THE SPECTRA OF TWO AND THREE-VALENCE-ELECTRON ATOMS, Si II, P III, S IV, Si III, P IV AND S V

By I. S. Bowen
Norman Bridge Laboratory of Physics
California Institute of Technology

(Received November 20, 1931)

Abstract

New measurements of the vacuum spark spectra of silicon, phosphorus and sulphur have been made with a vacuum spectrograph. With the aid of these data it has been possible to analyse a large number of hitherto unclassified lines. In Si III and P IV the stronger singlet lines have been classified, while in these ions and in S V a large number of lines involving terms in which both electrons are excited have been identified. In Si II, P III and S IV many of the important quartet lines have been located.

I. Introduction

FOWLER,[1] in his monumental analysis of the silicon spectrum, classified a large number of doublet lines in Si II and a group of triplet lines in Si III which are emitted when only one of the electrons is excited. Later Saha[2] called attention to two quartet multiplets in Si II, and Bowen[3] added a few quartet and doublet lines. The doublets of phosphorus III and sulphur IV were orginally classified by Millikan and Bowen.[4] Miss Saltmarsh[5] independently analysed the P III lines of wave-length greater than 1600A. Additional doublet lines and one quartet multiplet in each atom were later classified by Bowen[3]. The strong triplet lines of P IV and S V, emitted when a single electron is excited, were first arranged by Bowen and Millikan.[6] Again Miss Saltmarsh[5] independently listed a few of the multiplets of P IV.

In the course of the present investigation, new spectra of these elements have been obtained with a vacuum spark between metallic silicon electrodes or between magnesium electrodes containing compounds of phosphorus or sulphur. Many of the lines have been observed in all orders up to the third or fourth of a one meter grating. By the introduction of self induction in the spark circuit it was possible partially to differentiate the various stages of ionization.

II. Two Electron Atoms

The lines that have been classified in Si III, P IV and S V are given in Tables I, III and V, while the terms deduced from them are listed in Tables

[1] A. Fowler, Phil. Trans. **225**, 1 (1925).
[2] M. Saha, Nature **116**, 644 (1925).
[3] I. S. Bowen, Phys. Rev. **31**, 34 (1928).
[4] R. A. Millikan and I. S. Bowen, Phys. Rev. **25**, 600 (1925).
[5] M. O. Saltmarsh, Proc. Roy. Soc. **A108**, 332 (1925).
[6] I. S. Bowen and R. A. Millikan, Phys. Rev. **25**, 591 (1925).

II, IV and VI. For the sake of completeness all previously identified lines have been included as well as the new classifications. The wave-lengths below 2000A are new determinations which, it is hoped, have a somewhat higher

