

# THE ARC SPECTRUM OF PHOSPHORUS

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## ABSTRACT

For theoretical reasons phosphorus is known to have an extensive arc spectrum lying in the infra-red. Previous efforts to record this spectrum have proved unsuccessful owing to lack of sensitivity of the specially prepared photographic plates. Plates prepared by the Eastman Kodak Co. with a new infra-red sensitizer have permitted the hitherto unknown portion of the spectrum to be photographed at the Bureau of Standards. About 40 wave lengths have been measured between 9,100 and 10,800 Å. These have been classified as combinations between quartet and doublet terms, which, without exception, are those required theoretically for the phosphorus atom. A survey of the entire spectrum has revealed the presence of seven new ultra-violet lines which give the connection between the doublet and quartet systems. From the series-forming terms the value of the lowest term  $^4S_{1/2}$  is found to be 90,000  $\text{cm}^{-1}$  giving an ionization potential of 11.11 volts.

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## I. INTRODUCTION

Until recent years our knowledge of the spectrum emitted by neutral phosphorus atoms was limited to the two pairs of ultra-violet lines which Kayser<sup>1</sup> described as characteristic of the arc spectrum. These lines, at wave lengths 2,554.9, 2,553.3, 2,535.6, and 2,534.0 Å, were also designated by de Gramont<sup>2</sup> as the raies ultimes of phosphorus. In 1924, however, a notable extension of the arc spectrum was made by Miss Saltmarsh<sup>3</sup> who observed it down to 1,671 Å in the extreme ultra-violet. Her list of wave lengths begins with the characteristic group of four lines near 2,550 Å and contains several other related groups which she arranged into multiplets of the doublet system.

About that time an effort was made at the Bureau of Standards to detect the deep red and infra-red lines which were suspected of being present in the arc spectrum of phosphorus. This effort was inspired by the discovery of doublet and quartet system multiplets of nitrogen<sup>4</sup> in the near infra-red. The spectrum of a Geissler tube containing a small amount of red phosphorus was photographed, but no lines were

<sup>1</sup> Handbuch der Spectroscopie, vol. 6, p. 242, 1912.

<sup>2</sup> Compt. rend., vol. 146, p. 1260, 1908.

<sup>3</sup> Phil. Mag., series 6, vol. 47, p. 874, 1924.

<sup>4</sup> Science, vol. 60, p. 249, 1924; vol. 61, p. 468, 1925

detected in the region which could then be explored with specially sensitized photographic plates. With the advent, a few years ago, of neocyanine<sup>5</sup> as a sensitizing agent, a second attempt was made to get the phosphorus arc lines of long wave length, but the efforts were again fruitless. Quite recently some experimental photographic plates containing a new infra-red sensitizer were sent for test to the Bureau of Standards by Dr. C. E. K. Mees, of the Eastman Kodak Co. Phosphorus was included among the various elements whose infra-red spectra were easily recorded on these new plates. The results of this most recent attempt at extending our knowledge of the spectrum emitted by the neutral P atom are presented in this report.

## II. EXPERIMENTAL PROCEDURE

The source used in these most recent experiments to obtain the phosphorus spectrum was the arc in air. For some of the observations red phosphorus was mixed with powdered graphite and the mixture packed into a cored graphite electrode. But these electrodes emitted an intense carbon band extending from 9,150 to 10,500 Å, which masked all but the more intense phosphorus lines. Examination of the copper arc spectrum revealed that it has only a few lines in the region from 9,000 to 11,000 Å. The graphite electrodes were, therefore, abandoned in favor of cored copper electrodes into which small rods of a P-Cu alloy were inserted. This alloy contained 30 per cent phosphorus and melted rather rapidly in the arc leaving a crater-like depression in the electrode. Into this at intervals of a minute or two small beads of red phosphorus moistened with water were inserted.

