THE ARC SPECTRUM OF ARSENIC

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ABSTRACT

Metallic arsenic was vaporized in graphite or copper arcs, and the line emission spectrum was investigated throughout the entire range accessible to photography with concave grating and with quartz prism spectrographs. The measured wave lengths range from 1889.85 to 10023.98 A. The spectrum is relatively simple but difficult to analyze because many important lines lie either in the far ultra-violet or in the infra-red. The new data (vacuum wave numbers, estimated relative intensities, and self-reversal of certain lines) have made possible a fairly complete analysis of the As_I spectrum.

Forty-two levels have been identified; they include practically all of the spectral terms arising from the addition of a $4p$, $5s$, and $4d$ electron to the s^2p^2 configuration of the As^+ ion. The normal state is represented by a $^4S_2$ term for which the absolute value is estimated to be 80692.72, corresponding to an ionization potential of about 10 volts. Combinations of the identified terms account for 100 observed As_I lines, ranging in wave length from 1574.7 to 10614.0 A, our observations being supplemented by two infra-red lines detected radiometrically by Randall and 19 lines in the Schumann region obtained with a fluorite spectrograph in vacuo by L. and E. Bloch.

CONTENTS

	Page
I. Introduction	765
II. Wave-length measurements	766
III. Analysis of the arc spectrum of arsenic	769
1. Theoretical terms	770
2. The multiplets	771
3. The term table	776
4. List of classified As_I lines	778

I. INTRODUCTION

The first observations of the arc spectrum of arsenic were made by Kayser and Runge [1] in 1893. They excited the spectrum by placing metallic arsenic in a carbon arc and photographed it from 6000 A to shorter waves but found no lines in the visible spectrum. In the ultra-violet between 3119.69 and 2009.31 A they recorded 33 As lines but assigned no intensities to the last seven lying below 2113 A, probably because the strong absorption of ordinary gelatin emulsions for light in this region makes the photographic images appear very weak and thin. The only other attempt to derive wave lengths from a photographic study of the arc spectrum of arsenic

[1] Kayser and Runge, Abhandl. Berlin Akad.; 1893; Wiedemann's Ann., 52, p. 93; 1894.

was made by Exner and Haschek[2] in 1904. The observations were made with an alloy of 40 per cent As with nickel; wave lengths ranging from 3119.70 to 2271.46 A were measured for 18 lines.

A portion of the infra-red emission spectrum of arsenic was investigated radiometrically by Randall[3] in 1911; 10 lines were observed between 8823.3 and 10614.6 A.

The above-mentioned three papers contain all that was known of the arc spectrum of arsenic up to the present time. The wave lengths are relative to Rowland's scale of standards, since the measurements were made before the new international standards were adopted. The spectra of arsenic excited in high-potential condensed sparks have been studied more or less extensively by Hartley and Adeney,[4] by Exner and Haschek,[5] and by Herpertz.[6] The latter also investigated the spectra emitted by Geissler tubes containing arsenic. These high-potential sources develop spectra of greater complexity. About 500 lines have been recorded in the visible and ultra-violet. These include most of the lines ascribed to the arc spectrum, but the reverse is not true; that is, the arc spectrum can be produced without exciting any spark lines. The spark spectrum of arsenic has been observed by L. and E. Bloch[7] in the Schumann region, but it is impossible to distinguish arc from spark lines in this region without an arc comparison.

After summarizing these data in the section on arsenic in their Handbuch, Kayser and Konen[8] remark that "Das Spektrum ist eben noch sehr unvollkommen bekannt." We are aware of no additional published observations in recent years but have now completed a new description of the As_I spectrum covering the entire range accessible photographically to ordinary spectrographs. The new observations for As_I lines which have been classified are presented in this paper.

II. WAVE-LENGTH MEASUREMENTS

When the new infra-red photosensitizing dye, neocyanine, became available in 1926, it was immediately tested and found useful for the extension of spectrographic information already obtained by means of dicyanine. It was also employed for the study of certain spectra which had been previously neglected; arsenic became one of these at the suggestion of Dr. Otto Laporte. The arc spectrum of arsenic was found to contain a group of powerful lines in the infra-red, and it was

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[2] Exner and Haschek, Tabelle der Bogenspektra, Wien; 1904.
[3] Randall, Astrophys. J., **34**, p. 1; 1911.
[4] Hartley and Adeney, Phil. Trans., **175**, I, p. 63; 1884.
[5] Exner and Haschek, Tabelle der Funkenspektra, Wien; 1902.
[6] Herpertz, Zeitschr. f. wiss. Phot., **4**, p. 175; 1906.
[7] L. and E. Bloch, C. R., **158**, p. 416; 1914; **171**, p. 709; 1920.
[8] Kayser and Konen, Handbuch der Spectrotroscopie, **7**, p. 63; 1924, Hirzel, Leipzig.

immediately recognized that these were structurally related to the ultra-violet lines described by Kayser and Runge 33 years earlier. Then the observations were extended to cover the visible spectrum and the ultra-violet down to 3119 A. This interval was supposed to contain no lines of the As_I spectrum, but a considerable number of fairly strong lines were detected in the blue and green. No structural connection, however, has been found between the stronger visible lines and the invisible ones.

At this point it was apparent that a satisfactory analysis of the As_I spectrum could not be continued without reobserving the ultra-violet portion so as to establish the wave lengths of these lines relative to the modern international standards and to obtain more homogeneous data as to relative intensities. The results will show that this procedure was justified; some new lines have been discovered in the ultra-violet, and certain details of spectral structure have thus been revealed which otherwise would have remained obscure.

In this investigation the source was usually a graphite arc in which metallic arsenic was vaporized, although some exposures were made with a copper arc to which arsenic was added. The arcs were operated with 8 to 10 amperes on a 220-volt direct current circuit. The lower electrode was bored out and filled with lumps of arsenic metal. The metal vaporized and sublimed so rapidly that frequent fillings were necessary during an exposure. More than 400 gms of metal were thus consumed in about 10 hours of exposing time. Mallinckrodt's "pure" arsenic metal was used, and all the lines not duplicated in the graphite or copper comparison spectra were measured. The final list of wave lengths was compared with Kayser's [9] Hauptlinien for the identification of impurities. Evidence for a considerable number of impurities was found, especially in the ultra-violet where the raies ultimes of most elements occur. The main impurities were found to be Sb, Bi, Si, Sn, Pb, Cu, Fe, Ni, and traces of Mg, Al, Ag, and Te.

The infra-red spectrum was photographed with an Anderson grating (21-foot radius, 6-inch grating, with 7,500 lines per inch) in a Wadsworth mounting described in other papers [10] and successfully used in describing the long wave portions of various spectra. The first-order spectrum of this grating has a scale of approximately 10.4 A per mm.

"Eastman 36" plates, stained in the laboratory with neocyanine, were used in the infra-red. The greatest wave length recorded photographically in the arsenic spectrum was 10024 A, a good image of this line being impressed by an exposure of one hour.

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[9] Kayser, Tabelle der Hauptlinien der Linienspektren aller Elemente, Julius Springer, Berlin; 1927.
[10] Meggers and Burns, B. S. Sci. Papers 18 (No. 441), p. 191; 1922.

The same grating was used in exploring the spectrum through the visible and near ultra-violet where a number of lines not previously noted in the arc spectrum of arsenic and not identifiable with impurities were found. These observations were recently repeated and confirmed with another grating ruled by Prof. R. W. Wood. This grating resembles the Anderson grating in giving an exceptionally bright first-order spectrum, but it has twice as many lines (15,000 per inch) and consequently twice the dispersion and theoretically twice the resolving power in corresponding orders. The scale in the ultra-violet of the first-order spectrum is about 5.3 A per mm. Observations with the Wood grating were extended to 2288 A. "Eastman 33" plates were used in this range; they were sensitized to the green, yellow, and red by bathing in solutions of pinaverdol and pinacyanol.

The shorter ultra-violet was investigated with a Hilger E_1 quartz autocollimating spectrograph. Although it is not usually used below 2100 A, by remounting the prism and lens 10 cm nearer the plate holder it was possible to extend the range of this instrument to 1860 A. The shortest arsenic wave length which was recorded with an exposure of one hour was 1889 A. Four settings of the E_1 spectrograph were chosen to cover the interval from 1860 to 3600 A with overlaps. "Eastman process" plates were used from 3600 to 2160 A and "Hilger Schumann" plates from 2300 to 1860 A. In the ultra-violet this type of spectrograph compares favorably in dispersion and resolving power with the largest diffraction gratings, and it has a considerably greater light efficiency. The scale is 0.96 A per mm at 1900 A, 1.19 A per mm at 2000 A, 2.73 A per mm at 2500 A, 4.93 A per mm at 3000 A.

