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A PERIODIC TABLE OF THE STRUCTURE OF ATOMS AND ITS  
RELATION TO ION FORMATION AND VALENCE

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*Introduction.*—For the purpose of studying the interpretations which the recently acquired knowledge of the structure of atoms might afford as to tendencies of elements to form ions and to exist in definite valence states, the authors compiled from spectroscopic publications of the last three years the values of the energies attending the removal of the various electrons from the outer shells of the atoms and ions of the first twenty-six elements (higher elements not being included, since the spectral data have as yet been too incompletely interpreted). And a chart was prepared showing the number, the quantum states, and the energies of removal of these electrons. The data upon which the chart is based and the detailed discussion of it in relation to the chemical properties mentioned are to be published in full in the *Journal of the American Chemical Society*;<sup>\*</sup> but the interest which the matter might have for scientists in other fields has led to the presentation in these PROCEEDINGS of the chart and a summary of the conclusions reached as to ion formation and valence.

In the assembling and interpretation of the spectroscopic data we have been greatly assisted by the advice of Prof. Ira S. Bowen of this Institute, by whose experimental researches, made in association with Dr. R. A. Millikan, the data for the chart have in large measure been made available. This paper has, moreover, been possible only through the recent interpretations of electron distribution by Main-Smith<sup>1</sup> and Stoner<sup>2</sup> and of complex spectra by Russell and Saunders,<sup>3</sup> Pauli,<sup>4</sup> Heisenberg<sup>5</sup> and Hund.<sup>6</sup>

*Description of the Chart.*—The chart is shown on page 740. Along the axis of abscissas is plotted the atomic number of the element, which also represents the positive charge on the nucleus of its atom and ions, as well as the total number of electrons around the nucleus of the

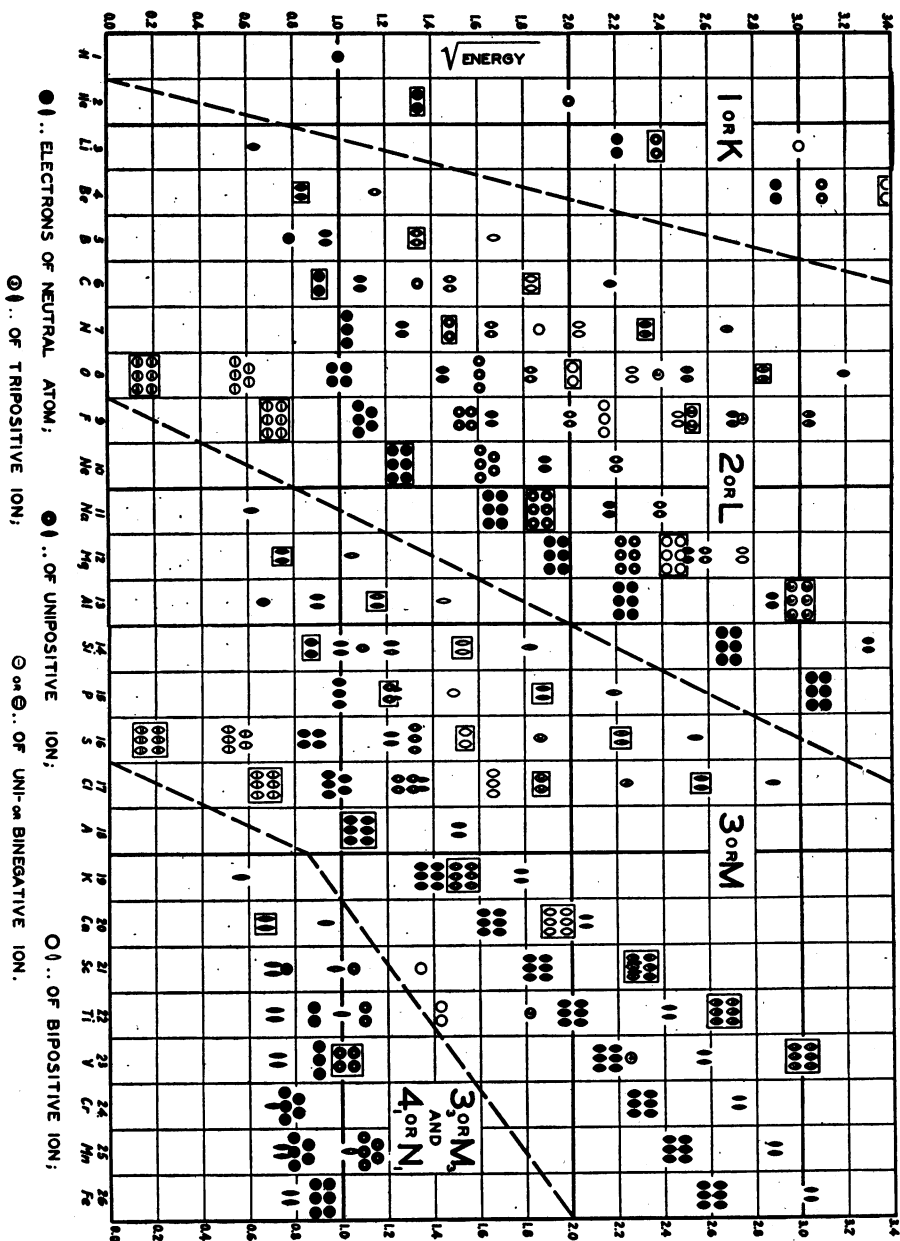
<sup>\*</sup> The chart was originally shown and discussed in an address before the Pacific Division of the American Association for the Advancement of Science at its Reno meeting on June 22, 1927.

