$
7493. 18	0	E	13341. 80	
7478. 13	0	E	13368. 65	
7462. 05	0	E	13397. 46	
7432. 82	0	E	13450. 14	$5p^4D_2-4d^4P_1$
7425. 89	10	A	13462. 70	$5p^4P_3-7s^4P_3$
7348. 56	25 *l*	A	13604. 37	$5s^4P_2-5p^2D_3$
7344. 55	4	B	13611. 80	$5p^4D_2-4d^4F_3$
7333. 70	2	E	13631. 93	
7319. 19	3	C	13658. 96	
7311. 59	2	E	13673. 16	
7305. 21	1	E	13685. 10	$5p^4D_2-4d^4F_2$
7288. 49	3	D	13716. 49	$5p^4D_1-4d^2P_1$
7260. 49	15	A	13769. 38	$5s^4P_2-5p^4S_2$

TABLE 1.—*Wave lengths in the arc spectrum of bromine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
7232. 47	2	E	13822. 73	$5p^4D_2-4d^4P_2$
7222. 39	1	E	13842. 02	
7217. 84	1	E	13850. 75	
7194. 29	1	E	13896. 09	
7184. 34	5	B	13915. 33	$5p^4P_1-4d^4D_1$
7162. 14	7	A	13958. 47	$5s^4P_2-5p^2P_1$
7150. 38	1	E	13981. 43	
7142. 28	6	A	13997. 28	$5s^2S_1-5p^2P_2,(^1S)$
7113. 53	3	B	14053. 85	$5p^4P_1-4d^4D_2$
7111. 63	5	B	14057. 60	
7058. 40	4	B	14163. 62	$5p^4D_3-4d^4D_4$
7054. 74	0	E	14170. 96	$5p^4D_3-4d^4D_2$
7015. 16	1	E	14250. 92	$5p^4D_3-4d^4D_3$
7011. 54	0	E	14258. 28	
7005. 21	20 *l*	A	14271. 16	$5s^4P_2-5p^2P_2$
6993. 25	0	E	14295. 57	$5p^4P_1-7s^2P_1$
6971. 97	6	A	14339. 20	$5p^4D_4-4d^4D_4$
6936. 71	0	E	14412. 09	
6929. 79	3	B	14426. 48	$5p^4D_4-4d^4D_3$
6922. 96	0	E	14440. 71	
6904. 95	3	B	14478. 38	$5p^4P_1-7s^4P_1$
6861. 21	5	B	14570. 67	$5p^4D_3-4d^4F_4$
6840. 74	0	E	14614. 28	$5p^4P_1-4d^4F_2$
6826. 09	2	C	14645. 64	
6820. 39	2	C	14657. 88	$5p^4D_3-4d^4F_3$
6791. 50	2	B	14720. 23	$5p^4P_2-4d^4D_1$
6790. 05	8	A	14723. 37	$5p^4D_4-4d^4F_5$
6786. 77	5	A	14730. 49	$5p^4D_3-5d^4F_2$
6785. 79	1	C	14732. 62	
6779. 48	3	B	14746. 33	$5p^4D_4-4d^4F_4$
6760. 11	3	B	14788. 58	$5s^4P_2-5p^2D_2$
6728. 29	6	A	14858. 52	$5p^4P_2-4d^4D_2$
6723. 75	1	E	14868. 56	$5p^4D_3-4d^4P_2$
6702. 10	0	E	14916. 59	
6692. 16	8	A	14938. 74	$5p^4P_2-4d^4D_3$
6682. 29	9	A	14960. 80	$5s^4P_2-5p^2S_1$
6672. 22	1	D	14983. 39	
6631. 64	15 *c l*	A	15075. 07	$5s^4P_3-5p^2D_3$
6620. 50	3	B	15100. 44	$5p^4P_2-7s^2P_1$
6584. 22	1	C	15183. 64	$5p^4P_2-4d^4P_1$
6582. 19	10	A	15188. 32	$5p^4P_3-4d^4D_4$
6579. 20	4	B	15195. 23	$5p^4P_3-4d^4D_2$
6571. 35	2	B	15213. 38	$5p^4D_2-5d^4F_3$
6559. 81	12 *c*	A	15240. 14	$5s^4P_3-5p^4S_2$
6548. 14	4	B	15267. 30	$5p^4D_4-4d^4P_3$
6544. 61	10	A	15275. 54	$5p^4P_3-4d^4D_3$
6541. 44	1	C	15282. 94	$5p^4P_2-7s^4P_1$
6532. 30	1	C	15304. 32	
6514. 60	1	C	15345. 90	$5p^4P_2-4d^4F_3$
6488. 71	1	D	15407. 14	

TABLE 1.—*Wave lengths in the arc spectrum of bromine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
6483. 60	2	C	15419. 28	$5p^4P_2-4d^4F_2$
6462. 40	1	C	15469. 86	
6438. 08	1	D	15528. 30	
6426. 37	1	C	15556. 59	$5p^4P_2-4d^4P_2$
6410. 32	5	B	15595. 54	$5p^4P_3-4d^4F_4$
6364. 76	0	E	15707. 18	
6350. 74	20 *c l*	A	15741. 85	$5s^4P_3-5p^2P_2$
6336. 58	1	C	15777. 03	
6335. 50	2	B	15779. 72	$5p^4P_2-4d^4P_3$
6296. 70	4	B	15876. 95	
6290. 13	2	B	15893. 54	$5p^4P_3-4d^4P_2$
6282. 50	2	C	15912. 84	
6277. 32	0	E	15925. 97	$5p^4P_1-5d^4D_1$
6253. 71	1	C	15986. 10	$5p^4P_1-5d^4D_2$
6251. 41	1	D	15991. 98	
6244. 30	1	C	16010. 19	$5p^4D_2-5d^4P_2$
6203. 08	3	C	16116. 57	$5p^4P_3-4d^4P_3$
6177. 40	6	C	16183. 57	$5p^4D_3-5d^4F_4$
6158. 20	3	C	16234. 03	$5p^4D_4-5d^4D_4$
6148. 62	12 *c*	A	16259. 32	{ $5s^4P_3-5p^2D_2$ $5p^4D_3-5d^4F_3$
6132. 70	2	C	16301. 53	
6122. 12	7 *l*	B	16329. 70	$5p^4D_4-5d^4F_5$
6095. 74	2	B	16400. 37	
6069. 75	1	E	16470. 59	
6064. 30	0	E	16485. 40	
6057. 82	0	E	16503. 03	
6030. 67	1, Br II?	E	16577. 32	
6007. 86	1	D	16640. 26	
5985. 30	0	E	16702. 98	
5975. 40	1	D	16730. 66	$5p^4P_2-5d^4D_1$
5954. 00	3	C	16790. 79	$5p^4P_2-5d^4D_2$
5950. 30	3	C	16801. 23	$5p^4P_2-5d^4D_3$
5945. 50	2	C	16814. 80	
5940. 53	5 *l*	C	16828. 86	$5s^2P_1-6p^4P_1$
5905. 45	3	C	16928. 83	$5p^4P_1-5d^4P_1$
5869. 25	0	E	17033. 24	$5p^4D_3-5d^4P_3$
5861. 32	0	E	17056. 29	$5p^4D_3-5d^4P_2$
5852. 10	8	C	17083. 16	$5p^4P_3-5d^4D_4$
5836. 85	1	E	17127. 79	$5p^4P_3-5d^4D_2$
5833. 43	6	C	17137. 83	$5p^4P_3-5d^4D_3$
5828. 60	0	E	17152. 03	
5809. 59	1	C	17208. 16	$5p^4D_4-5d^4P_3$
5794. 00	0, Br II?	E	17254. 46	
5783. 31	4	C	17286. 35	
5637. 35	0	E	17733. 92	$5p^4P_2-5d^4P_1$
5634. 03	1	D	17744. 37	$5p^4P_2-5d^4P_2$
5627. 23	1	D	17765. 81	
5558. 60	0	E	17985. 16	
5548. 20	0	E	18018. 87	
5536. 40	3	C	18057. 28	$5p^4P_3-5d^4P_3$

