5.17: Electron Configurations and the Periodic Table

The commonly used long form of the periodic table is designed to emphasize electron configurations. Since it is the outermost (valence) electrons which are primarily involved in chemical interactions between atoms, the *last* electron added to an atom in the building-up process is of far more interest to a chemist than the first. This last electron is called the **distinguishing electron** because it distinguishes an atom from the one immediately preceding it in the periodic table. The type of subshell (*s, p, d, f*)into which the distinguishing electron is placed is very closely related to the chemical behavior of an element and gives rise to the classification shown by the color-coding on the periodic table seen here. The **representative elements** are those in which the distinguishing electron enter an*s* or *p* subshell. Most of the elements whose chemistry and valence we have discussed so far fall into this category. Many of the chemical properties of the representative elements can be explained on the basis of Lewis diagrams. That is, the valences of the representative elements may be predicted on the basis of the number of valence electrons they have, or from the number of electrons that would have to be added in order to attain the same electron configuration as an atom of a noble gas. For representative elements the number of valence electrons is the same as the periodic group number, and the number needed to match the next noble-gas configuration is 8 minus the group number. This agrees with the valence rules derived from the periodic table, and results in formulas for chlorides of the first dozen elements that show the periodic variation of valence.

Formulas for chlorides of the first dozen elements that show the periodic variation of valence

Element	Atomic Weight	Hydrogen Compounds	Oxygen Compounds	Chlorine Compounds
Hydrogen	1.01	H_2	H_2O, H_2O_2	HCl
Helium	4.00	None formed	None formed	None formed
Lithium	6.94	LiH	Li_2O, Li_2O_2	LiCl
Beryllium	9.01	BeH_2	BeO	$BeCl_2$
Boron	10.81	B_2H_6	B_2O_3	BCl_3
Carbon	12.01	CH_4, C_2H_6, C_3H_8	CO_2, CO, C_2O_3	CCl_4, C_2Cl_6
Nitrogen	14.01	NH_3, N_2H_4, HN_3	N_2O, NO, NO_2, N_2O_5	NCl_3
Oxygen	16.00	H_2O, H_2O_2	O_2, O_3	$<Cl_2O$, ClO_2, Cl_2O_7
Fluorine	19.00	HF	OF_2, O_2F_2	ClF, ClF_3, ClF_5
Neon	20.18	None formed	None formed	None formed
Sodium	22.99	NaH	Na_2O, Na_2O_2	NaCl
Magnesium	24.31	MgH_2	MgO	$MgCl_2$

The first three horizontal rows or periods in the modern periodic table consist entirely of representative elements. In the first period the distinguishing electrons for H and He are in the 1*s* subshell. Across the second period Li and Be have distinguishing electrons in the 2*s* subshell, and electrons are being added to the 2*p* subshell in the atoms from B to Ne. In the third period the 3*s* subshell is filling for Na and Mg, and therefore Al, Si, P, S, Cl, and Ar. As a general rule, in the case of the representative elements, the distinguishing electron will be in an *ns* or *np* subshell. The value of *n*, the principal quantum number for the distinguishing electron, can be quickly determined by counting down from the top of the periodic table. For example, iodine is a representative element in the *fifth* period. Therefore the distinguishing electron must occupy either the 5*s* or 5*p* subshell. Since I is on the right side of the table, 5*p* is the correct choice.

When the principal quantum number is three or more, *d*-type subshells are also possible. The **transition elements** or **transition metals** are those elements whose distinguishing electron is found in a *d* orbital. The first examples of transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) are found in the *fourth* period even though the distinguishing electron in each case is a 3*d* electron and belongs to the *third* shell. This hiatus results, as we have already seen, because the 4*s* is lower in energy than the 3*d*. The 4*s* orbital thus starts to fill up, beginning the fourth period before any of the 3*d* orbitals can become occupied.

Figure 5.17.1 compares the probability distributions of a 4*s* and a 3*d* electron in a V atom. Although the 4*s* electron cloud lies farther from the nucleus on average than does the 3*d* cloud, a small portion of the 4*s* electron density is found very close to the

nucleus where it is hardly shielded from the total nuclear charge of +23. It is the very strong attractive force of this small fraction of the total 4s electron density that lowers the energy of the 4s electron below that of the 3d.
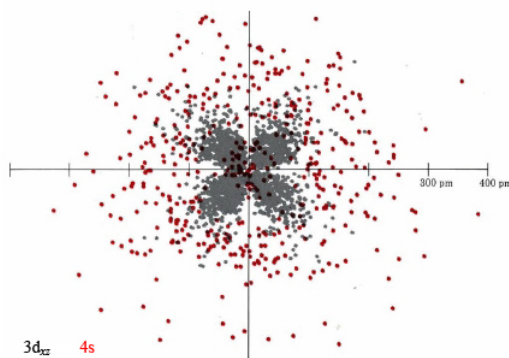

Figure 5.17.1 Comparison of 3d (gray) and 4s (red) electron clouds for a vanadium atom.