TABLE I. *Classified lines in Si III.*

Int.	λ Vac.	ν	Series Designation
3	566.54	176510	$(3s)^2\ ^1S-3s4p\ ^1P$
2	651.65	153457	$3s3p\ ^3P_0-3s5s\ ^3S$
3	652.21	153325	$3s3p\ ^3P_1-3s5s\ ^3S$
3	653.33	153062	$3s3p\ ^3P_2-3s5s\ ^3S$
1	672.29	148745	$3s3p\ ^3P_1-3s4d\ ^3D$
1	673.43	148494	$3s3p\ ^3P_2-3s4d\ ^3D$
1	800.06	124991	$3s3p\ ^1P-3s5s\ ^1S$
3	823.42	121445	$3s3p\ ^1P-3s4d\ ^1D$
4	993.54*	100650	$3s3p\ ^3P_0-3s4s\ ^3S$
5	994.82*	100521	$3s3p\ ^3P_1-3s4s\ ^3S$
5	997.40*	100261	$3s3p\ ^3P_2-3s4s\ ^3S$
3	1031.09	96984.7	$(3p)^2\ ^3P_1-3p4s\ ^3P_2$
3	1032.89	96815.7	$(3p)^2\ ^3P_0-3p4s\ ^3P_1$
4	1033.92	96719.3	$(3p)^2\ ^3P_2-3p4s\ ^3P_2$
2	1034.25	96688.4	$(3p)^2\ ^3P_1-3p4s\ ^3P_1$
2	1035.63	96559.6	$(3p)^2\ ^3P_1-3p4s\ ^3P_0$
4B	1037.02	96430.2	$(3p)^2\ ^3P_2-3p4s\ ^3P_1$
7	1108.35*	90224.2	$3s3p\ ^3P_0-3s3d\ ^3D_1$
8	1109.95*	90094.1	$3s3p\ ^3P_1-3s3d\ ^3D_{1,2}$
9	1113.20*	89831.1	$3s3p\ ^3P_2-3s3d\ ^3D_{1,2,3}$
4	1140.56	87676.2	$(3p)^2\ ^3P_0-3p3d\ ^3D_1$
4	1141.58	87597.9	$(3p)^2\ ^3P_1-3p3d\ ^3D_2$
4	1142.30	87542.7	$(3p)^2\ ^3P_1-3p3d\ ^3D_1$
5	1144.31	87388.9	$(3p)^2\ ^3P_2-3p3d\ ^3D_3$
4	1144.99	87337.0	$(3p)^2\ ^3P_2-3p3d\ ^3D_2$
3	1155.01	86579.3	$(3p)^2\ ^3P_0-3p3d\ ^3P_1$
3	1155.96	86508.2	$(3p)^2\ ^3P_1-3p3d\ ^3P_0$
3	1156.80	86445.4	$(3p)^2\ ^3P_1-3p3d\ ^3P_1$
3	1158.11	86347.6	$(3p)^2\ ^3P_1-3p3d\ ^3P_2$
3	1160.27	86186.8	$(3p)^2\ ^3P_2-3p3d\ ^3P_1$
3	1161.60	86088.2	$(3p)^2\ ^3P_2-3p3d\ ^3P_2$
10	1206.52*	82883.0	$(3s)^2\ ^1S-3s3p\ ^1P$
7	1294.55*	77246.9	$3s3p\ ^3P_1-(3p)^2\ ^3P_2$
7	1296.72*	77117.7	$3s3p\ ^3P_0-(3p)^2\ ^3P_1$
8	1298.90*	76988.2	$3s3p\ ^3P_{2,1}-(3p)^2\ ^3P_{2,1}$
7	1301.12*	76856.9	$3s3p\ ^3P_1-(3p)^2\ ^3P_0$
7	1303.30*	76728.3	$3s3p\ ^3P_2-(3p)^2\ ^3P_1$
4	1312.61	76184.1	$3s3p\ ^1P-3s4s\ ^1S$
4	1341.46	74545.6	$3s3d\ ^3D-3p3d\ ^3D_3$
3	1342.39	74494.0	$3s3d\ ^3D-3p3d\ ^3D_2$
3	1343.41	74437.4	$3s3d\ ^3D-3p3d\ ^3D_1$
3	1361.59	73443.5	$3s4s\ ^3S-3p4s\ ^3P_2$
2	1362.36	73402.0	$3s3d\ ^3D_1-3p3d\ ^3P_0$
3	1363.47	73342.3	$3s3d\ ^3D_{1,2}-3p3d\ ^3P_1$
3	1365.26	73246.1	$3s3d\ ^3D_{1,2,3}-3p3d\ ^3P_2$
3	1367.04	73150.7	$3s4s\ ^3S-3p4s\ ^3P_1$
2	1369.44	73022.5	$3s4s\ ^3S-3p4s\ ^3P_0$
1	1371.61	72907.0	$3s4p\ ^3P_1-3p4p\ ^3P_2$
1	1372.99	72833.7	$3s4p\ ^3P_2-3p4p\ ^3P_2$
1	1375.05	72724.6	$3s4p\ ^3P_0-3p4p\ ^3P_1$
1	1375.65	72692.9	$3s4p\ ^3P_1-3p4p\ ^3P_1$
2	1377.06	72618.5	$3s4p\ ^3P_{2,1}-3p4p\ ^3P_{1,0}$
5	1417.20	70561.7	$3s3p\ ^1P-(3p)^2\ ^1S$
4	1500.18*	66658.7	$3s3d\ ^3D_3-3s4f\ ^3F_4$
4	1501.16*	66615.2	$3s3d\ ^3D_{2,3}-3s4f\ ^3F_3$
3	1501.87*	66583.7	$3s3d\ ^3D_{1,2,3}-3s4f\ ^3F_2$
0	1833.42	54542.9	$(3p)^2\ ^1D-3s4p\ ^1P$
3	1842.54	54272.9	$3s3d\ ^1D-3s3p\ ^1P$
2	1895.46	52757.6	$(3s)^2\ ^1S-3s4p\ ^3P_1$
	λ Air		
10	2541.83	39329.9	$3s3p\ ^1P-3s3d\ ^1D$
7	2559.22	39062.7	$3s3p\ ^1P-(3p)^2\ ^1D$
1	3034.74*	32942.2	$3s4f\ ^3F_2-3s6g\ ^3G$
1	3037.26*	32914.9	$3s4f\ ^3F_3-3s6g\ ^3G$
1	3040.93*	32875.1	$3s4f\ ^3F_4-3s6g\ ^3G$
7	3086.225*	32392.7	$3s3d\ ^3D_3-3s4p\ ^3P_2$
3	3086.429*	32390.5	$3s3d\ ^3D_2-3s4p\ ^3P_2$
1	3086.620*	32388.5	$3s3d\ ^3D_1-3s4p\ ^3P_2$
6	3093.423*	32317.3	$3s3d\ ^3D_2-3s4p\ ^3P_1$
3	3093.613*	32315.3	$3s3d\ ^3D_1-3s4p\ ^3P_1$
4	3096.786*	32282.2	$3s3d\ ^3D_1-3s4p\ ^3P_0$
0	3126.25	31978.0	$3p3d\ ^3P_2-3p4p\ ^3P_2$
0	3147.38	31763.3	$3p3d\ ^3P_2-3p4p\ ^3P_1$
3	3185.16	31386.6	$3s4p\ ^1P-3s5s\ ^1S$
3	3230.55*	30945.6	$3s4p\ ^3P_0-3s5s\ ^3S$
5	3234.00*	30912.6	$3s4p\ ^3P_1-3s5s\ ^3S$
6	3241.67*	30839.4	$3s4p\ ^3P_2-3s5s\ ^3S$
00	3253.44	30727.9	$3p3d\ ^3D_2-3p4p\ ^3P_2$
1	3258.67	30678.6	$3p3d\ ^3D_3-3p4p\ ^3P_2$
1	3276.25	30513.9	$3p3d\ ^3D_2-3p4p\ ^3P_1$
0	3279.25	30486.0	$3p3d\ ^3D_1-3p4p\ ^3P_0$
8	3590.46	27843.7	$3s4p\ ^1P-3s4d\ ^1D$
3	3791.41*	26368.0	$3s4p\ ^3P_0-3s4d\ ^3D$
4	3796.11*	26335.3	$3s4p\ ^3P_1-3s4d\ ^3D$
5	3806.56*	26263.0	$3s4p\ ^3P_2-3s4d\ ^3D$
1	4338.52	23042.9	$(3p)^2\ ^1S-3s4p\ ^1P$
9	4552.654*	21959.2	$3s4s\ ^3S-3s4p\ ^3P_2$
7	4567.872*	21886.0	$3s4s\ ^3S-3s4p\ ^3P_1$
4	4574.777*	21853.0	$3s4s\ ^3S-3s4p\ ^3P_0$
1	4638.12	21554.4	$3p4s\ ^3P_0-3p4p\ ^3P_1$
0	4665.87	21426.3	$3p4s\ ^3P_1-3p4p\ ^3P_1$
2B	4683.774	21344.4	$3p4s\ ^3P_1-3p4p\ ^3P_0$
2B	4683.018	21347.8	$3p4s\ ^3P_2-3p4p\ ^3P_2$
2	4813.290*	20770.0	$3s4f\ ^3F_2-3s5g\ ^3G$
3	4819.740*	20742.2	$3s4f\ ^3F_3-3s5g\ ^3G$
4	4828.923*	20702.8	$3s4f\ ^3F_4-3s5g\ ^3G$
8	5739.762	17417.5	$3s4s\ ^1S-3s4p\ ^1P$