TABLE 1.—*Wave lengths in the arc spectrum of bromine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
5529. 00	1	E	18081. 44	$5p^4P_3-5d^4P_2$
5466. 23	8 *l*	B	18289. 07	$5s^2P_1-6p^2P_2$
5460. 70	2 *l*	E	18307. 60	
5450. 06	3	C	18343. 34	$5s^2P_2-6p^4P_3$
5395. 52	8 *l*	B	18528. 76	$5s^2P_1-6p^2P_1$
5382. 99	1	C	18571. 89	
5370. 27	3	C	18615. 88	$5s^2P_2-6p^4P_1$
5364. 20	2	B	18636. 94	$5s^2P_2-6p^4D_3$
5345. 43	6 *l*	B	18702. 38	$5s^4P_1-6p^4P_2$
5328. 89	1	D	18760. 43	$5s^2P_2-6p^4D_2$
5245. 13	3	C	19060. 01	$5s^4P_1-6p^4D_2$
5029. 35	2	C	19877. 76	$5s^2P_1-6p^2D_2$
5014. 80	0	D	19935. 43	
5009. 40	0	D	19956. 92	
5002. 70	4	B	19983. 65	$5s^2P_1-6p^4S_2$
4979. 76	15 *l*	A	20075. 70	$5s^2P_2-6p^2P_2$
4954. 73	4	B	20177. 12	$5s^2P_1-6p^2S_1$
4921. 00	2	C	20315. 42	$5s^2P_2-6p^2P_1$
4860. 04	5	B	20570. 23	
4849. 37	7	B	20615. 49	$5s^4P_1-6p^2P_1$
4834. 46	7 *c l*	A	20679. 07	$5s^4P_2-6p^4P_2$
4807. 62	4	B	20794. 52	$5s^2P_1-5p^2P_1$ ($^3P^1S$)
4802. 65	7	A	20816. 04	$5s^2P_1-7p^4P_2$
4785. 19	6	A	20891. 99	$5s^4P_2-6p^4P_1$
4780. 31	15 *c l*	A	20913. 32	$5s^4P_2-6p^4D_3$
4775. 21	7	A	20935. 65	$5s^2P_1-5p^2P_2$ ($^3P^1S$)
4765. 62	3	B	20977. 78	$5s^2P_1-7p^4P_1$
4759. 45	0	E	21004. 98	
4758. 55	0	E	21008. 95	
4752. 27	12	A	21036. 71	$5s^4P_2-6p^4D_2$
4750. 46	0	E	21044. 73	
4748. 85	0	E	21051. 86	
4735. 42	5, Br II?	A	21111. 56	
4727. 05	0	E	21148. 94	
4711. 08	1	C	21220. 64	
4698. 56	1	E	21277. 18	
4695. 11	0	E	21292. 82	
4654. 16	1	C	21480. 16	
4648. 02	0	E	21508. 53	
4643. 52	7 *l*	A	21529. 38	$5s^4P_2-6p^4D_1$
4640. 98	2	B	21541. 16	
4614. 60	12 *l*	A	21664. 30	$5s^2P_2-6p^2D_2$
4592. 17	1	C	21770. 12	$5s^2P_2-6p^4S_2$
4576. 76	0	E	21843. 42	
4575. 75	12 *l*	A	21848. 24	$5s^2P_2-6p^2D_3$
4549. 75	1	D	21973. 09	
4529. 77	10	A	22070. 01	$5s^4P_1-6p^4S_2$
4525. 62	12 *l*	A	22090. 25	$5s^4P_3-6p^4P_3$
4513. 44	12 *l*	A	22149. 86	$5s^4P_3-6p^4P_2$
4496. 52	0	E	22233. 20	

