

Textbook of INORGANIC CHEMISTRY

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Preface

The trend in American universities during the past few decades in the first course in chemistry has been to place more and more emphasis on theories and concepts and to devote less and less time to the variegated behavior of the elements, which cannot be fitted into a rationale encompassing nuclear physics and biochemistry. Subsequent courses expose the student to the aqueous chemistry of sulfides and some other compounds in qualitative analysis, to a few special stoichiometric reactions in quantitative analysis, to a few very special equilibria and reactions in physical chemistry, and to the reactions of some inorganic reagents with organic compounds in organic chemistry. Seldom is inorganic chemistry treated apart and in its own right. The present book is the outgrowth of twelve years experience in teaching a course suitable for students whose background in inorganic chemistry as such goes little beyond the inorganic content of courses in freshman general chemistry.

The general approach has been to treat the chemistry of *all* of the elements, insofar as it is known, at the same level. In this way it is hoped that the student will get an over-all view of the variety of chemical behavior to which he can relate further study and research. The treatment relies upon the principles and some of the facts learned in freshman chemistry; further courses will certainly enhance the student's appreciation of the material presented. Along with the descriptive chemistry of the elements, some of the generalizations and theories that make it coherent and that have contributed to the latter-day renaissance of inorganic chemistry have been brought in throughout the discussion.

Somewhat more than one half of the text provides the basis for a one-semester course at Chapel Hill; the material used in its entirety

is probably sufficient for a full year's course, especially if supplemented by further theoretical aspects in an advanced course. In the laboratory part of our course, representative inorganic preparations are carried out, each exercise chosen to illustrate one or more specific techniques and to enlarge the student's store of descriptive knowledge.

Many professional friends have been generous with suggestions during the years of development of this text, and their help is gratefully acknowledged. Particular thanks are due to Dr. S. B. Knight and Dr. D. L. Venezky of this department for their kindly criticisms during the revisions of the manuscript.

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Chapter 1 Periodicity

The subject of inorganic chemistry deals with all of the chemical elements, of which there are 102 at this writing. The task of memorizing the properties of so many distinct species is enormous; it is therefore advantageous to learn the behavior patterns that are exhibited by the elements. Insofar as these patterns are well-defined, the mass of information may be correlated and more easily learned. The object of this chapter is to point out regular gradations of chemical and physical properties among the elements. The correlations are not always applicable to all cases, but learning general rules and then exceptions to them will provide a method for understanding the astonishing variety of matter. Chemistry is, however, too complex for all of it to be reduced to general rules, and so there is still no substitute for a good memory.

ATOMIC WEIGHTS AND ISOTOPES

Reference to the table of atomic weights shows that chlorine has an atomic weight of 35.457. This does not mean that every atom of chlorine weighs 35.457/16.000 times as much as every atom of oxygen.* In 1913 J. J. Thomson showed that the element neon contains two kinds of atoms, both with atomic numbers of 10, but with masses of 20 and 22. Subsequently, F. W. Aston and many others have shown by means of mass spectrometers that most of the

* At the 1959 meeting of the International Union of Pure and Applied Chemistry the Council of the same organization tentatively adopted a new scale of atomic weights based on the whole number 12 as the atomic weight of the dominant natural isotope of carbon, carbon-12. Final adoption of the new scale will be considered at the 1961 meeting of the IUPAC after the International Union of Pure and Applied Physics meets in 1960 to consider the same proposal. Should the new scale be adopted the new values of atomic weights would be changed by -0.0042% of the current chemical scale values.

