

**Fig. 3.11** The shell model of the potassium atom. Now there are four shells. The first shell is complete with two electrons, the  $n = 2$  and  $n = 3$  shells hold eight electrons, and the fourth shell has only one electron. Adapted from Carl Snyder, *The Extraordinary Chemistry of Ordinary Things*, John Wiley & Sons, Inc., New York, 1992.

### ► CHECKPOINT

Is the radius of the valence shell of Na larger, smaller, or the same as the radius of the valence shell of Li?

that H, Li, Na, and K each have one electron in their outermost shell, and each of these elements is in Group IA of the periodic table. In addition, as we go down the column in this group, from H to K, the ionization energy decreases. This is consistent with all of these atoms having a core charge of  $+1$ , with the outermost electron in a shell that is progressively farther and farther from the nucleus. In fact, the number of electrons in the outermost shell of each atom among the first 20 elements in the periodic table corresponds exactly with the group number for that element.

As we will see in the next chapter, the electrons in the outermost shell of an atom are involved in the formation of bonds between atoms. Because these bonds are relatively strong, the electrons that form them are often called the **valence electrons** (from the Latin stem *valens*, “to be strong”). A more complete discussion of valence electrons is found in the next chapter.

The periodic table was originally created to group elements that had similar chemical and physical properties. The arrangement of the electrons in the atom deduced from the shell model is reflected in the arrangement of elements in the periodic table. This suggests that many of the chemical and physical properties of the elements are related to the number of electrons in the outermost shell, which are the valence electrons in these atoms. Also note that the core charge and the number of electrons in the outermost shell correspond to the group numbers IA through VIIIA.

## 3.11 Photoelectron Spectroscopy and the Structure of Atoms

The shell model of the atom that we have deduced from first ionization energy data assumes that the electrons in an atom are arranged in shells about the nucleus, with successive shells being farther and farther from the nucleus of the atom. The data we used to derive this model represented the *minimum* energy needed to remove an electron from the atom. Thus, in each case, the first ionization energy reflects the ease with which the outermost electron can be removed from the atom.

For atoms that have many electrons, we would expect that it would take more energy to remove an electron from an inner shell than it does to remove the electron from the valence shell. It takes more energy to remove an electron from the  $n = 2$  shell than from the  $n = 3$  shell, for example, and even more energy to remove an electron from the  $n = 1$  shell for a given atom.

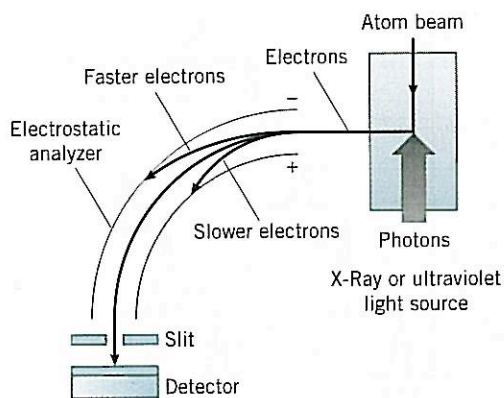
This raises an interesting question: Do all of the electrons in a given shell have the same energy? This question can be answered by using a slightly different technique to measure the energy required to remove an electron from a neutral atom in the gas phase to form a positively charged ion.

This time, we will shine radiation on the sample that has enough energy to excite an atom to the point that one of its electrons from any shell is ejected from the atom to form a positively charged ion. The experiment, which is diagrammed in Figure 3.12, is known as **photoelectron spectroscopy (PES)**.

The PES experiment begins with the absorption of a high-energy UV or X-ray photon. The energy of this photon is large enough to remove an electron from the atom ( $IE$ ). The excess energy is carried off by the electron ejected from the atom in the form of kinetic energy ( $KE$ ). We know the energy of the radiation ( $h\nu$ ) used to excite the atom. If we measure the kinetic energy of the photoelectron ejected ( $KE$ ) when this radiation is absorbed, we can calculate the energy required to remove this electron from the atom ( $IE$ ).