TABLE 1.—*Wave lengths in the arc spectrum of bromine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
4490. 43	7	A	22263. 36	$5s^4P_1-6p^2S_1$
4477. 75	20 *l*	A	22326. 40	$5s^4P_3-6p^4D_4$
4472. 62	15 *l*	A	22352. 01	$5s^4P_2-6p^4P_2$
4471. 74	1, Br II?	D	22356. 41	
4471. 07	1	C	22359. 76	
4470. 01	2	C	22365. 06	$5s^2P_2-7p^4P_3$
4467. 56	0	E	22377. 32	
4458. 40	0	E	22423. 30	
4441. 74	12 *l*	A	22507. 40	$5s^4P_3-6p^4D_2$
4427. 08	1	D	22581. 93	$5s^2P_2-5p^2P_1$, $(^3P^1S)$
4425. 14	8	A	22591. 83	$5s^4P_2-6p^2P_1$
4423. 04	4	B	22602. 56	$5s^2P_2-7p^4P_2$
4404. 45	0	E	22697. 96	
4399. 72	4	B	22722. 36	$5s^2P_2-5p^2P_2$, $(^3P^1S)$
4394. 95	3, Br II?	B	22747. 02	
4391. 61	7	A	22764. 32	$5s^2P_2-7p^4P_1$
4379. 78	2, Br II?	D	22825. 81	
4369. 25	1	D	22880. 82	$5s^4P_1-5p^2P_1$, $(^3P^1S)$
4365. 15	5	A	22902. 31	$5s^4P_1-7p^4P_2$
4334. 58	1	E	23063. 82	$5s^4P_1-7p^4P_1$
4312. 67	0	E	23180. 99	
4289. 91	0	E	23303. 98	
4283. 14	0	E	23340. 81	
4260. 64	1	C	23464. 07	
4250. 87	0	D	23518. 00	
4248. 42	0	D	23531. 56	
4240. 41	0	D	23576. 01	
4220. 57	0	E	23686. 83	
4202. 50	7	A	23788. 68	
4197. 07	0	E	23819. 46	
4196. 48	1	C	23822. 80	$5s^4P_3-6p^4P_2$
4175. 79	9	A	23940. 84	$5s^4P_2-6p^2D_2$
4157. 39	4	B	24046. 80	$5s^4P_2-6p^4S_2$
4143. 98	6	A	24124. 61	$5s^4P_2-6p^2D_3$
4132. 49	1	E	24191. 69	
4129. 09	0	E	24211. 60	
4124. 28	0	D	24239. 84	$5s^4P_2-6p^2S_1$
4123. 45	1	D	24244. 72	
4083. 23	0	D	24483. 53	
4046. 55	0	E	24705. 46	
4045. 10	0	E	24714. 31	
4037. 35	3	B	24761. 75	
4021. 78	2	B	24857. 61	$5s^4P_2-5p^2P_1$, $(^3P^1S)$
4018. 33	1	B	24878. 95	$5s^4P_2-7p^4P_2$
4012. 57	1	B	24914. 67	
3999. 10	1	C	24998. 58	$5s^4P_2-5p^2P_2$, $(^3P^1S)$
3992. 39	7	A	25040. 60	$5s^4P_2-7p^4P_1$
3991. 39	2	B	25046. 87	$5s^4P_3-5p^2P_2$, $(^3P^1D)$
3937. 64	1, Br II?	B	25388. 76	
3934. 11	2	B	25411. 54	$5s^4P_3-6p^2D_2$

TABLE 1.—*Wave lengths in the arc spectrum of bromine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
3917. 83	2	B	25517. 13	$5s^4P_3$–$6p^4S_2$
3909. 42	1	B	25572. 02	
3905. 92	0	E	25594. 94	$5s^4P_3$–$6p^2D_3$
3902. 93	2	B	25614. 55	
3900. 00	0	E	25633. 79	
3896. 68	1	B	25655. 63	
3864. 12	2	A	25871. 81	
3829. 76	1	B	26103. 92	
3828. 55	5	A	26112. 17	$5s^4P_3$–$7p^4P_3$
3815. 68	7	A	26200. 24	
3801. 04	1	E	26301. 15	
3798. 28	3	B	26320. 26	
3794. 04	6	A	26349. 68	$5s^4P_3$–$7p^4P_2$
3770. 99	1	D	26510. 73	
3735. 83	3	B	26760. 23	

As was the case with chlorine, most of the bromine spectrograms secured in this investigation show two or more types of lines, since it was impossible, during the exposure, to maintain the conditions in the source favorable for the excitation of but one type. The spark lines appearing on the plates have been measured, but the wave lengths derived for them will be reserved for later publication. An additional feature of the spectrum which appears when the conditions of excitation are favorable for the production of the arc spectrum is the band of continuous light extending from 3600 A to 3500 A, with maximum near 3550 A. It is clearly seen in the illustrations. On the original negatives the violet limit of this band merges into a broader and much fainter band with maximum near 3250 A. These two bands coincide approximately with the limits of the ^2P and ^4P series coming from the s electron. They may, therefore, represent the recombination light which is emitted when electrons with initial velocities v give up energy $h\nu = h\nu_{5s} + \frac{1}{2}mv^2$, where $h\nu_{5s}$ is the energy of the $5s^2P$ and $5s^4P$ levels. The view that these bands are due to atomic and not molecular bromine is further supported by the fact that the absorption band of Br vapor lies to the red of the emission bands. Ribaud's [16] measurements place the absorption maximum near wave length 4200 A and only a small portion of the more refrangible and less intense part of the band overlaps the 3600–3500 A region of the emission band.

IV. STRUCTURE OF THE ARC SPECTRUM

Attempts to find, in the bromine spectra, regularities which would indicate the nature of their structure have been made by Paulson,[17] by Kimura,[18] by Turner,[19] by Hori,[20] and by Siracusano.[21] The

[16] Annales de Physique (9), **12**, p. 165; 1919.
[17] Dissertation, Lund, 1914; Ann. der Physik, **45**, p. 426; 1914.
[18] Mem. College Sci. Kyoto Imperial Univ., **4**, p. 133; 1920.
[19] Physical Review, **27**, p. 404; 1926.
[20] Mem. College Sci. Kyoto Imperial Univ., **9**, p. 312; 1926.
[21] Atti. Accad. Lincei, VI **7**, p. 835; 1928.

results obtained by all these investigators, except those of Turner, do not appear to have any physical significance, as far as the arc spectrum is concerned. Turner found the difference $\Delta\nu = 3685$ recurring among the strong bromine lines observed by him in the Schumann region. As shown in our classification [22] of these lines, this difference turns out to be the separation of the components of the ^2P basic terms of Br I and the lines themselves constitute the resonance lines and raies ultimes of the bromine arc spectrum. Table 4 contains Turner's lines and our classification of them, which differs slightly from that given in our preliminary note. With the clue thus furnished it was soon possible to classify the prominent lines in the red and infra-red and also those in the blue and violet.

TABLE 2.—*Theoretical terms of Br I*

Electron configuration	Basic term of Br II		
	^3P	^1D	^1S
$4s^2 . 4p^5$	**^2P**		
$4s^2 . 4p^4 . 5s$	^{2}**P**, ^{4}**P**	^{2}**D**	^{2}**S**
$4s^2 . 4p^4 . 5p$	^{2}**S**, ^{2}**P**, ^{2}**D**, ^{4}**S**, ^{4}**P**, ^{4}**D**	^{2}**P**, ^{2}**D**, ^{2}**F**	^{2}**P**
$4s^2 . 4p^4 . 4d$	^{2}**P**, ^{2}**D**, ^{2}**F**, ^{4}**P**, ^{4}**D**, ^{4}**F**	^{2}S, ^{2}P, ^{2}D, ^{2}F, ^{2}G	^{2}D
$4s^2 . 4p^4 . 6s$	^{2}P, ^{4}P	^{2}D	^{2}S
$4s^2 . 4p^4 . 6p$	^{2}**S**, ^{2}**P**, ^{2}**D**, ^{4}**S**, ^{4}**P**, ^{4}**D**	^{2}P, ^{2}D, ^{2}F	^{2}P
$4s^2 . 4p^4 . 5d$	^{2}P, ^{2}D, ^{2}F, ^{4}**P**, ^{4}**D**, ^{4}**F**	^{2}S, ^{2}P, ^{2}D, ^{2}F, ^{2}G	^{2}D
$4s^2 . 4p^4 . 7s$	^{2}**P**, ^{4}**P**	^{2}D	^{2}S
$4s^2 . 4p^4 . 7p$	^{2}S, ^{2}P, ^{2}D, ^{4}S, ^{4}**P**, ^{4}D	^{2}P, ^{2}D, ^{2}F	^{2}P

