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THE 29 AND 30—ELECTRON-SYSTEM SPECTRA OF ARSENIC AND SELENIUM

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Abstract

New vacuum-spark data in the extreme ultra-violet have been obtained for arsenic and selenium. By aid of previous classifications in the 29 and 30—electron-system spectra of copper, zinc, gallium and germanium, it has been possible by extrapolation of the Moseley diagram, the irregular doublet law, screening constant data and the triplet interval ratios to predict the location of and to identify the lines arising from transitions between the lowest levels in the spectra of As IV, As V, Se V and Se VI. The *ionization potential* of As V is determined as 62.4 volts, that of Se VI as 81.4 volts.

The $(4P^2)\ ^3P$ separation of the 30—electron-system spectra is observed to show a rapid increase with respect to the separation both of $(4s\ 4p)^3P$ term and $(4p)^2P$ term of the next ion. The theoretical significance of this effect, which is observed here for the first time, and which does not appear in the corresponding iso-electronic spectra of the lighter elements, is discussed. The effect is believed to be due to a change of coupling of the quantum vectors with increasing nuclear charge.

I. Apparatus and Procedure

The vacuum-spark spectra of arsenic and selenium have been photographed with a one-meter vacuum spectrograph identical with that described by Sawyer.[1] A glass spark-box, similar to that described by Sawyer and Smith[2] was provided with a ground bearing fitting the conical end of the side-arm which carried the spectrograph slit. The only important modification of the spark box was the replacing with brass cones of the glass cones which carried the electrodes in the previous investigation. This gives a spark-box which is simple, convenient and almost entirely free from insulation or vacuum difficulties. The spark-box and spectrograph were evacuated separately—the spark-box by a two-stage glass Kurth pump, the spectrograph by a large three-stage Leybold steel pump. The vacuum attained was so good that discharge fog on the spectrograms was comletely eliminated.

The arsenic was used in the form of pure metallic arsenic—small pieces being held in the clamps in which the brass cones mentioned above terminated. Pure selenium electrodes were used similarly but because of the high resistivity of selenium better results were obtained by melting selenium into a hole in the end of an aluminum electrode. In some cases one carbon electrode was used to give the carbon lines with greater intensity than that with which they normally appear on all vacuum spark plates. Hydrogen 1215.68 and the carbon lines were used as standards, together with, in the case of aluminum electrodes, the aluminum and oxygen lines.

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[1] Sawyer, J.O.S.A. **15,** 305 (1927).

[2] Sawyer and Smith, J.O.S.A. **14,** 287 (1927).

The spectrograph allows a range of nearly 3000A to be photographed at once and in this work the range 0−2900A was always on the plates. The actual spectra extended to somewhat below 400A. Thus the stronger lines below 1450A could be measured in the second order and those below 950A in the third. As few lines of any intensity were found in either spectrum above 1500A practically all lines were measured in two or three orders. The definition of the grating was exceedingly good and the lines could be measured closely. It is believed an absolute accuracy of at least 0.05A and a relative accuracy in multiplet separations of 0.03A has been attained.

II. THE 29-ELECTRON-SYSTEM SPECTRA

The 29-electron-system spectra of gallium and germanium, Ga III and Ge IV, were first analyzed by Carroll[3] and remeasured and extended slightly by Lang.[4] In the present work the corresponding spectra of arsenic and selenium, As V and Se VI, have been identified by the aid of the regular and irregular doublet laws and the Moseley diagram. The classified lines in these spectra together with the approximate term values determined are given in Table I. In most cases there was no ambiguity in the identification of the lines, the lines chosen being the only choices in the region predicted by the application of the x-ray laws. The $\Delta\nu$ values for the $(4p)^2P$ doublet separations in each spectrum agree among themselves well within our assumed limit of error. The two $\Delta\nu$ separations for $(4d)^2D$ in As V show a disagreement

