

After hydrogen, the problem of the helium spectrum naturally suggests itself for solution. It is a time-honoured problem, and has baffled many attempts at solution. Recently solution on the basis of Schrödinger's theory have been published by Unsöld, Sugiura, and Kellner (24). Kellner has taken the calculations to the fourth place and finds an exact agreement between the theoretical and the experimental value. But this agreement does not exhaust all the points in the helium problem. One has to remember that the old Bohr theory gave the ionisation potential of hydrogen quite correctly, but it did not solve all the points in the hydrogen problem. In helium we have further to explain the origin of the parhelium and helium series, and the absence of inter combination amongst them. An explanation has been attempted by Heisenberg (25), and by Dirac, but both these authors have treated the electron merely as a point charge, while according to Hund's interpretation the difference in value between 1S and 3S is due only to the different orientation of the magnetic axis in the two cases. The $2\ ^1S_0$ -terms arises with electron (1) at K_1 , electron (2) at L_1 , but with its magnetic axis directed in an antiparallel direction. For the $2\ ^3S_1$ term, electron (1) is at K_1 , electron (2) at L_1 , but their magnetic axes are now parallel. The difference in value seems to be of magnetic origin and not to electrical origin, as supposed by Heisenberg and Dirac.

Wigner (26) has attempted a general explanation of the origin of different groups of terms in complicated spectra on the basis of Heisenberg's theory, but it is yet too early to pronounce a critical opinion on these works.

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43(a). EXTENSION OF THE IRREGULAR DOUBLET LAW TO COMPLEX SPECTRA

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(Ind. Journ. Phys., 2, 319, 1928)

The Irregular Doublet Law was discovered by G. Hertz in 1921.¹ It states that if the square roots of the values of the L_I and the L_{II} -absorption levels in X-ray Spectra are plotted against the atomic number, the two curves nearly run parallel to each other. Mathematically this means that

$$\sqrt{\nu_I} - \sqrt{\nu_{II}} = \text{constant.} \quad \dots(1)$$

The explanation on Bohr's theory is that the energy of the electron in the L-level is given by

$$\frac{\nu}{R} = \frac{(Z - \sigma_I)^2}{n^2}, \frac{(Z - \sigma_{II})^2}{n^2} \text{ respectively}$$

where Z = nuclear charge

n = Total quantum number for L_I and L_{II}

σ_I = Screening constant while the electron is in the L_I -level

σ_{II} = Screening constant while the electron is in the L_{II} -level.

n has the same value in both cases, viz., 2.

$$\sqrt{\nu_I} - \sqrt{\nu_{II}} = \frac{\sigma_I - \sigma_{II}}{n} \quad \dots(1')$$

The extension of the Irregular Doublet Law to optical region is due to Millikan and Bowen.² Starting from a

¹ G. Hertz, *Zs. f. Physik*. Vol. 3, p. 19.

² Millikan and Bowen, *Phys. Rev.* Vol. 24, p. 209 (1924) and subsequent papers.

theoretical treatment of the L-spectra of light elements which fall in the ultra-schumann region, these authors have gradually extended this law to predict and locate the spectra of elements which are reduced by heavy electrical discharge to the one valence or the two valence state. For example, let us take the group:—Na, Mg⁺, Al⁺⁺, Si⁺⁺⁺ ... they have got the K and L-rings complete, and only one electron in the M-ring (M₁) they differ only in the nuclear charge, which are respectively 11, 12, 13, 14, but the electronic constitution is the same. When this electron is further excited, it gives the same type (doublet) of spectra in the case of all elements. Millikan and Bowen's Law in its most general form states that when we compare the frequency of such lines of these successive elements, as arise from similar transition in which the total quantum number remains unchanged, they form an arithmetic progression. Thus let us compare the ²S₁—²P₁—lines of Na, Mg⁺, Al⁺⁺ ... The net nuclear charges are 1, 2, 3 ... etc, but the number of screening electrons (excepting the valency electron) is the same (10), and they are probably oriented in the same way. Hence the frequency in the M-state is

$$\begin{aligned} \frac{\nu}{R} &= \frac{(Z-\sigma)^2}{3^2} \text{ for the electron in the } M_1 \text{ -orbit} \\ \frac{\nu}{R} &= \frac{(Z-\sigma')^2}{3^2} \dots\dots\dots M_2 \\ \therefore \frac{\nu 2S_1 - \nu 2P}{R} &= \frac{2}{3^2}(\sigma' - \sigma)Z - \frac{\sigma'^2 - \sigma^2}{9} \\ &= AZ + B \end{aligned} \quad \dots(2)$$

because σ', and σ have presumably the same value in the series of elements considered.

∴ the ν_{2s}—ν_{2p} lines will form an A.P. [see Table 2].

In the hands of Millikan and Bowen, and other workers, this law has been a very powerful instrument in the location of spectra of stripped atoms having (1) one valency electron; (2) two valency electrons, (3) three valency electrons (for a few special transitions only).