Wave-length measurements were made relative to the international secondary standards in the spectrum of the iron arc.[11] Since no standards have been adopted shorter than 3370 A, from this point to 2370 A the iron arc wave lengths published by Burns [12] were used, and for the still shorter wave-length region to 1900 A Shenstone's value for Cu_{I},[13] Cu_{II},[14] and Ag_{II}[15] lines were employed. The comparison spectrum in the latter region was a condensed spark between a copper and a silver electrode.

All of the spectrograms were measured in two directions, those made with the gratings were reduced assuming a linear scale and applying corrections derived from the standards, while the prism spectrograms were reduced according to the standard method involving the Hartman-Cornu formula.[16] Most of the lines were observed on three or

[11] Trans. Internat. Astronom. Union, **3**, p. 77; 1928.
[12] Burns, Zeitschr. f. wiss. Phot., **12**, p. 207; 1913; **13**, p. 235; 1914.
[13] Shenstone, Phys. Rev., **28**, p. 449; 1926.
[14] Shenstone, Phys. Rev., **29**, p. 380; 1927.
[15] Shenstone, Phys. Rev., **31**, p. 317; 1928.
[16] Meggers, Glazebrook's Dictionary of Applied Physics, **4**, p. 890; 1923

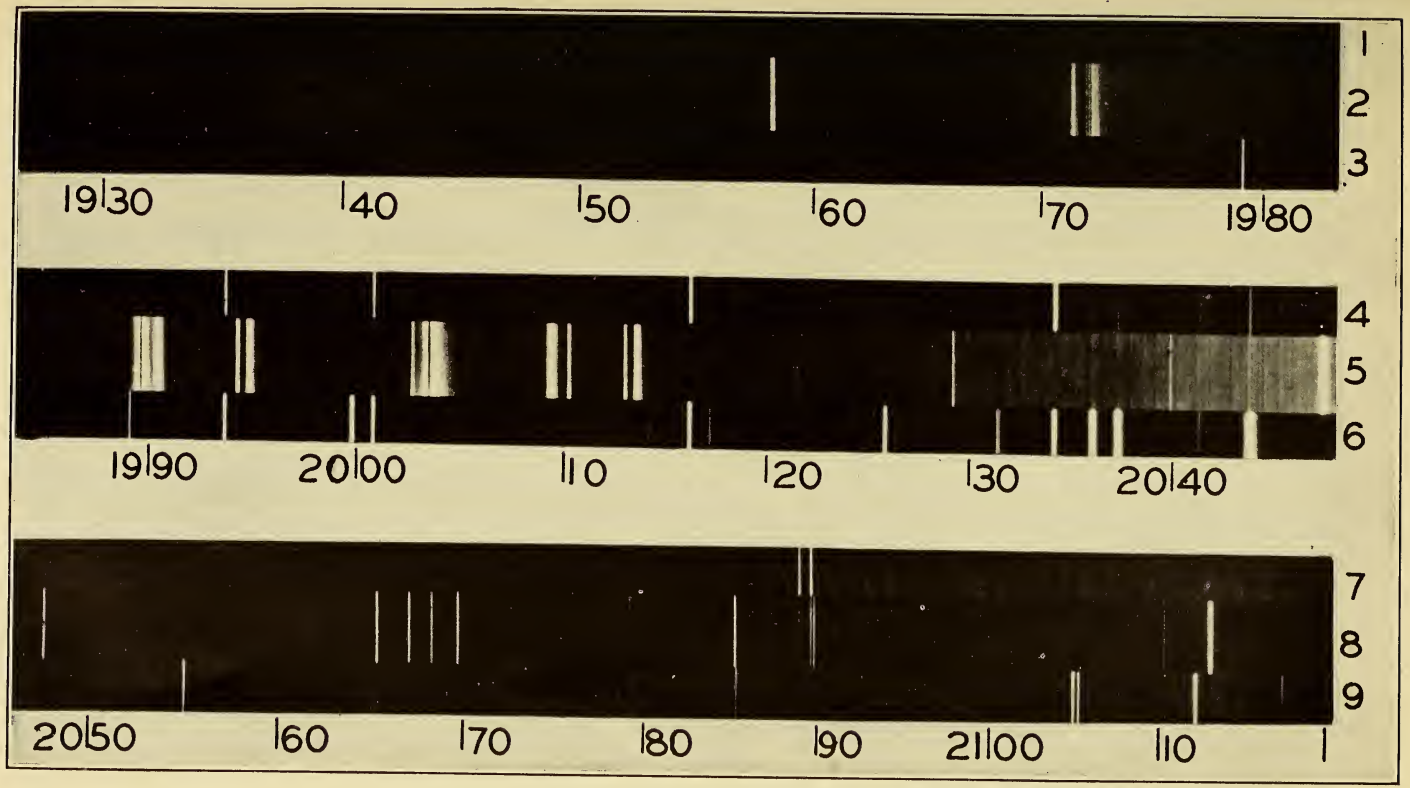

FIGURE 1.—*Arc spectrum of arsenic from 1930 to 2120 A*

Quartz prism spectrograph.
1 and 4, copper spark spectrum; 2, 5, and 8, arsenic in graphite; 3 and 6, copper + silver spark spectrum; 7, graphite arc spectrum; and 9, copper arc spectrum.

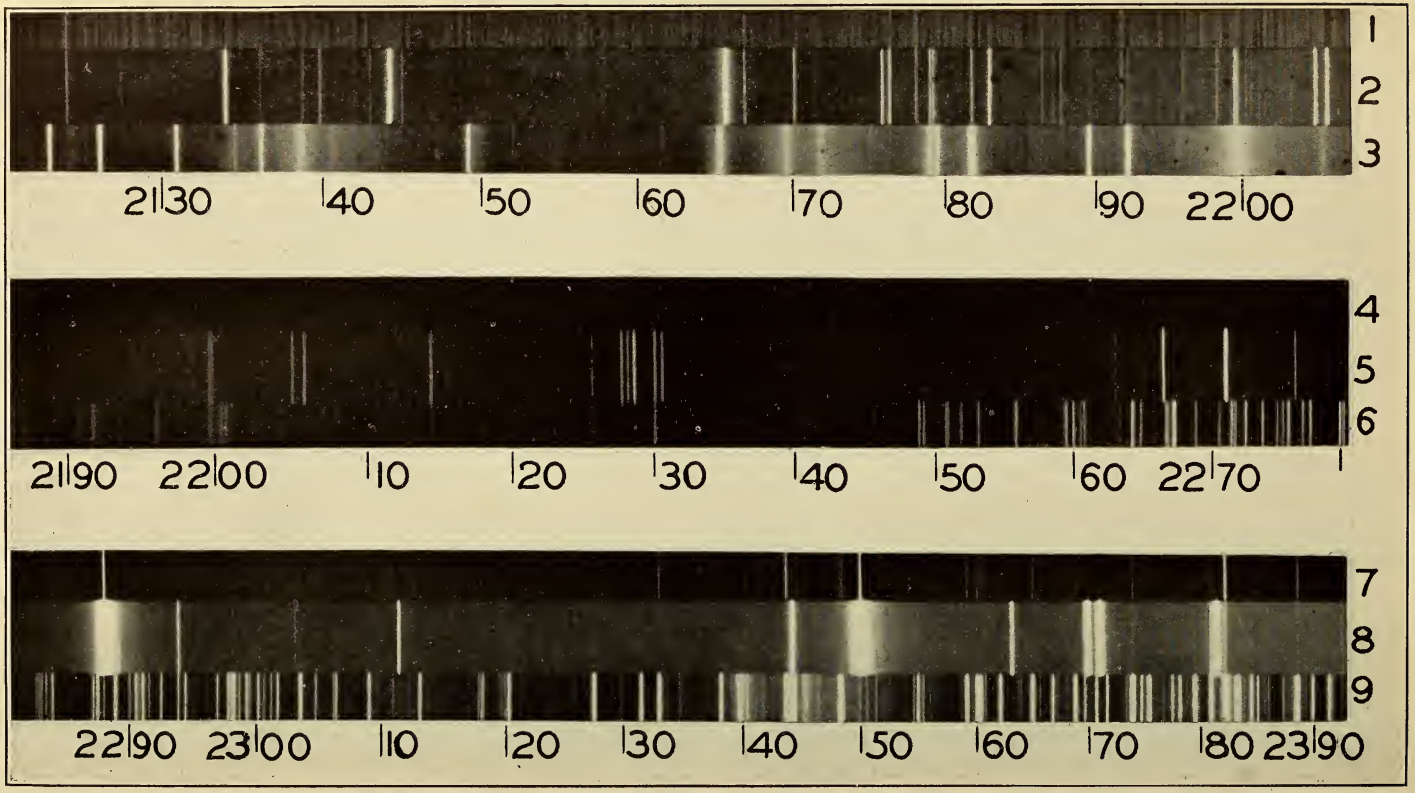

FIGURE 2.—*Arc spectrum of arsenic from 2120 to 2390 A*

Quartz prism spectrograph.
1, 4 and 7, graphite arc spectrum; 2, 5, and 8, arsenic in graphite; 3, copper arc spectrum; and 6 and 9, iron arc spectrum.