elements contain atoms of different masses, which are called isotopes. A few elements are monoisotopic, such as sodium and fluorine. Tin has the greatest number of stable isotopes, ten. The standard element for atomic weight scales, oxygen, has three natural isotopes of mass numbers* 16, 17, and 18. They are symbolized ^{16}O , ^{17}O , ^{18}O and occur in the ratio 99.757:0.039:0.204. Thus, there are two scales of atomic weights: the physical, which defines ^{16}O alone as the standard weight of 16.0000, and the chemical, which defines the natural mixture of oxygen isotopes as having the standard weight of 16.0000. Since the unit weight on the chemical scale is heavier, chemical atomic weights are smaller. By knowing the actual masses of the oxygen isotopes and their relative abundance, as determined by the mass spectrometer, the ratio of weights on the two scales can be calculated; it is 1.000275. Chlorine has two isotopes of mass numbers 35 and 37. Their relative abundance in nature is such that the average atomic weight on the chemical scale is 35.457. It is very difficult to separate the isotopes of an element; the average mixture goes through all ordinary chemical and physical processes without perceptible change in ratio. Thus, the chemist can use his scale of atomic weights with confidence in stoichiometric calculations.

ABUNDANCE OF THE ELEMENTS

The abundance of the elements on the surface of the earth is a subject of great economic as well as scientific interest. Geologists, particularly the great geochemist V. M. Goldschmidt, have done most of the work on this subject. Table 1.1 gives the abundance in the earth's crust, including the sea and atmosphere, of the elements from atomic numbers 1 to 92. The unit used is grams per metric ton, which is equivalent to parts per million. These figures are only estimates, and they are, of course, subject to constant revision as man explores his planet more fully. The table shows that an element whose atomic number is even is generally more abundant than the adjacent elements of odd atomic numbers. This generalization does not hold true for elements of widely different numbers: e.g., vana-

* The mass number of an isotope is the whole number nearest to its actual mass. It is also the number of protons and neutrons in the nucleus. It is approximately, but not exactly, equal to the actual mass.

TABLE 1.1
Abundance and Physical Properties of the Elements*

Atomic No.	Element	Abundance g/ton	Density of Solid g/cc	m.p. °C	b.p. °C
1	H	1400	0.0808	-259.14	-252.7
2	He	10 ⁻³	0.18	-272.0 (25 atm)	-268.9
3	Li	65	0.53	186	1336
4	Be	6	1.8	1278	2970
5	B	3	2.5	2300	2550
6	C	320	2.26	3600	4200
7	N	46	1.026	-209.86	-195.8
8	O	466,000	1.426	-218.4	-183.0
9	F	300	1.3	-223	-187
10	Ne	5 × 10 ⁻³	1.4	-248.67	-245.99
11	Na	28,300	0.97	97.5	880
12	Mg	20,900	1.74	651	1110
13	Al	81,300	2.702	660	1800
14	Si	277,200	2.4	1420	2600
15	P	1,180	1.83	44.1	280.5
16	S	520	2.06	118.95	444.60
17	Cl	314	2.1	-101.6	-34.6
18	Ar	4 × 10 ⁻²	1.65	-189.2	-185.7
19	K	25,900	0.86	62.3	760
20	Ca	36,300	1.55	810	1200
21	Sc	5	2.5	1200	2400
22	Ti	4,400	4.5	1725	>3000
23	V	150	5.96	1710	
24	Cr	200	7.1	1615	2200
25	Mn	1,000	7.2	1260	1900
26	Fe	50,000	7.86	1535	
27	Co	23	8.9	1480	2900
28	Ni	80	8.9	1425	2900
29	Cu	70	8.92	1083	2310
30	Zn	132	7.14	419.43	907
31	Ga	15	5.91	29.75	2030
32	Ge	7	5.36	937	2700
33	As	5	5.73	814	615
34	Se	9 × 10 ⁻²	4.82	220.2	685
35	Br	1.6	4.05	-7.2	58.78
36	Kr	2 × 10 ⁻⁴	3.13	-169	-151.8
37	Rb	310	1.53	38.5	700
38	Sr	300	2.6	800	1150
39	Y	28	4.34	1490	2500
40	Zr	220	6.49	1845	
41	Nb	24	8.4	1950	
42	Mo	15	10.2	2625	3700
43	Tc	?	11.50	2140	
44	Ru	10 ⁻⁵	12.2	2450	
45	Rh	10 ⁻⁵	12.5	1955	
46	Pd	10 ⁻²	12	1555	2200
47	Ag	10 ⁻¹	10.5	960.5	1950