We have found that in structure, the arc spectrum of Br closely resembles that of chlorine. The terms which have been detected thus far are given in Table 3, and, without exception, are those required by Hund's theory. The theoretical terms are given in Table 2, those printed in heavy type indicating the ones actually found and listed in Table 3. These terms represent the resultants of the interaction of the seven valence electrons in the N shell of the bromine atom. In the unexcited state of the atom two of these electrons occupy 4_1 orbits and five occupy 4_2 orbits, which is expressed by the symbol $4s^2 . 4p^5$. The term corresponding to this state is ^2P, the component with $j = 3/2$ being deepest. To avoid the use of cumbersome fractional inner quantum numbers, however, we have throughout this paper assigned to each term an integral inner quantum number one-half unit greater than the true value. When the atom is excited one of the $4p$ electrons is dislodged from its normal position and occupies a higher and less firmly bound orbit of the $s, p, d, ---$ type. The terms of Table 2, which represent the excited states of the atom, are the resultants obtained by adding in turn the electrons ns, np, nd, etc., to the configuration $4s^2 . 4p^4$, or what amounts to the same thing, by adding them to the terms ^3P, ^1D, and ^1S, the lowest and metastable states of the bromine ion.

The numerical values of the terms in Table 3 are absolute; that is, they are based on what is believed to be the most probable value

[22] Science, 69, p. 360; 1929.

of the ground term, $^2P_2$, derived from the calculation of series limits, discussed below. The designation of a term was determined largely from its relation to neighboring terms, and from analogy with the term structure of Cl I, since no Zeeman effects of Br I lines are available upon which to base a definitive decision. It is altogether likely, therefore, that future investigation will necessitate a revision of some of the less surely established designations. The terms of Table 3 are illustrated graphically in Figure 4.

TABLE 3.—*Terms of Br I*

Term No.	Term type	ν	$\Delta\nu$	Series electron	Term No.	Term type	ν	$\Delta\nu$	Series electron
1	$^2P_2$	95550			24	$^2F_4$	6891. 07		
			3685	$4p$				15. 99	
2	$^2P_1$	91865			25	$^2F_3$	6875. 08		
3	$^4P_3$	32120. 18			26	$^2D_3$	5763. 03		
			1470. 68					67. 37	$5p+{}^1D$
4	$^4P_2$	30649. 50			27	$^2D_2$	5695. 66		
			1976. 66	$5s+{}^3P$					
5	$^4P_1$	28672. 84			28	$^2P_2$	7073. 27		
								76. 19	
6	$^2P_2$	28373. 13			29	$^2P_1$	6997. 08		
			1786. 65						
7	$^2P_1$	26586. 48			30	$^2P_2$	5650. 84		
								−141. 12	$5p+{}^1S$
8	$^2D_3$	18225. 89			31	$^2P_1$	5791. 96		
			−18. 18	$5s+{}^1D$					
9	$^2D_2$	18244. 07			32	$^4P_3$	10029. 86		
								59. 46	
10	$^2S_1$	19648. 11		$5s+{}^1S$	33	$^4P_2$	9970. 40		
								212. 96	
11	$^4P_3$	20884. 33			34	$^4P_1$	9757. 44		
			336. 85						
12	$^4P_2$	20547. 48			35	$^4D_4$	9793. 78		
			804. 81					57. 60	
13	$^4P_1$	19742. 67			36	$^4D_3$	9736. 18		
								123. 40	
14	$^4D_4$	20035. 18			37	$^4D_2$	9612. 78		
			175. 62					492. 66	
15	$^4D_3$	19859. 56			38	$^4D_1$	9120. 12		$6p+{}^3P$
			1046. 01						
16	$^4D_2$	18813. 55			39	$^4S_2$	6602. 88		
			1332. 84						
17	$^4D_1$	17480. 71		$5p+{}^3P$	40	$^2P_2$	8297. 43		
								239. 79	
18	$^4S_2$	16880. 08			41	$^2P_1$	8057. 64		
19	$^2P_2$	16378. 36			42	$^2D_3$	6524. 95		
			−312. 66					−183. 76	
20	$^2P_1$	16691. 02			43	$^2D_2$	6708. 71		
21	$^2D_3$	17045. 12			44	$^2S_1$	6409. 50		
			1184. 28						
22	$^2D_2$	15860. 84			45	$^4P_3$	7421. 67		
								140. 44	$7s+{}^3P$
23	$^2S_1$	15688. 70			46	$^4P_2$	7281. 23		

TABLE 3.—*Terms of Br I*—Continued

Term No.	Term type	ν	$\Delta\nu$	Series electron	Term No.	Term type	ν	$\Delta\nu$	Series electron
			2016. 85		64	$^2F_4$	4087. 56		
47	$^4P_1$	5264. 38						−30. 44	
				$7s+^3P$	65	$^2F_3$	4118. 00		
48	$^2P_2$	7801. 70							
			2354. 63		66	$^2D_3$	3903. 42		
49	$^2P_1$	5447. 07						165. 06	$4d+^3P$
					67	$^2D_2$	3738. 36		
50	$^4P_3$	6008. 04							
			237. 52		68	$^2P_2$	?		
51	$^4P_2$	5770. 52		$7p+^3P$					
			161. 66		69	$^2P_1$	3764. 65		
52	$^4P_1$	5608. 86							
					70	$^4D_4$	3801. 16		
53	$^4D_4$	5695. 98						54. 78	
			87. 27		71	$^4D_3$	3746. 38		
54	$^4D_3$	5608. 71						−10. 22	
			−80. 16		72	$^4D_2$	3756. 60		
55	$^4D_2$	5688. 87						−60. 16	
			−138. 45		73	$^4D_1$	3816. 76		
56	$^4D_1$	5827. 32							
					74	$^4F_5$	3705. 48		
57	$^4F_5$	5311. 81						29. 89	
			22. 97		75	$^4F_4$	3675. 59		
58	$^4F_4$	5288. 84		$4d+^3P$				75. 42	$5d+^3P$
			87. 17		76	$^4F_3$	3600. 17		
59	$^4F_3$	5201. 67							
			73. 17		77	$^4F_2$	?		
60	$^4F_2$	5128. 50							
					78	$^4P_3$	2827. 13		
61	$^4P_3$	4767. 80						23. 97	
			−223. 08		79	$^4P_2$	2803. 16		
62	$^4P_2$	4990. 88						−10. 54	
			−372. 62		80	$^4P_1$	2813. 70		
63	$^4P_1$	5363. 50							