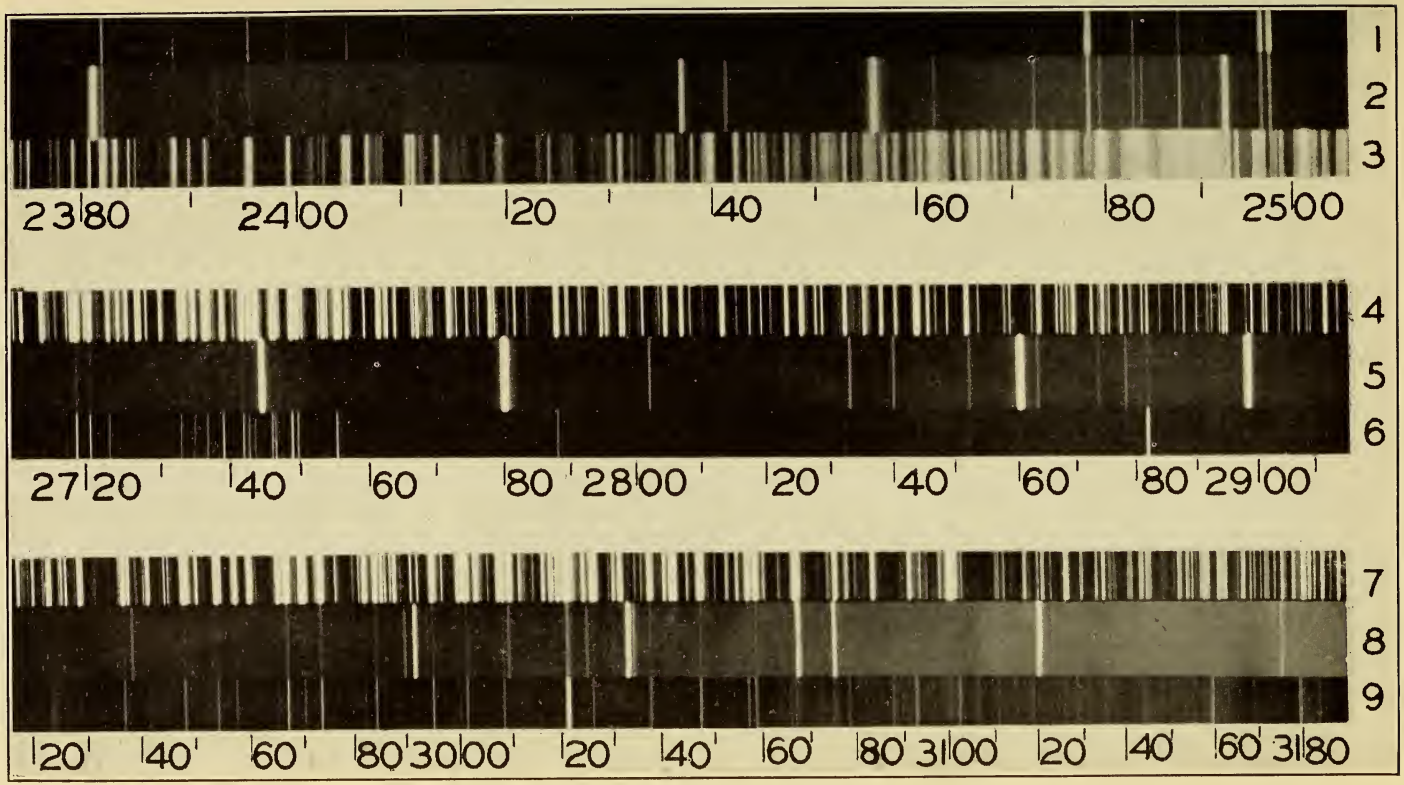

FIGURE 3.—*Arc spectrum of arsenic from 2380 to 3180 A*

Quartz prism spectrograph.
1, 6, and 9, graphite arc spectrum; 2, 5, and 8, arsenic in graphite; and 3, 4, and 7, iron arc spectrum.

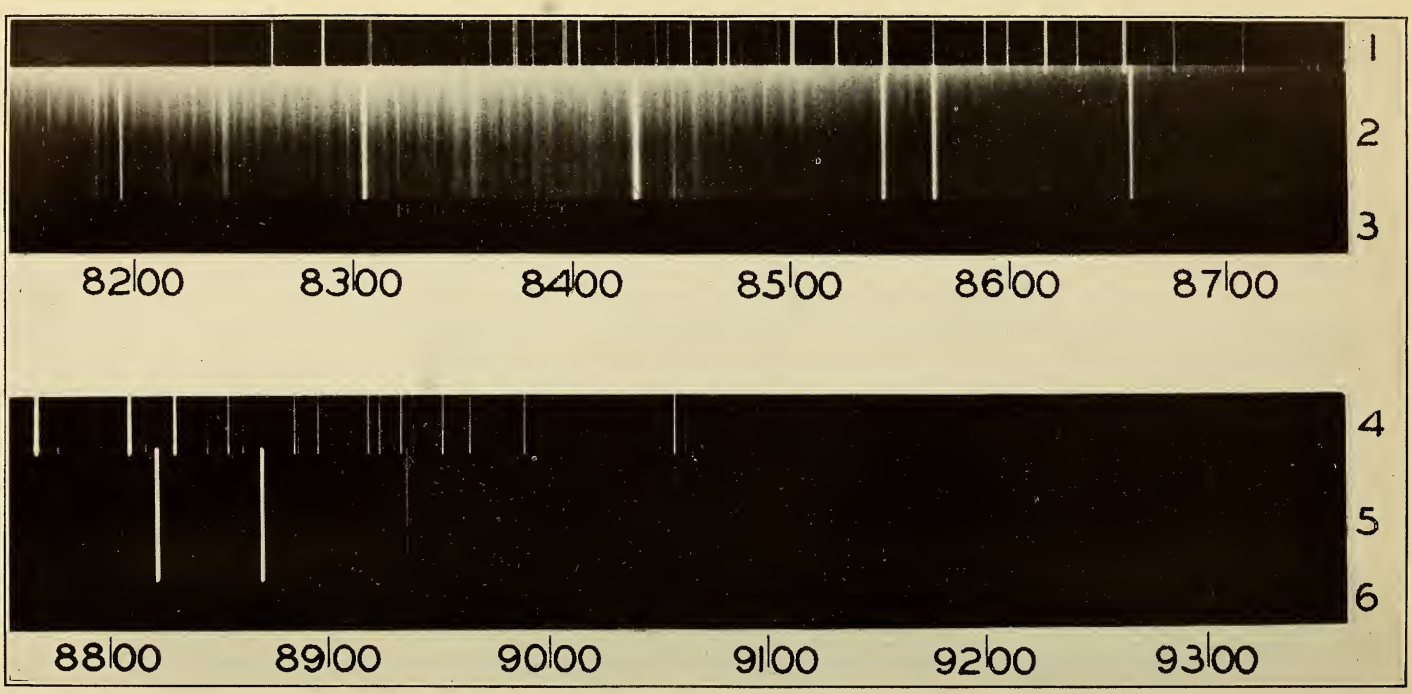

FIGURE 4.—*Arc spectrum of arsenic from 8200 to 9300 A*

Grating spectrograph.
1 and 4, iron arc spectrum; 2 and 5, arsenic in graphite; and 3 and 6, graphite arc spectrum.