The observations of the infra-red region were made with the spectrograph carrying the concave grating ruled by Anderson with 7,500 lines per inch. This instrument has been described elsewhere.<sup>6</sup> To get the lines of shorter wave length, which for theoretical reasons we know must exist, a survey was then made of the entire spectrum from 2,150 Å in the ultra-violet to the infra-red, using the grating with 20,000 lines per inch and the Hilger  $E_1$  quartz spectrograph in addition to the Anderson grating. The results of this survey were the detection of seven new lines in the ultra-violet, the significance of which is pointed out below, and the demonstration of the fact that the light source employed in these observations is not adequate to bring out the fainter phosphorus lines originating in the higher energy levels of the atom.

As stated above, this investigation owes its success to the infra-red plates kindly sent to us for test purposes by Doctor Mees. The stronger phosphorus lines were recorded on them in exposures of 15 or 20 minutes. To secure the faintest lines that were measured, exposures up to two hours were required. For photographing the green, yellow, red, and near infra-red regions special plates, also supplied by Doctor Mees, were used. All the spectrograms obtained in this investigation contained exposures to the Fe or Cu arcs also, to furnish the standards required in the derivation of the phosphorus wave lengths.

<sup>5</sup> J. Opt. Soc. Am. & Rev. Sci. Inst., vol. 12, p. 397, 1926.

<sup>6</sup> B. S. Sci. Papers Nos. 312, 441, and 499.

## III. RESULTS

## 1. WAVE LENGTHS AND INTENSITIES

The phosphorus wave lengths, which were derived from measurement of the spectrograms described above, are recorded in the first column of Table 3. Except for a few lines of intensity 0, which were measured on only one plate, all the wave lengths are the means of two to six observations and are referred to values of the Fe lines which have been adopted as secondary standards.<sup>7</sup> The intensities are visual estimates only. Owing to the changing spectral sensitivity of the photographic plates, the intensities recorded for groups of lines in different portions of the spectrum are not comparable with each other and are to be interpreted only as showing the relative strengths of the members of the group.

## 2. STRUCTURE OF THE ARC SPECTRUM

Nearly all the lines of Table 3 can be interpreted as combinations between terms, which according to atomic theory represent the different energy levels of the atom. Phosphorus, of atomic number 15, has 15 extra-nuclear electrons of which 10 fill all the allowed positions in the K and L shells, leaving 5 to be distributed among the available *s*, *p*, *d* orbits of the M shell. The terms arising from the various configurations assumed by these 5 valence electrons when the atom is at rest and excited are shown in Table 1. Those printed in heavy type are the ones identified in this investigation or by McLennan and McLay,<sup>8</sup> who, several years ago, interpreted Miss Saltmarsh's observations on the basis of the present theory of spectroscopic terms. The numerical values of the identified terms are given in Table 2. These are based on the value zero for the ground term  $3p^4S_{1/2}$ . The metastable terms  $3p^2D^\circ$  and  $3p^2P^\circ$  are involved in the doublet system multiplets arranged by Miss Saltmarsh. The connection between these terms and those of the quartet system is supplied by the seven new lines discovered in the ultra-violet as shown in Tables 3 and 4. As indicated in Table 1 only terms with  $^3P$  of P II as limit have been found. The relative positions of the identified terms are illustrated by Figure 1.

<sup>7</sup> Trans. Internat. Astron. Union, vol. 3, p. 77, 1928.

<sup>8</sup> Trans. Roy. Soc. Canada, series 3, vol. 21, p. 63, 1927.