All the data which are scattered about in the papers of Millikan and Bowen, and other workers are collected in the tables below. The object of this paper is not only the compilation of these tables, which are very useful for workers in spectroscopy, but also to show that the law is capable of much wider application, so that even complicated spectra can be predicted, and exactly located. Incidentally, it might be mentioned that the wide applicability of Millikan and Bowen's law seems to us to be the most complete vindication of the values which Bohr assigned to the total quantum numbers for the different X-ray levels within the atom. There is an ambiguity on this point as regards optical spectra. For example, according to Bohr, the D-lines

of Na ought to be described as 3s—3p—lines with the formulae

$$3s - 3p = R \left[\frac{(11 - \sigma_s)^2}{3^2} - \frac{(11 - \sigma_p)^2}{3^2} \right] \quad \dots(3)$$

whereas in the optical method of classification we describe it, as (using Paschen's notation)

$$1s - 2p = R \left[\frac{1}{(1+s)^2} - \frac{1}{(2+p)^2} \right] \quad \dots(3')$$

Formula (3) can be made to reduce to (3'), but no systematic work on this line is known. The carrying out of this programme is very important for the elucidation of the origin of Rydberg sequence.

In order to give a general explanation of the ideas contained in this paper, we start with the atomic chart given by one of the authors sometime ago, which gives a unitary explanation of the origin of the periodic classification, of X-ray spectra, and of optical spectra in a graphical way, embodying the principle successively developed by Bohr, Mainsmith and Stoner, Pauli and Heisenberg and Hund.

[To get the spectrum of any element, write out the number of electrons, beginning from K. Let now the last electron run through the higher unfilled levels. We get the optical terms when we apply the principles of term-synthesis discovered by Pauli, Heisenberg and Hund.]

For more complete explanation, and application of this chart, the reader is referred to the previous papers by the senior author.³ Here we shall simply add, that as the total quantum number remains the same for all horizontal transitions, lines arising from such transitions in the case of all successive elements which are reduced by electrical discharge to the same electron configuration, will form an Arithmetic Progression. The law is not confined to one, two or three valence elements alone, but to elements with higher valency as well. The application to four, five, six, seven and eight valence elements, and other elements with complicated spectra is taken after these tables are completed, though in the latter case, the complexity of the spectra makes the application a bit difficult.

General explanation to Tables 1 to 8.

We have collected the data for one valence elements under the groups

- (1) Li, Be⁺, B⁺⁺, C⁺⁺⁺ ... Ne⁺⁷
- (2) Na, Mg⁺, Al⁺⁺, S⁺⁺⁺ ... A⁺⁷ (2) K, Ca⁺ ...
- (3) Cu, Zn⁺, Cd⁺⁺, Ge⁺⁺⁺ ... Kr⁺⁷ (3) Rb, Sr⁺ ...
- (4) Ag, Cd⁺, In⁺⁺, Sn⁺⁺⁺ ... Xe⁺⁷, (4) Cs, Ba⁺ ...
- (5) Au, Hg⁺, Tl⁺⁺, Pb⁺⁺⁺

Even in these cases, some further niceties 'regarding the application of the law are introduced. They are discussed under the footnotes' in the case of each individual table.

³Vide M. N. Saha and B. B. Ray, Phys. Zeits, Vol. 28, p. 221; M. N. Saha, Phys. Zeits, Vol. 28, p. 469. P. K. Kichlu and M. N Saha, Phil. Mag., Vol. IV, (1927), p. 193.

		Transition Groups			Rare Earths		Trans. Group
		1	2	3	4	5	6
1 H	K_1						
2 He	2						
3 Li	L_1						
4 Be	L_2						
5 B	2						
6 C	M_1						
7 N	2						
8 O	M_2						
9 F	6						
10 Ne	M_3						
11 Na	2						
12 Mg	6						
13 Al	2						
14 Si	6						
15 P	2						
16 S	6						
17 Cl	2						
18 Ar	6						
19 K	N_1						
20 Ca	2						
21 Sc	N_2						
22 Ti	6						
23 V	N_3						
24 Cr	6						
25 Mn	N_4						
26 Fe	6						
27 Co	O_1						
28 Ni	2						
29 Cu	O_2						
30 Zn	6						
31 Ga	O_3						
32 Ge	6						
33 As	O_4						
34 Se	6						
35 Br	P_1						
36 Kr	2						
37 Rb	P_2						
38 Sr	6						
39 Y	P_3						
40 Zr	6						
41 Nb	P_4						
42 Mo	6						
43 Tc	P_5						
44 Ru	6						
45 Rh	P_6						
46 Pd	6						
47 Ag	P_7						
48 Cd	6						
49 In	P_8						
50 Sn	6						
51 Sb	P_9						
52 Te	6						
53 I	P_{10}						
54 Xe	6						
55 Cs	P_{11}						
56 Ba	6						
57 La	P_{12}						
58 Ce	6						
59 Pr	P_{13}						
60 Nd	6						
61 Pm	P_{14}						
62 Sm	6						
63 Eu	P_{15}						
64 Gd	6						
65 Tb	P_{16}						
66 Dy	6						
67 Ho	P_{17}						
68 Er	6						
69 Tm	P_{18}						
70 Yb	6						
71 Lu	P_{19}						
72 Hf	6						
73 Ta	P_{20}						
74 W	6						
75 Re	P_{21}						
76 Os	6						
77 Ir	P_{22}						
78 Pt	6						
79 Au	P_{23}						
80 Hg	6						
81 Tl	P_{24}						
82 Pb	6						
83 Bi	P_{25}						
84 Po	6						
85 Rad H	P_{26}						
86 Nt	6						
87 Rad C	P_{27}						
88 Ra	6						
89 Ac	P_{28}						
90 Th	6						
91 Pa	P_{29}						
92 U	6						

One Valence Electron Systems

Group I. Li ... Ne⁷Normal state L₁, total quantum number=2

TABLE 1.

