THE STRUCTURE OF ATOMS AS A PERIODIC PROPERTY AND ITS RELATION TO VALENCE AND ION-FORMATION*

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INTRODUCTION

The great development of the knowledge of the electronic structure of atoms which has resulted during the last two or three years from spectroscopic investigations has made it possible to draw a much more complete picture of the atoms of the elements of the first two short periods, and in less degree of those of the first long period of the periodic system. Namely, it is now possible in the case of most of these atoms and of many of the ions derived from them to specify not only the number and the quantum-states of the electrons in each of the shells of the atom, but also to evaluate the energies attending the removal of its electrons from the various quantum levels. Tables were published in 1924 by Main-Smith (19) and Stoner (20) showing the now accepted distribution of the electrons among the various quantum levels; and these tables have since been extended (21)[1] and reproduced by others (22). The corresponding values of the energies of the removal of the electrons have, however, not been compiled in connection with such tables. It seemed therefore well worth while to collate these values, which are scattered through the recent literature, and to present in the form of a

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[1] Thus by McLennan, McLay, and Smith, Proc. Roy. Soc. London, (A) **112**, 76 (1926), who added the quantum characteristics of the basic spectral term for each atom, especially its inner quantum number.

chart a graphic picture of the present knowledge of the structure of atoms, showing these energies in connection with the quantum states of the atoms.

Desirable as it would be to do so, it did not seem practicable at the present time to extend the chart and discussion of the results beyond zinc, because the interpretation of the spectroscopic data of the higher elements is still so fragmentary that energy values are seldom available, except for the more loosely bound electrons.

In the assembling and interpretation of the spectroscopic data we have been greatly assisted by the advice of Professor 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.

THEORETICAL CONSIDERATIONS

The structure data here presented, since they largely relate to the outer shell of electrons, are based almost wholly on spectroscopic studies. From empirical studies there resulted, even prior to the development of the quantum theory, a remarkable classification into series of the complex spectral lines; but the quantum theory suggested further principles which within the last few years have made almost complete the methods of ordering spectra[2] though a great deal of work must still be done in applying these methods to the individual elements.

It is to be noted that the data to be presented below of the energies of removal of the electrons from atoms are not based on any hypothetical considerations relating to the dynamics of the atom, such, for example, as the Bohr theory of orbits; and that

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[2] A good elementary presentation of the subject has been given by Goudsmit in 1927 in a dissertation entitled "The Atomic Models and the Structure of Spectra." This is now being translated and revised, with the coöperation of the author, by Dr. Linus Pauling of California Institute of Technology. For readers familiar with earlier quantum treatments of spectra, as given in Sommerfeld's "Atomic Structure and Spectral Lines," the following references may be found helpful: Sommerfeld, "Three Lectures on Atomic Physics," Methuen and Co., Ltd., London, 1926; F. Hund, "Linienspektren und Periodisches System der Elemente," Julius Springer, Berlin, 1927.

they will remain valid even though new conceptions as to atom mechanics be developed. For, so long as the basic quantum principle $E = h\nu$, stating that the energy E of each quantum of a radiation is proportional to its frequency ν, is accepted, the so called "terms," which are the values whose differences give directly the frequencies of observed spectral lines, will retain their significance as energies.

As is well known, the electrons of the various atoms have been arranged in a series of shells, each of which, with increasing atomic number or nuclear charge, becomes filled when a certain maximum number of electrons has been added. Thus, the helium atom has a shell of 2 electrons, known as the 1 or K shell; the neon atom has in addition a second shell of 8 electrons, known as the 2 or L shell; the nickel atom has also a third shell of 18 electrons, known as the 3 or M shell; etc. The numbers 1, 2, 3, 4 . . . . correspond to the principal or total quantum number n. It was, moreover, recognized by Bohr (23) in 1921 that all of the electrons within one of these main shells are not equivalent; and he proposed a classification into subshells, which he assumed to contain equal numbers of electrons. Thus the 8 electrons of the L shell were considered to form two subshells each containing 4 electrons, and the 18 electrons of the M shell to form three subshells each containing 6 electrons. Main-Smith (24) in 1924 and Stoner (20) some months later showed that the chemical facts and the spectra, respectively, are much better accounted for by assuming that the shells consist of subshells containing the following numbers of electrons: the K shell, 2 electrons; the L shell, a subshell of 2 and one of 6 electrons; and the M shell, subshells of 2, 6, and 10 electrons.[3]

The recent developments in the interpretation of the spectra of complex atoms by Russell and Saunders (25), Pauli (26), Heisenberg (27), and Hund (28) have completely confirmed the scheme of Main-Smith and Stoner. They have, moreover, made it possible to derive from the optical spectrum of any atom or ion the energies of removal of the electrons from its outer subshells.

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[3] For a table showing the electron groups for all the atoms, see Andrade (22).

In order to describe the state of the electrons in the subshells, another series of integral quantum numbers is used. These were originally called the azimuthal quantum numbers *k;* for this number, according to the Bohr orbital theory, determined, when considered in relation to the total quantum number, the eccentricity of the orbit of the electron. Its value, which ranges from unity up to that of the total quantum number, is indicated by attaching it as a subscript to the total quantum number. Thus 2_2, 3_3, 4_4 denote circular orbits; 2_1, 3_2, 4_3 the elliptical orbits of least eccentricity; 3_1, 4_2 elliptic orbits of greater eccentricity. More recent quantitative developments of the quantum theories of spectra and of the new wave-mechanics have led physicists to replace the azimuthal quantum numbers by values that are uniformly smaller by one unit, these values being denoted by the symbol *l*. Spectroscopists employ a different notation, derived from the designations of spectral series, in which conventional letters are used, instead of integral numbers. The relations between the three systems of notation are as follows:

Values of *k*	1	2	3	4	5	6
Values of *l*	0	1	2	3	4	5
Spectroscopic notation	s	p	d	f	g	h

Thus the states denoted by 3_1, 3_2, and 3_3 using the azimuthal numbers are represented in spectroscopic notation by 3s, 3p, and 3d respectively. For the values in table 1, which were compiled mostly from spectroscopic sources, the spectroscopic notation is retained; but in the charts and throughout the discussion the azimuthal notation is employed.