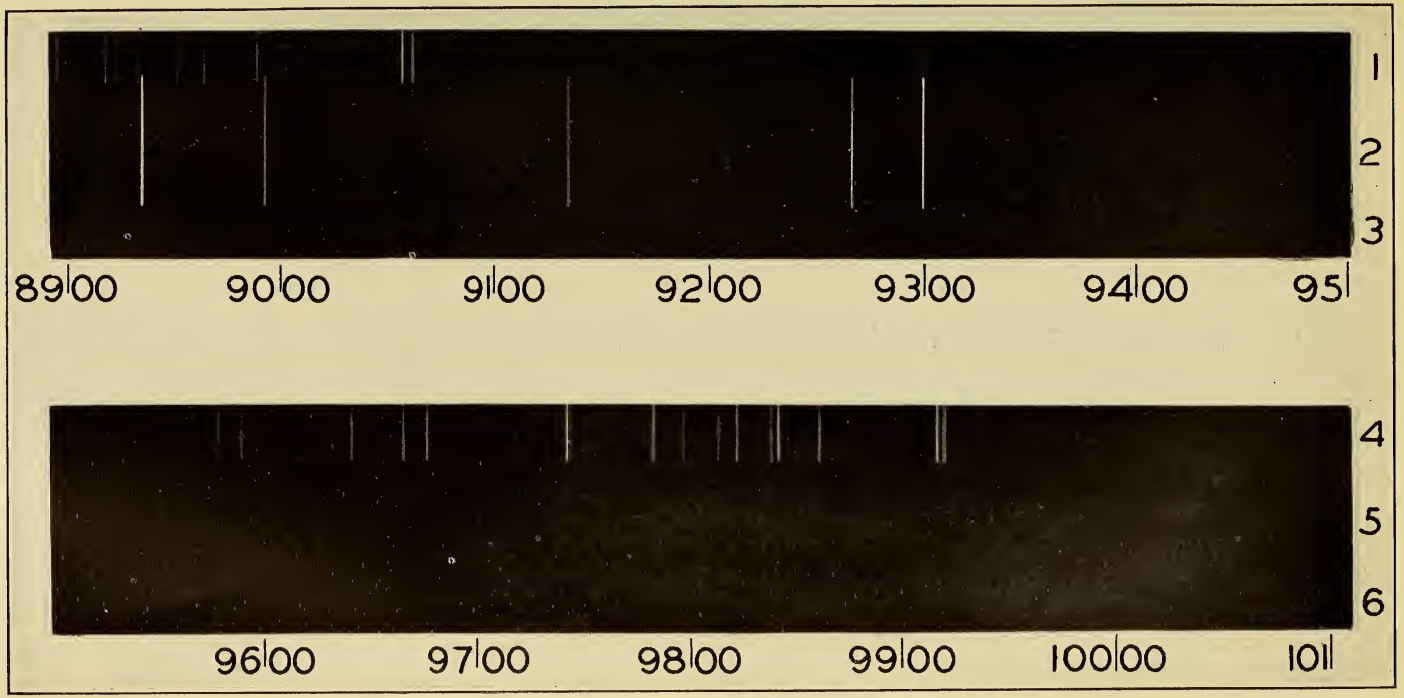

FIGURE 5.—*Arc spectrum of arsenic from 8900 to 10100 A*

Grating spectrograph.
1 and 4, iron arc spectrum; 2 and 5, arsenic in graphite; and 3 and 6, graphite arc spectrum.

more spectrograms, and the final mean wave length is probably not in error by more than one or two hundredths of an Ångstrom unit on the average.

No supplementary data, such as Zeeman effect, temperature classification, absorption phenomena, etc., are available for arsenic. Neither the Zeeman effect nor temperature classification has ever been investigated, and the absorption experiments have all given negative results for atomic arsenic. Thus, McLennan, Young, and Ireton [17] reported that no line reversals were obtained in any part of the spectrum down to 1850 A, and similar failure is recorded by Dobbie and Fox [18] and by Ruark, Mohler, Foote, and Chenault.[19]

Fortunately, certain lines of arsenic have been observed to be partially self-reversed in the arc. These reversals appear to be of two types distinguished in our tables by *R* and *r*, the former being considerably wider and more conspicuous than the latter. These observations, in addition to a satisfactory list of wave lengths and estimated intensities have enabled us to identify spectral terms which account for nearly all of the lines detected in the infra-red and ultra-violet. The strongest lines in these two regions are reproduced in Figures 1, 2, 3, 4, and 5. Attention is called to the widely reversed lines at 1937 and 1972 A, which appear to have superposed on their sides some finer absorption lines probably belonging to some compound of arsenic.

III. ANALYSIS OF THE ARC SPECTRUM OF ARSENIC

The arc spectrum of arsenic is relatively simple, and still it is difficult to analyze because so many important lines lie in the incompletely explored ultra-violet and infra-red regions. Kayser and Runge [20] first sought for regularities among the 33 lines observed by them in the ultra-violet, and they found 20 of the lines to be connected by wave-number differences of 461 and 8058. These differences are now interpreted as the intervals between three important low levels $^2P_1$, $^2P_2$, and $^2D_2$ of the As_I spectrum.

Two additional low levels were found by Ruark, Mohler, Foote, and Chenault,[21] but they interpreted the low energy levels as a set of middle terms and assigned the wrong quantum numbers in several cases. McLennan and McLay [22] gave the correct interpretation for the low energy levels but added nothing to the observational data or to the regularities. Without new and extended material, it was

[17] McLennan, Young, and Ireton, Trans. Roy. Soc. Can., **13**, 3, p. 7; 1919.
[18] Dobbie and Fox, Proc. Roy. Soc., **A98**, p. 147; 1920.
[19] Ruark, Mohler, Foote, and Chenault, B. S. Sci. Papers, **19** (No. 490), p. 463; 1924.
[20] Kayser and Runge, Wiedem. Ann., **52**, p. 93; 1894.
[21] Ruark, Mohler, Foote, and Chenault, B. S. Sci. Papers, **19** (No. 490), p. 463; 1924.
[22] McLennan and McLay, Trans. Roy. Soc. Can., **21**, 3, p. 63; 1927.

obvious that no real progress could be made in the analysis of the arsenic spectrum.

1. THEORETICAL TERMS

The neutral arsenic atom has 33 electrons ($Z=33$), but only 5 of these are of interest spectroscopically. According to the theory of spectral terms and electron configurations elaborated by Hund,[23] the terms which represent the excited states of the arsenic atom will result from the interaction of the series electron with the electron group s^2p^2 which characterizes the unexcited state of the ion, As^+. The terms arising from s^2p^2 are ^3P, ^1D, ^1S, the lowest levels of the As_{II} spectrum. We may, therefore, obtain the terms representing the excited states of the neutral atom by adding in turn the electron, *ns*, *np*, *nd*, etc., to the basic terms ^3P, ^1D, ^1S. The normal state of the As atom is formed by the configuration s^2p^3 giving rise to the five low levels[24] $^4S_2$, $^2D_{2,3}$, $^2P_{1,2}$. The complete set of theoretical terms which may be expected to account for the As_I spectrum is presented in Table 1.

TABLE 1.—*Predicted terms in the As_I spectrum*

Electron configuration As_{II}	$^3P_{1,2,3}$	$^1D_2$	$^1S_1$
$s^2p^2.4p$	$^4S_2$ $^2D_{2,3}$ $^2P_{1,2}$		
$s^2p^2.5s$	$^4P_{1,2,3}$ $^2P_{1,2}$	$^2D_{2,3}$	$^2S_1$
$s^2p^2.5p$	$^4D_{1,2,3,4}$ $^4P_{1,2,3}$ $^4S_2$ $^2D_{2,3}$ $^2P_{1,2}$ $^2S_1$	$^2F_{3,4}$ $^2D_{2,3}$ $^2P_{1,2}$	$^2P_{1,2}$
$s^2p^2.4d$	$^4F_{2,3,4,5}$ $^4D_{1,2,3,4}$ $^4P_{1,2,3}$ $^2F_{3,4}$ $^2D_{2,3}$ $^2P_{1,2}$	$^2G_{4,5}$ $^2F_{3,4}$ $^2D_{2,3}$	$^2D_{2,3}$

The normal electron configuration of the outer shell of As is s^2p^3, and the foregoing excited states arise from the displacement of one of the *p*-electrons. It is also possible that terms involving the displacement of an *s*-electron are present. Thus, from the configuration sp^4 we may expect the terms,

$$^4P_{1,2,3}\ ^2P_{1,2}\ ^2D_{2,3}\ ^2S.$$

Terms of this character have indeed been found by Bowen[25] in the analogous N_I spectrum and by Ingram[26] in the analogous S_{II} spectrum.