* Previously classified by Fowler (reference 1).
B Blend.

accuracy than previous measurements. In silicon the wave-lengths above 2000A are taken from Fowler[1], and in phosphorus from Geuter.[7]

[7] Geuter, Zeits. f. wiss. Photographie 5, 1 (1907).

TABLE II. *Term values in Si III.*

		$3s3p\,^3P_0$	217311	$3s3d\,^3D_1$	127088.9				
		$3s3p\,^3P_1$	217183	$3s3d\,^3D_2$	127090.9				
		$3s3p\,^3P_2$	216922	$3s3d\,^3D_3$	127093.0				
$(3s)^2\,^1S$	269940.6	$3s3p\,^1P$	187057.6	$3s3d\,^1D$	147727.6				
$3s4s\,^3S$	116659.6	$3s4p\,^3P_0$	94806.6	$3s4d\,^3D$	68438.1	$3s4f\,^3F_2$	60503.9		
		$3s4p\,^3P_1$	94773.6			$3s4f\,^3F_3$	60476.3		
		$3s4p\,^3P_2$	94700.4			$3s4f\,^3F_4$	60436.8		
$3s4s\,^1S$	110872.2	$3s4p\,^1P$	93454.7	$3s4d\,^1D$	65611.0				
$3s5s\,^3S$	63861.0							$3s5g\,^3G$	39734.0
$3s5s\,^1S$	62068.1							$3s6g\,^3G$	27561.6
				$(3p)^2\,^3P_0$	140326.	$3p3d\,^3P_0$	53686.		
				$(3p)^2\,^3P_1$	140194.	$3p3d\,^3P_1$	53748.		
				$(3p)^2\,^3P_2$	139935.	$3p3d\,^3P_2$	53846.		
				$(3p)^2\,^1S$	116497.6	$3p3d\,^3D_1$	52651.		
						$3p3d\,^3D_2$	52597.		
				$(3p)^2\,^1D$	147995.	$3p3d\,^3D_3$	52546.		
		$3p4s\,^3P_0$	43636.	$3p4p\,^3P_0$	22165.				
		$3p4s\,^3P_1$	43509.	$3p4p\,^3P_1$	22082.				
		$3p4s\,^3P_2$	43214.	$3p4p\,^3P_2$	21868.				