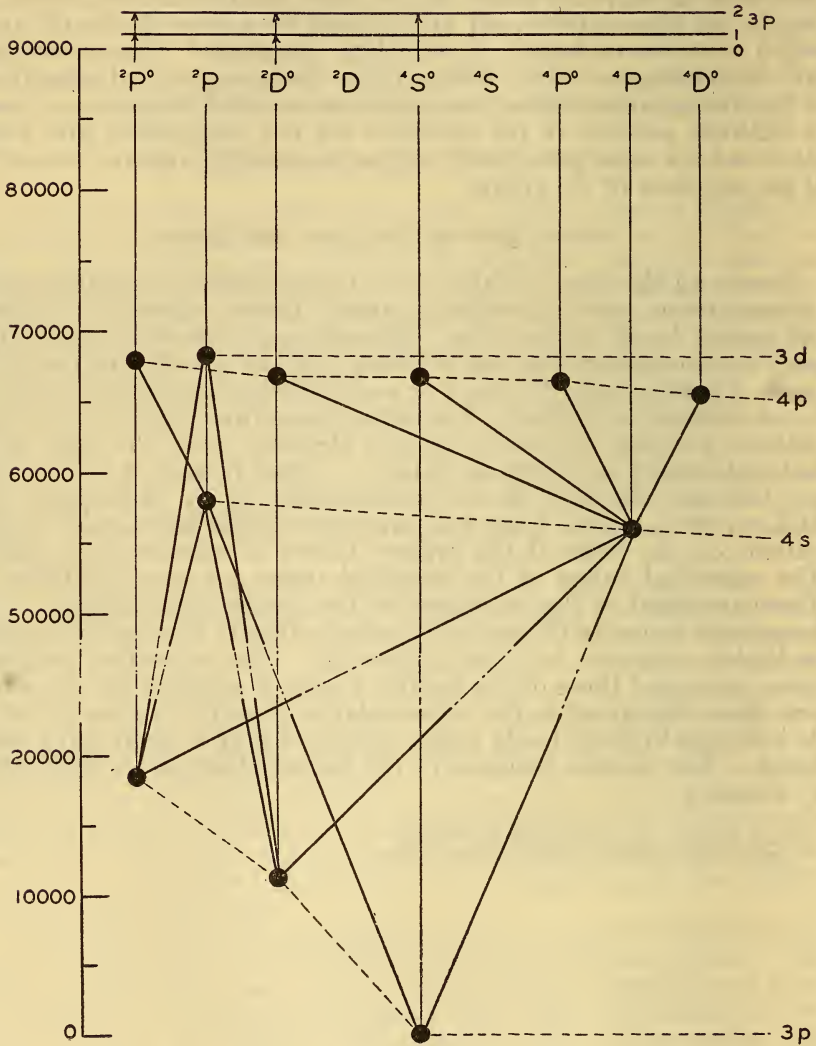


FIGURE 1.—Term diagram of  $P\ I$

TABLE 1.—Theoretical terms of P I

Electron configuration	Basic term of P II		
	<sup>3</sup> P	<sup>1</sup> D	<sup>1</sup> S
3s <sup>2</sup> .3p <sup>3</sup>	<sup>2</sup> P°, <sup>2</sup> D°, <sup>4</sup> S°		
3s <sup>2</sup> .3p <sup>2</sup> .4s	<sup>2</sup> P	<sup>2</sup> D	<sup>2</sup> S
3s <sup>2</sup> .3p <sup>2</sup> .4p	<sup>2</sup> S°, <sup>2</sup> P°, <sup>2</sup> D°, <sup>4</sup> S°, <sup>4</sup> P°, <sup>4</sup> D°	<sup>2</sup> P°, <sup>2</sup> D°, <sup>2</sup> F°	<sup>2</sup> P°
3s <sup>2</sup> .3p <sup>2</sup> .3d	<sup>2</sup> P, <sup>2</sup> D, <sup>2</sup> F, <sup>4</sup> P, <sup>4</sup> D, <sup>4</sup> F	<sup>2</sup> S, <sup>2</sup> P, <sup>2</sup> D, <sup>2</sup> F, <sup>2</sup> G	<sup>2</sup> D