THE QUANTUM STATES AND ENERGIES OF REMOVAL OF THE ELECTRONS

In table 1 are given, for the first 30 elements, the number of electrons in the outer subshells of the neutral atoms and of the various ions resulting from them, together with their energies of removal. Isolated values for a few higher elements are also included.

By the energy of removal of an electron is meant the energy

TABLE 1

Quantum states and energies of removal of electrons

ATOMIC NUMBER	ATOM OR ION	ELECTRONS		ENERGY OF REMOVAL		REFERENCE*
		Number	State	E	$\sqrt{E}$	
1	H	1	1 s	1.000	1.000	—
2	He	2	1 s	1.803	1.343	1
	He^{1+}	1	1 s	4.000	2.000	—
3	Li	1	2 s	0.397	0.630	2
		2	1 s	4.90	2.21	Est.†
	Li^{1+}	2	1 s	5.6	2.37	Est.
	Li^{2+}	1	1 s	9.000	3.000	—
4	Be	2	2 s	0.702	0.838	2
		2	1 s	8.5	2.9	Est.
	Be^{1+}	1	2 s	1.340	1.157	2
		2	1 s	9.6	3.1	Est.
	Be^{2+}	2	1 s	11.4	3.38	Est.
	Be^{3+}	1	1 s	16.000	4.000	—
5	B	1	2 p	0.616	0.785	2
		2	2 s	0.886	0.941	3
	B^{1+}	2	2 s	1.787	1.337	2
	B^{2+}	1	2 s	2.791	1.670	2
	B^{3+}	2	1 s	19.3	4.39	Est.
6	C	2	2 p	0.835	0.914	2
		2	2 s	1.18	1.09	3
	C^{1+}	1	2 p	1.794	1.339	2
		2	2 s	2.2	1.48	Est.
	C^{2+}	2	2 s	3.360	1.833	2
	C^{3+}	1	2 s	4.744	2.178	2
	C^{4+}	2	1 s	29.2	5.40	Est.
7	N	3	2 p	1.070	1.035	2
		2	2 s	1.62	1.27	3
	N^{1+}	2	2 p	2.183	1.478	2
		2	2 s	2.76	1.66	Est.
	N^{2+}	1	2 p	3.486	1.867	2
7	N^{2+}	2	2 s	4.16	2.04	Est.
	N^{3+}	2	2 s	5.43	2.33	Est.
	N^{4+}	1	2 s	7.193	2.682	4
8	O	4	2 p	1.002	1.001	2
		2	2 s	2.094	1.447	3
	O^{1+}	3	2 p	2.585	1.608	2
		2	2 s	3.35	1.83	Est.
	O^{2+}	2	2 p	4.047	2.012	2
		2	2 s	5.15	2.27	Est.
	O^{3+}	1	2 p	5.687	2.385	2
		2	2 s	6.30	2.51	Est.
	O^{4+}	2	2 s	8.07	2.84	Est.
	O^{5+}	1	2 s	10.144	3.185	4
	O^{1-}	5	2 p	0.34	0.58	Est.
	O^{2-}	6	2 p	0.03	0.16	Est.
9	F	5	2 p	1.248	1.117	2
		2	2 s	2.74	1.66	3
	F^{1+}	4	2 p	2.386	1.545	2
		2	2 s	4.00	2.00	Est.
	F^{2+}	3	2 p	4.62	2.15	Est.
		2	2 s	6.10	2.47	Est.
	F^{3+}	2	2 p	6.40	2.53	Est.
		2	2 s	7.34	2.71	Est.
	F^{4+}	1	2 p	7.56	2.75	Est.
		2	2 s	9.24	3.04	Est.
	F^{1-}	6	2 p	0.52	0.72	Est.
10	Ne	6	2 p	1.587	1.260	1
		2	2 s	3.57	1.89	Est.
	Ne^{1+}	5	2 p	3.025	1.738	15
		2	2 s	4.84	2.20	Est.
11	Na	1	3 s	0.378	0.615	1
		6	2 p	2.80	1.673	3

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* References for these tables have been placed at the end of the article, before the general references.

† Est. = estimated. The values given for negative ions, which were derived by extrapolation by the Millikan-Bowen principle, should be regarded as only rough indications.

TABLE 1—*Continued*

ATOMIC NUMBER	ATOM OR ION	ELECTRONS Number	ELECTRONS State	ENERGY OF REMOVAL E	ENERGY OF REMOVAL $\sqrt{E}$	REFERENCE
11	Na	2	2 s	4.71	2.17	Est.
	Na^{1+}	6	2 p	3.47	1.86	3
		2	2 s	5.71	2.39	Est.
12	Mg	2	3 s	0.562	0.750	1
		6	2 p	3.76	1.94	Est.
		2	2 s	6.30	2.51	Est.
	Mg^{1+}	1	3 s	1.106	1.051	1
		6	2 p	5.04	2.25	3
		2	2 s	6.71	2.59	Est.
	Mg^{2+}	6	2 p	5.98	2.45	3
		2	2 s	7.56	2.75	Est.
13	Al	1	3 p	0.440	0.663	1
		2	3 s	0.81	0.90	3
		6	2 p	5.0	2.24	5
		2	2 s	8.29	2.88	Est.
	Al^{1+}	2	3 s	1.342	1.159	1
	Al^{2+}	1	3 s	2.092	1.446	1
	Al^{3+}	6	2 p	9.00	3.00	3
14	Si	2	3 p	0.761	0.872	3
		2	3 s	1.00	1.00	Est.
		6	2 p	7.2	2.70	5
		2	2 s	10.9	3.3	Est.
	Si^{1+}	1	3 p	1.202	1.096	6
		2	3 s	1.49	1.22	Est.
	Si^{2+}	2	3 s	2.338	1.529	6
	Si^{3+}	1	3 s	3.320	1.822	6
	Si^{4+}	6	2 p	12.47	3.53	3
15	P	3	3 p	0.982	0.991	1
		2	3 s	1.52	1.23	Est.
		6	2 p	9.5	3.08	5
		2	2 s	13.7	3.7	Est.
	P^{1+}	2	3 p	1.462	1.209	7
	P^{2+}	1	3 p	2.216	1.489	8
	P^{3+}	2	3 s	3.53	1.88	Est.
	P^{4+}	1	3 s	4.778	2.186	9
16	S	4	3 p	0.761	0.873	1
		2	3 s	1.485	1.219	3
	S^{1+}	3	3 p	1.74	1.32	Est.
	S^{2+}	2	3 p	2.37	1.54	Est.
	S^{3+}	1	3 p	3.479	1.865	8
	S^{4+}	2	3 s	4.93	2.22	Est.
	S^{5+}	1	3 s	6.473	2.544	9
	S^{1-}	5	3 p	0.22	0.47	Est.
	S^{2-}	6	3 p	0.00	0.02	Est.
17	Cl	5	3 p	0.96	0.98	3
		2	3 s	1.81	1.35	3
	Cl^{1+}	4	3 p	1.66	1.29	3
	Cl^{2+}	3	3 p	2.93	1.71	16
	Cl^{3+}	2	3 p	3.50	1.87	3
	Cl^{4+}	1	3 p	5.00	2.24	3
	Cl^{5+}	2	3 s	6.55	2.56	Est.
	Cl^{6+}	1	3 s	8.400	2.898	4
	Cl^{1-}	6	3 p	0.33	0.57	Est.
18	A	6	3 p	1.159	1.076	10
		2	3 s	2.25	1.50	Est.
	A^{1+}	5	3 p	2.00	1.41	15
19	K	1	4 s	0.319	0.565	1, 18
		6	3 p	1.90	1.38	Est.
		2	3 s	3.17	1.78	Est.
	K^{1+}	6	3 p	2.34	1.53	17
20	Ca	2	4 s	0.450	0.671	1, 18
		6	3 p	2.72	1.65	Est.
		2	3 s	4.25	2.06	Est.
	Ca^{1+}	1	4 s	0.873	0.934	1, 18
	Ca^{2+}	6	3 p	3.76	1.94	17
21	Sc	2	4 s	0.49	0.702	11,18
		1	3 d	0.55	0.76	Est.
		6	3 p	3.4	1.85	Est.
		2	3 s	5.1	2.27	Est.