TABLE III. *Classified lines in P IV.*

Int.	λ Vac.	ν	Series Designation
5	628.983	158987.	$3s3p\,^3P_0-3s4s\,^3S$
6	629.914	158752.	$3s3p\,^3P_1-3s4s\,^3S$
7	631.765*	158287.	$3s3p\,^3P_2-3s4s\,^3S$
2	652.79	153189.	$(3p)^2\,^3P_1-3p4s\,^3P_2$
2	653.51	153020.	$(3p)^2\,^3P_0-3p4s\,^3P_1$
1	654.54	152779.	$(3p)^2\,^3P_1-3p4s\,^3P_1$
3	654.86	152704.	$(3p)^2\,^3P_2-3p4s\,^3P_2$
2	655.78	152490.	$(3p)^2\,^3P_1-3p4s\,^3P_0$
2	656.55	152311.	$(3p)^2\,^3P_2-3p4s\,^3P_1$
3	776.340	128809.5	$3s3p\,^1P-3s4s\,^1S$
6	823.177*	121480.6	$3s3p\,^3P_0-3s3d\,^3D$
7	824.733*	121251.4	$3s3p\,^3P_1-3s3d\,^3D$
8	827.932*	120782.9	$3s3p\,^3P_2-3s3d\,^3D$
3	845.964	118208.3	$(3p)^2\,^3P_0-3p3d\,^3D_1$
3	846.999	118063.9	$(3p)^2\,^3P_1-3p3d\,^3D_2$
4*B*	847.660	117971.8	$(3p)^2\,^3P_1-3p3d\,^3D_1$
4	849.799	117674.9	$(3p)^2\,^3P_2-3p3d\,^3D_3$
2	850.390	117593.1	$(3p)^2\,^3P_2-3p3d\,^3D_2$
1	851.094	117495.8	$(3p)^2\,^3P_2-3p3d\,^3D_1$
1	860.48	116214.	$(3p)^2\,^3P_1-3p3d\,^3P_0$
2	861.517	116074.3	$(3p)^2\,^3P_1-3p3d\,^3P_1$
2	863.288	115836.2	$(3p)^2\,^3P_1-3p3d\,^3P_2$
1	865.018	115604.5	$(3p)^2\,^3P_2-3p3d\,^3P_1$
2	866.820	115364.2	$(3p)^2\,^3P_2-3p3d\,^3P_2$
10	950.669*	105189.1	$(3s)^2\,^1S-3s3p\,^1P$
4	1006.237	99380.1	$3s3d\,^1D-3s4p\,^1P$
7	1025.579*	97505.9	$3s3p\,^3P_1-(3p)^2\,^3P_2$
7	1028.131*	97263.9	$3s3p\,^3P_0-(3p)^2\,^3P_1$
8	1030.545*	97036.0	$3s3p\,^3P_{2,1}-(3p)^2\,^3P_{2,1}$
7	1033.135*	96792.8	$3s3p\,^3P_1-(3p)^2\,^3P_0$
7	1035.542*	96567.8	$3s3p\,^3P_2-(3p)^2\,^3P_1$
3	1064.60	93932.	$3s3d\,^3D-3p3d\,^3D_3$
3	1065.554	93847.9	$3s3d\,^3D-3p3d\,^3D_2$
2	1066.640	93752.3	$3s3d\,^3D-3p3d\,^3D_1$
2	1086.943	92001.1	$3s3d\,^3D-3p3d\,^3P_0$
3	1088.608	91860.4	$3s3d\,^3D-3p3d\,^3P_1$
4	1091.442	91621.9	$3s3d\,^3D-3p3d\,^3P_2$
2	1093.318	91464.7	$3s4s\,^3S-3p4s\,^3P_2$
2	1098.183	91059.5	$3s4s\,^3S-3p4s\,^3P_1$
1	1101.65	90773.0	$3s4s\,^3S-3p4s\,^3P_0$
4	1484.508*	67362.4	$3s3d\,^3D-3s4p\,^3P_2$
4	1487.793*	67213.7	$3s3d\,^3D-3s4p\,^3P_1$
3	1489.093*	67155.0	$3s3d\,^3D-3s4p\,^3P_0$
8	1888.55	52950.7	$3s3p\,^1P-3s3d\,^1D$
1	1904.80*	52499.0	$3s4p\,^3P_1-3s5s\,^3S$
1	1910.18*	52351.1	$3s4p\,^3P_2-3s5s\,^3S$
	λ Air		
4	2724.96*	36688.4	$3s4p\,^3P_0-3s4d\,^3D_1$
4	2728.90*	36635.4	$3s4p\,^3P_1-3s4d\,^3D_2$
3	2729.29*	36630.2	$3s4p\,^3P_1-3s4d\,^3D_1$
5	2739.42*	36494.6	$3s4p\,^3P_2-3s4d\,^3D_3$
3	2740.00*	36486.9	$3s4p\,^3P_2-3s4d\,^3D_2$
6	3347.85*	29862.6	$3s4s\,^3S-3s4p\,^3P_2$
6	3364.57*	29714.2	$3s4s\,^3S-3s4p\,^3P_1$
5	3371.24*	29655.5	$3s4s\,^3S-3s4p\,^3P_0$
6	4249.73	23525.2	$3s4s\,^1S-3s4p\,^1P$

* Previously classified by Bowen and Milikan (reference 6).
B Blend.

Most of the new triplet terms arise from electron configurations in which both electrons are excited. In general, these terms combine with so many other terms, both old and new, to give observed lines that there can be little doubt as to the existence of the levels. Furthermore the irregular doublet law relationships, displayed in Table VII, confirm the assignment of the levels to

TABLE IV. *Term values in P IV.*

		$3s3p\,^3P_0$	346659	$3s3d\,^3D$	225174.6		
		$3s3p\,^3P_1$	346427				
		$3s3p\,^3P_2$	345960				
$(3s)^2\,^1S$	414247	$3s3p\,^1P$	309058	$3s3d\,^1D$	256105.		
$3s4s\,^3S$	187675	$3s4p\,^3P_0$	158019.5	$3s4d\,^3D_1$	121330.9		
		$3s4p\,^3P_1$	157960.8	$3s4d\,^3D_2$	121325.5		
		$3s4p\,^3P_2$	157812.4	$3s4d\,^3D_3$	121317.8		
$3s4s\,^1S$	180250.0	$3s4p\,^1P$	156724.8				
$3s5s\,^3S$	105461.6						
				$(3p)^2\,^3P_0$	249634.	$3p3d\,^3P_0$	133176
				$(3p)^2\,^3P_1$	249393.	$3p3d\,^3P_1$	133317
				$(3p)^2\,^3P_2$	248922.	$3p3d\,^3P_2$	133556
						$3p3d\,^3D_1$	131425
						$3p3d\,^3D_2$	131328
						$3p3d\,^3D_3$	131245
		$3p4s\,^3P_0$	96902.				
		$3p4s\,^3P_1$	96615.				
		$3p4s\,^3P_2$	96210.				