Atomic number	Element	L ₁ ←L ₂ S ₁ ← ³ P ₁	² S ₁	L ₂ ←M ₂ ³ P ₂ ← ² D ₂	Ionisation Potential	References
3	Li	14904 (17024)	43486 ..	16379 (49745)	5.37 ..	Fowler's Report, p. 97.
4	Be ⁺	31928 (16431)	146880 ..	66124 (81584)	18.14 ..	Bowen and Millikan, Phys. Rev. Vol. 28, p. 256.
5	B ²⁺	48359 (16122)	305938 ..	147708 (112458)	37.79 ..	Sawyer, J. O. S. A. Vol. 14, p. 287.
6	C ³⁺	64481 (15974)	520034 ..	260166 ..	64.23 ..	Millikan and Bowen, Nature, Vol. 114, p. 380.
7	N ⁴⁺	80455 (15913)	97.39 ..	Bowen and Millikan, Phys. Rev. Vol. 27, p. 144.
8	O ⁵⁺	96368	137.35	Ditto
9	F ⁶⁺	184.07	Ditto
10	Ne ⁷

N.B.—The law holds as the table shows for ²S₁←²P₁ *i.e.*, L₁←L₂ transition only and not for the PD-lines *vide* the following groups because the transition is from L₂→M₂ *i.e.*, the total quantum number increases by 1. For the remaining groups even PD lines forms an A.P.

Group II Na ... A⁺⁷Normal state 6L₂ M₁

Total quantum number=3

TABLE 2

Atomic Number	Element	M ₁ ←M ₂ ² S ₁ — ² P ₁	M ₂ ←M ₃ ² P ₂ — ² D ₂	M ₃ ←N ₄ ² D ₃ — ² F ₃	N ₃ ←N ₄ ² D ₃ — ² F ₃	² S ₁	I.P.	References
11	Na	16956 (18713)	12199 (23531)	5415 (16893)	5492 (14862)	41449 ..	5·12 ..	Fowler's Report on series in line spectra.
12	Mg ⁺	35669 (18011)	35730 (26307)	22308 (29350)	20354 (20997)	121267 ..	14·97 ..	Fowler's Report.
13	Al ⁺³	53680 (17600)	62037 (26635)	51658 (42124)	41351 (25289)	229543 ..	28·32 ..	Paschen, Ann. der Physik Vol. 71, P. 154
14	Si ⁺³	71280 (17369)	88672 (26083)	93782 ..	66640 ..	364177 ..	44·95 ..	Fowler, Phil. Trans. Vol. 225, p. 38.
15	P ⁺⁴	88649 (17217)	114755 (25558)	Bowen and Millikan, Phys. Rev. Vol. 25, p. 295.
16	S ⁺⁵	105866 (17132)	140313	Ditto.
17	Cl ⁺⁴	123001	Ditto.
18	A ⁺⁷	Ditto.

The irregular doublet law holds not only for ²S₁—²P₁ lines (M₁←M₂), but also for ²P—²D lines (M₂←M₃), because the total quantum number is 3 for all these terms. It does not hold good for the first ²D—²F combination, because the transition is from M₃←N₄, n changes from 4→3.

Group III K ... Mn⁺⁶Normal state=6M₃N₁

Total quantum number=4

TABLE 3

Atomic Number	Element	N ₁ ←N ₂ ²S ₁ —²P ₁	²S ₁	N ₂ ←N ₃ ²P ₂ —²D ₂	I.P.	References
19	K	12985 (12207)	35006	8492 (22933)	4.30	Fowler's Report.
20	Ca ⁺	25192 (11372)	95740	31425 (18299)	11.77	„ *
21†	Sc ⁺²	36564 (10978)	..	49724 (18340)	24.6	Russell and Lang, <i>Astro. Journ.</i> , Vol. 66, p. 13.
22	Ti ⁺³	47542 (10506)	..	68064	43.05	„
23	V ⁺⁴	58048 (8708)	Lang, <i>Nature</i> , July, 14, 1926.
24	Cr ⁺⁵	
25	Mn ⁺⁶	

*The first ²D term is given by the electron in M₃ with total quantum number 3, but the first ²P term has the total quantum number 4, we have therefore taken the 2nd number of the ²D sequence, for which n=4.

†In the case of Sc⁺, Ti⁺⁺ and other following elements,—the largest term is ²D with n=3, and not ²S with n=4. Hence the I.P. for Sc⁺ et seq., will refer to ²D—term.