TABLE 1—*Concluded*

ATOMIC NUMBER	ATOM OR ION	ELECTRONS		ENERGY OF REMOVAL		REFERENCE
		Number	State	E	$\sqrt{E}$	
21	Sc^{1+}	1	4 s	0.948	0.974	11, 18
		1	3 d	1.1	1.05	Est.
	Sc^{2+}	1	3 d	1.817	1.348	12
	Sc^{3+}	6	3 p	5.33	2.31	Est.
22	Ti	2	4 s	0.503	0.709	13,18
		2	3 d	0.730	0.855	13
		6	3 p	4.0	2.00	Est.
		2	3 s	5.9	2.42	Est.
	Ti^{1+}	1	4 s	1.003	1.001	13, 18
		2	3 d	1.2	1.10	Est.
	Ti^{2+}	2	3 d	2.038	1.428	13
	Ti^{3+}	1	3 d	3.301	1.817	14
	Ti^{4+}	6	3 p	7.07	2.66	Est.
23	V	2	4 s‡	0.524	0.724	13
		3	3 d	0.81	0.90	Est.
		6	3 p	4.1	2.15	Est.
		2	3 s	6.6	2.57	Est.
	V^{1+}	4	3 d	1.041	1.020	13
	V^{4+}	1	3 d	5.072	2.252	14
	V^{5+}	6	3 p	9.0	3.00	Est.
24	Cr	1	4 s	0.496	0.704	1, 18
		5	3 d	0.610	0.781	3
		6	3 p	5.3	2.30	Est.
		2	3 s	7.4	2.72	Est.
	Cr^{1+}	5	3 d	1.23	1.11	18
25	Mn	2	4 s	0.547	0.740	1, 18
		5	3 d	0.67	0.82	Est.
		6	3 p	6.0	2.45	Est.
		2	3 s	8.24	2.87	Est.
	Mn^{1+}	1	4 s	1.161	1.076	18
		5	3 d	1.25	1.12	Est.

ATOMIC NUMBER	ATOM OR ION	ELECTRONS		ENERGY OF REMOVAL		REFERENCE
		Number	State	E	$\sqrt{E}$	
26	Fe	2	4 s	0.578	0.759	18
		6	3 d	0.81	0.90	Est.
		6	3 p	6.8	2.60	Est.
		2	3 s	9.18	3.03	Est.
	Fe^{1+}	1	4 s	1.22	1.10	18
27	Co	2	4 s	0.577	0.759	18
	Co^{1+}	1	4 s	1.27	1.126	18
28	Ni	2	4 s	0.564	0.751	18
	Ni^{1+}	1	4 s	1.34	1.158	18
29	Cu	1	4 s	0.567	0.754	1, 18
		10	3 d	0.773	0.881	3
	Cu^{1+}	10	3 d	1.503	1.225	18
30	Zn	2	4 s	0.690	0.831	1, 18
	Zn^{1+}	1	4 s	1.320	1.148	18
31	Ga	1	4 p	0.440	0.664	1
		2	4 s	0.84	0.92	Est.
32	Ge	2	4 p	0.70	0.84	Est.
		2	4 s	1.00	1.00	Est.
33	As	3	4 p	0.86	0.929	1
		2	4 s	1.36	1.17	Est.
34	Se	4	4 p	0.70	0.84	Est.
		2	4 s	1.40	1.18	Est.
35	Br	5	4 p	0.86	0.93	Est.
		2	4 s	1.70	1.30	Est.
36	Kr	6	4 p	0.98	0.991	19
		2	4 s	2.00	1.41	Est.

‡ See footnote 4.

that must be imparted to the atom or ion in its normal or most stable configuration, in order to remove that electron, and leave the resulting ion in its most stable state.[4]

The energy is expressed as a ratio of the energy of removal of the specified electron to that of the electron of the neutral hydrogen atom (for which the energy is 2.156×10^{-11} ergs, corresponding to an ionization potential of 13.54 volts). The energy values have been obtained in most cases by dividing the wave-number of the spectral term by the Rydberg wave-number 109678 cm.^{-1}. An attempt has been made to indicate the accuracy of the value by giving one more figure than is probably certain. In the last column of the table are shown the sources of the energy values, the numbers there corresponding to the references given at the end of the table. The letters Est. show that the energy value is estimated and is not the result of direct determination. These estimated values have for the most part been derived with the aid of the principle established by Millikan and Bowen (2) that, for atoms and ions having the same electronic configuration and differing only in their nuclear charge (for example, Ne, Na^+, Mg^{2+}, Al^{3+}, Si^{4+}), the increase in the square-root of the energy of removal of an electron from any specified subshell is nearly proportional to the increase in the nuclear or atomic number.