neutral atom. As ordinates are plotted the square-roots of the energies absorbed in the removal of the respective electrons from the atom in its normal state in terms of the energy absorbed in removing the electron from the hydrogen atom as unity; in other words, the square-roots of the ratios  $\nu/R$  of the wave-number of the spectral term to the Rydberg number. The square-roots are plotted, rather than the energies themselves, since this enables higher energy values to be included in the chart without unduly extending it, and since Millikan and Bowen<sup>7</sup> have found that Moseley's principle that the square-roots of the energies are nearly linear functions of the atomic numbers applies to the corresponding electrons of ions that have the same configuration but different nuclear charges.

The number of electrons having a definite energy of removal is shown by a corresponding number of circles or ellipses; it being understood that the exact value of the energy is at the center around which these electrons are grouped. Black circles or ellipses are used for electrons of the neutral atom; black circles or ellipses with a white circle at the center for the uni-positive ions; white circles or ellipses for bipoisitive ions; white circles or ellipses with a numeral (3, 4 or 5) within for multipositive ions; and white circles with one or two cross bars for uninegative or binegative ions.

The quantum states of the electrons are differentiated by the use of circles and of ellipses of different eccentricity. Namely, in correspondence with the Bohr orbital theory, when the principal and azimuthal quantum numbers ( $n$  and  $k$ ) are equal (as in the  $1_1, 2_2, 3_3 \dots$  quantum states) the electrons are represented by circles; and when these quantum numbers are unequal, ellipses are used whose major and minor axes have the same ratio as the two quantum numbers, thus 2:1 for the  $2_1$  state; 3:2 for the  $3_2$  state; etc. The principal quantum numbers (1, 2, 3, 4) or the shells ( $K, L, M, N$ ) of the electrons are also indicated by the regions of the plot in which they lie, these regions being separated from each other by heavy oblique broken lines. It is not possible, however, to separate completely in this way the 3 or  $M$  from the 4 or  $N$  electrons, for the electrons of the  $3_3$  and  $4_1$  quantum types have energies of removal of the same order of magnitude. In the lower right-hand region, therefore, the circles are to be understood to represent  $3_3$  electrons and the ellipses  $4_1$  electrons.