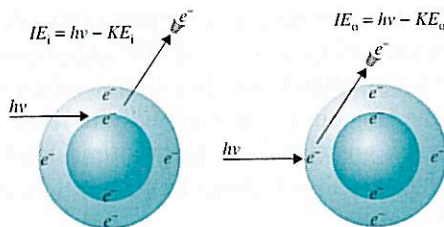
$$IE = h\nu - KE$$





**Fig. 3.12** A block diagram of photoelectron spectroscopy. Absorption of a high-energy electron leads to the ejection of an electron from the atom. The kinetic energy (KE) of the ejected electron is measured, and the energy required to remove the electron from the atom is calculated from the difference between the energy of the photon ( $h\nu$ ) and the kinetic energy of the photoelectron. Because electrons can be removed from any shell in the atom, this experiment is different from measurements of first ionization energies, which remove electrons from only the outermost shell. Reprinted from R. J. Gillespie et al., *Atoms, Molecules and Reactions*, Prentice-Hall, Englewood Cliffs, New Jersey, 1994, p. 198.

PES differs from the experiment used to obtain the first ionization energies given in Table 3.3 by its ability to remove electrons *from any shell in the atom*, as shown in Figure 3.13. Not only can an electron from the outermost shell be removed, but an electron from one of the shells deep within the core of electrons that surround the nucleus can be ejected. Only a single electron is removed from a given atom, but that electron can come from any energy level. As a result, PES allows us to measure the energy needed to remove any electron on an atom.



**Fig. 3.13** Absorption of a high-energy photon can result in the ejection of an electron from any shell of an atom. The ionization energy of the inner shell electrons,  $IE_i$ , will be larger than that of the outer shell electrons,  $IE_o$ .

Data from PES experiments are obtained as peaks in a spectrum that plots the energy needed to eject an electron ( $IE$ ) on the  $x$  axis versus the intensity of the observed signal on the  $y$  axis, as shown in Figure 3.14. The spectrum is plotted so that energy *increases* toward the *left* on the  $x$  axis. The intensity or the height of the peak is proportional to the number of electrons of equivalent energy ejected during the experiment. If we see two peaks, for example, that have a relative height of 2:1, we can conclude that one of the energy levels from which electrons are removed in this experiment contains twice as many electrons as the other.

As we examine PES data in the next section, it is important to remember that the electromagnetic radiation energy supplied may remove an electron from the outermost shell or remove an electron from one of the shells that are deep within the core of the atom.

*PES data include not only the ionization energies of the most loosely held electrons but also the ionization energies of all electrons in the atom. These new data present a problem to the student, who finds that the simple shell model cannot rationalize these ionization energies. Thus, a rethinking of the model is necessary.*

*There is a clear pattern in the first ionization energy data, which suggest that there are shells of electrons around an atom. Careful consideration of the PES data suggests that these shells not only can be but should be divided into subshells. PES ionization energies therefore provide a basis for developing electron configurations without the use of either quantum numbers or orbital shapes.*

## 3.12 Electron Configurations from Photoelectron Spectroscopy

Hydrogen has one peak in the photoelectron spectrum in Figure 3.14 because it contains only a single electron. As expected, this peak comes at an energy of 1312 kJ/mol, or, as we'll express it from now on in megajoules, 1.312 MJ/mol. This is the energy required to eject the electrons from a mole of hydrogen atoms.

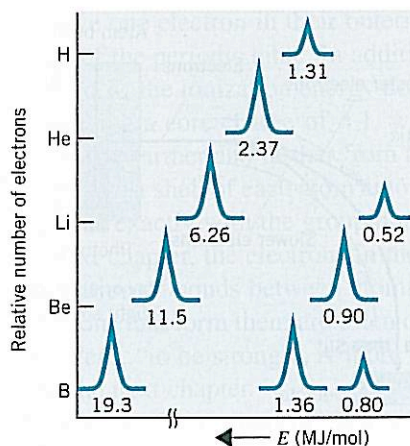
Helium also has only one peak in the PES experiment, which occurs at an energy of 2372 kJ/mol or 2.372 MJ/mol. Note that the peak for helium is shifted to

### ► CHECKPOINT

What factor determines the number of peaks in the photoelectron spectrum of an atom?