PERIODIC CHART SHOWING THE ENERGIES OF REMOVAL AND THE QUANTUM STATES OF THE ELECTRONS IN THE OUTER SHELLS OF ATOMS

With the aid of the data presented in table 1, the chart shown on the following pages has been prepared. The conventions employed are as follows.

Along the axis of abscissas is plotted the atomic number of the element, which also represents the positive charge on the

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[4] In general, there is no change in the quantum states of the remaining electrons; but to this there are occasional exceptions. Thus, when the neutral vanadium atom loses one of its two 4s electrons, the other 4s electron changes to a 3d state, associating itself with the three electrons already in this state. (In spectroscopic notation this is expressed by saying that the atom configuration changes from $4s^2 3d^3$ to $3d^4$, and not to $4s\ 3d^3$; the superscripts representing the number of electrons existing in the state to whose symbol they are attached.)

nucleus of its atom and ions (also the total number of electrons around the nucleus of the neutral atom). As ordinates are plotted the square-roots of the energies absorbed in the removal of the respective electrons from the atom, referred to that absorbed in removing the electron from the hydrogen atom as unity; in other words, the square-roots of the ratios ν / 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 (2) found that the square-roots of the energies of removal of the outer electrons of atoms and ions that have the same electronic configuration but different nuclear charges, are nearly linear functions of their atomic numbers.

The number of electrons having a specified 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. Whether the electron is removed from the neutral atom of an element or from one of its successive ions is indicated by different types of circles or ellipses, as shown by the legend at the bottom of the chart.[5]

The quantum-states of the electrons are differentiated by the use of circles and of ellipses of different eccentricity. Namely, when the total and azimuthal quantum numbers (n and k) are equal (as in the 1_1, 2_2, or 3_3 quantum states), the electrons are represented by circles. 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 a 2_1 state; 3:2 for a 3_2 state; etc. The total 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 was not possible, however, to separate completely in this way the

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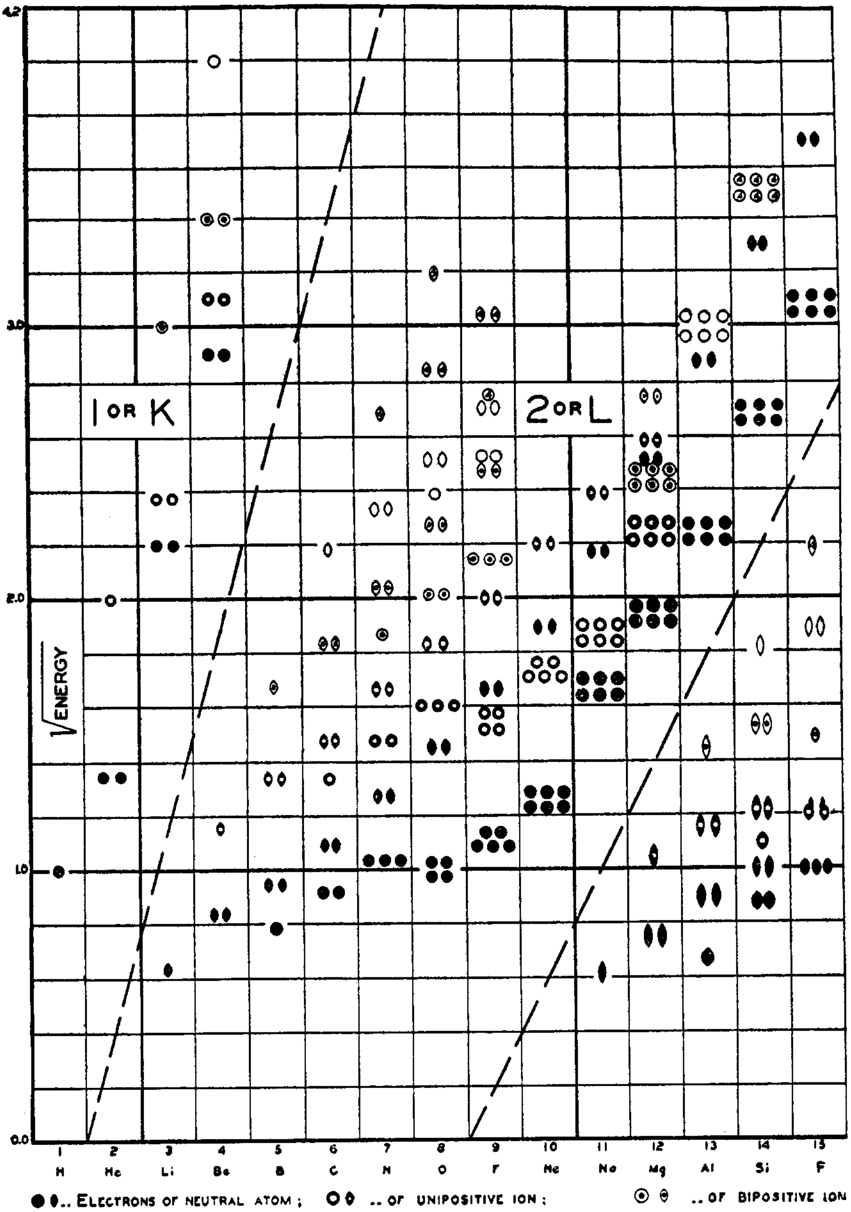
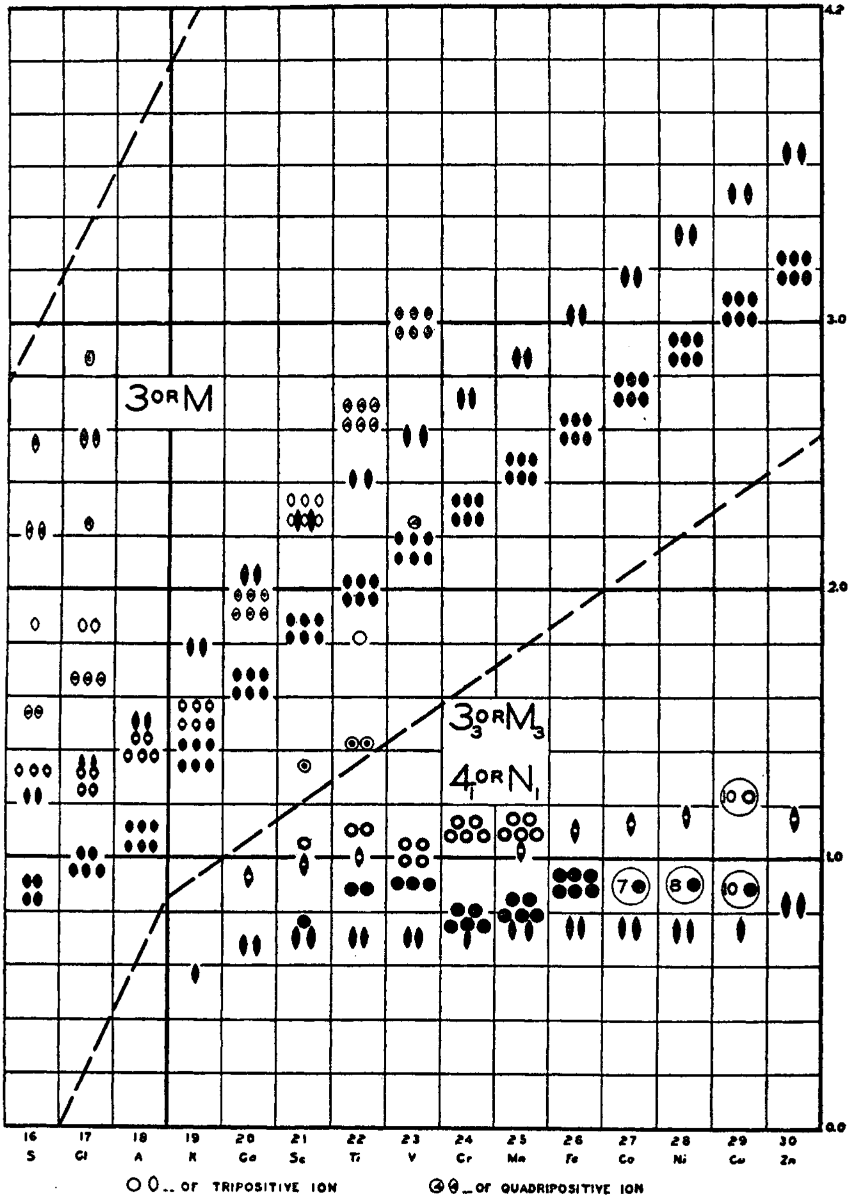
[5] In making a wall chart for lecture demonstration the authors have used, in order to make more prominent the distinction between the atom and its ions, in place of these different symbols, different colors (black, red, orange, green, blue) for the neutral atom and the successive positive ions.