There is a vertical and horizontal axes. The axis has the units picometers. Around the origin is a four lobe shaped region forming an "X" shape around the origin. This region is highly concentrated with grey dots. A circular area around the origin is also filled with red dots. A ring shaped region just beyond the outer edges of the lobed region is filled with red dots. The number of grey and red dots decreases as we move further away from the origin.

The fact that the 4s electron cloud is more extensive than the 3d has an important influence on the chemistry of the transition elements. When an atom such as V (Figure 5.17.1) interacts with another atom, it is the 4s electrons extending farthest from the nucleus which first contact the other atom. Thus the 4s electrons are often more significant than the 3d in determining valence and the formulas of compounds. The 3d electrons are "buried" under the surfaces of the atoms of the transition metals. Adding one more 3d electron has considerably less effect on their chemical properties than adding one more 3s or 3p electron did in the case of the representative elements. Hence there is a slow but steady *transition* in properties from one transition element to another. Notice, for example, that except for Sc, all of the transition metals form chlorides, MCl2, where the metal has a valence of 2; examples are TiCl2, VCl2, CrCl2, and so on. This can be seen in the table found at the top of this page. The valence of 2 corresponds with the two 4s valence electrons.

Each of the transition metals also exhibits other valences where one or more of the 3d electrons are also involved. For example, in some compounds V (vanadium) has a valence of 2 (VO, VCl_2) in others it has a valence of 3 (V_2O_3, VCl_3), in still others it has a valence of 4 (VO_2, VCl_4), and in at least one case (V_2O_5) it has a valence of 5. The chemistry of the transition metals is more complicated and a wider variety of formulas for transition-metal compounds is possible because of this variable valence. In some cases electrons in the d subshells act as valence electrons, while in other cases they do not. Although the 3d electron clouds do not extend farther from the nucleus than 3s and 3p (and hence do not constitute another shell as the 4s electrons do), they are thoroughly shielded from the nuclear charge and thus often act as valence electrons. This Jekyll and Hyde behavior of 3d electrons makes life more complicated (and often far more interesting) for chemists who study the transition elements.

Table 1: Atomic Electron Configurations

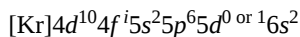| Z	Element	Configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	[He] $2s^1$
4	Be	[He] $2s^2$
5	B	[He] $2s^2 2p^1$
6	C	[He] $2s^2 2p^2$
7	N	[He] $2s^2 2p^3$
8	O	[He] $2s^2 2p^4$

Z	Element	Configuration
9	F	[He] $2s^2\,2p^5$
10	Ne	[He] $2s^2\,2p^6$
11	Na	[Ne] $3s^1$
12	Mg	[Ne] $3s^2$
13	Al	[Ne] $3s^2\,3p^1$
14	Si	[Ne]$3s^2\,3p^2$
15	P	[Ne] $3s^2\,3p^3$
16	S	[Ne] $3s^2\,3p^4$
17	Cl	[Ne] $3s^2\,3p^5$
18	Ar	[Ne] $3s^2\,3p^6$
19	K	[Ar] $4s^1$
20	Ca	[Ar] $4s^2$
21	Sc	[Ar] $3d^1\,4s^2$
22	Ti	[Ar] $3d^2\,4s^2$
23	V	[Ar] $3d^3\,4s^2$
24	Cr	[Ar] $3d^5\,4s^1$
25	Mn	[Ar] $3d^5\,4s^2$
26	Fe	[Ar] $3d^6\,4s^2$
27	Co	[Ar] $3d^7\,4s^2$
28	Ni	[Ar] $3d^8\,4s^2$
29	Cu	[Ar] $3d^{10}\,4s^1$
30	Zn	[Ar] $3d^{10}\,4s^2$
31	Ga	[Ar] $3d^{10}\,4s^2\,4p^1$
32	Ge	[Ar] $3d^{10}\,4s^2\,4p^2$
33	As	[Ar] $3d^{10}\,4s^2\,4p^3$
34	Se	[Ar] $3d^{10}\,4s^2\,4p^4$
35	Br	[Ar] $3d^{10}\,4s^2\,4p^5$
36	Kr	[Ar] $3d^{10}\,4s^2\,4p^6$
37	Rb	[Kr] $5s^1$
38	Sr	[Kr] $5s^2$
39	Y	[Kr] $4d^1\,5s^2$