Group IV Cu ... Kr⁺⁷Normal state=10M₃N₁

Total quantum number=4

TABLE 4

Atomic Number	Element	N ₁ ←N ₂ ²S ₁ —²P ₁	²S ₁	N ₂ ←N ₃ ²P ₂ —²D ₂	I.P.	References
29	Cu	30535 (17948)	62308	19151 (28402)	7.66	Fowler's Report, p. 111. ..
30	Zn ⁺	48483 (16678)	144890	47553 (29649)	17.8	Von Salis, <i>Ann. der Phys.</i> Vol. 76, p. 145. ..
31	Ga ⁺²	65161 (16153)	247797	77202 (29302)	30.5	Carroll, <i>Phil. Trans.</i> Vol. 225, p. 359. ..
32	Ge ⁺³	81314 (18506)	368701	106504	45.3
33	As ⁺⁴	99820
34	Se ⁺⁵
35	Br ⁺⁶
36	Kr ⁺⁷

In this case, the ²L₃—²F₃ lines also obey roughly the Irregular Doublet Law, as the total quantum number is now 4 in both cases.

Group V Rb ... M_0^{+5}
 Normal state = $6N_2O_1$.
 Total quantum number = 5

TABLE 5

Atomic Number	Element	$O_1 \leftarrow O_2$ $^2S_1 - ^2P_1$	2S_1	$O_2 \leftarrow O_3$ $^2P_2 - ^2D_2^*$	I.P.	References
37	Rb	12579 (11136)	33689	6538 (22232)	4.14	Fowler's Report, p. 104.
38	Sr ⁺	23715 (10219)	88952	28770 (16655)	10.93	Fowler's Report, p. 132.
39	Y ⁺²	33934 (9784)	157822	45425	19.41	Bowen and Millikan, Phys. Rev. Vol. 28, p. 923.
40	Zr ⁺³	43718	238546		29.33	
41	Nb ⁺⁴					
42	Mo ⁺⁵					

Group VI Ag ... X_0^{+7}
 Normal state = $10N_2O_1$.
 Total quantum number = 5

TABLE 6

Atomic Number	Element	$O_1 \leftarrow O_2$ $^2S_1 - ^2P_1$	2S_2	$O_2 \leftarrow O_3$ $^2P_2 - ^2D_2$	I.P.	References
47	Ag	29552 (14584)	61096	18271 (24798)	7.51	Fowler's Report.
48	Cd ⁺	44136 (13046)	140226	43069 (23865)	17.24	Von Salis, Ann. der Physik, Vol. 76, p. 145.
49	In ⁺²	57182 (12374)	225690	66934	27.76	Carroll. Phil. Trans. Vol. 225, p. 388.
50	Sn ⁺³	69556 (13418)	327261		40.2	
51	Sb ⁺⁴	82974				
52	Te ⁺⁵					
53	I ⁺⁶					
54	Xe ⁺⁷					

Group VII Au ... Nt⁷
 Normal state: 10 O₃P₁.
 Total quantum number=6

TABLE 7

Atomic Number	Element	P ₁ ←P ₁ ³ S ₁ — ³ P ₁	¹ S ₁	P ₂ ←P ₃ ³ P ₂ — ³ D ₂	I.P.	References
79	Au	37359 (14126)	74510	20784 (23589)	9.16	Thorsen. Naturwissen schaft. Vol. Vol. 25, p. 500 (1923).
80	Hg ⁺	51484 (12675)	153701	44373 (22019)	18.9	Carroll. Phil. Trans. Vol. 225, p. 389.
81	Tl ²⁺	64160 (12010)	248045	66392 (24804)	30.5	Ditto.
82	Pb ³⁺	76150	355963	91196	43.8	Ditto
83	Bi ⁴⁺					
84	Po ⁵⁺					
85						
86	Nt ⁷⁺					

Two-Valence Systems

The two-valence systems ought properly to begin with the group (He, Li⁺, Be⁺⁺ ...). But there is no data in this group beyond He, and Li⁺. The normal state is X₁ X₁, or s², the next state is X₁ X₂ or s²p. The sp-combination gives rise to ³P_{0,1,2} ¹P₁-terms, and in the transition X₁X₁←X₁X₂, we get ¹S₂—³P₁, ¹S₂—¹P₁ lines. Both these lines form an Arithmetic Progression as shown in the tables which follow.

It also seems to be rather remarkable that the difference ³P₁—¹P₁, in the case of successive elements, roughly vary as the net nuclear charge. Thus we have⁴

$$\begin{aligned} \text{for Mg.} & \quad ^3P_1 - ^1P_1 = 13181 \\ \text{,, Al}^+ & \quad ^3P_1 - ^1P_1 = 22390/2 = 11195 \\ \text{,, Si}^{++} & \quad ^3P_1 - ^1P_1 = 29850/3 = 9950 \end{aligned}$$

Similarly the ³S₁—³S₀ differences arising from a X₁X₁ combination, seem to increase as the net nuclear charge

$$\begin{aligned} \text{Mg...} & \quad ^3S_1 - ^1S_0 = 2305 \\ \text{Al}^+... & \quad ^3S_1 - ^1S_0 = 4077 \\ \text{Si}^{++}... & \quad \text{,,} \quad = ? \end{aligned}$$

[We have taken the second members of the sequence.]
 These facts should have some bearing on the

Heisenberg-Dirac⁵ theory of the bifurcation of two-valence spectra into singlets and triplets on the basis of electrical coupling of the two electrons.