**Fig. 3.14** Simulated photoelectron spectra of the first five elements in the periodic table. The energy needed to remove an electron from an atom increases from right to left. The energy required to remove an electron from the hydrogen atom is 1.312 MJ/mol and that for the helium atom is 2.372 MJ/mol. The height of the He spectrum is twice that of the H spectrum because He has twice as many electrons as H. The spectra have been adjusted so that the peak heights of spectra of different atoms are directly comparable.



### ► CHECKPOINT

Why is there only one peak in the photoelectron spectrum of He even though there are two electrons in an He atom?

the left in Figure 3.14 when compared to the peak in the spectrum for hydrogen. This corresponds to a shift toward a larger ionization energy, as expected. It takes more energy to remove an electron from a helium atom than the energy needed to remove an electron from hydrogen. The height of the peak for helium is twice that for the peak in the spectrum for hydrogen. This is consistent with our hypothesis that the two electrons in a helium atom both occupy the  $n = 1$  shell.

Our shell model of the atom leads us to expect two peaks in the PES spectrum for lithium, which is exactly what is observed. These peaks occur at ionization energies ( $IE$ ) of 6.26 and 0.52 MJ/mol, and they have a relative intensity of 2:1. The outermost electron in the Li atom is relatively easy to remove because it is in the  $n = 2$  shell. But it takes a great deal of energy to reach into the  $n = 1$  shell, as shown in Figure 3.14, because the electrons in that shell lie close to a nucleus that carries a charge of +3.

Two peaks are also observed in the PES spectrum of beryllium, with a relative intensity of 1:1. In this case, it takes an enormous amount of energy to reach into the  $n = 1$  shell ( $IE = 11.5$  MJ/mol) to remove one of the electrons that lie close to the nucleus with its charge of +4. It takes quite a bit less energy ( $IE = 0.90$  MJ/mol) to remove one of the electrons in the  $n = 2$  shell, as shown in Figure 3.14.

An interesting phenomenon occurs when we compare the photoelectron spectrum of boron with the spectra for the first four elements shown in Figure 3.14. There are now three distinct peaks in the spectrum, at energies of 19.3, 1.36, and 0.80 MJ/mol. There is a peak in the PES spectrum that corresponds to removing one of the electrons from the  $n = 1$  shell ( $IE = 19.3$  MJ/mol). But there are also two additional peaks, with a relative intensity of 2:1, that correspond to removing an electron from the  $n = 2$  shell ( $IE = 1.36$  and 0.80 MJ/mol).

The same phenomenon occurs in the PES spectra for carbon, nitrogen, oxygen, fluorine, and neon, as shown in Table 3.4. In each case, we see three peaks. As the charge on the nucleus increases, it takes more and more energy to remove an electron from the  $n = 1$  shell, until, by the time we get to neon, it takes 84.0 MJ/mol to remove an electron from this shell. (This is more than 100 times the energy given off in a typical chemical reaction.)

The PES spectra for B, C, N, O, F, and Ne contain a second peak, of gradually increasing energy because of the increasing nuclear charge, that has the same intensity as the peak for the  $n = 1$  shell. And, in each case, we get a third peak, of gradually increasing energy, that corresponds to the electrons which are the easiest to remove from the atoms. The intensity of the third peak increases from element

*Ejected electrons may be separated out according to their kinetic energies by an electrostatic analyzer, which has two oppositely charged plates. As an ejected electron enters the electric field between the plates, it is deflected depending on its speed (kinetic energy). A detector is arranged so that electrons with the proper deflection may be recorded as "counts."*

*Electrons of different kinetic energies may be counted by varying the voltage difference between the plates.*

*Students sometimes do not realize that in a photoelectron spectroscopy experiment only one electron is removed from an atom and that this could be any electron in the atom—not just electrons from the valence shell. It is, therefore, important to assign homework from this section.*



Table 3.4

Ionization Energies for Gas Phase Atoms of the First 10 Elements Obtained from Photoelectron Spectra

IE (MJ/mol) Element	First Peak	Second Peak	Third Peak
H	1.31		
He	2.37		
Li	6.26	0.52	
Be	11.5	0.90	
B	19.3	1.36	0.80
C	28.6	1.72	1.09
N	39.6	2.45	1.40
O	52.6	3.12	1.31
F	67.2	3.88	1.68
Ne	84.0	4.68	2.08

Source: D. A. Shirley et al., *Physical Review B* (15), 544–552 (1977).

to element, representing a single electron for boron up to a total of six electrons for neon, as shown in Figures 3.14 and 3.15.