TABLE I. *29-electron-system spectra*

Comb.	λ	I	ν	$\Delta\nu$	Terms	
			As V			
$(4d)^2D_3-(4f)^2F_{3,4}$	1056.71	5	94633			
$(4d)^2D_2-(4f)^2F_3$	1051.64	4	95090	457		
					$(4s)^2S_1$	505136
$(4s)^2S_1-(4p)^2P_1$	1029.50	10	97135		$(5s)^2S_1$	241540
$(4s)^2S_1-(4p)^2P_2$	987.69	10	101246	4111	$(4p)^2P_1$	408001
					$(4p)^2P_2$	403891
$(4p)^2P_2-(4d)^2D_2$	737.18	5	135652		$(4d)^2D_2$	268239
$(4p)^2P_2-(4d)^2D_3$	734.77	8	136097	445	$(4d)^2D_3$	267794
$(4p)^2P_1-(4d)^2D_2$	715.50	7	139762	4110	$(4f)^2F_{3,4}$	173149
$(4p)^2P_2-(5s)^2S_1$	615.95	4	162351			
$(4p)^2P_1-(5s)^2S_1$	600.74	3	166461	4110		
			Se VI			
$(4s)^2S_1-(4p)^2P_1$	886.82	5	112762			
$(4s)^2S_1-(4p)^2P_2$	844.15	5	118462	5700	$(4s)^2S_1$	658994
					$(5s)^2S_1$	325400
$(4p)^2P_2-(4d)^2D_2$	608.39	3	164368		$(4p)^2P_1$	546232
$(4p)^2P_2-(4d)^2D_3$	605.89	4	165047	679	$(4p)^2P_2$	540532
$(4p)^2P_1-(4d)^2D_2$	588.01	4	170065	5697	$(4d)^2D_2$	376164
					$(4d)^2D_3$	375485
$(4p)^2P_2-(5s)^2S_1$	464.83	2	215132			
$(4p)^2P_1-(5s)^2S_1$	452.83	2	220833	5701		

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[3] Carroll, Phil. Trans. **225**, 357 (1925).

[4] Lang, Phys. Rev. **30**, 762 (1927).

which is certainly larger than the probable error of measurement. There is however no other choice for the DF combination on our plates and we have therefore included these lines tentatively. In the selenium spectrum two lines are found (λλ814.77, 898.71; νν122734, 123654) which have the correct separation and occur in the expected position. These lines however are definitely a part of the Se V spectrum and so are not here classified. The $(4d)^2D-(4f)^2F$ pair of Se V is either not excited in our source or there is an error in the selection of this doublet in one of the earlier spectra which makes the prediction of the expected location of the doublet incorrect. It is well known that the irregular doublet law does not hold so exactly in the case of this combination, doubtless, as has been pointed out by Bowen, and Millikan[5] because of the change of the $(4d)$ orbit to a penetrating orbit with increasing nuclear charge.

The application of the regular and irregular doublet laws to these spectra is shown in Table II and constitutes of course the chief evidence for the

TABLE II. *Application of the x-ray laws to 29-electron spectra.*

Term	Element	Regular doublet law $\Delta\nu$	σ	$\Delta\sigma_1$	$\Delta\sigma_2$
$(3d^{10}4p)^2P$	Cu I	248	20.19	1.96	
	Zn II	873	18.23	1.17	0.79
	Ga III	1718	17.06	0.79	0.38
	Ge IV	2790	16.27	0.60	0.19
	As V	4110	15.67	0.48	0.12
	Se VI	5700	15.19		
$(3d^{10}4d)^2D$	Cu I	6.4	24.47	2.07	1.51
	Zn II	40.8	22.40	0.56	−0.66
	Ga III	107	21.84	1.22	0.45
	Ge IV	255	20.62	0.77	0.38
	As V	454	19.85	0.39	
	Se VI	679	19.46		

Comb.	Element	Irregular doublet law ν	$\Delta\nu_1$	$\Delta\nu_2$
$(4s)^2S_1-(4p)^2P_1$	Cu I	30535	17949	
	Zn II	48483	16684	1264
	Ga III	65167	16140	544
	Ge IV	81307	15828	312
	As V	97135	15627	201
	Se VI	112762		
$(4p)^2P_2-(4d)^2D_2$	Cu I	19150	28404	
	Zn II	47554	29639	1235
	Ga III	77193	29298	341
	Ge IV	106491	29161	137
	As V	135652	28716	445
	Se VI	164368		
$(4d)^2D_3-(4f)^2F_3$	Cu I	5484	14819	
	Zn II	20303	20943	6124
	Ga III	41246	25394	4451
	Ge IV	66640	27988	2594
	As V	92633		