TABLE 2.—Observed terms of P I

Term type	$\nu$	$\Delta\nu$	Series electron	Term type	$\nu$	$\Delta\nu$	Series electron
<sup>4</sup> S <sub>1½</sub>	0. 0			<sup>4</sup> D <sub>½</sub>	65, 378. 1		
<sup>2</sup> D <sub>1½</sub>	11, 365. 8	15. 5	3p	<sup>4</sup> D <sub>1½</sub>	65, 454. 7	76. 6	
<sup>2</sup> D <sub>3½</sub>	11, 381. 3			<sup>4</sup> D <sub>3½</sub>	65, 589. 6	134. 9	
<sup>2</sup> P <sub>0½</sub>	18, 727. 2	25. 5		<sup>4</sup> D <sub>3½</sub>	65, 791. 8	202. 2	
<sup>2</sup> P <sub>1½</sub>	18, 752. 7			<sup>4</sup> P <sub>0½</sub>	66, 347. 9		
<sup>4</sup> P <sub>0½</sub>	55, 944	151	4s	<sup>4</sup> P <sub>1½</sub>	66, 364. 7	16. 8	
<sup>4</sup> P <sub>1½</sub>	56, 095			<sup>4</sup> P <sub>1½</sub>	66, 548. 6	183. 9	4p
<sup>4</sup> P <sub>2½</sub>	56, 344	249		<sup>4</sup> S <sub>1½</sub>	66, 839. 0		
<sup>2</sup> P <sub>0½</sub>	57, 880. 9	297. 6		<sup>2</sup> D <sub>1½</sub>	66, 817. 6		
<sup>2</sup> P <sub>1½</sub>	58, 178. 5			<sup>2</sup> D <sub>3½</sub>	66, 874. 7	57. 1	
<sup>2</sup> X <sub>1½</sub>	65, 160. 9		3d	<sup>2</sup> P <sub>0½</sub>	67, 975. 2		
<sup>2</sup> P <sub>0½</sub>	67, 916. 2	219. 2		<sup>2</sup> P <sub>1½</sub>	68, 092. 4	117. 2	
<sup>2</sup> P <sub>1½</sub>	68, 135. 4						