[23] Hund, Linienspektren und periodisches System der Elemente, Julius Springer, Berlin; 1927.

[24] For greater convenience of writing, printing, and reading the inner quantum numbers of levels belonging to even multiplicities are increased by one-half in this paper.

[25] Bowen Phys. Rev., 29, p. 231; 1927.

[26] Ingram, Phys. Rev., 32, p. 172; 1928.

2. THE MULTIPLETS

The combinations accompanying the electron transition $5s \rightarrow 4p$ are presented as a supermultiplet in Table 2. This supermultiplet contains 35 ultra-violet lines, including most of those observed as reversed in the arc. Fourteen of these lines are contained in the wave-number scheme of Kayser and Runge. Six lines fall in the vacuum region; they are represented by wave numbers calculated from relative term values. It is possible that five of these calculated lines are identifiable with lines observed by L. and E. Bloch[27] in the arsenic spark spectrum as follows:

Intensity	λ	Observed	Calculated	Combinations
1	1, 831. 1	54, 612	54, 606	$^4S_2$–$^2P_2$
3	1, 844. 3	54, 221	54, 219	$^2D_2$–$^2S_1$
1	1, 881. 08	53, 143	53, 135	$^4S_2$–$^2P_1$
1	1, 644. 0	60, 827	60, 834	$^4S_2$–$^2D_2$
			60, 814	$^4S_2$–$^2D_3$

The sixth line (64,810 $^4S_2$–$^2S_1$) falls just beyond the limit of the observations.

It is to be noted, further, that while the terms originating with ^3P are regular, (level values increase with decreasing inner quantum number), the $^2D_{3,\,2}$ arising from ^1D is inverted. Attention is called also to the fact that the level separations $5s\ ^4P_{1,\,3}$ and $5s\ ^2P_{1,\,2}$ have exactly the ratio 3:2 which might be anticipated from considerations of convergence to limits in the As_{II} spectrum. This ratio has been found in several 7-electron systems[28] to be 4:3, but in these cases the convergence to limits is uncertain because of inverted terms.

The $5p \rightarrow 5s$ multiplets, involving 23 infra-red lines of arsenic are given as a supermultiplet in Table 3. The following remarks are pertinent to the terms and combinations shown here. It is not possible at present to assign all the quantum numbers of the $5p$-terms with positiveness, but in most cases a plausible interpretation can be suggested. Thus, although no satellites have been observed to support the $5p\ ^4P$–$5s\ ^4P$ multiplet, the line intensities, term differences, and interval ratio are of the order that can be expected. Furthermore, it is possible by interpolation to predict the spectral region in which this multiplet should occur. This is illustrated in Table 4 where the first column contains the atomic number, the second the chemical symbol, the third the $p \rightarrow s$ "electron jump" symbolized by spectral term differences. The actual values, so far as known,

[27] L. and E. Bloch, J. de. Phys., 4, p. 622; 1914, Comptes rendus, 171, p. 709; 1920.
[28] deBruin, Zeitschr. f. Phys., 53, p. 661; 1929.

are given in wave numbers in column 4. A fairly regular progression of wave number with increasing atomic number appears to exist, and it sustains the construction placed upon 9973.35 of As_I. It may be added that if this identification is correct $5p\ ^4P$ has a lower position in the energy diagram of As_I than $5p\ ^4D$.

TABLE 2.—*As_I supermultiplet $5s \rightarrow 4p$*

5s \ 4p	$^4S_2$ 80,692.72	$^2D_2$ 70,101.26	$^2D_3$ 69,779.03	$^2P_1$ 62,507.46	$^2P_2$ 62,046.13
	1, 000 *R*	50		20	50
$^4P_1$	1, 972. 03	2, 492. 91		3, 075. 32	3, 119. 60
	50, 692. 72	40, 101. 60		32, 507. 53	32, 046. 13
30, 000. 00	50, 692. 72	40, 101. 26		32, 507. 46	32, 046. 13
	1, 000 *R*	50	200 *r*	20	40
$^4P_2$	1, 937. 02	2, 437. 23	2, 456. 53	2, 990. 99	3, 032. 68
	51, 608. 91	41, 017. 74	40, 695. 45	33, 424. 02	32, 962. 68
29, 083. 52	51, 609. 20	41, 017. 72	40, 695. 51	33, 423. 94	32, 962. 61
	1, 000 *R*	10	150 *r*		2
$^4P_3$	1, 889. 85	2, 363. 05	2, 381. 20		2, 918. 82
	52, 896. 62	42, 305. 24	41, 983. 17		34, 250. 40
27, 795. 83	52, 896. 89	42, 305. 43	41, 983. 20		34, 250. 30
	1	500 *R*		100 *r*	50 *r*
$^2P_1$	1, 881. 08	2, 349. 84		2, 860. 44	2, 898. 71
	53, 143	42, 543. 05		34, 949. 42	34, 488. 06
27, 558. 28	53, 134. 44	42, 542. 98		34, 949. 28	34, 487. 85
	1	50	500 *R*	50 *r*	200 *r*
$^2P_2$	1, 831. 1	2, 271. 36	2, 288. 12	2, 745. 00	2, 780. 22
	54, 612	44, 012. 85	43, 690. 49	36, 419. 07	35, 957. 76
26, 088. 49	54, 604. 23	44, 012. 77	43, 690. 54	36, 418. 97	35, 957. 64
	1	50 *r*	300 *R*		100 *r*
$^2D_3$	1, 644. 0	1, 990. 49	2, 003. 34		2, 370. 78
	60, 827	50, 222. 74	49, 900. 41		42, 167. 32
19, 878. 59	60, 814. 13	50, 222. 67	49, 900. 44		42, 167. 54
	1	200 *R*	20 *r*	50	80 *r*
$^2D_2$	1, 644. 0	1, 989. 71	2, 002. 54	2, 344. 03	2, 369. 67
	60, 827	50, 242. 42	49, 920. 34	42, 648. 49	42, 187. 07
19, 858. 89	60, 833. 83	50, 242. 37	49, 920. 14	42, 648. 49	42, 187. 24
		3		100 *r*	100 *r*
$^2S_1$		1, 844. 3		2, 144. 10	2, 165. 52
		54, 221		46, 624. 87	46, 163. 74
15, 882. 49	64, 810. 23	54, 218. 77		46, 624. 97	46, 163. 64

TABLE 3.—*As*$_{\text{I}}$ *supermultiplet* $5p \rightarrow 5s$

$5p$ \ $5s$	$^4P_1$ 30,000.00	$^4P_2$ 29,083.52	$^4P_3$ 27,795.83	$^2P_1$ 27,558.28	$^2P_2$ 26,088.49
$^4P_1$	80 9, 833. 76 10, 166. 27				
19, 833. 73	10, 166. 27	9, 249. 79			
$^4P_2$		100 10, 023. 98 9, 973. 35			
19, 110. 17	10, 889. 83	9, 973. 35	8, 685. 66		
$^4P_3$			150 9, 923. 03 10, 074. 81		
17, 721. 02		11, 362. 50	10, 074. 81		
$^4D_1$	150 8, 821. 76 11, 332. 50	10 9, 597. 94 10, 416. 05			
18, 667. 48	11, 332. 52	10, 416. 04			
$^4D_2$	50 8, 541. 65 11, 704. 13	25 9, 267. 29 10, 787. 68			
18, 295. 86	11, 704. 14	10, 787. 66	9, 499. 97		
$^4D_3$		100 8, 564. 71 11, 672. 62	8 9, 626. 69 10, 384. 94		
17, 410. 89		11, 672. 63	10, 384. 94		
$^4D_4$			150 8, 654. 16 11, 551. 96		
16, 243. 87			11, 551. 96		
$^4S_2$		50 8, 305. 62 12, 036. 73	50 9, 300. 62 10, 749. 03		
17, 046. 80	12, 953. 20	12, 036. 72	10, 749. 03		
$^2D_2$	100 8, 428. 94 11, 860. 63	15 9, 134. 81 10, 944. 13		25 10, 614 9, 418. 9	
18, 139. 38	11, 860. 62	10, 944. 14	9, 656. 45	9, 418. 90	7, 949. 11
$^2D_3$		25 7, 960. 26 12, 558. 95	100 8, 869. 69 11, 271. 26		60 10, 453 9, 564. 0
16, 524. 57		12, 558. 95	11, 271. 26		9, 563. 92
$^2P_1$				20 8, 993. 08 11, 116. 62	
16, 441. 66				11, 116. 62	9, 646. 83
$^2P_2$		4 7, 863. 45 12, 713. 57		50 8, 935. 58 11, 188. 15	
16, 370. 04		12, 713. 48		11, 188. 24	9, 718. 45
$^2S_1$		8 7, 410. 16 13, 491. 27		10 8, 355. 00 11, 965. 60	
15, 592. 46		13, 491. 06		11, 965. 82	10, 445. 93