The PP-lines). Taking the Mg.-group, they are seen to arise from the transition M₁M₂←M₂M₂, or in this process the lines owe their origin to the transition of the electron from the M₂M₂ (initial) to the M₁M₂ (final) or in a M₁←M₃ transition, leaving the outer electron fixed. We have called such transitions as "Inner transitions."

Two-Valence Electron Systems.

Group I He ... C⁴⁺
 Normal state: 2K₁.

TABLE 8

Atomic Number	Element	4←L ₂ ¹ S ₀ — ¹ P ₁	4←L ₂ ³ S ₁ — ³ P ₁	I.P.	References
2	He	4857	9231	..	Fowler's Report, p. 9.
3	Li ⁺	18209	34072	..	Schüler, Naturwissenschaft. 1924, p. 579.
4	Be ²⁺				No other element has yet been investigated.
5	B ³⁺				
6	C ⁴⁺				

⁵ Heisenberg, Zs. f. Physik, p. 239; Dirac, Proc. R. S. L., Vol. 113, p.261.

⁴ Here again the second number of the ³D-sequence has been taken for all the elements, as in the group K, Ca⁺...

Group IV: Ca ... Kr⁺⁶
 Metastable State M₃ N₁
 Total quantum number=4

TABLE 11

Atomic Number	Element	N ₁ ←N ₂	N ₁ ←N ₂	N ₁ ←N ₂	¹ S ₀	I.P.	References
		³ D ₂ — ³ D ₂	¹ D ₂ — ¹ D ₂	³ D ₃ — ³ D ₃			
20	Ca	17870 (10084)	13985 (9555)		49305	6.06	Fowler's Report, p. 121, Russell and Saunders, Astro. Jour., Vol. 61, p. 38.
21	Sc ⁺	27954 (11015)	23540 (9954)				Goudsmit, Mark and Zeeman., Proc. Amst., Vol. 28, p. 127.
22	Ti ⁺²	38969	33494	52595			Russell and Lang, Astro. Journ., Vol. 66, p. 27.
23	V ⁺³						
24	Cr ⁺⁴						
25	Mn ⁺⁵						
26	Kr ⁺⁶						

Group V: Zn.....Br⁺⁵
 Normal state: 10M₃ 2N₁
 Total quantum number=4

TABLE 12

Atomic Number	Element	N ₁ ←N ₂	N ₁ ←N ₂	³ PP	¹ P ₁ — ³ P ₁	I.P.	References
		¹ S ₀ — ¹ P ₁	¹ S ₀ — ³ P ₁		net nuclear charge		
30	Zn	46745 (23952)	32502	47894 (19516)	14243	9.30	Fowler's Report, p. 140.
31	a ⁺	70697 (21179)		67410 (18738)			R. J. Lang, Phys. Rev., Vol. 30, P. 762.
32	Ge ⁺²	91876	45462	86148	15471	31.96	Ditto.
33	As ⁺³						
34	Se ⁺⁴						
35	Br ⁺⁵						

Group VI; Cd I⁺⁵
 Normal state: 10 N₃ 2O₁
 Total quantum number=5
 O₁←O₂ O₁←O₂

TABLE 13

Atomic Number	Element	¹ S ₀ — ¹ P ₁	¹ S ₀ — ³ P ₁	³ P ₁ ³ P ₁	¹ S ₀	I.P.	References
48	Cd	43692 (19345)	30656	44088 (15810)	72539	8.95	Fowler's Report, p. 143.
49	In ⁺	63037 (16871)		59898 (15023)			R. J. Lang, Phys. Rev., Vol. 30, p. 769.
50	Sn ⁺²	79908	55191	74921	243235	30.0	Green and Loring, Phys. Rev., Vol. 30, p. 574.
51	Sb ⁺³						
52	Te ⁺⁴						
53	I ⁺⁵						

THE THREE-VALENCE ELEMENTS

The normal state is 2X₁X₂ or s²p¹. The next stage is s²d¹ or s²s. The ²P—²D lines follow the law roughly in the group Al, Si⁺ etc. Data in other groups are incomplete.

The lines arising from the "inner transition" 2M₁M₂←M₁2M₂ follow the law more regularly.