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[5] Bowen and Millikan, Phys. Rev. **28,** 923 (1926).

correctness of the classifications. The screening constants are computed from the usual formula

$$\Delta\nu=\frac{\alpha^2R(Z-\sigma)^4}{n^3l(l+1)}$$

The regular decrease of the second difference of the screening constant for the $(4p)^2P$ terms is notable. There is an irregularity in the second differences of the screening constant for the $(4d)^2D$ terms. An even greater irregularity occurs in the case of the 47-electron-system (silver-like) spectra classified by Lang[6] and there may be some perturbing effect in these terms. The second differences of wave-number also show an irregularity in the application of the irregular doublet law to $(4p)^2P_2-(4d)^2D_2$. All these irregularities may be connected with the change of the 4*d* orbit to a penetrating orbit.

Term values in these spectra may be obtained either by applying a Rydberg formula to the two *S* terms or by extrapolating the $(\nu/R)^{1/2}$ values for the preceding spectra. The result in either case is nearly the same. The values have been chosen so the $(\nu/R)^{1/2}$ values for $(4s)^2S$ and $(4p)^2P$ will form a smooth sequence with those of the preceding spectra. Table III gives the values of $(\nu/R)^{1/2}$ for the 29-electron spectra together with their first and second differences and shows how smoothly the so-called Moseley diagram lines for these spectra run. The actual term values cannot be in error by more than 1000 or 2000 cm^{-1}. The values of the $(4s)^2S$ term correspond to an ionization potential of 62.4 volts for As V and of 81.4 volts for Se VI.

TABLE III. *Values of* $(\nu/R)^{1/2}$ *for 29-electron spectra together with their differences.*

	Cu I		Zu II		Ga III		Ge IV		As V		Se VI
$(4s)^2S_1$	0.7535		1.1490		1.5021		1.8300		2.1450		2.4506
Δ_1		0.3955		0.3531		0.3279		0.3150		0.3056	
Δ_2			0.0424		0.0252		0.0129		0.0094		
$(4p)^2P_2$	0.5359		0.9311		1.2840		1.6103		1.9185		2.2194
Δ_1		0.3952		0.3529		0.3263		0.3082		0.3009	
Δ_2			0.0423		0.0266		0.0181		0.0073		
$(4d)^2D_3$	0.3357		0.6609		0.9716		1.2730		1.5623		1.8498
Δ_1		0.3252		0.3107		0.3014		0.2893		0.2875	
Δ_2			0.0145		0.0093		0.0121		0.0018		
$(5s)^2S_1$	0.4180		0.7172		0.9877		1.2400		1.4836		1.7200
Δ_1		0.2992		0.2705		0.2523		0.2436		0.2364	
Δ_2			0.0287		0.0182		0.0087		0.0072		

III. THE 30-ELECTRON-SYSTEM SPECTRA

The 30-electron-system spectra of gallium and germanium have been analyzed by Lang[4] who has given several of the triplets arising from the

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[6] Lang. Proc. Nat. Acad. Sci. **13**, 341 (1927).

lowest levels and the singlet resonance lines in each spectrum. The homologous lines in the spectra of As IV and Se V have been identified in our data by the aid of extrapolation of the x-ray laws and the triplet intervals. The classified lines in the two spectra and approximate term values are given in Table IV. The $\Delta\nu$ values for the various intervals will all be seen to agree well within the limits of error. The *PD* and *PS* triplets are especially unmistakable in arsenic where these groups stand out by themselves.