The principal multiplets of Br I, which contain most of the prominent lines, are presented in Tables 4 to 9. Multiplet lines which have not been observed owing to faintness or inaccessibility, but which may be calculated from the known term differences, are indicated in the tables by braces { }. Turner's lines, Table 4, resulting from the transition $5s \rightarrow 4p$, represent those terms based on ^3P and ^1S of the ion. Additional lines in the Schumann region may be expected coming from the ^2D terms based on ^1D of the ion. Although the calculated wave numbers of these lines lie in the regions observed by Turner and by Vaudet, they are not to be found in either list. However, according to the intensity rules, they may be expected to be faint, since the term combination $^2D \rightarrow {}^2P$ represents a change of -1 in the quantum numbers of terms resulting from an electron transition in which the azimuthal quantum number changes by $+1$ ($s \rightarrow p$).

The intense lines of the deep red and infra-red form the multiplets given in Table 5. They represent the transition of the series electron from the $5p$ state to the $5s$ state, and thus constitute the set of lines most likely to occur among the Fraunhofer lines if bromine is present

in the sun's reversing layer. But careful comparison of the wave lengths of Table 1 with the Revision of Rowland's Preliminary Table of Solar Spectrum Wave Lengths [23] has failed to establish any coincidences and we must conclude that there is, at present, no evidence for the existence of bromine in the sun. These multiplets exhibit the same peculiarities that were noted for the corresponding multiplets of chlorine: (1) The intersystem combination ^2P–^4P is unusually strong, (2) the separations of the $4p$ terms ^4D and ^4P deviate markedly from the Landé interval rule. The latter fact indicates an anomalous coupling which persists with the $6p$ terms. This is readily seen by comparing the multiplets of Table 6, representing the transition $6p \rightarrow 5s$, with those of Table 5.

TABLE 4.—*Turner's lines*

$5s$ \ $4p$	$^2P_1$ 3685	$^2P_2$
$^2P_2$	9 1575. 0 63492	8 1488. 6 67176
$^2P_1$	7 1531. 9 65277	3 1449. 9 68965
$^4P_3$		6 1576. 5 63432
$^4P_2$	10 1633. 6 61214	6 1540. 8 64902
$^4P_1$	8 1582. 4 63194	{1495. 3 66878}
$^2S_1$	8 1384. 6 72224	6? [a] 1317. 4 75909

[a] The wave length 1317.8 given by Turner evidently is a blend with an iodine line of nearly the same value.

[23] Carnegie Institution of Washington, Pub. No. 396; 1928.

TABLE 5.—*Multiplets from the transition 5p→5s*

5p \ 5s	$^2P_1$ 1786.65	$^2P_2$	299.71	$^4P_1$ 1976.66	$^4P_2$ 1470.68	$^4P_3$
$^2D_3$ 1184. 28		15 8825. 26 11328. 00			25 7348. 56 13604. 37	15 6631. 64 15075. 07
$^2D_2$	4 9320. 83 10725. 72	12 7989. 94 12512. 31	299. 70	15 7803. 03 12812. 01	3 6760. 11 14788. 58	12 6148. 62 16259. 32
$^2P_2$ 312. 66	{9793. 2, 10208. 3}	20 8334. 69 11994. 75	299. 71	12 8131. 51 12294. 46	20 7005. 21 14271. 16	20 6350. 74 15741. 85
$^2P_1$	{10102. 8, 9895. 6}	5 8557. 73 11682. 14	299. 66	20 8343. 70 11981. 80	7 7162. 14 13958. 47	
$^2S_1$	4 9173. 59 10897. 87	2 7881. 58 12684. 33		{7699. 6, 12984. 1}	9 6682. 29 14960. 80	
$^4D_4$ 175. 66						75 8272. 46 12084. 98
$^4D_3$ 1046. 01		{11743. 2, 8513. 6}			8 9265. 39 10789. 90	12 8153. 94 12260. 65
$^4D_2$ 1332. 84	{12862. 0, 7773. 0}	{10458. 1, 9559. 5}		{10140. 0, 9859. 2}	50 8446. 55 11835. 90	50 7513. 01 13306. 58
$^4D_1$	{10979. 0, 9106. 0}	4 9178. 16 10892. 44	299. 70	3 8932. 39 11192. 14	2 7591. 59 13168. 85	
$^4P_3$ 336. 85		{13350. 2, 7488. 9}			{10237. 7, 9765. 2}	15 8897. 64 11235. 86
$^4P_2$ 804. 81	{16555. 7, 6039. 1}	{12775. 7, 7825. 6}		{12304. 0, 8125. 3}	{9896. 3, 10102. 0}	25 8638. 66 11572. 69
$^4P_1$	{14608. 3, 6844. 0}	{11584. 1, 8630. 5}		{11195. 0, 8930. 1}	7 9166. 07 10906. 81	
$^4S_2$	{10299. 6, 9706. 5}	10 8698. 51 11493. 07	299. 67	20 8477. 47 11792. 74	15 7260. 49 13769. 38	12 6559. 81 15240. 14