TABLE 1.1 (Continued)

Atomic No.	Element	Abundance g/ton	Density of Solid g/cc	m.p. °C	b.p. °C
48	Cd	1.5×10^{-1}	8.6	320.9	767
49	In	10^{-1}	7.3	156.2	2100
50	Sn	40	7.285	231.8	2362
51	Sb	1	6.684	630.5	1380
52	Te	2×10^{-3}	6.24	452	1390
53	I	3×10^{-1}	4.93	113.5	184.35
54	Xe	3×10^{-5}	4.32	-140	-109.1
55	Cs	7	1.90	26	670
56	Ba	250	3.5	850	1140
57	La	18	6.2	826	1800
58	Ce	46	6.8	770	
59	Pr	5.5	6.8	940	
60	Nd	24	7.004	840	
61	Pm	?			
62	Sm	6.5	6.93	1350	
63	Eu	1.1	5.244	1100	
64	Gd	6.4	7.948		
65	Tb	9×10^{-1}	8.332		
66	Dy	4.5	8.562		
67	Ho	1.2	8.764		
68	Er	2.5	9.164	1250	
69	Tm	2×10^{-1}	9.346		
70	Yb	2.7	7.010	1800	
71	Lu	8×10^{-1}	9.740		
72	Hf	4.5	13.09	1975	
73	Ta	2.1	16.6	2800	
74	W	69	19.3	3370	5900
75	Re	10^{-3}	21.40	3137	
76	Os	10^{-3}	22.48	2700	
77	Ir	10^{-3}	22.4	2450	
78	Pt	5×10^{-3}	21.45	1755	4300
79	Au	5×10^{-3}	19.3	1063	2600
80	Hg	5×10^{-1}	14.2	-38.87	356.90
81	Tl	6×10^{-1}	11.85	303.5	1650
82	Pb	16	11.34	327.5	1620
83	Bi	2×10^{-1}	9.8	271	1450
84	Po	10^{-10}			
85	At	?			
86	Rn	10^{-11}	5.7	-71	-61.8
87	Fr	?			
88	Ra	10^{-6}	5	960	1140
89	Ac	10^{-10}			
90	Th	12	11.2	1845	
91	Pa	10^{-7}			
92	U	4	18.7	1150	

*The tabulated values of course are subject to change.

dium is much more abundant than platinum. There are also some exceptions, particularly among the lighter elements. One very good example of where it does hold true is in the rare-earth series, 57 to 71 (see Chapter 9).

Furthermore, it will be noticed that elements in the third and fourth periods, 11 to 18 and 19 to 36, appear to be the most abundant. Generally, the abundance of elements in a group decreases with increase in atomic weight, except in period 2. For example, Na is about as abundant as K, which is more abundant than Rb, etc. Exceptions are apparent in the second and sixth groups, where Ca and O respectively are the most abundant.

SOME PHYSICAL PROPERTIES OF THE ELEMENTS

Figure 1.1 shows the variation in density of the solid elements as a function of atomic number. Notice that the curve is a periodic one, with the alkali metals in the valleys and the group VIII elements at the peaks. These peaks become higher with increasing atomic number. On the same graph is plotted the atomic volume, which is the density divided by the atomic weight. The density of the solid is used for all the elements, so that atomic volume is roughly proportional to the size of the atom. This curve is essentially the complement of the density curve, since the greater the density, the more atoms there are in unit space, and the less the volume taken up by one atom.