The PES data for the first 10 elements reinforce our belief in the shell model of the atom. But they suggest that we have to refine the model to explain the fact that the electrons in the  $n = 2$  shell seem to occupy different energy levels. In other words, we have to introduce the concept of **subshells** within the shells of electrons.

When the first evidence for subshells was discovered shortly after the turn of the twentieth century, a shorthand notation was introduced in which these subshells were described as either  $s$ ,  $p$ ,  $d$ , or  $f$ . Within any shell of electrons, it always takes the largest amount of energy to remove an electron from the  $s$  subshell.

The PES data in Table 3.4 suggest that there is only one subshell in the  $n = 1$  shell. Chemists usually represent this by writing  $1s$ , where the number represents the shell and the letter represents the subshell. These data also suggest that the  $1s$  subshell can hold a maximum of two electrons. The third and fourth electrons on an atom seem to be added to a  $2s$  subshell. Once we have four electrons, however, the  $2s$  subshell seems to be filled, and we have to add the fifth electron to the next subshell:  $2p$ .

By convention, the information we have deduced from the PES data is referred to as the atom's **electron configuration** and is written as follows.

H ( $Z = 1$ )	$1s^1$
He ( $Z = 2$ )	$1s^2$
Li ( $Z = 3$ )	$1s^2 2s^1$
Be ( $Z = 4$ )	$1s^2 2s^2$
B ( $Z = 5$ )	$1s^2 2s^2 2p^1$

The superscripts in the electron configurations designate the number of electrons in each subshell. The existence of two subshells within the  $n = 2$  shell explains the minor inversion in the first ionization energies of boron and beryllium shown in Figure 3.6. It is slightly easier to remove the outermost electron from B ( $IE = 0.80$  MJ/mol) than from Be ( $IE = 0.90$  MJ/mol), in spite of the greater charge on the nucleus of the boron atom, because the outermost electron of

Low-resolution PES spectra are used so as not to have to introduce complicated coupling interactions between electron spins and angular momenta. A high-resolution photoelectron spectrum of the  $2p$  atomic state of argon shows two peaks lying very close to one another. A low-resolution photoelectron spectrum will not differentiate between the two peaks, and hence a single peak is seen. See the Instructor's Manual.

The photoelectron spectra shown as figures in this text are computer generated. Normally photoelectron spectra of different elements are not directly comparable. The areas under the peaks of these spectra have been adjusted so that the areas under the peaks due to the  $1s$  electrons are equivalent for all elements containing two  $1s$  electrons.

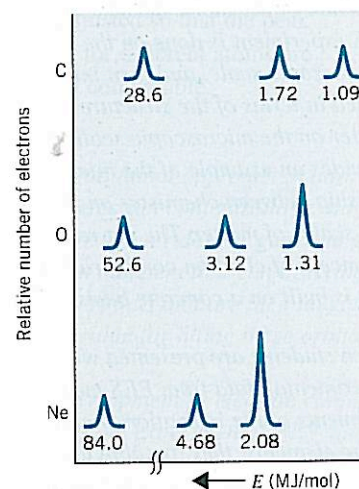
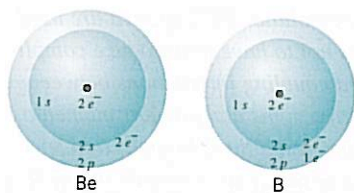


Fig. 3.15 Simulated photoelectron spectra of C, O, and Ne. The nuclear charge increases from carbon to oxygen to neon, and the spectra shift to the left to higher energies. The peak farthest to the right shows the electrons most easily removed, and the peak heights (relative number of electrons) increase in a ratio of 2:4:6. The spectra have been adjusted so that the peak heights for different atoms are directly comparable.





**Fig. 3.16** The outermost electron in B is easier to remove than the outermost electron in Be because the electron is in the  $2p$  subshell. The easiest electron to remove from Be is in the  $2s$  subshell.