TABLE 6.—*Multiplets from the transitions 6p→5s and 7p→5s*

6p \ 5s	$^2P_1$ 1786.65	$^2P_2$	299.71	$^4P_1$ 1976.66	$^4P_2$ 1470.68	$^4P_3$
$^2D_3$		12 4575. 75 21848. 24			6 4143. 98 24124. 61	0 3905. 92 25594. 94
−183. 76						
$^2D_2$	2 5029. 35 19877. 76	12 4614. 60 21664. 30		4551. 6 21964. 2	9 4175. 79 23940. 84	2 3934. 11 25411. 54
$^2P_2$	8 5466. 23 18289. 07	15 4979. 76 20075. 70		4906. 5 20375. 4	15 4472. 62 22352. 01	1 4196. 48 23822. 80
239. 79						
$^2P_1$	8 5395. 52 18528. 76	2 4921. 00 20315. 41	300. 00	7 4849. 39 20615. 41	8 4425. 14 22591. 83	
$^2S_1$	4 4954. 73 20177. 12	4551. 7 21963. 6		7 4490. 43 22263. 36	0 4124. 28 24239. 84	
$^4D_4$						20 4477. 75 22326. 40
57. 60						
$^4D_3$		2 5364. 20 18636. 94			15 4780. 31 20913. 32	4466. 2 22384. 0
123. 40						
$^4D_2$	5889. 8 16973. 9	1 5328. 89 18760. 43	299. 58	3 5245. 13 19060. 01	12 4752. 27 21036. 71	12 4441. 74 22507. 40
492. 66						
$^4D_1$	5723. 7 17466. 5	5192. 6 19253. 0		5113. 0 19552. 7	7 4643. 52 21529. 38	
$^4P_3$		3 5450. 06 18343. 34			4848. 4 20619. 5	15 4525. 62 22090. 25
59. 46						
$^4P_2$	6016. 6 16616. 2	5432. 5 18402. 7		6 5345. 43 18702. 38	7 4834. 46 20679. 07	12 4513. 44 22149. 86
212. 96						
$^4P_1$	5 5940. 53 16828. 86	3 5370. 27 18615. 88		5285. 2 18915. 3	6 4785. 19 20891. 99	
$^4S_2$	4 5002. 70 19983. 65	1 4592. 17 21770. 12	299. 89	10 4529. 77 22070. 01	4 4157. 39 24046. 80	2 3917. 83 25517. 13

TABLE 6.—*Multiplets from the transitions 6p→5s and 7p→5s*—Continued

7p \ 5s	$^2P_1$ 1786.65	$^2P_2$	299.71	$^4P_1$ 1976.66	$^4P_2$ 1470.68	$^4P_3$
$^4P_3$ 237. 52		2 4470. 01 22365. 06			{ 4057. 1 24641. 4 }	5 3828. 55 26112. 17
$^4P_2$ 161. 66	7 4802. 65 20816. 04	4 4423. 04 22602. 56		5 4365. 15 22902. 31	1 4018. 33 24878. 95	6 3794. 04 26349. 68
$^4P_1$	3 4765. 62 20977. 78	7 4391. 61 22764. 32	299. 50	1 4334. 58 23063. 82	7 3992. 39 25040. 60	

The terms from the 4*d* and 5*d* electrons, which have been found, combine with those from the 5*p* electron to give the multiplets of Tables 7 and 8. The ^4D terms of the *nd* sequence are partially regular and the term separations are small. This fact is a characteristic of series-forming terms which approach a common limit.

The 6*s* electron gives terms which lie between those of the 5*p* and 6*p* electrons. It has not been possible to establish these terms, however, because the multiplets resulting from their combination with the 5*p* and 6*p* terms lie in the infra-red out of reach of the sensitized photographic plate.

The multiplets described in Tables 4 to 8, represent combinations of terms which have ^3P, the lowest term of Br II, as parent. The low metastable terms of Br II, ^1D and ^1S, also give families of terms in Br I. Of these, the lowest are ^2D and ^2S coming from the 5*s* electron, and these combine with the ^2F, ^2D, and ^2P terms from the 5*p* electron to give the multiplets of Table 9. The corresponding terms from the 6*p* electron have not been found. It is therefore impossible, at present, to form any estimate of the relative positions of the terms ^3P, ^1D, and ^1S of the Br ion, from calculation of the limiting terms of the series of Br I.

TABLE 7.—*Multiplets from the transition 4d→5p*

4d \ 5p	$^4S_2$	$^4P_1$ 804.81	$^4P_2$ 336.85	$^4P_3$	$^4D_1$ 1332.84	$^4D_2$ 1046.01	$^4D_3$ 175.62	$^4D_4$
$^4F_5$								8 6790.05 14723.37
22.97								
$^4F_4$				5 6410.32 15595.54			5 6861.21 14570.67	3 6779.48 14746.33
87.17								
$^4F_3$	1 8560.58 11678.25		1 6514.60 15345.90	{6374.7 15682.6}		4 7344.55 13611.90	2 6820.39 14657.88	{6739.6 14833.5}
73.17								
$^4F_2$	{8507.1 11751.7}	0 6840.74 14614.28	2 6483.60 15419.28	0 6345.40 15755.10	{8093.9 12351.6}	1 7305.21 13685.10	5 6786.77 14730.49	
$^4D_4$				10 6582.19 15188.32			4 7058.40 14163.62	6 6971.97 14339.20
87.27								
$^4D_3$	{8869.5 11271.4}		8 6692.16 14938.74	10 6544.61 15275.54		2 7570.87 13204.89	1 7015.16 14250.92	3 6929.79 14426.48
−80.16								
$^4D_2$	{8933.3 11191.0}	3 7113.53 14053.85	6 6728.29 14858.52	4 6579.20 15195.23	{8478.3 11791.6}	{7617.2 13124.6}	0 7054.74 14170.96	
−138.45								
$^4D_1$	{9045.0 11052.8}	5 7184.34 13915.33	2 6791.50 14720.23		0 8578.88 11653.33	{7698.3 12986.3}		
$^4P_3$	{8253.8 12112.3}		2 6335.50 15779.72	3 6203.08 16116.57		{7117.6 14045.8}	{6624.3 15091.8}	4 6548.14 15267.30
−223.08								
$^4P_2$	1 8408.66 11889.24	{6777.0 14751.8}	1 6426.37 15556.59	2 6290.13 15893.54	{8004.4 12489.7}	2 7232.47 13822.73	1 6723.75 14868.56	
−372.62								
$^4P_1$	{8680.6 11516.7}	{6952.5 14379.2}	1 6584.22 15183.64		0 8250.32 12117.42	0 7432.82 13450.14		