TABLE 4.—*Homologous electron jumps in several spectra*

Z	Element	$p \longrightarrow s$	ν	Remarks
31	Ga	$^2S_1$–$^2P_2$	(8, 265)	Calculated from terms.[1]
32	Ge	$^3P_2$–$^3S_1$		
33	As	$^4P_2$–$^4P_2$	9, 973. 35	
34	Se	$^5S_2$–$^5P_2$	(11, 029)	Extrapolated from series.[2]
35	Br	$^4P_3$–$^4D_4$	12, 084. 98	Observed.[3]
36	Kr	$^3P_2$–$^3D_3$	12, 322. 60	Do.[4]
37	Rb	$^2S_1$–$^2P_2$	12, 816. 72	Do.[5]

[1] Paschen-Götze, Seriengesetze der Linienspektren, p. 129, Julius Springer, Berlin; 1922.
[2] Paschen-Götze, Seriengesetze der Linienspektren, p. 140.
[3] Kiess and deBruin, B. S. Jour. Research (in press).
[4] Meggers, de Bruin, and Humphreys, B. S. Jour. Research, 3, (No. 89), p. 129; 1929.
[5] Paschen-Götze, Seriengesetze der Linienspektren, p. 61.

The $5s\ ^4P_1$–$5p\ ^4S_2$ combination should be a fairly strong line, but it was not observed; it may be possible that $^2D_2$ and $^4S_2$ should be interchanged, but in this case the ^2D interval becomes smaller and ^4S deeper than would be expected.

Finally, it is admitted that the identification of $5p\ ^2P_{2,1}$ is somewhat doubtful because the level separation is abnormally small. However, in the infra-red only a few faint unclassified lines remain and there seems to be no choice for another arrangement.

Now, we can discuss a group of levels (still higher than the $5p$-terms) which combines with the deep ^2P and ^2D as shown in Table 5. Combinations with the normal state ^4S nearly all fall in the unobserved ultra-violet. In developing this group of terms, we succeeded first in evaluating 8 levels (possibly 9) with inner quantum numbers, $j=1$ or 2 and then 5 levels with $j=3$. This is precisely the number of levels of each class which can be produced by the configuration $s^2p^2.4d$, and this group is accordingly interpreted as having this origin. In addition to the 13 levels with $j=1$, 2, 3 we expect 3 levels with $j=4$ and 1 with $j=5$. Unfortunately, the levels with $j=4$ can give only one combination with deep terms, but their selection is not entirely arbitrary, because so few lines remain unclassified that there is scarcely any choice. The level $j=5$ is not expected to combine with any of the deep terms. We have hazarded an interpretation of these 16 high levels (Tables 5 and 6), but we wish to emphasize at the same time the desirability of regarding the identifications and groupings as tentative rather than final.

Table 5 contains 13 ultra-violet lines observed only by L. and E. Bloch. These are distinguished from our observations by 5-place wave numbers instead of 7.

TABLE 5.—*As*, *supermultiplet 4d→4p*

4d \ 4p	$^4S_2$ 80,692.72	$^2D_2$ 70,101.26	$^2D_3$ 69,779.03	$^2P_1$ 62,507.46	$^2P_2$ 62,046.13
$^4F_4$ 18, 730. 75			20*r* 1, 958. 29 51, 048. 28 51, 048. 28		
$^4F_3$ 17, 942. 81	1 1, 593. 4 62, 759 62, 749. 91	5 1, 916. 61 52, 158. 31 52, 158. 45	4 1, 928. 58 51, 834. 69 51, 836. 22		25 2, 266. 70 44, 103. 32 44, 103. 32
$^4F_2$ 17, 190. 10	2 1, 574. 7 63, 504 63, 502. 62			15 2, 205. 97 45, 317. 35 45, 317. 36	20 2, 228. 66 44, 856. 03 44, 856. 03
$^4D_1$ 16, 712. 10		1 1, 872. 33 53, 391 53, 389. 16		20 2, 182. 94 45, 795. 40 45, 795. 36	10 2, 205. 16 45, 334. 00 45, 334. 03
$^4D_2$ 16, 571. 50	64, 121. 22	53, 529. 76	53, 207. 53	15 2, 176. 26 45, 935. 95 45, 935. 96	5 2, 198. 34 45, 474. 63 45, 474. 63
$^4D_3$ 16, 351. 41	64, 341. 31	1 1, 859. 90 53, 748 53, 749. 85	1 1, 871. 07 53, 427 53, 427. 62		5 2, 187. 75 45, 694. 72 45, 694. 72
$^4D_4$ 15, 853			2 1, 854. 4 53, 926 53, 926		
$^4P_1$? 15, 196. 55	65, 496. 17	54, 904. 71		100 2, 113. 01 47, 310. 81 47, 310. 91	30 2, 133. 81 46, 849. 69 46, 849. 58
$^4P_1$ 14, 209. 76	66, 482. 96	2 1, 789. 2 55, 891 55, 891. 50		30 2, 069. 83 48, 297. 66 48, 297. 70	10 2, 089. 79 47, 836. 41 47, 836. 37
$^4P_2$ 14, 106. 48	66, 586. 24	55, 994. 78	55, 672. 55	40 2, 065. 41 48, 401. 00 48, 400. 98	25 2, 085. 29 47, 939. 63 47, 939. 65
$^4P_3$ 13, 686. 10	67, 006. 62	1 1, 772. 5 56, 417 56, 415. 16	56, 092. 93		25 2, 067. 16 48, 360. 03 48, 360. 03
$^2F_4$ 14, 396			5 1, 805. 6 55, 383 55, 383		

TABLE 5.—*As*$_{I}$ *supermultiplet* $4d \rightarrow 4p$—Continued

4 *d* \ 4*p*	$^4S_2$ 80,692.72	$^2D_2$ 70,101.26	$^2D_3$ 69,779.03	$^2P_1$ 62,507.46	$^2P_2$ 62,046.13
$^2F_3$		3 1, 758. 2 56, 876			50 2, 047. 59 48, 822. 17
13, 223. 96	67, 468. 76	56, 877. 30	56, 555. 07		48, 822. 17
$^2P_1$				20 2, 010. 04 49, 734. 10	4 2, 028. 87 49, 272. 58
12, 773. 46	67, 919. 26	57, 327. 80		49, 734. 00	49, 272. 67
$^2D_2$		1 1, 732. 8 57, 710		100*r* 1, 994. 79 50, 114. 51	50*r* 2, 013. 32 49, 653. 10
12, 392. 99	68, 299. 73	57, 708. 27	57, 386. 04	50, 114. 47	49, 653. 14
$^2P_2$				25 1, 994. 25 50, 128. 08	20 2, 012. 77 49, 666. 66
12, 379. 43	68, 313. 29	57, 721. 83	57, 399. 60	50, 128. 03	49, 666. 70
$^2D_3$		1 1, 729. 8 57, 810	2 1, 739. 4 57, 491		100*r* 2, 009. 18 49, 755. 38
12, 290. 75	68, 401. 97	57, 810. 51	57, 488. 28		49, 755. 38

Two new lines in the visible spectrum, 5,361.12 (10) and 5,497.10 A (4) deserve special mention because they can be interpreted as the "forbidden" combinations $4p\ ^4S_2$–$4p\ ^2P_{1,2}$. The $^4S_2$ level calculated from the line at 1,972.03 A ($4p\ ^4S_2$–$5s\ ^4P_1$) is 80,692.72, while the above-mentioned pair yields 80,693.80. If this interpretation is correct, these visible lines are of the same character as the nebular lines.[29]

We may mention, also, at this point the possibility of interpreting two extreme ultra-violet lines as "forbidden"; they are as follows:

Intensity	λ	$\nu_{obs.}$	$\nu_{calc.}$	Combination
2	1, 612. 3	62, 023	62, 025. 24	$4p\ ^4S_2$–$5p\ ^4D_1$
1	1, 558. 4	64, 168	64, 168. 15	$4p\ ^4S_2$–$5p\ ^2D_3$

3. THE TERM TABLE

All of the terms thus far established in the As$_{I}$ spectrum are given in Table 6. Comparison with Table 1 shows that practically all the terms resulting from the (s^2p^2) $4p$, $5s$, $5p$, $4d$ configurations have been found. Unfortunately, it is not possible at this stage to determine final absolute term values from term series, first, because the

[29] Bowen, Astrophys, J., 67 ,p. 1; 1928.