Group I: B Ne⁺⁵
 Normal state: 2L₁ L₂
 Total quantum number=2

TABLE 14

Atomic Number	Element	L ₂ ←M ₃	2L ₁ L ₂ ←L ₁ 2L ₂		³ P ₁	I.P.	References
		³ P ₂ — ³ D ₂	³ P ₂ — ³ D ₂	³ P ₁ — ³ S ₁			
5	B	54751 (90798)	47841 (27026)		67545	8.34	Bowen, Phys. Rev., Vol. 29, p. 229.
6	C ⁺	145549 (121609)	74867 (25983)	96430 (34399)	196659	24.29	A. Fowler, Proc. Roy. Soc., Vol. 105, p. 299.
7	N ⁺²	267158	100850 (25699)	130829 (33152)	382226	47.2	Bowen, Phys. Rev. Vol. 29, p. 229.
8	O ⁺³		126549	163981		77.0	Ditto.
9	F ⁺⁴						
10	Ne ⁺⁵						

In the present group the first PD terms do not follow the law, as the transition is from 2 to 3 total quantum numbers. The inner transition (L₁←L₂) on the other hand follows the law.

TABLE 17

Ionisation potential of Carbon.

Element	$L_2M_1 \leftarrow L_2M_2$			$L_2M_2 \leftarrow L_2M_3$	
	$3P_1-3P_1$	$3P_1-3D_1$	$1P_1-1P_1$	$3P_1-3P_1$	$3D_1-3D_1$
C	(10400)	(8673)	(9307)	(7331)	(8469)
N ⁺	21667 (11268)	17581 (8908)	25014 (15707)	18301 (10970)	20916* (12447)†‡
O ⁺⁺	32935	26489	40721	29271	33863
F ⁺⁺	(44000)	(35000)		(40000)	(46000)
Ne ⁺⁺					

Though the systematisation of the spectrum of Carbon, and the exact value of its Ionisation Potential will depend upon the investigations above mentioned, it is not difficult to predict what the I.P. will be.

It is a general rule that the terms arising from the inner transition, viz., $L_1, 3L_2$ are in the case of neutral elements almost always negative, or at least have very small positive values. We have not much of exact data, but a glance at Table 14, which gives the inner transition lines of C, combined with a knowledge of corresponding term values for different electron configurations for N⁺ and O⁺⁺ should be sufficient indication that the value of $3P_1$ terms in C will be about 90,000, which corresponds to 11.0 volts approximately.*

Certain experiments with an Adam Hilger Infra-red spectrometer have shown that Carbon possesses strong lines in the regions predicted, but their fine structure has not yet been determined.

Group Si, P⁺, S⁺⁺, Cl⁺⁺⁺

The spectrum of Si has been discussed by Fowler, that of P⁺ by Bowen. In the case of S⁺⁺, and Cl⁺⁺⁺, certain vacuum spark data are recorded by Millikan and Bowen. The application of the Irregular Doublet Law is shown in the following table:

From this table we can easily perceive why the spectrum of Carbon has up to this time remained unknown. The chief lines ($2L_2 \leftarrow L_2M_1$), $3P-3P$, lie in the Schumann region, as well as all other lines arising from deeper transitions. The lines arising from ($L_2M_1 \leftarrow L_2M_2$) lie in the region λ 9000 ... λ 12000 ($L_2M_1 \leftarrow L_2M_3$) lie in the region λ 11000 ... λ 13000.

Hence the spectrum of C must be investigated in the infra-red for the location of these lines. Other possible lines may be in the visible region but they would be extremely weak, and special methods of excitation will have to be employed to bring them out.

TABLE 18

Element	$M_2M_2 \leftarrow M_2M_2$	$M_2N_1 \rightarrow M_2M_2$	$2M_1 2M_2 \rightarrow M_1 3M_2$ Inner Transition			References
	$3P_1-3D_2$	$3P_1-3P_1$	$3P_1-3P_1$	$3P_2-3D_2$	$3P-3D$	
Si	45216 (19890)	50191 (26157)				Fowler, Phil. Trans., Vol. 225
P ⁺	65106 (18646)	76648 (25583)	18558	16595	103726.6	Bowen, Phys. Rev.
S ⁺⁺	83752	(102231)				Millikan and Bowen, Phys. Rev. Vol. 23, p. 16.
Cl ⁺⁺⁺	(101546)	(126936)				

*Fowler has recently announced that the I. P. of C is 11.2 Volts. (Nature, Feb. 25, p. 304, 1928)

The identification of λ 1194, $\nu=83275$ as the $3P_1-3D_2$ line of S⁺⁺ seems to be well-warranted, the full multiplet being as given below

TABLE 19

	$3P_0$	$3P_1$	(737) $3P_2$
$3D_1$	84002		
D_2		(1) 83752	(1) 83015
D_3			(4) 83275

The line 978.2, $\nu=102231$, may be the $3P_1-3P_2$ line, but the wave lengths in this region ought to be revised. The chlorine lines are given provisionally. They require confirmation.

In the second table ($M_2N_1 \leftarrow M_2N_2$) transition, data are known in the case of P only. The Silicon lines must be in the infra-red. The existing data do not help us. The corresponding S⁺⁺ lines ought to lie in the region $\nu=26000-30000$, but they have not yet been looked for.