TABLE V. *Classified lines in S V.*

Int.	λ Vac.	ν	Series Designation	Int.	λ Vac.	ν	Series Designation
1	437.37*	228639.	$3s3p\,^3P_0-3s4s\,^3S$	1	691.74	144563	$(3p)^2\,^3P_2-3p3d\,^3P_1$
1	438.19*	228212.	$3s3p\,^3P_1-3s4s\,^3S$	2	693.522	144192	$(3p)^2\,^3P_2-3p3d\,^3P_2$
1	439.65*	227454.	$3s3p\,^3P_2-3s4s\,^3S$	8	786.476*	127149.4	$(3s)^2\,^1S-3s3p\,^1P$
3	658.262*	151915.	$3s3p\,^3P_0-3s3d\,^3D$	6	849.241*	117752.2	$3s3p\,^3P_1-(3p)^2\,^3P_2$
4	659.853*	151549.	$3s3p\,^3P_1-3s3d\,^3D$	5	852.185*	117345.4	$3s3p\,^3P_0-(3p)^2\,^3P_1$
5	663.155*	150794.	$3s3p\,^3P_2-3s3d\,^3D$	7	854.792*	116987.5	$3s3p\,^3P_{1,2}-(3p)^2\,^3P_{1,2}$
1	676.21	147883.	$(3p)^2\,^3P_0-3p3d\,^3D_1$	5	857.872*	116567.5	$3s3p\,^3P_1-(3p)^2\,^3P_0$
1	677.342	147636.	$(3p)^2\,^3P_1-3p3d\,^3D_2$	5	860.462*	116216.6	$3s3p\,^3P_2-(3p)^2\,^3P_1$
2	678.08	147475.	$(3p)^2\,^3P_1-3p3d\,^3D_1$	2	883.59	113175.	$3s3d\,^3D-3p3d\,^3D_3$
3	680.326	146988.	$(3p)^2\,^3P_2-3p3d\,^3D_3$	2	884.46	113063.	$3s3d\,^3D-3p3d\,^3D_2$
5B	680.940	146856.	$(3p)^2\,^3P_2-3p3d\,^3D_2$	1	885.77	112896.	$3s3d\,^3D-3p3d\,^3D_1$
3B	681.565	146721.	$(3p)^2\,^3P_2-3p3d\,^3D_1$	2	900.93	110996.	$3s3d\,^3D-3p3d\,^3P_0$
1	686.150	145741.	$(3p)^2\,^3P_0-3p3d\,^3P_1$	1	902.80	110767.	$3s3d\,^3D-3p3d\,^3P_1$
1	686.93	145575.	$(3p)^2\,^3P_1-3p3d\,^3P_0$	2	905.92	110385.	$3s3d\,^3D-3p3d\,^3P_2$
0	688.04	145340.	$(3p)^2\,^3P_1-3p3d\,^3P_1$				
1	689.838	144962.	$(3p)^2\,^3P_1-3p3d\,^3P_2$				

* Previously classified by Bowen and Millikan (reference 6).
B Blend

TABLE VI. *Term values in S V.*

		$3s3p\,^3P_0$	501629	$3s3d\,^3D$	349713		
		$3s3p\,^3P_1$	501267				
		$3s3p\,^3P_2$	500500				
$3s4s\,^3S$	273030						
				$(3p)^2\,^3P_0$	384700	$3p3d\,^3P_0$	238713
				$(3p)^2\,^3P_1$	384283	$3p3d\,^3P_1$	238950
				$(3p)^2\,^3P_2$	383514	$3p3d\,^3P_2$	239324
						$3p3d\,^3D_1$	236817
						$3p3d\,^3D_2$	236649
						$3p3d\,^3D_3$	236532

TABLE VII. *Irregular doublet law relationships in two electron-systems.*

	$3s3d\ {}^3D_3-3p3d\ {}^3P_2$ ν	Diff.	$3s3d\ {}^3D_3-3p3d\ {}^3D_3$ ν	Diff.	$(3p)^2\ {}^3P_2-3p3d\ {}^3P_2$ ν	Diff.	$(3p)^2\ {}^3P_2-3p3d\ {}^3D_3$ ν	Diff.
Si III	73246.1		74545.6		86088.2		87388.9	
		18375.8		19386.4		29276.0		30286.0
P IV	91621.9		93932.		115364.2		117674.9	
		18763.1		19243.		28827.8		29313.1
S V	110385.		113175.		144192.		146988.	
	$3s4s\ {}^3S-3p4s\ {}^3P_2$		$3s3p\ {}^1P-3s3d\ {}^1D$		$3s4s\ {}^1S-3s4p\ {}^1P$		$(3s)^2\ {}^1S-3s3p\ {}^3P_1$	
Mg I			11351.8		5843.6		21870.7	
				14277.5		5726.2		15583.1
Al II	54686.4		25629.3		11569.8		37453.8	
		18757.1		13700.6		5847.7		15303.8
Si III	73443.5		39329.9		17417.5		52757.6	
		18021.2		13620.8		6107.7		
P IV	91464.7		52950.7		23525.2			

configurations. Table VII includes these relationships for the newly identified lines only, as previous articles gave similar tables for the lines classified in them. Additional evidence for the correctness of the assignments is found in the comparison of the observed multiplet separations with the predictions of the theory developed by Goudsmit and Humphreys.[8] The comparison is shown in Table XIV and discussed in section IV.

Tables VII and XIV show at once that the P'' term in Al II, found by Sawyer and Paschen,[9] satisfies the predictions completely for the ${}^3P$ term of the $3p4s$ configuration, but definitely cannot be assigned to the $3p3d$ configuration as originally suggested by these authors.