On the chart are also differentiated the atom configurations for which the inner quantum number  $J$  is zero and the magnetic moment  $\mu$  is zero from those for which these quantities have finite values; namely, by enclosing in the former case (where  $J = 0$  and  $\mu = 0$ ) the lowest group of electrons within a rectangle. It may be recalled that the quantity  $J$  is an integer or half-integer expressing the quantized resultant, for any given atom or ion, of the moments of momentum (in terms of  $h/2\pi$ ) of the orbital rotations and spinings about their axes of all the individual electrons, and that  $\mu$  is the corresponding resultant for the magnetic



moments of the electrons. The values of  $J$  for all the neutral atoms have recently been determined by McLennan, McLay and Smith<sup>8</sup> for all the neutral atoms in their most stable states, and their results are those employed in this article. The values of  $\mu$ , which is equal to the product of  $J$  by a variable factor  $g$ , were calculated with the aid of the values of this factor given by Hund<sup>9</sup> and Sommerfeld.<sup>10</sup>

The chart gives a complete representation of all the electrons for the neutral atom and its ions only in the case of the first four elements (hydrogen to beryllium). For all the other elements the two electrons in the  $K$  shell are omitted, as they would lie far above the top of the chart; and for the neutral atoms above phosphorus and for the ions above aluminum the eight electrons of the  $L$  shell are also omitted. These omissions must be borne in mind in considering the complete structure of the atom. It should also be mentioned that many of the points are based on estimated, not directly measured data. No attempt is made to indicate this distinction on the chart; but it is shown in the detailed article.

*Ion-Formation and Valence.*—To facilitate the study of the relations of atomic structure to ion-formation and valence, table 1 has been prepared from the atomic-structure data and the known chemical properties of the elements. The headings and conventions are for the most part self-explanatory; but the following supplementary statements may be made. The "ions formed" are all the simple elementary ions of whose existence in aqueous solutions or in crystals there is good evidence. The indicated "valences" include only those corresponding to the best defined states of oxidation, such as are exhibited by the elements in their salts, bases or acids. The ions whose symbols are given in the next three columns do not all actually exist, but are those which have, or would have if they existed, the types of configuration named in the three headings. Note that these hypothetical ions are formed from the neutral atoms by the loss or gain of a number of electrons equal to the charges on the ions, and that, if these electrons be those which actually participate in the union of the atom with other atoms (*the reacting electrons*), their number will correspond to an existing valence. In the column headed "ions or atoms with zero moment" are given only those with incomplete shells, it being understood that, as above stated, all those cited in the two adjoining columns to the left have also zero moment of momentum and magnetic moment.

The conclusions as to ion-formation to be drawn from this table may be briefly stated as follows. Of the elements preceding titanium the first three of each period (except boron) form positive ions, and only such as result from the removal of all the electrons outside of the complete 1, 2, or  $3_1 + 3_2$  shells; and the last three elements of each period alone form negative ions, and only such as result from the completion of the 2 or  $3_1 + 3_2$  shells with electrons. Intermediate ions, such as  $Al^+$  or  $Ca^+$ ,