TABLE 3.—Wave lengths observed in the arc spectrum of phosphorus

$\lambda$ I. A	Intensity	Vacuum wave number	Term combinations
10, 813. 03	0	9, 245. 57	$4s^4P_{2\frac{1}{2}}-4p^4D_{\frac{3}{2}}$
10, 681. 43	1	9, 359. 48	$4s^4P_{1\frac{1}{2}}-4p^4D_{1\frac{1}{2}}$
10, 596. 92	1	9, 434. 14	$4s^4P_{0\frac{1}{2}}-4p^4D_{0\frac{1}{2}}$
10, 581. 52	8	9, 447. 85	$4s^4P_{2\frac{1}{2}}-4p^4D_{\frac{3}{2}}$
10, 529. 45	6	9, 494. 57	$4s^4P_{1\frac{1}{2}}-4p^4D_{\frac{3}{2}}$
10, 511. 43	3	9, 510. 81	$4s^4P_{0\frac{1}{2}}-4p^4D_{1\frac{1}{2}}$
10, 455. 90	1	9, 561. 36	
10, 448. 48	0	9, 568. 15	
10, 432. 64	2	9, 582. 67	
10, 204. 72	2	9, 796. 71	$4s^2P_{1\frac{1}{2}}-4p^2P_{0\frac{1}{2}}$
10, 172. 01	0	9, 828. 22	
10, 146. 71	0 <i>b, d?</i>	9, 852. 72	
10, 124. 36	0	9, 874. 46	
10, 084. 22	25	9, 913. 77	$4s^2P_{1\frac{1}{2}}-4p^2P_{1\frac{1}{2}}$
9, 976. 65	5	10, 020. 66	$4s^4P_{2\frac{1}{2}}-4p^4P_{1\frac{1}{2}}$
9, 903. 74	8	10, 094. 43	$4s^2P_{0\frac{1}{2}}-4p^2P_{0\frac{1}{2}}$
9, 834. 61	1	10, 165. 39	
9, 796. 79	50	10, 204. 64	$4s^4P_{2\frac{1}{2}}-4p^4P_{2\frac{1}{2}}$
9, 790. 08	3	10, 211. 62	$4s^2P_{0\frac{1}{2}}-4p^2P_{1\frac{1}{2}}$
9, 779. 37	0	10, 222. 81	
9, 776. 90	0	10, 225. 39	
9, 760. 87	0	10, 242. 18	
9, 750. 73	25	10, 252. 83	$4s^4P_{1\frac{1}{2}}-4p^4P_{0\frac{1}{2}}$
9, 734. 74	20	10, 269. 68	$4s^4P_{1\frac{1}{2}}-4p^4P_{1\frac{1}{2}}$
9, 706. 80	1	10, 299. 23	
9, 676. 27	2	10, 331. 73	
9, 639. 06	1	10, 371. 61	
9, 608. 97	3	10, 404. 08	$4s^4P_{0\frac{1}{2}}-4p^4P_{0\frac{1}{2}}$
9, 593. 54	25	10, 420. 82	$4s^4P_{0\frac{1}{2}}-4p^4P_{1\frac{1}{2}}$
9, 563. 45	12	10, 453. 61	$4s^4P_{1\frac{1}{2}}-4p^4P_{2\frac{1}{2}}$
9, 545. 27	10	10, 473. 52	$4s^4P_{2\frac{1}{2}}-4p^2D_{1\frac{1}{2}}$
9, 525. 78	30	10, 494. 95	$4s^4P_{2\frac{1}{2}}-4p^4S_{1\frac{1}{2}}$
9, 493. 48	4	10, 530. 66	$4s^4P_{2\frac{1}{2}}-4p^2D_{2\frac{1}{2}}$
9, 452. 87	1	10, 575. 90	
9, 441. 76	3	10, 588. 35	
9, 435. 07	2	10, 595. 85	
9, 323. 55	2	10, 722. 59	$4s^4P_{1\frac{1}{2}}-4p^2D_{1\frac{1}{2}}$
9, 304. 88	3	10, 744. 10	$4s^4P_{1\frac{1}{2}}-4p^4S_{1\frac{1}{2}}$
9, 278. 82	1	10, 774. 28	
9, 193. 86	1	10, 873. 85	$4s^4P_{0\frac{1}{2}}-4p^2D_{1\frac{1}{2}}$
9, 175. 85	0	10, 895. 18	$4s^4P_{0\frac{1}{2}}-4p^4S_{1\frac{1}{2}}$
9, 153. 25	0	10, 922. 09	
2, 688. 02	2	37, 191. 08	$3p^2P_{1\frac{1}{2}}-4s^4P_{0\frac{1}{2}}$
2, 677. 12	5	37, 342. 50	$3p^2P_{1\frac{1}{2}}-4s^4P_{1\frac{1}{2}}$
2, 675. 31	1	37, 367. 76	$3p^2P_{0\frac{1}{2}}-4s^4P_{1\frac{1}{2}}$
2, 554. 93	30	39, 128. 28	$3p^2P_{1\frac{1}{2}}-4s^2P_{0\frac{1}{2}}$
2, 553. 28	40	39, 153. 57	$3p^2P_{0\frac{1}{2}}-4s^2P_{0\frac{1}{2}}$
2, 535. 65	50	39, 425. 78	$3p^2P_{1\frac{1}{2}}-4s^2P_{1\frac{1}{2}}$
2, 534. 01	25	39, 451. 29	$3p^2P_{0\frac{1}{2}}-4s^2P_{1\frac{1}{2}}$
2, 235. 77	5	44, 713. 39	$3p^2D_{2\frac{1}{2}}-4s^4P_{1\frac{1}{2}}$
2, 234. 99	3	44, 729. 00	$3p^2D_{1\frac{1}{2}}-4s^4P_{1\frac{1}{2}}$
2, 223. 35	3	44, 963. 14	$3p^2D_{2\frac{1}{2}}-4s^4P_{2\frac{1}{2}}$
2, 222. 59	0	44, 978. 52	$3p^2D_{1\frac{1}{2}}-4s^4P_{2\frac{1}{2}}$

*b*=broad; *d*=double.