THE STRUCTURE OF ATOMS



THE STRUCTURE OF ATOMS

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.[6]

The chart gives a complete representation of all the electrons for the neutral atom and all 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 magnesium 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. No attempt is made to indicate on the chart whether the points are based on estimated or directly measured data; but this was shown in the table of data in the preceding section.

THE GROUPS OF THE PERIODIC SYSTEM IN RELATION TO THE STRUCTURE OF ATOMS

Now that we have more complete knowledge of the energies of removal of the electrons as well as of their quantum states, it seems desirable to review the general relations between the structure of atoms and the periodicity of the properties of the elements.

Attention may first be called to the extent of the similarities

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[6] These conventions may be illustrated by reference to the element beryllium. It is seen that the neutral atom of beryllium has two (loosely-bound) electrons of the 2_1 quantum type (in the L shell) with an energy of removal equal to $(0.838)^2$ or about 0.70 that of the hydrogen electron, and two (much more firmly bound) electrons of the 1_1 quantum type (in the K shell) with an energy of removal equal to $(2.9)^2$ or 8.5 times that of the hydrogen electron. The unipositive ion Be^+ is seen to have its single remaining 2_1 electron at a higher level than before, with an energy of removal $(1.157)^2$ or 1.34 times that of the hydrogen electron, and it has its two 1_1 or K electrons at a level corresponding to an energy of removal equal to $(3.1)^2$ or 9.6 times that of the hydrogen electron. The chart also shows that the bipositive ion Be^{++} has only the two 1_1 or K electrons remaining, that these have an energy of removal equal to $(3.38)^2$ or 11.4 times that of the hydrogen electron. Finally, the tripositive ion Be^{+++} is seen to have only one K electron, which has an energy of removal $(4.00)^2$ or 16.0 times that of the hydrogen electron.

exhibited not only by the quantum states, but also by the energies of removal of the outer-shell electrons of the neutral atoms of the elements of the same group in the first three periods of the periodic system. To make these relations clearer, there have been brought together in table 2 the numbers, quantum states, and energies of removal of the electrons for the neutral atoms of the first three elements of each of the eight periodic groups, as well as for the element of the other subgroup in the third period of each group. These values have been taken from table 1.

Examination of table 2 shows that the atoms of the first three elements in each group have the same number of electrons in the same azimuthal quantum state, and have energies of removal of the same general magnitude, there being however usually a considerable decrease in the energy in passing from the first to the second and third elements. On the other hand, comparison of the first three elements of groups III to VII with the fourth element (which belongs to the other subgroup of the periodic system) shows that the azimuthal quantum states of the outer electrons of the atom are not the same—facts which are no doubt, related to the marked difference in properties. This difference in the azimuthal quantum states is not shown in groups I and II, so that the difference in properties of the alkali elements and copper, or of the alkaline-earth elements and zinc, must be due to other factors.

The atomic structure also accounts for the fact that the third period includes eighteen elements, instead of eight. Referring to the chart and comparing the second and third periods, the following differences are noted. In the second period, in passing from magnesium 12 to argon 18, the two 3_1 electrons steadily become more and more firmly bound; and when other electrons are added, as in the elements from aluminum 13 to argon 18, these are of the 3_2 type and have progressively increasing[7] energies of removal much less than those of the 3_1 electrons, a condition which accounts for the progression in physical properties. In the third period, on the other hand, though it starts

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[7] Except that there is a break in the progression at sulfur 18.