FIVE-VALENCE ELEMENTS

We have the following groups:

1. N,	O ⁺ ,	Fl ⁺⁺ ,	Ne ⁺³
2. P,	S ⁺ ,	Cl ⁺⁺ ,	A ⁺³
3. As,	Se ⁺ ,	Br ⁺³ ,	Kr ⁺³
4. Sb,	Te ⁺ ,	I ⁺⁺	Xe ⁺³
5. Bi	Po ⁺		

The spectra of none of these elements, has been completely elucidated, O⁺ is a solitary exception, which has been treated by Fowler and Bowen ; N has been done only partially. The Table 18 is given to indicate the region in which the line of Fl⁺ have to be looked for.

TABLE 20

FIVE-VALENCE ELEMENTS

 $2 L_2(M_1 \leftarrow M_2)$ $2 L_2(M_2 \leftarrow M_3)$

Element	$4P_2-4D_1$	$4P_2-4P_2$	$4P_2-4S$	$4D_2-4F_3$	$4D_2-4D_2$	$4D_2-4P_1$	References
N	11475	12175	13432				Kiess and Kiess, J.O.S.A. Vol. II, p. 1.
O ⁺	21346	23052	26822	24564	25960		Fowler, Proc. Roy., Soc. Lond. Vol. 110, p. 479.
Fl ⁺⁺							Bowen, Phys. Rev., Vol. 29, p. 243.
Ne ⁺³							

SIX-VALENCE ELEMENTS.

The groups are

1. O, Fl⁺, Ne⁺⁺
2. S, Cl⁺, A⁺⁺

3. Se, Br⁺, Kr⁺⁺
4. Te l⁺, Xe⁺⁺

The application of the irregular Doublet Law to group 1 is shown in Table 21.

TABLE 21

 $(3L_2M \leftarrow 3L_2M_2)$ $(3L_2M_2 \leftarrow 3L_2M_3)$

Element	$5S_2-5P_2$	$3S_1-3P_1$	$5P-5D$	$3P-3D$	References
O	12859 13108	11836	10788 (17748)	8857	Fowler's Report.
Fl ⁺	25967 12578		28536		Discovered by D. S. Jog.
Ne ⁺⁺	38545				

The ${}^5S_2-{}^5P_2$ lines, transition $3L_2M_1 \leftarrow 3L_2M_2$ of Fl⁺, and Ne⁺⁺ have been obtained by Mr. D. S. Jog, following the indications of the irregular doublet law. The ${}^5P-{}^5D$ lines of Fl⁺ seem also to be correctly located. The elucidation of the spectra of Fl⁺ and Ne⁺⁺ will be very helpful to the understanding of the spectrum of O, which is now arousing wide interest owing to McLennan's discovery that the green auroral line must be due to O. A knowledge of the spectra of Fl⁺ and Ne⁺⁺ will help us in finding out the transition to which the green line owes its origin. The Oxygen spectrum itself is difficult, as the separations are very small, the quintets appearing as triplets, and triplets appearing as singlets.

SEVEN-VALENCE ELEMENTS

The groups are—

- (1) Fl, Ne⁺, Na⁺⁺, Mg⁺⁺⁺.....
- (2) Cl, A⁺, K⁺⁺, Ca⁺⁺
- (3) Br, Kr⁺, Rb⁺⁺, Sr⁺⁺⁺.....
- (4) I, Xe⁺, Cs⁺⁺, Ba⁺⁺⁺.....

The spectrum of Ne⁺ has been almost completely elucidated by the junior author. Subsequent work by De Bruin has confirmed his analysis. The spectrum of Fl has been analysed by De Bruin and Dingle but they have not yet been able to trace ${}^4L_2 (M_2 \leftarrow M_3)$ -lines. They will be in the

infra-red. We are, therefore, in a very nice position to predict the spectrum of Na^{++} , but data is yet completely

wanting. The expected frequencies are shown within brackets in the following table.

TABLE 22

SEVEN-VALENCE ELEMENTS

Element	$4L_2M_1 \leftarrow 4L_2M_2$			$4L_2M_2 \leftarrow 4L_2M_3$			References
	$^4P_2 - ^4D_2$	$^4P_2 - ^4P_2$	$^2P_1 - ^2P_1$	$^4D_2 - ^4F_2$	$^4D_2 - ^4D_2$	$^2D_2 - ^2D_2$	
Fl	14628 (15418)	13360 (13407)	14025 (15567)	Dingle, P.R.S.L., 113. ,, 117
Ne^+	30046	26747	29592	31579	29629	..	De Bruin, Zs. f. Physik, Vol. 40.
Na^{++}	(45000)	(40000)	(45000)	P. K. Kichlu, Proc. Phys. Soc, Lond. Vol. 39, p. 424. No data available.

TABLE 23

EIGHT-ELECTRON ELEMENTS

Element	$5L_2(M_1 \leftarrow M_2)$			$5L_2(M_2 \leftarrow M_3)$			References
	$^3P_1 - ^3D_2$	$^3P_1 - ^3P_1$	$^1P_1 - ^1P_1$	$^3D_2 - ^3F_3$	$^3D_2 - ^3D_2$	$^1D_2 - ^1D_2$	
Ne	15798 (16145)	16579 (17614)	14883 (16858)	11276 (22271)	12105 (21962)	..	Paschen and Götze, Serien- spektren.
Na^+	31943	34193	31741	33547	34067	?	M. N. Saha, Phil. Mag. Vol. 4, p. 223.
Mg^{++}	(48000)	(52000)	(48500)	(55000)	(56000)	..	Majumdar's Analysis (Supra). To be confirmed.