TABLE 8.—*Multiplets from the transition 5d→5p*

5d \ 5p	$^4S_2$	$^4P_1$ 804.81	$^4P_2$ 336.85	$^4P_3$	$^4D_1$ 1332.84	$^4D_2$ 1046.01	$^4D_3$ 175.62	$^4D_4$
$^4F_5$								7 6122.12 16329.70
29.89								
$^4F_4$				{5809.4 17208.7}			6 6177.40 16183.57	{6110.9 16359.6}
75.42								
$^4F_3$			{5899.0 16947.3}	{5784.0 17284.1}		2 6571.35 15213.38	{6148.5 16259.6}	{6082.9 16435.0}
?								
$^4F_2$		?	?	?	?	?	?	
$^4D_4$				8 5852.10 17083.16			{6225.5 16058.4}	3 6158.20 16234.03
54.78								
$^4D_3$	{7611.8 13133.7}		3 5950.30 16801.23	6 5833.43 17137.83		{6635.1 15067.2}	{6204.4 16113.2}	{6137.5 16288.8}
−10.22								
$^4D_2$	{7617.8 13123.5}	1 6253.71 15986.10	3 5954.00 16790.79	1 5836.85 17127.79	{7284.5 13724.0}	{6639.6 15057.0}	{6208.3 16103.0}	
−60.16								
$^4D_1$	1 7652.83 13063.47	0 6277.32 15925.97	1 5975.40 16730.66		{7316.5 13663.9}	{6666.3 14996.8}		
$^4P_3$	{7113.1 14053.1}		{5641.6 17720.5}	3 5536.40 18057.28		{6253.5 15986.6}	0 5869.25 17033.24	1 5809.59 17208.16
23.97								
$^4P_2$	{7101.8 14077.1}	{5901.7 16939.6}	1 5634.03 17744.37	1 5529.00 18081.44	{6811.2 14677.7}	1 6244.30 16010.19	0 5861.32 17056.29	
−10.54								
$^4P_1$	{7107.2 14066.4}	3 5905.45 16928.83	0 5637.35 17733.92		{6816.1 14667.0}	{6248.3 15999.9}		

TABLE 9.—*Combinations of doublet terms originating in* ^1D *and* ^1S *of Br II*

5p \ 5s	$^2S_1$	$^2D_2 - 18.18$	$^2D_2$
$^2F_4$			10 8819. 95 11334. 82
15. 99			
$^2F_3$		6 8793. 46 11368. 97	2 8807. 52 11350. 82
$^2D_3$		4 8009. 98 12481. 00	1 8021. 61 12462. 91
67. 37			
$^2D_2$	{ 7165. 3 13952. 4 }	2 7966. 95 12548. 40	10 7978. 50 12530. 24
$^2P_2$	5 7950. 19 12574. 86	2 8949. 31 11170. 98	5 8963. 99 11152. 69
76. 19			
$^2P_1$	{ 7902. 3 12651. 0 }	2 8888. 83 11246. 99	
$^2P_2$	6 7142. 28 13997. 28	12 7938. 64 12593. 15	5 7950. 19 12574. 86
−141. 12			
$^2P_1$	{ 7215. 1 13856. 1 }	0 8028. 55 12452. 13	

Of the terms given in Table 3, 11 sets are in Rydberg sequence and, therefore, available for calculating series limits. These are shown in Figure 4 where the series-forming terms are plotted on the same vertical line. Since, with one exception, only two terms in each sequence are known with certainty, it was not deemed necessary, for the present, to seek for more accurate values of the terms than those given by Rydberg's formula. By adding to the terms thus found, their separation from the basic term $^2P_2$ we get the separations between the limiting terms of the ion and the lowest term of the neutral atom. The values found in this way from all the component series are given in Table 10. The 15 values for the separation $^3P_2$—$^2P_2$ are in very good accord, their mean being 95543 cm^{-1}. The value of the basic term $^2P_2$ is therefore conveniently placed at 95550. Nine of the series converge to $^3P_1$ of Br II, and three to $^3P_0$. Of these, the *np* ^2P series have three members each, but they appear to be abnormal, since it was not possible to find a formula of the Ritz type, with three constants, to represent them satisfactorily. The approximate values for $^3P_1$ and $^3P_0$ derived from these abnormal series, when averaged with corresponding values derived from the other series converging to these limits, give the means shown in the table. We may feel sure that the order of magnitude for the

separations of the components of ^3P indicated by these results is very nearly correct, for we may arrive at an estimate of them from the known $\Delta\nu$'s of the basic ^3P of Se I. McLennan, McLay, and McLeod [24] have found that the extreme components of the ground term of Se I are separated by 2534 cm^{-1}. Assuming that the corresponding separation of Br II shows an increase over that of Se I in the same ratio as does that of Cl II over S I ($\Delta\nu$ Cl II: $\Delta\nu$ S I = 1.75) we find for it $\Delta\nu_{0,2} \approx 4500$ cm^{-1}, which is of the order shown in Table 10. Some of the individual values for the series limits recorded in Table 10 may be somewhat in error because of uncertainties attaching to the identification of the higher terms; but such errors can not be large enough to affect the order of magnitude of the series limits as found in the above analysis. At present there seems to be no way of deciding this point without the help of Zeeman effects or other evidence coming from a study of the fine structure of the bromine lines. Unfortunately, we do not as yet know the basic term of Br II from observation and, therefore, can not check absolutely the term separations derived from calculation of the series limits.

TABLE 10.—*Series limits of Br I*

Term sequence		Limiting term of Br^+		
		$^3P_0$	$^3P_1$	$^3P_2$
np	$^4P_3$			95692
	$^4P_2$			95609
	$^4P_1$		95882	
	$^4D_4$			95613
	$^4D_3$			95608
	$^4D_2$			95230
	$^4D_1$			95250
	$^4S_2$		98820	
	$^2P_2$	106000		
	$^2P_1$		101000	
	$^2D_3$		99023	
	$^2D_2$		98107	
	$^2S_1$	98480		
ns	$^4P_3$			
	$^4P_2$			95506
	$^4P_1$		97526	
	$^2P_2$		94604	
	$^2P_1$	97032		
nd	$^4P_3$			96528
	$^4P_2$		96836	
	$^4P_1$		97210	
	$^4D_4$			95501
	$^4D_3$			95519
	$^4D_2$			95589
	$^4D_1$			95618
	$^4F_5$			95244
	$^4F_4$			95288
	$^4F_3$			95343
Means		100500	97670	95543
Ionization potential $= 1.2345 \times 95543 \times 10^{-4} = 11.80v$				

[24] Phil. Mag. (7), 4, p. 486; 1927.