TABLE IV. *30-electron-system spectra.*

Comb.	λ	I	ν		$\Delta\nu$	Terms	
			As IV				
$(4s4p)^3P_2-(4p^2)^3P_1$	980.58	8	101981		2526	$(4s4p)^3P_0$	343400
$(4s4p)^3P_1-(4p^2)^3P_0$	971.13	8	102973			$(4s4p)^3P_1$	342250
$(4s4p)^3P_1-(4p^2)^3P_2$	956.87	8	104507		1151	$(4s4p)^3P_2$	339720
$(4s4p)^3P_2-(4p^2)^3P_2$	953.25	8	104904				
$(4s4p)^3P_0-(4p^2)^3P_1$	946.45	8	105658		2531		
$(4s4p)^3P_1-(4p^2)^3P_2$	930.80	8	107435				
$(4s^2)^1S_0-(4s4p)^1P_1$	892.68	10	112022				
$(4s4p)^3P_2-(4s4d)^3D_1$	762.75	2	131105—			$(4s4d)^3D_1$	208615
$(4s4p)^3P_2-(4s4d)^3D_2$	761.99	4	131235—	130	2526	$(4s4d)^3D_2$	208485
$(4s4p)^3P_2-(4s4d)^3D_3$	760.80	5	131441—	206		$(4s4d)^3D_3$	208279
$(4s4p)^3P_1-(4s4d)^3D_1$	748.33	5	133631—		2532		
$(4s4p)^3P_1-(4s4d)^3D_2$	747.57	5	133767—	136			
$(4s4p)^3P_0-(4s4d)^3D_1$	741.93	5	134784		1153		
$(4s4p)^3P_2-(4s5s)^3S_1$	711.07	7	140633			$(4s5s)^3S_1$	199087
$(4s4p)^3P_1-(4s5s)^3S_1$	698.50	6	143164		2531		
$(4s4p)^3P_0-(4s5s)^3S_1$	692.94	4	144313		1149		
			Se V				
$(4s4p)^3P_2-(4p^2)^3P_1$	839.49	8	119120		3614	$(4s4p)^3P_0$	500025
$(4s4p)^3P_1-(4p^2)^3P_0$	830.30	6	120438			$(4s4p)^3P_1$	498430
$(4s4p)^3P_1-(4p^2)^3P_1$	814.77	6	122734			$(4s4p)^3P_2$	494820
$(4s4p)^3P_2-(4p^2)^3P_2$	808.71	7	123654		1596		
$(4s4p)^3P_0-(4p^2)^3P_1$	804.31	5	124330		3608		
$(4s4p)^3P_1-(4p^2)^3P_2$	785.78	5	127262				
$(4s^2)^1S_0-(4s4p)^1P_1$	759.07	8	131740				
$(4s4p)^3P_2-(4s4d)^3D_1$	615.10	1	162575—	212		$(4s4d)^3D_1$	332247
$(4s4p)^3P_2-(4s4d)^3D_2$	614.30	4	162787—	335	3613	$(4s4d)^3D_2$	332033
$(4s4p)^3P_2-(4s4d)^3D_3$	613.04	5	163122—		3616	$(4s4d)^3D_3$	331698
$(4s4p)^3P_1-(4s4d)^3D_1$	601.73	4	166188—	215			
$(4s4p)^3P_1-(4s4d)^3D_2$	600.95	4	166403—		1594		
$(4s4p)^3P_0-(4s4d)^3D_1$	596.01	5	167782				
$(4s4p)^3P_2-(4s5s)^3S_1$	519.58	4	192463		3608	$(4s5s)^3S_1$	302355
$(4s4p)^3P_1-(4s5s)^3S_1$	510.02	3	196071		1593		
$(4s4p)^3P_0-(4s5s)^3S_1$	505.91	2	197664				

The regular and irregular doublet laws are obeyed by the triplets in these 30-electron spectra in an unimpeachable manner as will be seen from Table V. In all cases the smooth run of the second differences is unbroken.

The only choice in these triplet spectra which presents any ambiguity is that of the line $(4s4p)^3P_1-(4p^2)^3P_0$ since $(4p^2)^3P_0$ has only this one combination. The identification was made from the two or three possibilities

TABLE V. *Application of the x-ray laws to 30-electron spectra.*

Term	Element	Regular doublet law $\Delta\nu$	σ	Δ_1	Δ_2
	Zn I	579.2	19.38	1.58	
$(4s4p)^3P$	Ga II	1382	17.80	0.95	0.63
	Ge III	2403	16.85	0.70	0.25
	As IV	3677	16.15	0.54	0.16
	Se V	5210	15.61		
	Zn I	7.95	25.22	2.31	
$(4s4d)^3D$	Ga II	65	22.91	1.33	0.98
	Ge III	179	21.58	0.78	0.55
	As IV	336	20.80	0.60	0.18
	Se V	550	20.20		