TABLE I  
 ION FORMATION AND VALENCE IN RELATION TO ATOMIC STRUCTURE

Ele- ment	Atomic no.	Ions formed	Va- lences	Ions or Atoms with			$M$	Energy of removal of outer electrons <sup>11</sup> from			
				Com- plete %Shell	Com- plete % <sub>1</sub> Shell	Zero moment		$M^+$	$M^{2+}$	$M^{3+}$	$M^{4+}$
H	1	H <sup>+</sup> , H <sup>-</sup>	1 -1	H <sup>+</sup> , H <sup>-</sup>	..	...	1.00	∞	...	...	...
He	2	None	0	He	..	...	1.80	4.00	∞	...	...
Li	3	Li <sup>+</sup>	1	Li <sup>+</sup>	..	...	0.40	5.6	9.00	∞	...
Be	4	Be <sup>2+</sup>	2	Be <sup>2+</sup>	..	...	0.70	1.34	11.4	16.0	∞
B	5	...	3	B <sup>3+</sup>	B <sup>+</sup>	...	0.62	1.79	2.80	19.3	25.0
C	6	...	4	C <sup>4+</sup>	C <sup>2+</sup>	...	0.83	1.79	3.36	4.74	29.0
N	7	...	3, 5 -3	N <sup>5+</sup> N <sup>3-</sup>	N <sup>3+</sup> N <sup>+</sup>	N <sup>+</sup>	1.07	2.18	3.49	5.43	7.19
O	8	... O <sup>2-</sup>	... -2	O <sup>6+</sup> O <sup>2-</sup>	O <sup>4+</sup>	O <sup>2+</sup>	1.00	2.58	4.05	5.69	8.07
F	9	F <sup>-</sup>	-1	F <sup>7+</sup> F <sup>-</sup>	F <sup>5+</sup>	F <sup>3+</sup>	1.25	2.39	4.62	6.40	7.56
Ne	10	None	0	Ne	..	...	1.59	2.70	...	...	...
Na	11	Na <sup>+</sup>	1	Na <sup>+</sup>	..	...	0.38	3.50	...	...	...
Mg	12	Mg <sup>2+</sup>	2	Mg <sup>2+</sup>	..	...	0.56	1.11	5.98	...	...
Al	13	Al <sup>3+</sup>	3	Al <sup>3+</sup>	Al <sup>+</sup>	...	0.44	1.34	2.09	9.00	...
Si	14	...	4	Si <sup>4+</sup>	Si <sup>2+</sup>	...	0.76	1.20	2.34	3.32	12.47
P	15	...	1, 3, 5 -3	P <sup>5+</sup> P <sup>3-</sup>	P <sup>3+</sup>	P <sup>+</sup>	0.98	1.46	2.22	3.53	4.78
S	16	... S <sup>2-</sup>	4, 6, -2	S <sup>6+</sup> S <sup>2-</sup>	S <sup>4+</sup>	S <sup>2+</sup>	0.76	1.74	2.37	3.48	4.93
Cl	17	... Cl <sup>-</sup>	1, 3, 5, 7 -1	Cl <sup>7+</sup> Cl <sup>-</sup>	Cl <sup>5+</sup>	Cl <sup>3+</sup>	0.96	1.66	2.76	3.50	5.00
A	18	None	0	A	..	...	1.16	..	...	...	...
K	19	K <sup>+</sup>	1	K <sup>+</sup>	..	...	0.32	2.34	...	...	...
Ca	20	Ca <sup>2+</sup>	2	Ca <sup>2+</sup>	..	...	0.45	0.87	3.76	...	...
Sc	21	Sc <sup>3+</sup>	3	Sc <sup>3+</sup>	..	...	0.49	0.95	1.82	5.33	...
Ti	22	Ti <sup>2+</sup> Ti <sup>3+</sup> Ti <sup>4+</sup>	2, 3, 4	Ti <sup>4+</sup>	..	...	0.50	1.00	2.04	3.18	7.07
V	23	V <sup>2+</sup> V <sup>3+</sup>	2, 3, 4, 5	V <sup>5+</sup>	..	V <sup>+</sup>	0.52	1.04	...	...	5.08
Cr	24	Cr <sup>2+</sup> Cr <sup>3+</sup>	2, 3, 6	Cr <sup>6+</sup>	..	Cr <sup>2+</sup>	0.50	..	...	...	...
Mn	25	Mn <sup>2+</sup> Mn <sup>3+</sup> Mn <sup>4+</sup>	2, 3, 4, 6, 7	Mn <sup>7+</sup>	..	Mn <sup>3+</sup>	0.55	1.07	...	...	...
Fe	26	Fe <sup>2+</sup> Fe <sup>3+</sup>	2, 3, 6	Fe <sup>6+</sup>	..	Fe <sup>4+</sup>	0.59	..	...	...	...

do not form as they do at high temperatures, even though the energy required for the removal of the first electron is much smaller than that for the second and even when, as with  $Al^+$ , the resulting ion would have its lowest energy electrons in a complete subshell ( $3_1$ ), which has, moreover, zero moment of momentum and zero magnetic moment. Titanium, vanadium, chromium, manganese and iron all form bivalent ions through the loss of their  $4_1$  electrons, even though the remaining electrons do not suffice to complete the  $3_3$  shell; the incomplete  $3_3$  shell being apparently as stable as the complete 2 quantum shell. They also form other ions which have no apparent relation to the structure of their atoms.

The conclusions in regard to valence may be summarized as follows. None of the first four elements of the first two periods and neither of the first two elements of the third period exhibit any other well-defined valence than that which would result if the electrons giving rise to the valence were those, and only those outside of the complete 1, 2 or  $3_1 + 3_2$  quantum shells. The possibility that, in the cases of boron and aluminum or of carbon and silicon, the electrons outside of a complete subshell ( $2_1$  or  $3_1$ ) (with its zero moment of momentum and zero magnetic moment) might alone function as valence electrons does not cause these elements to exist in the univalent or bivalent state.