We may also form an estimate of the magnitude of the separation of the series limits from the separations of the components of a set of series terms. In our paper on chlorine we presented evidence to show the manner in which component series approached their limits and pointed out that our conclusions were in accord with the new scheme given by Hund.[25] Similar evidence is afforded by the bromine series. For instance, the ^4P terms coming from the 5*s* and 7*s* electrons are characterized by the separations (1470.68, 1896.66) and (140.44, 2016.85), respectively. This indicates that in approaching the limit the separation $\Delta\ \nu_{3,2}$ decreases toward zero, which means that the component series $ns\ ^4P_3$ and $ns\ ^4P_2$ both approach the same limit $^3P_2$ of the ion; whereas the separation $\Delta\ \nu_{2,1}$ remains constant or increases, which means that the series $ns\ ^4P_1$ approaches the limit $^3P_1$ of the ion. From the magnitude of the separations $\Delta\ \nu_{2,1}$ we may therefore estimate the separation of the two limits $^3P_2$ and $^3P_1$ to be in excess of 2000 cm^{-1}. Similarly, we can form an estimate of the separation of the series limits $^3P_1$ and $^3P_0$ from the components of series which converge to these limits. Such series, for example, are composed of the terms $^2P_2$ and $^2P_1$ coming from the *ns* electrons. In bromine the values of $\Delta\ \nu_{2,1}$ for these terms are 1786.65 and 2354.63, respectively, for the 5*s* and 7*s* electrons. We may, therefore, expect the limiting terms $^3P_1$ and $^3P_0$ to be separated by an amount of the order of 2000 cm^{-1}. This would indicate that the distance between $^3P_0$ and $^2P_2$ in Table 10 should be somewhat in excess of 99000 cm^{-1}.

From the separation 95550 cm^{-1} between the ground terms of Br I and Br II, we derive a value of 11.80 volts for the ionization potential of the neutral bromine atom. This value differs by 0.6 volt from that found by linear interpolation between the values recently found spectroscopically for Ge and Kr. Rao's recent analysis of the germanium arc spectrum [26] gives an ionization potential of 8.09 volts for this element; and for krypton the classification of the spectrum by Gremmer [27] and by Meggers, deBruin, and Humphreys,[28] gives a value of 13.94 volts. The straight line connecting these points gives for As an ionization potential of 9.55 volts, for Se 11.00 volts, and for Br 12.40 volts. The value for As agrees well with the estimate of 9.9 volts made by Meggers and deBruin [29] from analyses of As I and with the similar estimate of 9.6 volts recently made by Russell.[30] For Se no spectroscopic value is available, but Udden's [31] measured value of 12.7 volts is higher by 1.7 volts than that given by the curve. For Ga the curve gives 6.6 volts, which is 0.6 volt larger than the value determined spectroscopically.

V. CONCLUSION AND ACKNOWLEDGMENTS

Sixty per cent of the lines of Table 1 have been classified as resulting from combinations of the terms given in Table 3. This includes practically all the stronger lines in the list. Of the fainter lines, many have been measured but once and may not be characteristic of Br I, but they are retained in the list subject to the confirmation or

[25] Zeit. für Physik, **52**, p. 601; 1928.
[26] Proc. Roy. Soc. (London), **A124**, p. 465; 1929.
[27] Zeit. für Physik, **54**, p. 198; 1929.
[28] B. S. Jour. Research, **3**, p. 129; 1929.
[29] B. S. Jour. Research, **3**, p. 765; 1929.
[30] Astrophys. J., **70**, p. 11; 1929.
[31] Phys. Rev., **18**, p. 385; 1921.

rejection of future observations. As stated above, some of the higher terms of Table 3 may also require revision in the light of subsequent observational data. However, whatever readjustment may be made will not seriously alter the structure of the spectrum as portrayed in

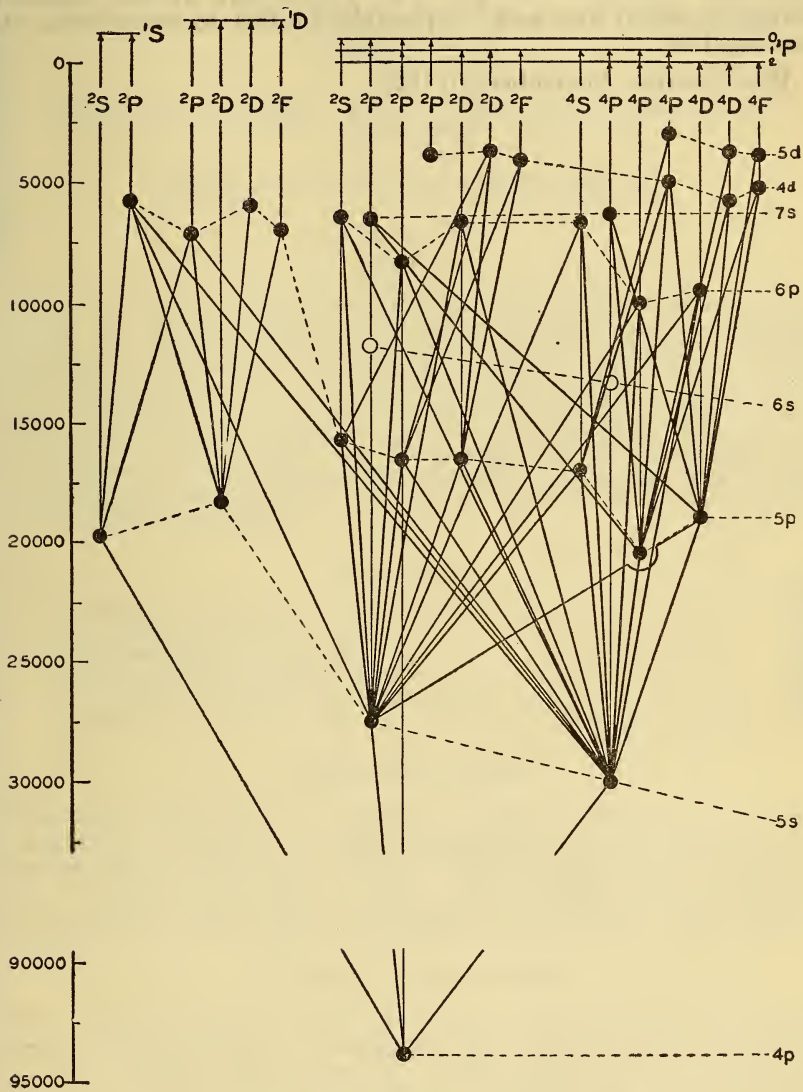

FIGURE 4.—*Term diagram of Br I*

Figure 4. The essential fact brought out by this analysis is the complete agreement of the observed structure of the spectrum with that required theoretically for an atom with seven valence electrons.

In conclusion we again wish to express our appreciation to our colleague, Dr. B. H. Carroll, who prepared for us the pure bromine used

in this investigation. To Bourdon F. Scribner, also of the bureau staff, we are indebted for valued assistance in the computation of the wave lengths presented in this paper. Finally, one of us (T. L. deB.) wishes to take this opportunity to thank the International Education Board for the grant of a fellowship at the Bureau of Standards which has made it possible for him to cooperate in this investigation.

WASHINGTON, November 30, 1929.