TABLE VIII. *Quartet lines in Si II.*

Int.	λ Vac.	ν	Series Designation	Int.	λ Vac.	ν	Series Designation
3	1246.73	80209.8	$3p\ {}^4P_1-(3p)^3\ {}^4S$	0	5540.74*	18043.1	$4s\ {}^4P_1-4p\ {}^4S$
3	1248.40	80102.5	$3p\ {}^4P_2-(3p)^3\ {}^4S$	1	5576.61*	17927.1	$4s\ {}^4P_2-4p\ {}^4S$
4	1251.16	79925.8	$3p\ {}^4P_3-(3p)^3\ {}^4S$	2	5639.492*	17727.2	$4s\ {}^4P_3-4p\ {}^4S$
3	1346.92	74243.5	$3p\ {}^4P_2-4s\ {}^4P_3$	1	5800.48*	17235.2	$4s\ {}^4P_2-4p\ {}^4P_3$
3	1348.55	74153.7	$3p\ {}^4P_1-4s\ {}^4P_2$	2	5806.75*	17216.6	$4s\ {}^4P_1-4p\ {}^4P_2$
4	1350.07	74070.2	$3p\ {}^4P_3-4s\ {}^4P_3$	0	5827.80*	17154.4	$4s\ {}^4P_1-4p\ {}^4P_1$
3	1350.58	74042.3	$3p\ {}^4P_2-4s\ {}^4P_2$	0	5846.12*	17100.6	$4s\ {}^4P_2-4p\ {}^4P_2$
3	1352.68	73927.3	$3p\ {}^4P_2-4s\ {}^4P_1$	1	5867.497*	17038.4	$4s\ {}^4P_2-4p\ {}^4P_1$
3	1353.75	73868.9	$3p\ {}^4P_3-4s\ {}^4P_2$	3	5868.404*	17035.7	$4s\ {}^4P_3-4p\ {}^4P_3$
				1	5915.266*	16900.7	$4s\ {}^4P_3-4p\ {}^4P_2$

* Previously classified by Saha (reference 2).

TABLE IX. *Quartet term values in Si II.*

		$3s(3p)^2\,{}^4P_1$	87737.7	$(3p)^3\,{}^4S$	7526.8
		$3s(3p)^2\,{}^4P_2$	87627.1		
		$3s(3p)^2\,{}^4P_3$	87453.6		
$3s3p4s\,{}^4P_1$	13700.0	$3s3p4p\,{}^4S$	−4343.1		
$3s3p4s\,{}^4P_2$	13584.0				
$3s3p4s\,{}^4P_3$	13384.1	$3s3p4p\,{}^4P_1$	−3454.4		
		$3s3p4p\,{}^4P_2$	−3516.6		
		$3s3p4p\,{}^4P_3$	−3651.4		

[8] S. Goudsmit and C. J. Humphreys, Phys. Rev. **31**, 960 (1928).
[9] R. A. Sawyer and F. Paschen, Ann. d. Physik **84**, 1 (1927).

In the singlet system it is, of course, impossible to make all of the tests of the classification such as those discussed above. This naturally makes the assignment of singlet lines somewhat less certain. In most of the cases, however, the great strength of the lines and the irregular doublet law relationships shown in Table VII leave little doubt as to the reality of most of the levels. However the assignment of the levels to configurations is quite uncertain for the terms tentatively ascribed to the $3s3d$, $3s4d$ and $(3p)^2$ configurations. In fact due to the overlapping of the $3s3d$ and $(3p)^2$ configurations the terms due to them are doubtless much disturbed and any attempt to assign these terms to a definite configuration may have little significance.

The identification of the intercombination line $(3s)^2\ {}^1S-3s3p\,{}^3P_1$ in Si III is also doubtful. However the term values of the singlets and triplets can be independently determined with an accuracy which precludes any large shift in the relative position of the two systems regardless of this identification.

The term values listed correspond to an ionization potential of 33.30 volts for Si III and 51.1 volts for P IV.

III. Three-Electron Atoms

The lines that have been classified in the quartet systems of Si II, P III and S IV, including those identified by previous authors, are given in Tables VIII, X and XII, while the terms deduced from them are listed in Tables IX, XI and XIII. Since the present investigation has yielded no new doublet or intercombination lines no doublet lines or terms have been included. The wave-lengths in silicon and phosphorus above 2000A are taken from Fowler[1] and Geuter[7] respectively. Since no intercombinations are known, the quartet term values cannot be fixed accurately with respect to those of the doublets.