Comb.	Irregular doublet law Element	ν	$\Delta\nu$	$\Delta_2\nu$
$(4s4p)^3P_1-(4s4d)^3D_1$	Zn I	30267	35732	
	Ga II	65999	34338	1394
	Ge III	100337	33294	1044
	As IV	133631	32557	737
	Se V	166188		
	Zn I	47890	19520	
$(4s4p)^3P_1-(4p^2)^3P_1$	Ga II	67410	18740	780
	Ge III	86150	18357	383
	As IV	104507	18227	130
	Se V	122734		

by a consideration of the ratio of $(4p^2)^3P_0-(4p^2)^3P_1$ to $(4p^2)^3P_1-(4p^2)^3P_2$ in these spectra and the choice was made so that this ratio should show a smooth progression with nuclear charge. This progression is seen in the fifth column of Table VI and is believed to be a sufficient justification for the choice made. No other choice would give a reasonable progression of these intervals. The $^3P^0P$ group[7] in Zn I was first identified by Sawyer and Beese[8] who found four lines corresponding to the combinations of $(4s4p)^3P_{0,1,2}$ with $(4p^2)^3P_0$ and $(4p^2)^3P_1$. In the position of the combinations with $(4p^2)^3P_2$

TABLE VI. *Triplet intervals*

Element	$\Delta P^0_{01}/\Delta P^0_{02}$	$\Delta D_{12}/\Delta D_{13}$	$\Delta P^0_{12}/\Delta P_{12}$	$\Delta P_{01}/\Delta P_{02}$
Zn I	0.328	0.428	——	——
Ga II	0.324	0.354	1.023	0.365
Ge III	0.318	0.402	0.950	0.355
As IV	0.313	0.389	0.864	0.344
Se V	0.307	0.391	0.796	0.336

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[7] In accordance with a new system of notation recently suggested by a committee of spectroscopists we replace PP' by P^0P. According to this system terms arising from configurations of electrons, for which the sum of the l values is odd, are called odd terms and designated by a superscript 0. If the sum of the l values of the electrons is even, the term is said to be even. Thus $(sp)^3P$ is odd whereas $(p^2)^3P$ is even.

[8] Sawyer and Beese, Nature **116**, p. 936 (1925).

are two diffuse lines whose reversal in the heavy arc and diffuse character led to their classification as $(4s4p)^3P_2-(4p^2)^1D_2$ and $(4s4p)^3P_1-(4p^2)^1D_2$.[9] If in spite of their appearance these two lines are classified as the combinations with $(4p^2)^3P_2$ we obtain as the ratio of $(4p^2)^3P_0-(4p^2)^3P_1$ to $(4p^2)^3P_1-(4p^2)^3P_2$, the value of 0.355. This seems to depart from the smooth progression of this ratio by an amount larger than can be accounted for by the accuracy of measurement. We are still forced to assume that the combinations with $(4p^2)^3P_2$ are masked by this diffuse pair.

Table VI also shows the perfectly smooth progression of the $(4s4p)^3P$ interval ratio (column one) and a slight irregularity in the $(4s4d)^3D$ interval ratio (column two) which may however be due to a relatively greater inaccuracy of measurement of the D intervals which are about one-tenth those of the P. Column four of Table V shows a very interesting effect pointed out here for the first time; in this type of spectra viz, the steady and rapid increase of the $(4p^2)^3P$ separation with respect to the $(4s4p)^3P$ separation. The theoretical importance of this phenomenon will be discussed in a later section of this paper.

TABLE VII. *Values of* $(\nu/R)^{1/2}$ *for 30-electron spectra together with their differences.*

	Zn I		Ga II		Ge III		As IV		Se V
$(4s4p)^3P$	0.6178		1.0100		1.3895		1.7595		2.1235
Δ_1		0.3922		0.3795		0.3700		0.3640	
Δ_2			0.0127		0.0095		0.0060		
$(4s5s)^3S$	0.4487		0.7255		1.0355		1.3469		1.6599
Δ_1		0.2768		0.3100		0.3114		0.3130	
Δ_2			0.0332		0.0014		0.0026		
$(4s4d)^3D$	0.3440		0.6532		1.0152		1.3777		1.7386
Δ_1		0.3092		0.3620		0.3625		0.3609	
Δ_2			0.0528		0.0005		−0.0016		

The 30-electron-system spectra should have a singlet system as well as a triplet, but the singlets are much harder to locate because of the lack of characteristic separations and, in the vacuum spark, of higher series members. The approximate location of the $(4s^2)^1S-(4s4p)^1P$ line may however be predicted by the rule first given by Sawyer and Beese.[7] and discussed more fully by Sawyer.[8] This prediction may be checked by the application of the irregular doublet law. The classifications of the line $(4s^2)^1S-(4s4p)^1P$ given in Table IV were obtained in this way. The choices made in each case were practically the only possibilities. The application of the irregular doublet law and of the rule given by Sawyer and Beese is shown in Table VIII.