The variation of the melting points of the elements as a function of atomic number is shown in Figure 1.2. Again the plot is periodic. The periodicity of these properties is typical of the curves obtained when most physical properties of the elements are plotted against atomic number; it was first pointed out by Lothar Meyer in 1870.

Correlations between the periodicity of different properties can be drawn also. Thus, it is seen that within a period, the reactive elements, such as K, Ca, and Br have large atomic volumes, while unreactive elements, such as Co, Ni, and Cu have small atomic volumes.

ELECTRONIC CONFIGURATION OF ATOMS

The chemical properties of the elements also obey the Periodic Law: indeed, the periodic table was constructed from the known

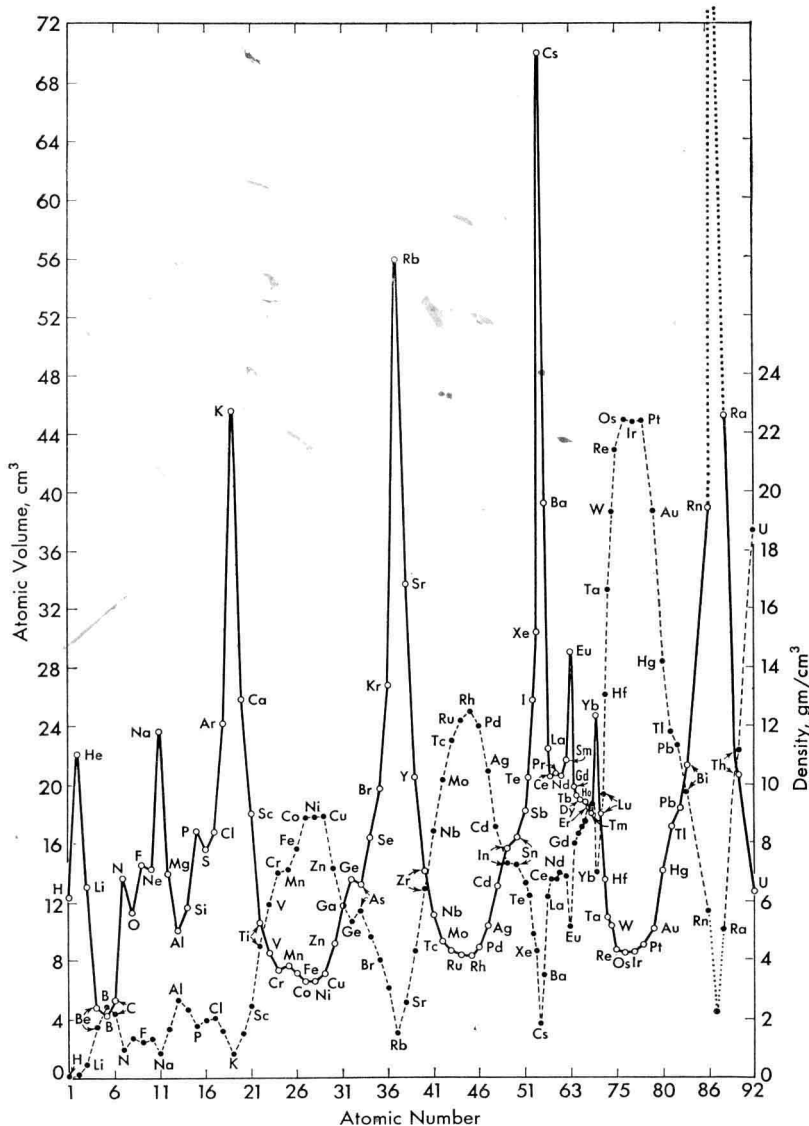


Fig. 1.1 Atomic volumes and densities of the elements vs. atomic number.