Table X. *Quartet lines in P III.*

Int.	λ Vac.	ν	Series Designation
2	781.728	127921.7	$3p\ {}^4P_2-4s\ {}^4P_3$
2B	782.965	127719.6	$3p\ {}^4P_1-4s\ {}^4P_2$
3B	783.739	127593.5	$3p\ {}^4P_3-4s\ {}^4P_3$
1	784.10	127535.	$3p\ {}^4P_1-4s\ {}^4P_1$
1	784.25	127510.	$3p\ {}^4P_2-4s\ {}^4P_2$
2	785.383	127326.4	$3p\ {}^4P_2-4s\ {}^4P_1$
2	786.239	127187.8	$3p\ {}^4P_3-4s\ {}^4P_2$
4	844.644	118393.1	$3p\ {}^4P_1-3d\ {}^4D_2$
4	845.029	118339.1	$3p\ {}^4P_1-3d\ {}^4D_1$
4	845.665	118250.1	$3p\ {}^4P_2-3d\ {}^4D_3$
3	846.120	118186.5	$3p\ {}^4P_2-3d\ {}^4D_2$
2	846.477	118136.7	$3p\ {}^4P_2-3d\ {}^4D_1$
4B	847.660	117971.8	$3p\ {}^4P_3-3d\ {}^4D_4$
3	848.017	117922.2	$3p\ {}^4P_3-3d\ {}^4D_3$
1	848.450	117862.0	$3p\ {}^4P_3-3d\ {}^4D_2$
2	853.355	117184.5	$3p\ {}^4P_1-3d\ {}^4P_1$
3	854.228	117064.8	$3p\ {}^4P_1-3d\ {}^4P_2$
3	854.831	116982.2	$3p\ {}^4P_2-3d\ {}^4P_1$
3	856.980	116688.8	$3p\ {}^4P_2-3d\ {}^4P_3$
3	858.133	116532.1	$3p\ {}^4P_3-3d\ {}^4P_2$
3	859.403	116359.8	$3p\ {}^4P_3-3d\ {}^4P_3$
3	972.830	102792.9	$3p\ {}^4P_1-(3p)^3\ {}^4S$
4	974.768	102588.5	$3p\ {}^4P_2-(3p)^3\ {}^4S$
4	977.890	102261.0	$3p\ {}^4P_3-(3p)^3\ {}^4S$
	λ Air		
3	2664.09	37526.6	$3d\ {}^4P_3-4p\ {}^4S$
2	2685.08	37233.1	$3d\ {}^4P_1-4p\ {}^4S$
Int.	**λ Air.**	**ν**	**Series Designation**
5B	2739.42	36494.6	$3d\ {}^4P_3-4p\ {}^4P_3$
2	2752.81	36317.2	$3d\ {}^4P_2-4p\ {}^4P_3$
4	2758.62	36240.7	$3d\ {}^4P_3-4p\ {}^4P_2$
0	2771.93	36066.7	$3d\ {}^4P_2-4p\ {}^4P_2$
0	2779.9	35963.3	$3d\ {}^4D_3-4p\ {}^4S$
3	2780.89	35950.5	$3d\ {}^4P_{2,1}-4p\ {}^4P_{1,2}$
1	2790.09	35831.9	$3d\ {}^4P_1-4p\ {}^4P_1$
2	2857.07	34992.0	$3d\ {}^4D_2-4p\ {}^4P_3$
3	2862.17	34929.6	$3d\ {}^4D_3-4p\ {}^4P_3$
4	2866.25	34879.9	$3d\ {}^4D_4-4p\ {}^4P_3$
1	2873.27	34794.7	$3d\ {}^4D_1-4p\ {}^4P_2$
3	2877.64	34741.9	$3d\ {}^4D_2-4p\ {}^4P_2$
1	2882.86	34679.0	$3d\ {}^4D_{1,3}-4p\ {}^4P_{1,2}$
1	2887.40	34624.5	$3d\ {}^4D_2-4p\ {}^4P_1$
5B	3717.77	26891.3	$4s\ {}^4P_1-4p\ {}^4S$
5	3744.36	26700.3	$4s\ {}^4P_2-4p\ {}^4S$
6	3802.22	26294.1	$4s\ {}^4P_3-4p\ {}^4S$
6	3895.17	25666.6	$4s\ {}^4P_2-4p\ {}^4P_3$
6	3904.93	25602.4	$4s\ {}^4P_1-4p\ {}^4P_2$
4	3922.86	25485.4	$4s\ {}^4P_1-4p\ {}^4P_1$
4	3933.52	25416.3	$4s\ {}^4P_2-4p\ {}^4P_2$
5	3951.65	25299.7	$4s\ {}^4P_2-4p\ {}^4P_1$
6	3957.77	25260.6	$4s\ {}^4P_3-4p\ {}^4P_3$
5	3997.31	25010.8	$4s\ {}^4P_3-4p\ {}^4P_2$

B Blend

TABLE XI. *Quartet terms in P III.*

		$3s(3p)^2\,{}^4P_1$	185423.6	$(3p)^3\,{}^4S$	82630.6
		$3s(3p)^2\,{}^4P_2$	185219.2		
		$3s(3p)^2\,{}^4P_3$	184891.4	$3s3p3d\,{}^4P_1$	68238.5
				$3s3p3d\,{}^4P_2$	68356.3
				$3s3p3d\,{}^4P_3$	68531.2
				$3s3p3d\,{}^4D_1$	67084.0
				$3s3p3d\,{}^4D_2$	67031.1
				$3s3p3d\,{}^4D_3$	66968.9
				$3s3p3d\,{}^4D_4$	66919.2
$3s3p4s\,{}^4P_1$	57891.7	$3s3p4p\,{}^4S$	31005.7		
$3s3p4s\,{}^4P_2$	57705.8				
$3s3p4s\,{}^4P_3$	57300.0	$3s3p4p\,{}^4P_1$	32406.2		
		$3s3p4p\,{}^4P_2$	32289.3		
		$3s3p4p\,{}^4P_3$	32039.3		

TABLE XII. *Quartet lines in S IV.*

Int.	λ Vac.	ν	Series Designation	Int.	λ Vac.	ν	Series Designation
2	519.30	192567.	$3p\,{}^4P_2-4s\,{}^4P_3$	4	655.553	152543.	$3p\,{}^4P_3-3d\,{}^4D_4$
2	520.11	192267.	$3p\,{}^4P_1-4s\,{}^4P_2$	2	655.887	152465.	$3p\,{}^4P_3-3d\,{}^4D_3$
3	520.83	192001.	$3p\,{}^4P_3-4s\,{}^4P_3$	1	656.30	152369.	$3p\,{}^4P_3-3d\,{}^4D_2$
1	521.13	191891.	$3p\,{}^4P_2-4s\,{}^4P_2$				
2	521.99	191575.	$3p\,{}^4P_2-4s\,{}^4P_1$	3	660.945	151299.	$3p\,{}^4P_1-3d\,{}^4P_2$
2	522.54	191373.	$3p\,{}^4P_3-4s\,{}^4P_2$	3	663.707	150669.	$3p\,{}^4P_2-3d\,{}^4P_3$
				3	664.822	150416.	$3p\,{}^4P_3-3d\,{}^4P_2$
3	652.523	153251.	$3p\,{}^4P_1-3d\,{}^4D_2$	4	666.114	150124.	$3p\,{}^4P_3-3d\,{}^4P_3$
3	653.000	153139.	$3p\,{}^4P_1-3d\,{}^4D_1$				
4	653.560	153008.	$3p\,{}^4P_2-3d\,{}^4D_3$	3	798.277	125270.	$3p\,{}^4P_1-(3p)^3\,{}^4S$
3	653.988	152908.	$3p\,{}^4P_2-3d\,{}^4D_2$	4	800.477	124926.	$3p\,{}^4P_2-(3p)^3\,{}^4S$
1	654.37	152819.	$3p\,{}^4P_2-3d\,{}^4D_1$	4	803.996	124379.	$3p\,{}^4P_3-(3p)^3\,{}^4S$