EIGHT-VALENCE ELEMENTS

The groups are—

- (1) Ne, Na^+ , Mg^{++}
- (2) A, K^+ , Ca^{++}
- (3) Kr, Rb^+ , Sr^{++}
- (4) Xe, Cs^+ , Ba^{++}

In the following paper Mr. Kanakendu Majumdar describes his analysis of the Na^+ -spectrum. The spectrum of Na was treated as the mean between the spectra of Ne^+ and Mg^+ , and the differences from that of Ne^+ were predicted as the mean of the differences in the foregoing (Fl, Ne^+)

and succeeding groups (Na , Mg^+). The prediction has been very elegantly confirmed by Majumdar's analysis which is almost complete. The results are shown in Table 23. This enables us to predict the spectrum of Mg^+ which is yet unknown. This is being investigated by Mr. Majumdar in this laboratory.

Summary.—In this paper, the full data of Millikan and Bowen's Arithmetic Progression Rule (Irregular Doublet Law in Optical Region) have been collected. The law has been extended to the case of complex spectra, and has been shown to hold good. Predictions are made regarding the spectra of certain elements which are yet unknown.

42(b) EXTENSION OF IRREGULAR DOUBLET LAW

M. N. SAHA & P. K. KICHLU

(*Nature*, **121**, 244, 1928)

Recent work in this laboratory has shown that the irregular doublet law, first discovered in 1920 by G. Hertz in the X-ray region, and since then extended by Millikan and Bowen for the optical region is capable of much wider application. Millikan and Bowen have applied the law for the prediction and identification of spectra of atoms which are stripped to one or two valency electrons by vacuum discharge, and in the case of higher valence elements, for inner transition lines. But the law can be applied for the prediction of spectra of elements with a larger number of valency electrons giving rise to complicated spectra. The extension of the law in its most general form can be thus enunciated:

If we compare the spectra of a group of successive elements which are reduced by electric discharge to the same electronic constitution (for example, C, N⁺, O⁺⁺, Fl⁺⁺⁺, N⁴⁺), then frequencies of corresponding lines arising out of a transition in which the total quantum number remains unchanged will form an arithmetic progression.

The law can be very easily illustrated with the atomic chart given by one of the authors (*Phys. Zs.*, p. 470; 1927).

K_1					
2					
	L_1	L_2			
	2	1			
			M_1	M_2	M_3
			[1]	→ (1)	→ (1)

In this chart, horizontal transitions refer to $\Delta n=0$. Thus taking C, N⁺, O⁺⁺ ... we find that the origin of

all possible groups of lines can be visualised as follows:

$$L_2L_2 \longrightarrow L_2M_1 \longrightarrow L_2M_2 \longrightarrow L_2M_3$$

$$(M_1 \longrightarrow M_2) \quad (M_2 \longrightarrow M_3)$$

Now the corresponding lines of the successive elements arising out of the transitions

$$L_2M_1 \longrightarrow L_2M_2, \text{ that is, } ({}^3P, {}^1P) - ({}^3D, {}^3P, {}^2S) \text{ lines,}$$

and

$$L_2M_2 \longrightarrow L_2M_3, \text{ that is, } ({}^3D, {}^3P, {}^3S) - ({}^3F, {}^3D, {}^3P)$$

will form arithmetic progressions.

Application of this law can be extended to all other complicated spectra.

It follows that if the spectra of two elements, preferably successive, of any group be known, it becomes quite easy to predict the spectra of the remaining elements.

In the group just mentioned, namely, C, N⁺, O⁺⁺ ... the spectra of N⁺ has been completely elucidated by Fowler and Freeman, and that of O⁺⁺, is nearing completion thanks to the work of Mihul. (Mihul's levels are wrongly given, though his multiplets are correct. They can be easily reshuffled and correctly fitted to Hund's theory.) We can then predict the spectra of C, which is still unknown. Then $L_2(M_1 \longrightarrow M_2)$, as well as $L_2(M_2 \longrightarrow M_3)$ lines which are next in intensity to the fundamental $L_2L_2 \longrightarrow L_2M_1$ (${}^3P, {}^1D, {}^1S$) - (${}^3P, {}^1P$) lines are found to be beyond 8000 Å.

In a similar way, spectra of all groups can be predicted and correctly located.

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Jan. 11.

43. THE ORIGIN OF NEBULIUM SPECTRUM

(*Nature*, **121**, 418, 1928)

In a letter to NATURE of Oct. 1, 1927, p. 473, Mr. Bowen has announced the very interesting relationship that some of the lines of unknown origin which are found in the nebulae and in the Wolf-Rayet stars and were so long

attributed to a hypothetical element nebulium, are really due to ionised light elements like O⁺⁺, N⁺⁺, O⁺, N⁺ ...; they do not arise from the transitions usually allowed, but are due to transitions which are usually prohibited.