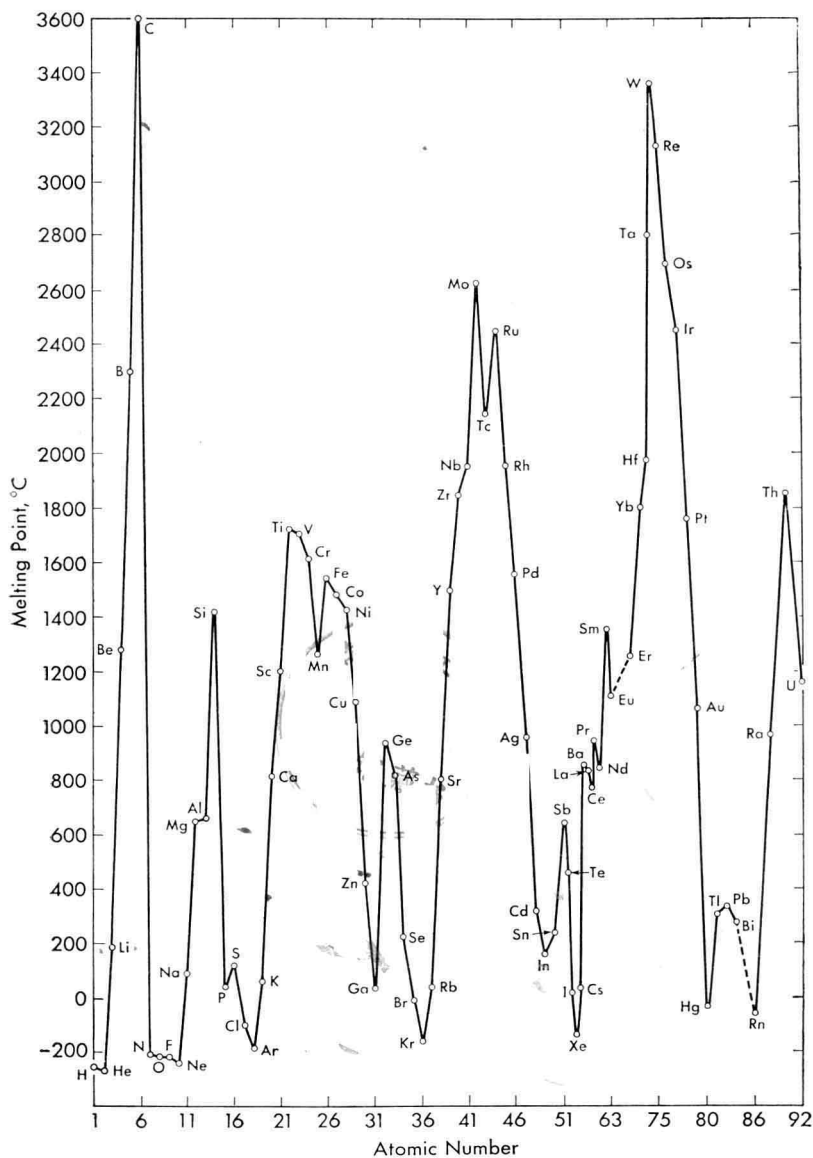


Fig. 1.2 Melting points of the elements vs. atomic number.

chemical and physical properties of the elements. The concept of periodicity has, however, been given a fundamental basis by modern theories of electron structure, and we shall deal first with the results of these basic concepts.

In 1911 E. Rutherford showed that atoms consist of small, heavy nuclei, positively charged, surrounded by a much larger cloud of negative electrons. A few years later N. Bohr arranged the electrons into orbits about the nucleus. Today we know that the positions of these orbits are not nearly so definite as was once thought. The distance between the electron and the nucleus can vary within wide limits—much wider than, say, the relative variation in distance between the earth and the sun—and the position of the electron is best described by means of a distribution function. One thing is still fixed about the electron, however—its energy. Since it is by the energetics of electron movement that physical and chemical properties are determined, the indefinite position of the electron does not matter. The positions of the atoms, and hence the sizes and shapes of molecules, can still be delineated by the average size of the electron cloud.