The triplet term values in the spectra of As IV and Se V could be determined only by extrapolation of the Moseley diagrams since no second term members were found. The term values so determined are given in Table IV

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[9] Sawyer, J.O.S.A. **13**, 431 (1926).

TABLE VIII. *Application of the rule of Sawyer and Beese and of the irregular doublet law in the location of singlet combinations.*

	^1SP	$^3P^0{}_1P_1$	^2SP	$^1SP-{}^2SP$
Zn	46744	47900	48480	− 1740
Ga	70700	67400	65170	+ 5530
Ge	91876	86150	81300	+10580
As	112022	104500	97130	+14900
Se	131740	122730	112760	+19000

and Table VIII gives the values of $(\nu/R)^{1/2}$, for the terms of the 30-electron sequence showing the first and second differences of the values.

Dr. R. J. Lang has kindly informed us that the lines which we have classified as As IV and As V appear faintly or not at all on his plates taken with a less violent vacuum spark in the course of his unpublished work on the As III spectrum. This is good evidence that the lines in question belong to a higher stage of ionization than As III. The location of As VI lines may be predicted from the data given by Mack, Laporte and Lang[10] but they do not appear on our plates. It may thus be inferred that our classified lines belong to the As IV and As V spectra without doubt.

IV. THE $(4p^2)^3P$ SEPARATIONS

The observed relative increase in the $(4p^2)^3P$ separation with respect to the $(4s4p)^3P$ separation has been mentioned. The former also shows a similar increase with respect to the $(4p)^2P$ separation in the spectrum of the ion of next higher degree. These features require some special consideration. Table IX contains a complete list of these separations in the isoelectronic spectra we are considering with the exception of $(4p^2)^3P$ in Zn I.[11] The $(4s4p)^3P$ separations are observed to be smaller in all cases than the corresponding $(4p)^2P$ or $(4p^2)^3P$ separations, and for higher ionizations become nearly equal to $(4p)^2P$ which, as we shall point out, is to be expected. The $(4p^2)^3P$ separations range from somewhat smaller to considerably larger than $(4p)^2P$ as we proceed through the series of elements. In the case of the pure Russell-Saunders coupling both the $(4p^2)^3P$ and the $(4s4p)^3P$ should be slightly smaller than $(4p)^2P$ according to a recent theore-

TABLE IX. *Multiplet separations together with the relative separation of $(p^2)^3P$ and ^2P*

	Zn	Ga	Ge	As	Se
$(p)\Delta^2P$	874	1718	2790	4110	5700
$(sp)\Delta^3P$	579	1382	2403	3677	5210
$(p^2)\Delta^3P$		1437	2684	4460	6824
$(p^2)\Delta^3P/(p)\Delta^2P$		0.8365	0.9620	1.0852	1.1972

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[10] Mack, Laporte and Lang, Phys. Rev. **31,** 748 (1928).

[11] This separation is omitted because, as mentioned above, the complete measurement of the P^0P group was impossible owing to the presence of a pair of diffuse lines which masked a part of the group.

tical investigation by Goudsmit and Humphreys.[12] Although the theory predicts that to a first approximation these separations should all be the same, the screening effect of the second valence electron would be expected to reduce the triplet separations with respect to the doublet.