TABLE 2

The outer-shell electrons of corresponding elements of different periodic groups

GROUP	ATOM	OUTER ELECTRONS		
		Number	State	Energy
I	Li	One	2_1	0.40
	Na	One	3_1	0.38
	K	One	4_1	0.32
	Cu	One	4_1	0.57
II	Be	Two	2_1	0.70
	Mg	Two	3_1	0.56
	Ca	Two	4_1	0.45
	Zn	Two	4_1	0.69
III	B	One	2_2	0.62
		Two	2_1	0.89
	Al	One	3_2	0.44
		Two	3_1	0.81
	Ga	One	4_2	0.44
		Two	4_1	0.84
	Sc	Two	4_1	0.49
		One	3_3	0.55
IV	C	Two	2_2	0.84
		Two	2_1	1.18
	Si	Two	3_2	0.76
		Two	3_1	1.00
	Ge	Two	4_2	0.70
		Two	4_1	1.00
	Ti	Two	4_1	0.50
		Two	3_3	0.73
V	N	Three	2_2	1.07
		Two	2_1	1.62
	P	Three	3_2	0.98
		Two	3_1	1.52
	As	Three	4_2	0.86
		Two	4_1	1.36
	V	Two	4_1	0.52
		Three	3_3	0.81
VI	O	Four	2_2	1.00
		Two	2_1	2.09
	S	Four	3_2	0.76
		Two	3_1	1.49
	Se	Four	4_2	0.70
		Two	4_1	1.40
	Cr	One	4_1	0.50
		Five	3_3	0.61
VII	F	Five	2_2	1.25
		Two	2_1	2.74
	Cl	Five	3_2	0.96
		Two	3_1	1.81
	Br	Five	4_2	0.86
		Two	4_1	1.70
	Mn	Two	4_1	0.55
		Five	3_3	0.67
O	Ne	Six	2_2	1.59
		Two	2_1	3.57
	A	Six	3_2	1.16
		Two	3_1	2.25
	Kr	Six	4_2	0.98
		Two	4_1	2.00

normally by adding 4_1 electrons, the conditions are complicated by the fact that there exists in the atoms an unfilled 3 shell, namely the 3_3 subshell. From this subshell the energy of removal, though nearly the same as from the 4_1 subshell, is much greater than from the 4_2 subshell. Consequently, the electrons next added are of the 3_3 type, not of the 4_2 type which would correspond to the 3_2 type of the second period. An additional fact is that the energies of the 3_3 and 4_1 electrons retain nearly the same values for the successive elements until the 3_3 subshell is completely filled with its ten electrons. This results in a long series of similar elementary substances which have atoms with two electrons of the 4_1 type and a group of 3_3 electrons, both types having nearly the same energies of removal.[8] And it is only beyond zinc (when the 4_1 and 3_3 subshells have been filled) that the new electrons begin to take the six places existing in the 4_2 subshell, thereby giving rise to six elements, gallium 31 to krypton 36 (not shown in the chart) with properties very similar to those of the last six elements of the second period (aluminum 13 to argon 18) which are characterized by loosely bound 3_2 electrons, thus with the same azimuthal quantum number.

It is perhaps well to emphasize the fact, pointed out early by investigators of atomic structure, that periodic tables of the form used by J. Thomsen, Bohr, and others[9] in which the first and second periods consist of eight elements and the third period of eighteen elements, and the former periods are shown to be in a dual relationship to the latter, are a much better expression of atomic-structure results than the more commonly used tables, in which, as in that of Lothar Meyer, the elements are so far as possible classified in successive periods of eight.

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[8] There is, to be sure, a progressive increase in the number of 3_3 electrons which makes possible compounds of higher valences, increasing progressively from scandium to iron.

[9] Charts of this type which show the relationships rather strikingly have recently been described by von Antropoff (Z. angew. Chem., **39**, 722 (1926)), and are sold by Köhler and Volckmar of Leipsic, Germany.

ION-FORMATION AND VALENCE IN RELATION TO THE STRUCTURE OF ATOMS

With the aid of the chart and the data of tables 1 and 2 there may now be studied empirically[10] the relations that exist between the structures of the atoms of the elements, and (*a*) the nature of the ions which the elements form in crystals and aqueous solutions, and (*b*) the valences which the elements actually exhibit in their compounds.

The characteristics of the two classes of compounds, known as polar and non-polar, are fairly distinct, even though they doubtless grade into each other. In polar compounds, of which salts in the crystalline, fused, and dissolved states are examples, there exist, more or less separate from each other, positive and negative ions formed from neutral atoms by the loss or gain of one or more electrons. In non-polar compounds the electronic condition of the united atoms has been the subject of many hypotheses. For our purposes it will, however, suffice to point out that the valence shown by an element in its non-polar compounds doubtless corresponds to the existence of a certain number of electrons in such a state that they take part in the process of formation of the molecules of the compounds. The electrons in this state may be called the *reacting electrons* for that valence.

To facilitate the study of the relation of these characteristics

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[10] There cannot be discussed here the highly important theoretical relations that have been recently developed. Reference may, however, be made to the original work of Grimm and Herzfeld (Z. Physik., **19**, 141 (1923)), according to which only those kinds of ions exist in crystals or solutions whose formation from the neutral elementary substances is attended by a net decrease in energy-content as computed from the energies of removal of the electrons of the neutral atoms and from the other energy effects involved; namely, from the energies of vaporization of the metal and of dissociation of the diatomic gases (Cl_2, O_2, etc.), and from the "lattice energy" attending the bringing together in the crystal of the gaseous ions, or the electrostatic energy attending their introduction into a dielectric medium such as water. The latter subject has been also treated by Webb (J. Am. Chem. Soc., **48**, 2589 (1926)). Of transcendent importance to our interpretation of valence and non-polar bonding may also become the theories based on wave mechanics of London (Z. Physik., **46**, 455 (1928)), which confirm the earlier conclusion of Lewis that single chemical bonds consist in the pairing of two electrons of two different atoms. (See also Pauling, Proc. Nat. Acad. Sci., **14**, 359 (1928.)