TABLE 4.—*Multiplets from the transitions  $4s \rightarrow 3p$  and  $4p \rightarrow 4s$* 

Terms	$4s^2P_{0\frac{1}{2}}$ 57,880.9	297.6	$4s^2P_{1\frac{1}{2}}$ 58,178.5	2,234.5	$4s^2P_{2\frac{1}{2}}$ 55,944	151.1	$4s^2P_{1\frac{1}{2}}$ 56,095	249.0	$4s^2P_{2\frac{1}{2}}$ 56,344
$3p^4S_{\frac{1}{2}}$			1.5		6.5		7		7
0.0	(57, 881)		1,719.0 58,173		1,787.5 55,944		1,782.7 56,095		1,774.8 56,344
$3p^2D_{\frac{3}{2}}$			8				5		3
11,381.3			2,136.79 46,799.2				2,235.77 44,713.39		2,223.35 44,963.14
$3p^2D_{\frac{1}{2}}$			6				3		0
11,365.8	2,149.81 46,515.7		2,136.10 46,814.2		(44, 578.2)		2,234.99 44,729.00		2,222.59 44,978.52
$3p^2P_{\frac{1}{2}}$			50		2		5		
18,752.7	2,554.93 39,128.28		2,535.65 39,425.78		2,688.02 37,191.08		2,677.12 37,342.50		(37, 591.3)
$3p^2P_{\frac{3}{2}}$			25				1		
18,727.2	2,553.28 39,153.57		2,534.01 39,451.29		(37, 216.8)		2,675.31 37,367.76		
$4p^4D_{\frac{3}{2}}$									8
65,791.8									10,581.52 9,447.85
$4p^4D_{\frac{1}{2}}$							5		0
65,589.6							10,529.45 9,494.57		10,813.03 9,245.57
$4p^4D_{\frac{5}{2}}$					3		1		
65,454.7					10,511.47 9,510.81		10,681.43 9,359.48		(9, 110.5)
$4p^4D_{\frac{7}{2}}$					1				
65,378.1					10,596.91 9,434.14		(9, 283.0)		
$4p^4P_{\frac{3}{2}}$							12		50
66,548.6							9,563.45 10,453.61		9,796.79 10,204.64
$4p^4P_{\frac{1}{2}}$					25		20		4
66,364.7					9,593.54 10,420.82		9,734.74 10,269.68		9,976.65 10,020.66
$4p^4P_{\frac{5}{2}}$					3		25		
66,347.9					9,608.97 10,404.08		9,750.73 10,252.83		
$4p^4S_{\frac{1}{2}}$					0		3		30
66,839.0					9,175.85 10,895.18		9,304.88 10,744.10		9,525.78 10,494.95
$4p^2D_{\frac{3}{2}}$									4
66,874.7							(10, 779.7)		9,493.48 10,530.66
$4p^2D_{\frac{1}{2}}$					1		2		10
66,817.6					9,193.86 10,873.85		9,323.55 10,722.59		9,545.27 10,473.52
$4p^2P_{\frac{1}{2}}$			25						
68,092.4	3 9,790.08 10,211.62		10,084.22 9,913.77						
$4p^2P_{\frac{3}{2}}$			2						
67,975.2	8 9,903.74 10,094.43		10,204.72 9,796.71						



Among the faint lines remaining unclassified occur the differences 57.1 and 21.4, which, reference to Table 2 shows, are the separations between the terms  $^4S_{1/2}$ ,  $^2D_{1/2}$ , and  $^2D_{3/2}$  coming from the  $4p$  electron. It is possible to bring these lines into the classification scheme, but the new terms can not be checked from the existing wave-length data.