$4p$, $5p$ series will give values which are too high, and, second, because the higher terms of the spectrum are not completely described. It is, however, possible to make an estimation of the absolute term values of the As_I spectrum by comparison with the analogous terms in the spectra of neighboring elements as shown in Table 7.

We have taken 30,000 as a reasonable value for $5s\ ^4P_1$ and have based all the other terms on this value. This fixes the ground term $^4S_2$ tentatively at 80,692.72, which corresponds to an ionization potential of about 10 volts, 1.5 volts lower than the value measured by Ruark, Mohler, Foote, and Chenault.[30]

TABLE 6.—*Relative terms in the As_I spectrum*

Electron configuration	Term symbol	Term value	Level separations
$s^2p^2.4p$	$^4S_2$	80, 692. 72	
	$^2D_2$	70, 101. 26	322. 23
	$^2D_3$	69, 779. 03	
	$^2P_1$	62, 507. 46	461. 33
	$^2P_2$	62, 046. 13	
$s^2p^2.5s(^3P)$	$^4P_1$	30, 000. 00	916. 48
	$^4P_2$	29, 083. 52	1, 287. 69
	$^4P_3$	27, 795. 83	
	$^2P_1$	27, 558. 28	1, 469. 79
	$^2P_2$	26, 088. 49	
$s^2p^2.5s(^1D)$	$^2D_3$	19, 878. 59	−19. 70
	$^2D_2$	19, 858. 89	
$s^2p^2.5s(^1S)$	$^2S_1$	15, 882. 49	
$s^2p^2.5p$	$^4P_1$	19, 833. 73	723. 56
	$^4P_2$	19, 110. 17	1, 389. 15
	$^4P_3$	17, 721. 02	
	$^4D_1$	18, 667. 48	371. 62
	$^4D_2$	18, 295. 86	884. 97
	$^4D_3$	17, 410. 89	1, 167. 02
	$^4D_4$	16, 243. 87	
	$^4S_2$	17, 046. 80	
	$^2D_2$	18, 139. 38	1, 614. 81
	$^2D_3$	16, 524. 57	
	$^2P_1$	16, 441. 66	71. 62
	$^2P_2$	16, 370. 04	
	$^2S_1$	15, 592. 46	

[30] Ruark, Mohler, Foote, and Chenault, B. S. Sci. Paper 19 (No. 490), p. 463; 1924.

TABLE 6.—*Relative terms in the As_I spectrum*—Continued

Electron configuration	Term symbol	Term value	Level separations
	$X(^1D)$	7, 448. 76	
$s^2p^2.4d$	$^4F_5$		
	$^4F_4$	18, 730. 75	−787. 94
	$^4F_3$	17, 942. 81	−752. 71
	$^4F_2$	17, 190. 10	
	$^4D_1$	16, 712. 10	140. 60
	$^4D_2$	16, 571. 50	220. 09
	$^4D_3$	16, 351. 41	498
	$^4D_4$	15, 853	
	$^4P_1$?	15, 196. 55	
	$^4P_1$	14, 209. 76	103. 28
	$^4P_2$	14, 106. 48	420. 38
	$^4P_3$	13, 686. 10	
	$^2F_4$	14, 396	−1, 172
	$^2F_3$	13, 223. 96	
	$^2P_1$	12, 773. 46	394. 03
	$^2P_2$	12, 379. 43	
	$^2D_2$	12, 392. 99	102. 22
	$^2D_3$	12, 290. 75	

TABLE 7.—*Center of gravity of 5s-terms in several spectra*

Z	Element	Center of gravity of 5s-terms	Remarks
31	Ga	23, 591	(1)
32	Ge	26, 568	(2)
33	As	(28, 500)	
34	Se	29, 462	Extrapolated from series.[3]
35	Br	30, 246	(4)
36	Kr	31, 238	(5)

[1] Paschen-Götze, Seriengesetze der Linienspektren, p. 129.
[2] Rao, Proc. Roy. Soc., A 124, p. 465; 1929.
[3] Paschen-Götze, Seriengesetze der Linienspektren, p. 140.
[4] Kiess and deBruin, B. S. Jour. Research (in press).
[5] Meggers, deBruin, and Humphreys, B. S. Jour. Research 3 (No. 89), p. 129; 1929.

4. LIST OF CLASSIFIED As_I LINES

The classified lines of the arc spectrum of arsenic are collected in Table 8. Relative intensities estimated from photographic plates appear in the first column and galvanometer deflections for 10 infrared lines observed radiometrically by Randall are in the second. In the extreme ultra-violet Bloch's intensities occupy column 2. Column 3 contains the wave length measurements, the first two lines being observed only by Randall and the last 17 only by L. and E.

Bloch. The corresponding vacuum wave numbers are given in column 5 and the term combinations in the last. This list contains most of the observed As_I lines and from this point of view may be regarded as a fairly complete description of the As_I spectrum. We plan, however, to extend the observations into the Schumann region, so that certain ambiguities referred to above may be removed, and also to identify higher series terms which will fix the absolute term values.

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Acknowledgment is made to Bourdon F. Scribner for assistance with the wave-length calculations.

TABLE 8.—*List of classified As_I lines*

Intensity		λ	ν (vac)	Combination
M	R			
	25	10, 614	9, 418. 9	$5s\ ^2P_1-5p\ ^2D_2$
	60	10, 453	9, 564. 0	$5s\ ^2P_2-5p\ ^2D_3$
4	100	10, 023. 98	9, 973. 35	$5s\ ^4P_2-5p\ ^4P_2$
5	150	9, 923. 03	10, 074. 81	$5s\ ^4P_3-5p\ ^4P_3$
5	80	9, 833. 76	10, 166. 27	$5s\ ^4P_1-5p\ ^4P_1$
8	140	9, 826. 69	10, 384. 94	$5s\ ^4P_3-5p\ ^4D_3$
10	100	9, 597. 94	10, 416. 05	$5s\ ^4P_2-5p\ ^4D_1$
50		9, 300. 62	10, 749. 03	$5s\ ^4P_3-5p\ ^4S_2$
25		9, 267. 29	10, 787. 68	$5s\ ^4P_2-5p\ ^4D_2$
15		9, 134. 81	10, 944. 13	$5s\ ^4P_2-5p\ ^2D_2$
20		8, 993. 08	11, 116. 62	$5s\ ^2P_1-5p\ ^2P_1$
50	15	8, 935. 58	11, 188. 15	$5s\ ^2P_1-5p\ ^2P_2$
100	15	8, 869. 69	11, 271. 26	$5s\ ^4P_3-5p\ ^2D_3$
150	10	8, 821. 76	11, 332. 50	$5s\ ^4P_1-5p\ ^4D_1$
100		8, 654. 16	11, 551. 96	$5s\ ^4P_3-5p\ ^4D_4$
100		8, 564. 71	11, 672. 62	$5s\ ^4P_2-5p\ ^4D_3$
50		8, 541. 65	11, 704. 13	$5s\ ^4P_1-5p\ ^4D_2$
100		8, 428. 94	11, 860. 63	$5s\ ^4P_1-5p\ ^2D_2$
10		8, 355. 00	11, 965. 60	$5s\ ^2P_1-5p\ ^2S_1$
50		8, 305. 62	12, 036. 73	$5s\ ^4P_1-5p\ ^4S_2$
5		8, 055. 72	12, 410. 13	$5s\ ^2D_2-X$
10		8, 042. 95	12, 429. 83	$5s\ ^2D_3-X$
25		7, 960. 26	12, 558. 95	$5s\ ^4P_2-5p\ ^2D_3$
4		7, 863. 45	12, 713. 57	$5s\ ^4P_2-5p\ ^2P_2$
8		7, 410. 07	13, 491. 43	$5s\ ^4P_2-5p\ ^2S_1$
50		3, 119. 60	32, 046. 13	$5s\ ^4P_1-4p\ ^2P_2$
20		3, 075. 32	32, 507. 53	$5s\ ^4P_1-4p\ ^2P_1$
40		3, 032. 85	32, 962. 68	$5s\ ^4P_2-4p\ ^2P_2$
20		2, 990. 99	33, 424. 02	$5s\ ^4P_2-4p\ ^2P_1$
50*r*		2, 898. 71	34, 488. 06	$5s\ ^2P_1-4p\ ^2P_2$