The energy which an electron in an atom can have is not continuous, as is that of an object on a smooth inclined plane, which can have any potential energy between the values at the top and the bottom, rather, the electron energy can have only discrete values, like an object on a flight of stairs. Furthermore, there are limits to the number of electrons that may occupy the same energy level, the number increasing with the value of the energy. The energy values and the number of electrons in a level have been worked out mostly through the aid of spectroscopy, and spectroscopic notation is still used to a large extent. The energy levels that electrons may assume about a nucleus are also called quantum levels and are numbered 1, 2, 3, 4, . . . , beginning with the lowest energy. In spectroscopy these are called the K, L, M, N, . . . shells, the word now meaning energy shell and not position shell. The maximum number of electrons that may occupy these levels are 2 for the first, 8 for the second, 18 for the third, and 32 for the fourth. This sequence of numbers may be easily memorized by noting that the number of electrons is equal to twice the square of the number of the level.

Both of the electrons in the first energy level have the same

energy, but the higher levels are further divided into sublevels. The number of sublevels in a principal level is equal to the number of the principal level; thus, there are one in the first, two in the second, three in the third, etc. Spectroscopic notation is used exclusively for the sublevels. Spectral lines arising from the electronic transitions involving these sublevels are called sharp, principal, diffuse, and fundamental, and the sublevels are designated s, p, d, and f, in order of increasing energy. The number of electrons which can be accommodated in a sublevel is limited, and this number is independent of the number of the principal level, depending only on the designation of the sublevel. Each sublevel is made up of orbitals, each of which can hold a pair of electrons. An s-sublevel has one orbital, and so can hold at most two electrons. There are 3 orbitals all of the same energy in a p-sublevel, 5 in a d, and 7 in an f. Thus these sublevels can have at most 6, 10, and 14 electrons, respectively.

An atom left to itself will acquire the structure of lowest energy: viz., the ground state. In order then to write down the electronic structures of atoms, we need to know the sequence of the energies of the sublevels. In some of the heavier elements the sequence cannot be decided with certainty. When there is uncertainty, however, the possible structures are all of approximately the same energy, and the difference is not significant chemically. In the lower principal levels with few sublevels the sequence is normal. As the number of sublevels increases, overlap of the higher sublevels of one principal level with the lower sublevels of the following principal level occurs. Nevertheless, the order can be found: it is given in Figure 1.3 for a light atom.*

Given this sequence, the electron structures of the elements can be built up by adding electrons one at a time, filling up the lowest available sublevel to its maximum before going on to the next. The first element, hydrogen, has one electron, which goes into the orbital designated 1s. The two electrons of helium both occupy the 1s orbital, so its electron structure is written $1s^2$. In lithium the third electron must go into the 2s orbital because the 1s is full, giving $1s^2 2s$. Then beryllium is $1s^2 2s^2$. With boron the fifth electron occupies

* For a simple mnemonic for the order of filling of the orbitals, see p. 97 of the third reference in the list at the end of this chapter.

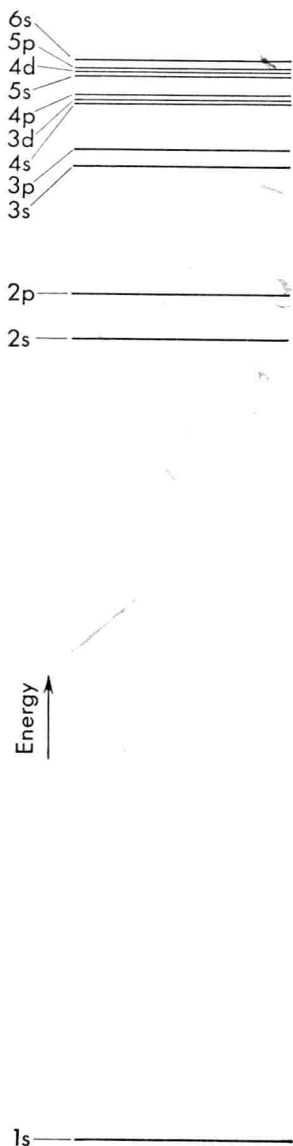


Fig. 1.3 Sequence of sub-level energies in a light atom.