Z	Element	Configuration
40	Zr	[Kr] $4d^2\, 5s^2$
41	Nb	[Kr] $4d^4\, 5s^1$
42	Mo	[Kr] $4d^5\, 5s^1$
43	Tc	[Kr] $4d^5\, 5s^2$
44	Ru	[Kr] $4d^7\, 5s^1$
45	Rh	[Kr] $4d^8\, 5s^1$
46	Pd	[Kr] $4d^{10}$
47	Ag	[Kr] $4d^{10}\, 5s^1$
48	Cd	[Kr] $4d^{10}\, 5s^2$
49	In	[Kr] $4d^{10}\, 5s^2\, 5p^1$
50	Sn	[Kr] $4d^{10}\, 5s^2\, 5p^2$
51	Sb	[Kr] $4d^{10}\, 5s^2\, 5p^3$
52	Te	[Kr] $4d^{10}\, 5s^2\, 5p^4$
53	I	[Kr] $4d^{10}\, 5s^2\, 5p^5$
54	Xe	[Kr] $4d^{10}\, 5s^2\, 5p^6$
55	Cs	[Xe] $6s^1$
56	Ba	[Xe] $6s^2$
57	La	[Xe] $5d^1\, 6s^2$
58	Ce	[Xe] $4f^1\, 5d^1\, 6s^2$
59	Pr	[Xe] $4f^3\, 6s^2$
60	Nd	[Xe] $4f^4\, 6s^2$
61	Pm	[Xe] $4f^5\, 6s^2$
62	Sm	[Xe] $4f^6\, 6s^2$
63	Eu	[Xe] $4f^7\, 6s^2$
64	Gd	[Xe] $4f^7\, 5d^1\, 6s^2$
65	Tb	[Xe] $4f^9\, 6s^2$
66	Dy	[Xe] $4f^{10}\, 6s^2$
67	Ho	[Xe] $4f^{11}\, 6s^2$
68	Er	[Xe] $4f^{12}\, 6s^2$
69	Tm	[Xe] $4f^{13}\, 6s^2$
70	Yb	[Xe] $4f^{14}\, 6s^2$
71	Lu	[Xe] $4f^{14}\, 5d^1\, 6s^2$
72	Hf	[Xe] $4f^{14}\, 5d^2\, 6s^2$

Z	Element	Configuration
73	Ta	[Xe] $4f^{14} 5d^3 6s^2$
74	W	[Xe] $4f^{14} 5d^4 6s^2$
75	Re	[Xe] $4f^{14} 5d^5 6s^2$
76	0s	[Xe] $4f^{14} 5d^6 6s^2$
77	Ir	[Xe] $4f^{14} 5d^7 6s^2$
78	Pt	[Xe] $4f^{14} 5d^9 6s^1$
79	Au	[Xe] $4f^{14} 5d^{10} 6s^1$
80	Hg	[Xe] $4f^{14} 5d^{10} 6s^2$
81	Tl	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$
82	Pb	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$
83	Bi	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$
84	Po	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$
85	At	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$
86	Rn	[Xe] $4f^{14} 5d^{10} 6s^2 6p^6$
87	Fr	[Rn] $7s^1$
88	Ra	[Rn] $7s^2$
89	Ac	[Rn] $6d^1 7s^2$
90	Th	[Rn] $6d^2 7s^2$
91	Pa	[Rn] $5f^2 6d^1 7s^2$
92	U	[Rn] $5f^3 6d^1 7s^2$
93	Np	[Rn] $5f^4 6d^1 7s^2$
94	Pu	[Rn] $5f^6 7s^2$
95	Am	[Rn] $5f^7 7s^2$
96	Cm	[Rn] $5f^7 6d^1 s^2$
97	Bk	[Rn] $5f^9 s^2$
98	Cf	[Rn] $5f^{10} s^2$
99	Es	[Rn] $5f^{11} s^2$
100	Fm	[Rn] $5f^{12} s^2$
101	Md	[Rn] $5f^{13} s^2$
102	No	[Rn] $5f^{14} s^2$
103	Lr	[Rn] $5f^{14} 6d^1 s^2$
104	Rf	[Rn] $5f^{14} 6d^2 s^2$