### ► CHECKPOINT

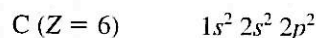
Explain the relative intensity of the three peaks in the PES spectrum of Ne (Figure 3.17), which is 2:2:6. Assign each of these peaks to a subshell.

*This approach illustrates the process of science because it uses experimental data to generate the electronic structure of the atom. Because the PES experiment is done on the macroscopic scale, and then interpreted in terms of the structure of matter on the microscopic scale, it provides an example of the interrelationship between chemistry on the two scales of matter. The net result is a concept of electron configuration that is built on a concrete basis.*

*When students are presented with experimental data from PES measurements of the ionization energies of the elements, they are able to develop many of these rules for themselves and thus obtain a fuller understanding of electron configurations—particularly with respect to the energies of the various subshells.*

B is in the  $2p$  subshell, whereas the outermost electron in Be has to be removed from the  $2s$  subshell shown in Figure 3.16.

As we continue across the second row of the periodic table, from B to Ne, the number of electrons in the  $2p$  subshell gradually increases to six. The best evidence for this is the growth in the intensity of the peak corresponding to the  $2p$  subshell. In boron, this peak has half the height of the  $1s$  or  $2s$  peaks. When we get to neon, we find it has three times the height of the  $1s$  or  $2s$  peaks. This suggests that the  $2p$  subshell can hold a maximum of six electrons. We can therefore continue the process of translating PES data into the electron configurations for the atoms as follows.

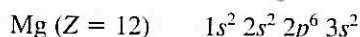


PES data for the next 11 elements in the periodic table are given in Table 3.5, in which the columns are labeled in terms of the representations for the subshells:  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ ,  $3d$ , and  $4s$ .

As we might expect, sodium has four peaks in the photoelectron spectrum, corresponding to the loss of electrons from the  $1s$ ,  $2s$ ,  $2p$ , and  $3s$  subshells, as shown in Figure 3.17. It is easier to remove the electron in the  $n = 3$  shell in sodium ( $IE = 0.50$  MJ/mol) than the electrons in the  $n = 2$  shell ( $IE = 6.84$  and  $3.67$  MJ/mol), which in turn are easier to remove than the electrons in the  $n = 1$  shell ( $IE = 104$  MJ/mol).



Magnesium also gives four peaks in the PES experiment, which is consistent with the following electron configuration:



Aluminum and each of the subsequent elements up to argon have five peaks in the PES spectrum. The new peak corresponds to the  $3p$  subshell, and these elements

**Table 3.5**

**Ionization Energies for Gas Phase Atoms of Elements 11 Through 21 Obtained from Photoelectron Spectra**

IE (MJ/mol) Element	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$
Na	104	6.84	3.67	0.50			
Mg	126	9.07	5.31	0.74			
Al	151	12.1	7.79	1.09	0.58		
Si	178	15.1	10.3	1.46	0.79		
P	208	18.7	13.5	1.95	1.01		
S	239	22.7	16.5	2.05	1.00		
Cl	273	26.8	20.2	2.44	1.25		
Ar	309	31.5	24.1	2.82	1.52		
K	347	37.1	29.1	3.93	2.38		0.42
Ca	390	42.7	34.0	4.65	2.90		0.59
Sc	433	48.5	39.2	5.44	3.24	0.77	0.63

Source: D. A. Shirley et al., *Physical Review B* (15), 544–552 (1977).



have the following electron configurations.