TABLE 8.—*List of classified As_I lines*—Continued

Intensity		λ	ν (vac)	Combination
M	B			
100*r*		2, 860. 44	34, 949. 42	$5s\ ^2P_1-4p\ ^2P_1$
200*r*		2, 780. 22	35, 957. 76	$5s\ ^2P_2-4p\ ^2P_2$
50*r*		2, 745. 00	36, 419. 07	$5s\ ^2P_2-4p\ ^2P_1$
50		2, 492. 91	40, 101. 60	$5s\ ^4P_1-4p\ ^2D_2$
200*r*		2, 456. 53	40, 695. 45	$5s\ ^4P_2-4p\ ^2D_3$
50		2, 437. 23	41, 017. 74	$5s\ ^4P_2-4p\ ^2D_2$
150*r*		2, 381. 18	41, 983. 17	$5s\ ^4P_3-4p\ ^2D_3$
100*r*		2, 370. 77	42, 167. 50	$5s\ ^2D_3-4p\ ^2P_2$
80*r*		2, 369. 67	42, 187. 07	$5s\ ^2D_2-4p\ ^2P_2$
10		2, 363. 05	42, 305. 24	$5s\ ^4P_3-4p\ ^2D_2$
500*R*		2, 349. 84	42, 543. 05	$5s\ ^2P_1-4p\ ^2D_2$
50		2, 344. 03	42, 648. 49	$5s\ ^2D_2-4p\ ^2P_1$
500*R*		2, 288. 12	43, 690. 49	$5s\ ^2P_2-4p\ ^2D_3$
50		2, 271. 36	44, 012. 85	$5s\ ^2P_2-4p\ ^2D_2$
25		2, 266. 70	44, 103. 32	$4p\ ^2P_2-4d\ ^4F_3$
20		2, 228. 66	44, 856. 03	$4p\ ^2P_2-4d\ ^4F_2$
15		2, 205. 97	45, 317. 35	$4p\ ^2P_1-4d\ ^4F_2$
10		2, 205. 16	45, 334. 00	$4p\ ^2P_2-4d\ ^4D_1$
5		2, 198. 34	45, 474. 63	$4p\ ^2P_2-4d\ ^4D_2$
5		2, 187. 75	45, 694. 72	$4p\ ^2P_2-4d\ ^4D_3$
20		2, 182. 94	45, 795. 40	$4p\ ^2P_1-4d\ ^4D_1$
15		2, 176. 26	45, 935. 95	$4p\ ^2P_1-4d\ ^4D_2$
100*r*		2, 165. 52	46, 163. 74	$4p\ ^2P_2-5s\ ^2S_1$
100*r*		2, 144. 10	46, 624. 87	$4p\ ^2P_1-5s\ ^2S_1$
30		2, 133. 81	46, 849. 69	$4p\ ^2P_2-4d\ ^4P_1$
100		2, 113. 01	47, 310. 81	$4p\ ^2P_1-4d\ ^4P_1$
10		2, 089. 79	47, 836. 41	$4p\ ^2P_2-4d\ ^4P_1$
25		2, 085. 29	47, 939. 63	$4p\ ^2P_2-4d\ ^4P_2$
30		2, 069. 83	48, 297. 66	$4p\ ^2P_1-4d\ ^4P_1$
25		2, 067. 16	48, 360. 03	$4p\ ^2P_2-4d\ ^4P_3$
40		2, 065. 41	48, 401. 00	$4p\ ^2P_1-4d\ ^4P_2$
50		2, 047. 59	48, 822. 17	$4p\ ^2P_2-4d\ ^2F_3$
4		2, 028. 87	49, 272. 58	$4p\ ^2P_2-4d\ ^2P_1$
50*r*		2, 013. 32	49, 653. 10	$4p\ ^2P_2-4d\ ^2D_2$
20		2, 012. 77	49, 666. 66	$4p\ ^2P_2-4d\ ^2P_2$
20		2, 010. 04	49, 734. 10	$4p\ ^2P_1-4d\ ^2P_1$
100*r*		2, 009. 18	49, 755. 38	$4p\ ^2P_2-4d\ ^2D_3$
300*R*		2, 003. 34	49, 900. 41	$4p\ ^2D_3-5s\ ^2D_3$
20*r*		2, 002. 54	49, 920. 34	$4p\ ^2D_3-5s\ ^2D_2$
100*r*		1, 994. 79	50, 114. 51	$4p\ ^2P_1-4d\ ^2D_2$
25		1, 994. 25	50, 128. 08	$4p\ ^2P_1-4d\ ^2P_2$
50*r*		1, 990. 49	50, 222. 74	$4p\ ^2D_2-5s\ ^2D_3$
200*R*		1, 989. 71	50, 242. 42	$4p\ ^2D_2-5s\ ^2D_2$
1000*R*		1, 972. 03	50, 692. 72	$4p\ ^4S_2-5s\ ^4P_1$
20*r*		1, 958. 29	51, 048. 28	$4p\ ^2D_3-4d\ ^4F_4$
1000*R*		1, 937. 02	51, 608. 91	$4p\ ^4S_2-5s\ ^4P_2$
4		1, 928. 58	51, 834. 69	$4p\ ^2D_3-4d\ ^4F_3$
5		1, 916. 61	52, 158. 31	$4p\ ^2D_2-4d\ ^4F_3$
1000*R*		1, 889. 85	52, 896. 62	$4p\ ^4S_2-5s\ ^4P_3$
	1	1, 881. 08	53, 143	$4p\ ^4S_2-5s\ ^2P_1$

TABLE 8.—*List of classified* As_I *lines*—Continued

Intensity		λ	ν (vac)	Combination
M	B			
	1	1, 872. 33	53, 391	$4p\ ^2D_2$–$4d\ ^4D_1$
	1	1, 871. 07	53, 427	$4p\ ^2D_3$–$4d\ ^4D_3$
	1	1, 859. 90	53, 748	$4p\ ^2D_2$–$4d\ ^4D_3$
	2	1, 854. 4	53, 926	$4p\ ^2D_3$–$4d\ ^4D_4$
	3	1, 844. 3	54, 221	$4p\ ^2D_2$–$5s\ ^2S_1$
	1	1, 831. 1	54, 612	$4p\ ^4S_2$–$5s\ ^2P_2$
	5	1, 805. 6	55, 383	$4p\ ^2D_3$–$4d\ ^2F_4$
	2	1, 789. 2	55, 891	$4p\ ^2D_2$–$4d\ ^4P_1$
	1	1, 772. 5	56, 417	$4p\ ^2D_2$–$4d\ ^4P_3$
	3	1, 758. 2	56, 876	$4p\ ^2D_2$–$4d\ ^2F_3$
	2	1, 739. 4	57, 491	$4p\ ^2D_3$–$4d\ ^2D_3$
	1	1, 732. 8	57, 710	$4p\ ^2D_2$–$4d\ ^2D_2$
	1	1, 729. 8	57, 810	$4p\ ^2D_2$–$4d\ ^2D_3$
	1	1, 644. 0	60, 814	$4p\ ^4S_2$–$5s\ ^2D_3$
	1	1, 593. 4	62, 759	$4p\ ^4S_2$–$4d\ ^4F_3$
	2	1, 574. 7	63, 504	$4p\ ^4S_2$–$4d\ ^4F_2$

WASHINGTON, June 29, 1929.