The third major category of elements arises when the distinguishing electron occupies an *f* subshell. The first example occurs in the case of the **lanthanoids** (elements having atomic numbers between 57 and 71).The lanthanoids have the general electron configuration

$$[Kr]4d^{10}4f^{\,i}5s^25p^65d^{0\text{ or }1}6s^2$$

where *i* is a number between 0 and 14. Thus in the building-up process for the lanthanoids, electrons are being added to a subshell (4*f*) whose principal quantum number is two less than that of the outermost orbital (6*s*). Addition of another electron to an inner shell buried as deeply as the 4*f* has little or no effect on the chemical properties of these elements. All are quite similar to lanthanum (La) and might fit into exactly the same space in the periodic table as La. The lanthanoid elements are so similar to one another that special techniques are required to separate them. As a result, even approximately pure samples of most of them were not prepared until the 1870s. Following the element actinium (Ac) is a series of atoms in which the 5*f* subshell is filling. The **actinoids** are somewhat less similar to Ac than the lanthanoids are to La because some exceptions to the usual order of filling orbitals occur in the case of Th, Pa, and U (Table 5.17.1).

Figure 5.17.2: Periodic Table displaying the subshells which distinguish regions of the periodic table. Note: even though it is found in the p-subshell region of the periodic table, the box for He is purple, not green, since the s-subshell is filled in He, not the p-subshell.

Because the lanthanoids and most of the actinoids behave chemically as if they should fit in group IIIB of the periodic table (where Lu and Lr are found), both groups are separated from the rest of the table and placed together in a block below. Taken together, the lanthanoids and actinoids are called **inner transition elements** because the *f* subshells being filled lie so deep within the remaining electronic structure of their atoms.

Figure 5.17.2 summarizes the type of subshell in which the distinguishing electron is to be found for atoms of elements in various regions of the periodic table. This summary information makes it relatively simple to use the periodic table to obtain electron configurations, as the following example shows.

> ✔ Example 5.17.1: Electron Configuration
>
> Obtain the electron configuration for (a) Nb; (b) Pr.
>
> **Solution**
> **a)** Nb, element number 41, is found in the fifth period and in a region of the periodic table where a *d* subshell is filling (the second transition series). Moving backward (toward lower atomic numbers) through the periodic table, the nearest noble gas is Kr, and so we use the Kr kernel:
>
> Nb [Kr] _____
>
> The next element after $_{36}$K is $_{37}$Rb in which the 5s subshell is filling. Moving right one more space, we come to $_{38}$Sr which has a $5s^2$ pair. So far we have Nb [Kr] _____ $5s^2$ for the Nb configuration. We now move farther right into the 4*d subshell* region of the periodic table and count over three spaces (Y, Zr, Nb) to reach Nb. The total electron configuration is thus Nb $[Kr]4d^35s^2$ (Note that the principal quantum number of the *d* subshell is 4 — one less than the number of the period. Also, if you look at

the table of electron configurations, it should be noted that Nb is an exception to the typical orbital filling rules) **b)** A similar procedure is followed for Pr, element number 59. Moving backward through the table, the nearest noble gas is Xe, and so we use the Xe kernel. Counting forward again, Cs and Ba correspond to $6s^2$. Then La, Ce, and Pr correspond to three more electrons in the $4f$ subshell. The configuration is thus Pr ⎯ $[Xe]4f^36s^2$

One more point needs to be emphasized about the relationship between electron configuration and the periodic table. *The atoms of elements in the same vertical column of the table have similar electron configurations*. For example, consider the alkaline-earth elements (group IIA). Using our rules for deriving electron configurations (Example 1) we have

deriving electron configurations

Element	Electron Configuration	Lewis Diagram
Be	$[He]2s^2$	Be:
Mg	$[Ne]3s^2$	Mg:
Ca	$[Ar]4s^2$	Ca:
Sr	$[Kr]5s^2$	Sr:
Ba	$[Xe]6s^2$	Ba:
Ra	$[Rn]7s^2$	Ra:

Thus the similarities of chemical behavior and valence noted earlier for these elements correlate with the similarities of their outermost electron clouds. Such similarities account for the success of Mendeleev's predictions of the properties of undiscovered elements.

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