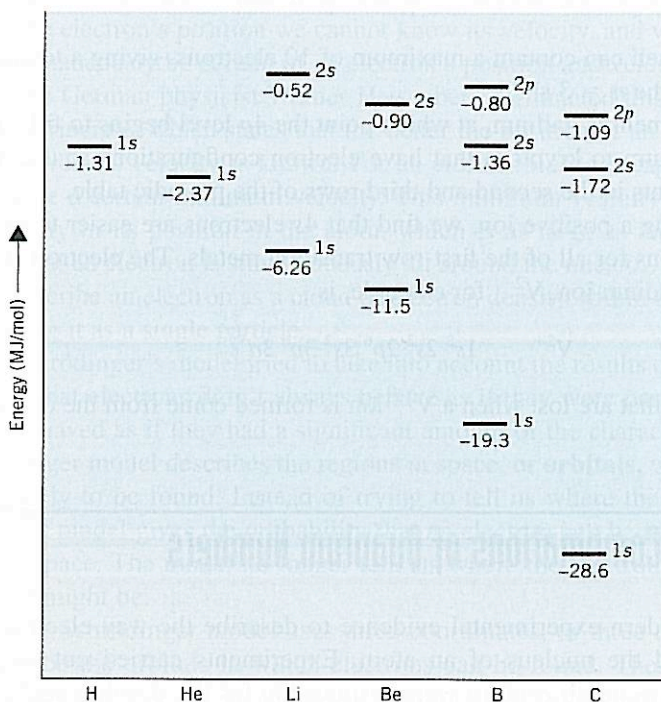
Al ( $Z = 13$ )	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si ( $Z = 14$ )	$1s^2 2s^2 2p^6 3s^2 3p^2$
P ( $Z = 15$ )	$1s^2 2s^2 2p^6 3s^2 3p^3$
S ( $Z = 16$ )	$1s^2 2s^2 2p^6 3s^2 3p^4$
Cl ( $Z = 17$ )	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar ( $Z = 18$ )	$1s^2 2s^2 2p^6 3s^2 3p^6$

The electron configurations of the elements in the third row of the periodic table therefore follow the same pattern as the corresponding elements in the second row.

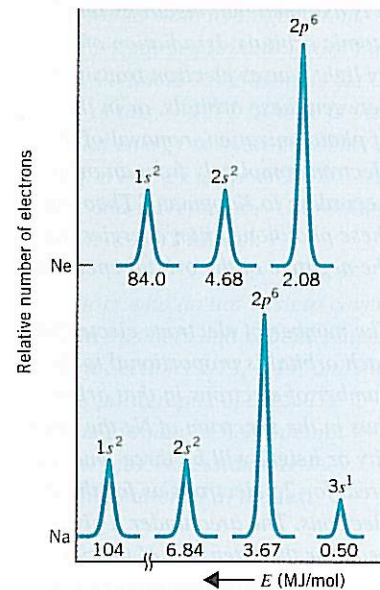
By the time we get to potassium and calcium, we find six peaks in the PES spectrum, with the smallest ionization energy comparable to, but slightly less than, the ionization energies of the  $3s$  electrons on sodium and magnesium. We therefore write the electron configurations of potassium and calcium as follows.

K ( $Z = 19$ )	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Ca ( $Z = 20$ )	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Figure 3.18 shows the relative energies of the shells and subshells in the first six elements in the periodic table: H, He, Li, Be, B, and C. The same labels ( $1s$ ,  $2s$ , and  $2p$ ) are used to describe the different energy states in these atoms. The energy associated with a given label, however, changes significantly from one element to another. Once again, the energies are given as negative numbers to indicate that the atom must absorb energy to remove an electron from one of these subshells. The energy of the  $1s$  subshell gradually decreases from  $-1.31$  MJ/mol in H to  $-2.37$  MJ/mol in He,  $-6.26$  MJ/mol in Li, and so on, until we reach an energy of  $-28.6$  MJ/mol in C. This is explained by the shell model of the atom, which assumes that these electrons are close to a nucleus with a charge that increases from  $+1$  to  $+6$ . The energy of the  $2s$  orbital also decreases as the charge on the nucleus



**Fig. 3.18** Relative energies of the electrons within the shells and subshells in H, He, Li, Be, B, and C atoms in units of megajoules per mole (MJ/mol). The  $1s$  electrons are more tightly held as the nuclear charge increases from H through C. The labels  $1s$ ,  $2s$ , and  $2p$  are used to describe the energy states.



**Fig. 3.17** Simulated photoelectron spectra of Ne and Na. Sodium has four peaks corresponding to loss of electrons from the  $1s$ ,  $2s$ ,  $2p$ , and  $3s$  subshells. The heights of the peaks correspond to the number of electrons in a subshell. The spectra have been adjusted so that the peak heights for different atoms are directly comparable.