TABLE XIII. *Quartet terms in S IV.*

		$3s(3p)^2\,{}^4P_1$	309701	$(3p)^3\,{}^4S$	184431
		$3s(3p)^2\,{}^4P_2$	309357		
		$3s(3p)^2\,{}^4P_3$	308810	$3s3p3d\,{}^4P_2$	158398
				$3s3p3d\,{}^4P_3$	158687
				$3s3p3d\,{}^4D_1$	156550
				$3s3p3d\,{}^4D_2$	156447
				$3s3p3d\,{}^4D_3$	156347
				$3s3p3d\,{}^4D_4$	156267
$3s3p4s\,{}^4P_1$	117782				
$3s3p4s\,{}^4P_2$	117436				
$3s3p4s\,{}^4P_3$	116800				

However the relative positions of the two systems can be determined approximately by assuming that the $3s3p4s^4P$ term of the quartet system differs from the $(3s)^2 4s^2S$ term of the doublet system by an amount equal to the difference between the terms in the next ion on which these terms are respectively based, namely, $(3s)^2\,{}^1S-3s3p^3P$. The tabulated values of the terms are fixed in this way.

With one exception in each element all the terms found are due to configurations having a $3s$ and a $3p$ electron plus an excited electron whose transitions cause the emission of the observed lines. This makes it feasible to simplify the notation for the series designation of the lines by the omission of the $3s3p$.

TABLE XIV. *Multiplet separations.*

Triplets									Quartets						
	Al II Calc.	Al II Obs.	Si III Calc.	Si III Obs.	P IV Calc.	P IV Obs.	S V Calc.	S V Obs.		Si II Calc.	Si II Obs.	P III Calc.	P III Obs.	S IV Calc.	S IV Obs.
$3p4s\,^3P$	156	127	308	295	530	405	845		$3s3p4s\,^4P$	216	199.9	388	405.8	627	636
	78	58	154	127	265	287	423			130	116.0	233	185.9	376	346
$3p4p\,^3P$	78		154	214	265		423		$3s3p4p\,^4P$	108	134.8	194	250.0	314	
	39		77	83	133		211			65	62.2	117	117.1	188	
$3p4p\,^3D$	117		231		398		634		$3s3p4p\,^4D$	151		272		439	
	78		154		265		423			108		194		314	
										65		117		188	
$3p3d\,^3P$	−78		−154	−98	−265	−239	−423	−374	$3s3p3d\,^4P$	−108		−194	−174.9	−314	--289
	−39		−77	−62	−133	−141	−211	−237		−65		−117	−117.8	−188	
$3p3d\,^3D$	39		77	51	133	83	211	117	$3s3p3d\,^4D$	50		91	49.7	146	80
	26		51	54	88	97	141	168		36		65	62.2	104	100
										22		39	52.9	63	103

The results of this analysis of the quartets were checked with the predictions of the theory of Goudsmit and Humphreys[8] with the very satisfactory results shown in Table XIV.

IV. General Considerations

This analysis has brought to light a large number of multiplet separations, whose value can also be predicted by the theory of Goudsmit and Humphreys[8]. Table XIV gives a comparison of the predicted and observed values. The predicted values are calculated on the assumption that the a_2 of their Eq. (3) is small enough to be neglected in comparison with A'. This is probably justified in cases such as these where the electron to which the a_2 applies is much less tightly bound than the electrons to which the A' refers. As is at once seen, the theory predicts the observed values with surprising accuracy, particularly when one considers the various approximations made in the calculation.

One other regularity that is brought out by this analysis is the uniformity of arrangement of the terms arising from a given configuration in isoelectronic ions of this row of the periodic system. Thus in every atom where the terms arising from the $3p4p$ configuration of a two-electron system, the $3s3p$-$4p$ configuration of a three-electron system or the $(3s)^2 3p4p$ configuration of a four-electron system have been observed, the order of increasing term values is S, P, D. Likewise for the terms of the $3p3d$, $3s3p3d$ and the $(3s)^2 3p3d$ configurations the order is D, P, F for all cases except Si I and P II. In both of these cases other irregularities throw great doubt on the published identifications of the terms that are not in agreement with this arrangement. As might be expected from the symmetry of the eigenfunctions of s electrons, this indicates that the addition of s electrons has little effect on the relative positions of these levels. A similar regularity is found in the first row of the periodic table. In this case, however, the $2p3p$, $2s2p3p$ and $(2s)^2 2p3p$ configurations give uniformly the order P, S, D, while the $2p3d$, $2s2p3d$ and $(2s)^2 2p3d$ configurations yield P, D, F.