TABLE 3

Ion-formation and valence in relation to atomic structure

ELEMENT	ATOMIC NUMBER	IONS FORMED	VALENCES	IONS OR ATOMS WITH		ENERGY OF REMOVAL OF OUTER ELECTRONS FROM				
				Complete shell	Complete subshell	*M*	M^+	M^{2+}	M^{3+}	M^{4+}
H	1	H^+	1	H^+	..	1.00	∞	...	...	...
		H^-	−1	H^-						
He	2	None	0	He	..	1.80	4.00	∞	...	...
Li	3	Li^+	1	Li^+	..	0.40	5.6	9.00	∞	...
Be	4	Be^{2+}	2	Be^{2+}	..	0.70	1.34	11.4	16.0	∞
B	5	...	3	B^{3+}	B^+	0.62	1.79	2.80	19.3	25.0
C	6	...	4	C^{4+}	C^{2+}	0.83	1.79	3.36	4.74	29.2
N	7	...	3, 5	N^{5+}	N^{3+}	1.07	2.18	3.49	5.43	7.19
			−3	N^{3-}						
O	8	...	...	O^{6+}	O^{4+}	1.00	2.58	4.05	5.69	8.07
		O^{2-}	−2	O^{2-}						
F	9	...	...	F^{7+}	F^{5+}	1.25	2.39	4.62	6.40	7.56
		F^-	−1	F^-						
Ne	10	None	0	Ne	..	1.59	3.02	...	...	...
Na	11	Na^+	1	Na^+	..	0.38	3.47	...	...	...
Mg	12	Mg^{2+}	2	Mg^{2+}	..	0.56	1.11	5.98	...	...
Al	13	Al^{3+}	3	Al^{3+}	Al^+	0.44	1.34	2.09	9.00	....
Si	14	...	4	Si^{4+}	Si^{2+}	0.76	1.20	2.34	3.32	12.47
P	15	...	1, 3, 5	P^{5+}	P^{3+}	0.98	1.46	2.22	3.53	4.78
			−3	P^{3-}						
S	16	...	4, 6	S^{6+}	S^{4+}	0.76	1.74	2.37	3.48	4.93
		S^{2-}	−2	S^{2-}						
Cl	17	...	1, 3, 5, 7	Cl^{7+}	Cl^{5+}	0.96	1.66	2.93	3.50	5.00
		Cl^-	−1	Cl^-						
A	18	None	0	A	..	1.16	2.00	...	...	...
K	19	K^+	1	K^+	..	0.32	2.34	...	...	...
Ca	20	Ca^{2+}	2	Ca^{2+}	..	0.45	0.87	3.76	...	...
Sc	21	Sc^{3+}	3	Sc^{3+}	..	0.49	0.95	1.82	5.33	...
Ti	22	Ti^{2+} Ti^{3+} Ti^{4+}	2, 3, 4	Ti^{4+}	..	0.50	1.00	2.04	3.30	7.07
V	23	V^{2+} V^{3+}	2, 3, 4 5	V^{5+}	..	0.52	1.04	...	...	5.07
Cr	24	Cr^{2+} Cr^{3+}	2, 3, 6	Cr^{6+}	..	0.50	1.23	...	...	...
Mn	25	Mn^{2+} Mn^{3+}	2, 3, 4, 6, 7	Mn^{7+}	..	0.55	1.16	...	...	...
Fe	26	Fe^{2+} Fe^{3+}	2, 3, 6	Fe^{8+}	..	0.58	1.22	...	...	...

to ion-formation and valence, table 3 has been prepared from the atomic-structure data given in tables 1 and 2 and the known chemical properties of the elements. The headings 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 actual existence in aqueous solutions or in crystals there is good evidence. The indicated "valences" include only those corresponding to the well-defined states of oxidation that are exhibited by the elements in their salts, bases, or acids. The symbols of the "ions or atoms" in the next two columns show those configurations which have, or would have if they existed, complete shells or complete subshells. Note that the charges on these hypothetical ions show also the *valences* that would exist if the lost or gained electrons were actually the reacting electrons in the neutral atom.

A study of the table leads to the following conclusions.

1. In the case of the first three elements of the first two periods (except boron) positive ions are formed at the point where the electrons remaining just suffice to complete the next lower main shell (the 1 or 2 shell). This point is, moreover, identical with the point where the removal of a further electron would require a much greater absorption of energy. Thus, the ions formed are Li^+, Be^{2+}, Na^+, Mg^{2+}, and Al^{3+}, all of which are "stripped atoms" so-called. These elements do not form ions at points intermediate between the stripped atom and the neutral atom, even in cases where the energies of removal of the successive electrons differ by considerable amounts, or in cases where it would leave as the outermost electrons a complete subshell (2_1 or 3_1). Thus the ions Be^+, Mg^+, and Al^+ do not form in solutions or crystals, even though the energy of removal of the second electron is two or three times that of the first electron; and Al^+ does not form, even though the removal of its 3_2 electron would leave its 3_1 shell complete.

2. The first three elements of the third period, potassium, calcium, and scandium, form through the loss of their 4_1 electrons (and of the 3_3 electron of scandium) the ions K^+, Ca^{2+} and Sc^{3+}; even though there then remains not a complete main shell (the 3 shell), but only two fully filled subshells (3_1 and 3_2).

3. Each of the first three elements of the first three periods exhibits in its chemical compounds only that valence which is identical with the charge on the ion which it actually forms; showing that the readily detachable electrons in the neutral atom are also those concerned in the formation of molecules.

4. The middle elements, carbon and silicon, of the first two periods do not seem to form ions; but they show the valence +4, in correspondence with the tendency of all the electrons of a neutral atom that are outside of a completed shell to be reactive.

5. The elements near the ends of the first and second periods do not form positive ions, but produce such negative ions as correspond to the completion of the partially filled shell; thus these elements form the ions $O^=$, F^-, $S^=$, Cl^-.

6. Nitrogen in the first period, and phosphorus, sulfur, and chlorine in the second period, all exhibit very stable (maximum) positive valences that correspond to the tendency of all the electrons that are outside of a complete shell to be reactive. These elements also exhibit the negative valences that correspond to that number of electrons which would complete the next main shell. Thus nitrogen or phosphorus has the valence +5 in nitrates or phosphates, and the valence −3 in ammonia or phosphine; sulfur has the valences +6 in sulfates and −2 in sulfides; and chlorine has the valences +7 in perchlorates and −1 in chlorides.