*In the traditional approach to introducing electron configurations, students are given rules for generating quantum numbers that can describe atomic orbitals and are then taught an algorithm for filling these orbitals.*

*This development of electron configurations from experimental PES data gives students a more concrete, while still scientifically correct, foundation on which to base their understanding of electron configuration than the more abstract quantum numbers and orbital shapes.*



*It is assumed that electrons reside in atomic orbitals. Irradiation of atoms by light causes electron transitions between these orbitals, or in the case of photoionization, removal of an electron completely from an orbital. According to Koopmans' Theorem, these photoionization energies are the negative of the orbital energies.*

*The number of electrons ejected from each orbital is proportional to the number of electrons in that orbital; thus in the spectrum of Ne the intensity or height will be three times as great for 2p electrons as for the 2s electrons. The area under a given peak (or the intensity) of the photoelectron spectrum is proportional to the number of electrons in that particular energy state.*

*If an atom is bombarded with photons of sufficient energies (UV and X ray), electrons may be removed from all the energy states (orbitals) of an atom. Koopmans' theorem is usually interpreted as meaning that for multielectron atoms the one-electron energy as obtained from SCF is a good approximation of IE and thus is assumed to be valid for the interpretation of PES data.*

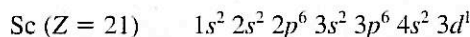
### ► CHECKPOINT

Using data from Table 3.5, sketch the photoelectron spectrum of scandium, Sc. Give the relative intensities of the peaks and assign energies to each peak. Use the photoelectron spectrum to list the order in which electrons are removed from subshells of scandium. Use the electron configuration of Sc to list the order in which its subshells are filled with electrons. Is there a difference in the orders in which electrons are added to and taken away from Sc?

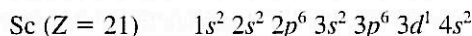
increases, as we would expect. But the energy of the 1s orbital is always lower than the 2s, which is lower than the 2p.

An interesting phenomenon occurs in the next element in the periodic table, scandium (Sc). Our shell model predicts that the subshells used to hold electrons in calcium are all filled. The twenty-first electron therefore has to go into a new subshell. But the ionization energy for the new peak that appears in the PES spectrum doesn't occur at a lower energy than the subshells used previously, which has been observed for every other subshell as it has appeared. The new peak appears at a higher energy than the 4s subshell on scandium.

Evidence from other forms of spectroscopy suggest that the twenty-first electron on the scandium atom goes into the  $n = 3$  shell, not the  $n = 4$  shell. The subshell used to hold this electron is the 3d subshell. As we can see from the data in Table 3.5, the 3d subshell is very close in energy to the 4s subshell. For scandium, it is easier to remove a 4s electron than a 3d electron. The electron configuration of scandium may be written as follows:

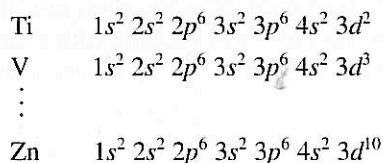


This way of writing electron configurations is convenient because it follows the arrangement of the elements in the periodic table. Another way of writing electron configurations is to list the subshells in order of decreasing ionization energy.



In this text the first method is employed.

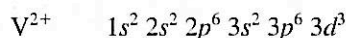
Scandium is followed by nine elements—known as the **transition metals**—that have no analogs in the second and third rows of the periodic table. In these elements, electrons continue to fill the 3d subshell until we reach zinc.



Thus, the 3d subshell can contain a maximum of 10 electrons, giving a total of up to 18 electrons in the  $n = 3$  shell.

The next element is gallium, at which point the 4p level begins to fill, giving six elements (gallium to krypton) that have electron configurations analogous to those of the elements in the second and third rows of the periodic table.

When forming a positive ion, we find that 4s electrons are easier to remove than the 3d electrons for all of the first-row transition metals. The electron configuration of the vanadium ion,  $\text{V}^{2+}$ , for example, is



The two electrons that are lost when a  $\text{V}^{2+}$  ion is formed come from the outermost shell, 4s.

## 3.13 Allowed Combinations of Quantum Numbers

We have used modern experimental evidence to describe the way electrons are distributed around the nucleus of an atom. Experiments carried out near the beginning of the twentieth century were responsible for the development of the