We can show that the total $(4s4p)^3P$ separation will not be thus affected As is known from other spectra higher nuclear charge is favorable to a change of coupling. The (sp) configuration with Russell-Saunders coupling gives ^1P and ^3P terms. When we go over to the limiting (jj) coupling we still have four levels characterized by the same inner quantum numbers but two of them having values 0, 1, lie relatively close together and are separated by the $(4p)^2P$ interval of the next ion from two others of values, 2 and 1. Fig. 1 will make this arrangement clear. Without going into the rules of correlation at this point, it may be stated the levels of corresponding j values in the Russell-Saunders case go over to the new levels in such a way that the connecting lines do not cross. Consequently, while the triplet intervals may change, we no not expect achange in the total $(4s4p)^3P$ separation with respect to $(4p)^2P$ but rather expect the former to approach the latter as a limit.

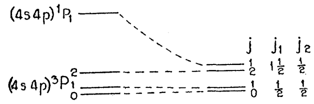

Fig. 1.

The increase in the relative $(p^2)^3P$ separations has been observed for the first time in the spectra we have investigated. Spectra of lighter elements, found in the first two rows of the periodic table and studied by Millikan and Bowen[13], do not show this effect. The P^0P groups are quite symmetrical showing that the $(sp)^3P$ and $(p^2)^3P$ separations are the same. They are also somewhat smaller than the corresponding $(p)^2P$ separation of the next ion. These features are of course to be expected since, as we have pointed out, any departure from the Russell-Saunders coupling should occur only with relatively high nuclear charge.

Although a change of coupling does not affect the total $(4s4p)^3P$ separation, the results are quite different for $(4p^2)^3P$. The correlation of levels must be considered in detail in order to explain the observed features of the spectra. The ^1S, ^1D, and ^3P multiplets no longer appear in the case of the limiting (jj) coupling, but we expect instead the following arrangement: a lowest level characterized by a j value 0; above that, at a distance equal to the doublet of the ion, two relatively close levels, of j values 1 and 2; and, at again the same distance higher, two levels with j values 2 and 0. The lowest levels of lead seem to show a configuration approximating this ideal arrangement.

The rearrangement of levels in changing over to another coupling is quite analogous to what happens in going to series limits in complicated spectra. Consequently it would seem promising to try Hund's method, for the correlation of series limits to our problem of change of coupling.

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[12] S Goudsmit and C. J. Humphreys. Multiplet separations. Phys. Rev. **31,** 960 (1928).

[13] I. S. Bowen and R. A. Millikan, *PP'* groups in atoms of the same electronic structure, Phys. Rev. **26,** 150 (1925).

But we arrive by this method at very strange results. In order to use Hund's scheme we must first consider the result of applying a weak magnetic field. The remarkable result is that a part of the magnetic levels of $(4p^2)^3P_2$ will go to one and the other part to the other of the two levels having *j* equal to 2, occurring in the extreme case of the (*jj*) coupling. A similar behavior is predicted for the $^1D_2$ levels. As we cannot expect the levels to split up when we gradually change the coupling, we must assume that the two levels, having *j* equal to 2, cross over and interchange their magnetic levels at the point of intersection. The point where the levels intersect might be considered as a certain type of degeneration where either coupling is equally probable. This seems to be the most satisfactory explanation of the increase of the $(4p^2)^3P$ separations. Fig. 2 illustrates the scheme of correlation. It is assumed in these spectra that the point of intersection has not yet been reached.[14]

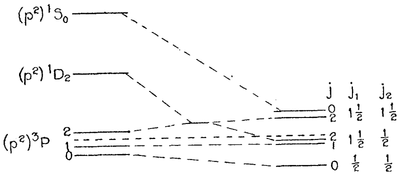

Fig. 2.

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June 2, 1928.

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[14] The explanation given above of the remarkable increase of the $(4p^2)^3P$ separation with respect to the doublet of the next ion is necessarily based on the applicability of the rules given by Hund. According to Hund's reasoning, near the series limit the emitting electron is so loosely coupled with the other electrons, that its influence may be neglected. Hund derives his rules, using this assumption, by a consideration of the magnetic energy in an outer field. The magnetic energy is however of the same order of magnitude for each electron, independent of strong or weak interaction between electrons. In other words, the magnetic behaviour of the levels near the series limit is not at all like that of the state of the ion, in which one electron is completely removed. Such considerations lead to some uncertainty as to the applicability of Hund's rules, and may possibly affect the explanation given here. Quite recently Shenstone has shown, Nature **121,** 619 (1928), that in certain cases spectroscopic data are in disagreement with the results of these rules, it being observed that the levels converge to other series limits than those predicted by Hund.