### 3. SERIES AND IONIZATION POTENTIAL

The terms from the  $3p$  and  $4p$  electrons form sequences from which the distances to the series limits and, consequently, the ionization potential of the atom may be found. The ground term  $^3P$  of the first spark spectrum of phosphorus, which is the limit of the series detected in P I, has been established by Bowen<sup>9</sup> and is characterized by the  $\Delta\nu$ 's 304.6 and 165.3. According to Hund<sup>10</sup> the terms  $^4S_{1/2}$ ,  $^2D_{3/2}$ , and  $^2P_{1/2}$  converge to  $^3P_2$ , while  $^2D_{1/2}$  and  $^2P_{3/2}$  converge to  $^3P_1$ . Applying these facts to the P I series the separations of the ground states of the arc and first spark spectra have been calculated as set forth in Table 5. The mean of the five determinations falls conveniently near 90,000  $\text{cm}^{-1}$ , which is adopted, for the present, as the value of  $3p\ ^4S_{1/2}$ . From this an ionization potential of 11.11 volts is derived for the neutral P atom.

TABLE 5.—Series limits of P I

Term	$3p\ ^4S_{1/2}$	$3p\ ^2P_{3/2}$	$3p\ ^2P_{1/2}$	$3p\ ^2D_{1/2}$	$3p\ ^2D_{3/2}$
Distance from limit, $\text{cm}^{-1}$ .....	91,887	71,037	71,158	78,485	78,533
Reduction to $3s^2\ 3p^2\ ^3P_0$ , P II.....	-470	-165	-470	-165	-470
Reduction to $3s^2\ 3p^3\ ^4S_{1/2}$ , P I.....	0	+18,727	+18,753	+11,366	+11,381
$^4S_{1/2}-^3P_0$ .....	91,417	89,599	89,441	89,686	89,444

$$\text{Mean } ^4S_{1/2}-^3P_0=90,000\ \text{cm}^{-1}$$

$$\text{Ionization potential}=1.2345\times 90,000\times 10^{-4}=11.11\ \text{v}$$

### 4. SPECTROCHEMICAL AND ASTROPHYSICAL TESTS FOR PHOSPHORUS

The ultimate rays of phosphorus are given by the term combination  $3p^4S^\circ-4s^4P$ . These lines, lying at 1,774.8, 1,782.7, and 1,787.5 Å, and classified several years ago by McLennan and McLay, fall outside the range of ordinary spectrographs and can not be relied on for making spectrochemical analyses. The group of four lines near 2,550 Å, chosen by de Gramont, must continue to serve this purpose. As shown in this investigation, they originate in one of the metastable states of the atom and must be designated as penultimate lines, according to the terminology of Russell.<sup>11</sup>

If phosphorus is a constituent of the sun and stars its presence will be betrayed most probably by the infra-red lines resulting from the transition  $4p\rightarrow 4s$ . The homologous element, nitrogen, is represented in the sun by only one very faint line at 8,680.4 Å given by the term combination  $2s\ ^4P_{2/2}-2p\ ^4D_{3/2}$ . The corresponding line of phosphorus lies beyond the last recorded wave length in the solar

<sup>9</sup> Phys. Rev., vol. 29, p. 510, 1927.

<sup>10</sup> Linienspektren und periodisches System der Elemente, p. 184, 1927.

<sup>11</sup> Astrophys. J., vol. 61, p. 223, 1925.



spectrum, but the other infra-red phosphorus lines fail to show any agreement with the solar lines listed in the Revision of Rowland's Preliminary Table of Solar Spectrum Wave Lengths.<sup>12</sup>

#### IV. ACKNOWLEDGMENTS

In conclusion I wish to express my thanks to Dr. C. E. K. Mees, of the Eastman Kodak Co., for his gift of the special infra-red plates which has made possible the above investigation of the phosphorus arc spectrum; and to C. M. Saeger, jr., of the metallurgy division of the Bureau of Standards, I am also thankful for the preparation of the P-Cu alloy rods used in the electrodes. To other members of the bureau staff, notably Dr. B. H. Carroll, I am indebted for assistance rendered at various times during the course of the work.

WASHINGTON, January 25, 1932.

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<sup>12</sup> Carnegie Institution of Washington, Publication No. 396, 1928.