These elements also exhibit other positive valences, which may be considered in relation to the various subshells. Thus in the case of nitrogen or phosphorus the electrons present in the neutral atom in excess of those needed to complete the 2_1 or 3_1 subshell correspond to the valence +3; and this valence is in fact shown in nitrites or phosphites. In the case of sulfur the excess electrons outside the 3_1 subshell correspond to the valence +4, which exists in sulfites. And in the case of chlorine the excess electrons outside the 3_1 subshell correspond to the valence +5, which exists in chlorates.

These elements may exhibit, however, besides these valences related to complete shells or subshells, other less stable valences. These valences correspond to a diminished reactivity of the successive pairs of electrons remaining after the most reactive electrons of a given subshell have entered into molecular unions. Thus phosphorus shows the valence +1 in the unstable hypophosphites, indicating that of the three electrons in the 3_2 subshell of its atom two of them are less reactive, at any rate after one of them has entered into chemical union. Similarly, sulfur has the valence +2 in derivatives of the non-existent H_2SO_2 and also perhaps in the unstable hydrosulfurous acid $H_2S_2O_4$ (if this be regarded as an anhydride of H_2SO_2 and H_2SO_3); and chlorine shows the valence +3 and +1 in the unstable chlorites and hypochlorites. These valences of sulfur and chlorine correspond to the fact that of the electrons of the 3_2 subshell one pair (or two pairs) are less reactive.

7. The elements of the third period from titanium 22 to copper 29 form a series of elementary ions of varying charge, and exist in a series of positive valences which are not merely even or odd as in the case of the elements of the first two periods, but increase continuously or irregularly. Thus titanium forms the ions Ti^{2+}, Ti^{3+}, and Ti^{4+}, and exists in corresponding valences; vanadium forms V^{2+} and V^{3+}, and exists not only in the corresponding valences, but also in the +4 and +5 stages; chromium forms Cr^{2+} and Cr^{3+}, and shows the valences +2, +3, and +6, but not +4 and +5; manganese forms Mn^{2+} and Mn^{3+}, and shows also the valences +4, +6, and +7, but not +5; iron forms Fe^{2+} and Fe^{3+}, and has the valences +2, +3, and +6 (in ferrates). Unfortunately, energy data are still lacking for many of the ions of these elements (except in the case of titanium); but the results lead to the following conclusions.

The maximum valence of the elements from titanium to manganese corresponds to the participation of all the 4_1 and 3_3 electrons in chemical combinations, leaving the unreacting electrons in a complete 3_2 subshell. The formation by all the elements from titanium to zinc of stable bipositive ions corresponds to the loss of the two 4_1 electrons (except in the cases of chromium and copper); and the bipositive valence of these three elements corresponds to the participation of these two 4_1 electrons in chemical unions. The electrons in the 3_3 subshell are evidently less reactive, even though this subshell is not completely filled, indicating that an outermost 3_3 subshell (unlike the lower quantum subshells), even when not completed, constitutes an unusually stable configuration, moreover, one whose stability seems to be little affected by the number of electrons which it contains. Beyond this, however, our present knowledge of atomic structure does not go in interpreting the peculiar valence relations of these elements. It seems clear, however, as pointed out by G. N. Lewis (29) that the irregular valences of these metal-forming elements constitute a phenomenon of a different type from the even or odd valences exhibited by the elements of the nitrogen, sulfur, and chlorine groups.

SUMMARY

In this article has been presented a compilation of values, derived from recent spectroscopic studies, of the energies attending the removal of the separate electrons from the atoms and ions of the first thirty elements. With the aid of these values and data as to quantum states, a periodic chart has been prepared showing graphically the number, the quantum states, and the energies of removal of the electrons in the outer shells of these atoms and ions.

These atomic structures are discussed in relation to the periods and groups of the periodic system of the elements. The structures are also discussed in detail in relation to the formation of ions in crystals or solutions by the separate elements, and in relation to the best-defined valences which they exhibit.

The conclusions as to ion-formation may be briefly summarized as follows:

Of the elements preceding titanium, the first three elements of the first three periods form only such positive ions 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 form only such negative ions as result from the complete filling of the 2 or $3_1 + 3_2$ shells with electrons. Intermediate ions, such as Al^+ or Ca^+, do not form, even when, as with Al^+, the resulting ion would have its outermost electrons in a complete subshell (3_1). Titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper all form bipositive ions, even though there remain electrons in an unfilled 3_3 subshell. They also form other ions which have no apparent relation to the structure of their atoms.

The conclusions as to valence may be summarized as follows:

None of the first three elements of the first three periods exhibit any well-defined valence other 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 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) might alone function as reacting electrons does not cause these elements to actually exist in the univalent or bivalent state.

The elements nitrogen, phosphorus, sulfur, and chlorine, on the other hand, exhibit the positive valences that would result if the reacting electrons were:

(1) All those in an unfilled main shell (2 or 3) outside a filled main shell (1 or 2).
(2) All those in an unfilled subshell (2_2 or 3_2) outside a filled subshell (2_1 or 3_1).
(3) Those in an unfilled subshell (2_2 or 3_2) in excess of one pair or two pairs of (less reactive) electrons in the same subshell.

Thus the positive valences that would correspond to these three types are:

(1) Nitrogen, +5; phosphorus, +5; sulfur, +6; chlorine, +7.
(2) Nitrogen, +3; phosphorus, +3; sulfur, +4; chlorine, +5.
(3) Nitrogen, +1; phosphorus, +1; sulfur, +2; chlorine, +3.

And in fact these elements exist in the form of salts in these valences. 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, sulfates, and perchlorates; type (2) is that of the much less stable nitrites, phosphites, sulfites, and chlorates; and type (3) is that of the unstable hypophosphites, chlorites, and hypochlorites, and of the extremely unstable or even nonexistent salts MNO and M_2SO_2.

The first eight elements of the third period exhibit (maximum) positive valences that correspond to a reactivity of the electrons outside of the completed 3_1 or 3_2 subshells. Moreover, all of them beyond scandium form bivalent compounds, which indicates that the 3_3 subshell is an exceptionally stable configuration, even when it is incompletely filled with electrons. The other irregular valences exhibited by these elements are not related in any apparent way to the structure of their atoms.

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