a $2p$ orbital, giving $1s^22s^22p$. Note that if there is only one electron in a sublevel, no superscript is put after the designation. From boron to neon the $2p$ fills up to its maximum of 6. Then sodium has the structure $1s^22s^22p^63s$, magnesium $1s^22s^22p^63s^2$, aluminum $1s^22s^22p^63s^23p$, silicon $1s^22s^22p^63s^23p^2$, . . . , and argon $1s^22s^22p^63s^23p^6$, when the $3p$ sublevel is filled. In potassium the nineteenth electron goes into the $4s$ orbital, not a $3d$, because, as is shown in Figure 1.3, the $4s$ lies lower in energy. Thus, potassium and calcium have the structures $1s^22s^22p^63s^23p^64s$ and $1s^22s^22p^63s^23p^64s^2$, respectively. Only with scandium does the $3d$ begin to fill. Even though the $4s$ has a lower energy than the $3d$ in this region of atomic numbers, the designation for the $3d$ electrons is still put before the $4s$ in order to preserve the numerical order of the principal levels. Thus, scandium is written $1s^22s^22p^63s^23p^63d4s^2$. The $3d$ orbitals then fill up to their maximum of 10. Because the energy levels are lying so close together here, there is some irregularity in this region. Nevertheless, the regularity is restored at zinc, which is $1s^22s^22p^63s^23p^63d^{10}4s^2$. Then the $4p$ sublevel fills up to 6 from gallium to krypton. Table 1.2 shows the electronic structures of the first 102 elements.

PERIODIC TABLES

The periodic table proposed by Mendeleeff in 1872 is shown in Figure 1.4. It is a slight modification of his 1869

TABLE 1.2
The Electronic Configuration of the Elements

		NUMBER OF ELECTRONS IN EACH QUANTUM GROUP																			
Atomic Number	Element	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	7s	7p
1	H	1																			
2	He	2																			
3	Li	2	1																		
4	Be	2	2																		
5	B	2	2	1																	
6	C	2	2	2																	
7	N	2	2	3																	
8	O	2	2	4																	
9	F	2	2	5																	
10	Ne	2	2	6																	
11	Na	2	2	6	1																
12	Mg	2	2	6	2																
13	Al	2	2	6	2	1															
14	Si	2	2	6	2	2															
15	P	2	2	6	2	3															
16	S	2	2	6	2	4															
17	Cl	2	2	6	2	5															
18	Ar	2	2	6	2	6															
19	K	2	2	6	2	6		1													
20	Ca	2	2	6	2	6		2													
21	Sc	2	2	6	2	6	1	2													
22	Ti	2	2	6	2	6	2	2													
23	V	2	2	6	2	6	3	2													
24	Cr	2	2	6	2	6	5	1													
25	Mn	2	2	6	2	6	5	2													
26	Fe	2	2	6	2	6	6	2													
27	Co	2	2	6	2	6	7	2													
28	Ni	2	2	6	2	6	8	2													
29	Cu	2	2	6	2	6	10	1													
30	Zn	2	2	6	2	6	10	2													
31	Ga	2	2	6	2	6	10	2	1												
32	Ge	2	2	6	2	6	10	2	2												
33	As	2	2	6	2	6	10	2	3												
34	Se	2	2	6	2	6	10	2	4												
35	Br	2	2	6	2	6	10	2	5												
36	Kr	2	2	6	2	6	10	2	6												
37	Rb	2	2	6	2	6	10	2	6			1									
38	Sr	2	2	6	2	6	10	2	6			2									
39	Y	2	2	6	2	6	10	2	6	1		2									