The elements nitrogen, phosphorus, sulphur and chlorine, on the other hand, exhibit the positive valences that would result if the reacting electrons are those outside: (1) the complete shells 1 or 2; (2) the complete subshells  $2_1$  or  $3_1$ ; and (3) the configurations other than these that have zero moment of momentum and zero magnetic moment. These elements also exhibit negative valences of the type (1), namely, those that correspond to the taking up of enough more electrons to complete the 2 or  $3_1 + 3_2$  shells. Thus, the valences corresponding to the three types are:

(1) Nitrogen and phosphorus, +5 and -3; sulphur, +6 and -2; chlorine, +7 and -1.

(2) Nitrogen, +3; phosphorus, +3; sulphur, +4; chlorine, +5.

(3) Nitrogen, +1; phosphorus, +1; sulphur, +2; chlorine, +3.

And, in fact, these elements exist in the form of salts in all these valences, with the exception of unipositive nitrogen (which, however, forms  $N_2O$ ) and possibly of bivalent sulphur (which, however, forms derivatives of the acid  $H_2SO_2$ ). Furthermore, the chemical stability of these various valences is clearly related to the type, being greatest for type (1) and least for type (3). Thus, type (1) is that of the very stable nitrates, phosphates, sulphates and perchlorates, as well as of the amines, phosphines, sulphides and chlorides; type (2) is that of the much less stable nitrites, phosphites, sulphites and chlorates; and type (3) is that of the unstable hypophosphites and chlorites and of the non-existent or extremely unstable salts  $M^I NO$

and  $M^I_2SO_2$ . These configuration types do not account for unipositive chlorine (in hypochlorites); but this is perhaps related to its instability; nor do they explain the existence of isolated compounds with even valences, such as NO,  $NO_2$ ,  $ClO_2$ . The three types together account for the long-known fact that the well-defined valences are all even (as in the case of sulphur) or all odd (as in the case of nitrogen, phosphorus and chlorine).

The six elements beyond calcium in the third period exhibit positive valences that correspond to the complete  $3_1 + 3_2$  shell. Moreover, all of them (except scandium) form bivalent compounds that can be accounted for by assuming that only the two  $4_1$  electrons are reacting, which implies that the underlying  $3_3$  shell is an exceptionally stable configuration even when it is incompletely filled with electrons. The other irregular valences exhibited by these elements cannot be explained by our present knowledge of the structure of their atoms. These valences evidently constitute a phenomenon of a type distinct from the regular even or odd valences of the nitrogen, sulphur and chlorine groups.

In general, the energies of removal of the successive electrons seem to play only a secondary part in determining the valences that exist.

<sup>1</sup> Main-Smith, *Chemistry and Atomic Structure*, D. Van Nostrand Co., New York, 1924, pp. 189-198.

<sup>2</sup> Stoner, *Phil. Mag.*, **48**, 719 (1924).

<sup>3</sup> Russell and Saunders, *Astrophys. J.*, **61**, 38 (1925).

<sup>4</sup> Pauli, *Zs. Physik*, **31**, 765 (1925).

<sup>5</sup> Heisenberg, *Ibid.*, **32**, 841 (1925).

<sup>6</sup> Hund, *Ibid.*, **33**, 345 (1925); **34**, 296 (1925).

<sup>7</sup> Millikan and Bowen, these PROCEEDINGS, **13**, 531 (1927).

<sup>8</sup> McLennan, McLay and Smith, *Proc. Roy. Soc.*, **A112**, 76 (1926).

<sup>9</sup> Hund, *Linien spectren und Periodisches System der Elemente*, 1927, p. 106.

<sup>10</sup> Sommerfeld, *Atombau und Spectrallinien*, 4th edition, 1924, p. 623.

<sup>11</sup> The energies of removal of the outer electrons from negative ions are:  $O^-$ , 0.34;  $O^{2-}$ , 0.03;  $F^-$ , 0.52;  $S^-$ , 0.30;  $S^{2-}$ , 0.03;  $Cl^-$ , 0.45. All these values were obtained by linear extrapolation on the square-root plot.