CHAPTER 8 Electronic Structure

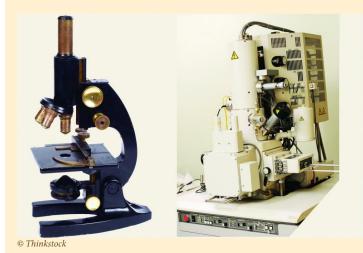
Opening Essay

Normal light microscopes can magnify objects up to about 1,500 times. Electron microscopes can magnify objects up to 1,000,000 times. Why can electron microscopes magnify images so much?

A microscope's resolution depends on the wavelength of light used. The smaller the wavelength, the more a microscope can magnify. Light is a wave, and, as such, it has a wavelength associated with it. The wavelength of visible light, which is detected by the eyes, varies from about 700 nm to about 400 nm.

One of the startling conclusions about modern science is that electrons also act as waves. However, the wavelength of electrons is much, much shorter—about 0.5 to 1 nm. This allows electron microscopes to magnify 600–700 times more than light microscopes. This allows us to see even smaller features in a world that is invisible to the naked eye.

(a) A simple light microscope can magnify up to 1,500 times. (b) An electron microscope can magnify up to 1,000,000 times. (c) Flu viruses imaged by an electron microscope. The virus is about 100 nm in diameter.





Atoms act the way they do because of their structure. We already know that atoms are composed of protons, neutrons, and electrons. Protons and neutrons are located in the nucleus, and electrons orbit around the nucleus. But we need to know the structural details to understand why atoms react the way they do.

Virtually everything we know about atoms ultimately comes from light. Before we can understand the composition of atoms (especially electrons), we need to understand the properties of light.

1. LIGHT

LEARNING OBJECTIVES

- 1. Describe light with its frequency and wavelength.
- 2. Describe light as a particle of energy.

wavelength

The distance between corresponding points in two adjacent light cycles.

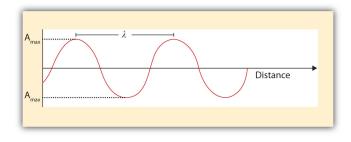
frequency

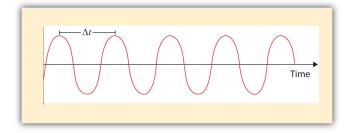
The number of cycles of light that pass a given point in one second.

What we know as light is more properly called *electromagnetic radiation*. We know from experiments that light acts as a wave. As such, it can be described as having a frequency and a wavelength. The **wavelength** of light is the distance between corresponding points in two adjacent light cycles, and the **frequency** of light is the number of cycles of light that pass a given point in one second. Wavelength is typically represented by λ , the lowercase Greek letter *lambda*, while frequency is represented by ν , the lowercase Greek letter *nu* (although it looks like a Roman "vee," it is actually the Greek equivalent of the letter "en"). Wavelength has units of length (meters, centimeters, etc.), while frequency has units of *per second*, written as s⁻¹ and sometimes called a *hertz* (Hz). Figure 8.1 shows how these two characteristics are defined.

FIGURE 8.1 Characteristics of Light Waves

Light acts as a wave and can be described by a wavelength λ and a frequency v.





One property of waves is that their speed is equal to their wavelength times their frequency. That means we have

speed =
$$\lambda \nu$$

For light, however, speed is actually a universal constant when light is traveling through a vacuum (or, to a very good approximation, air). The measured speed of light (c) in a vacuum is 2.9979 × 10⁸ m/s, or about 3.00 × 10⁸ m/s. Thus, we have

$$c = \lambda v$$

Because the speed of light is a constant, the wavelength and the frequency of light are related to each other: as one increases, the other decreases and vice versa. We can use this equation to calculate what one property of light has to be when given the other property.

EXAMPLE 1

What is the frequency of light if its wavelength is 5.55×10^{-7} m?

Solution

We use the equation that relates the wavelength and frequency of light with its speed. We have

$$3.00 \times 10^8 \text{m/s} = (5.55 \times 10^{-7} \text{ m})v$$

We divide both sides of the equation by 5.55×10^{-7} m and get

$$v = 5.41 \times 10^{14} \text{ s}^{-1}$$

Note how the m units cancel, leaving s in the denominator. A unit in a denominator is indicated by a -1 power—s⁻¹—and read as "per second."

Test Yourself

What is the wavelength of light if its frequency is 1.55×10^{10} s⁻¹?

Answei

0.0194 m, or 19.4 mm

Light also behaves like a package of energy. It turns out that for light, the energy of the "package" of energy is proportional to its frequency. (For most waves, energy is proportional to wave amplitude, or the height of the wave.) The mathematical equation that relates the energy (E) of light to its frequency is

$$E = h\nu$$

where v is the frequency of the light, and h is a constant called **Planck's constant**. Its value is 6.626×10^{-34} J·s—a very small number that is another fundamental constant of our universe, like the speed of light. The units on Planck's constant may look unusual, but these units are required so that the algebra works out.

Planck's constant

The proportionality constant between the frequency and the energy of light.

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EXAMPLE 2

What is the energy of light if its frequency is 1.55×10^{10} s⁻¹?

Solution

Using the formula for the energy of light, we have

$$E = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(1.55 \times 10^{10} \text{ s}^{-1})$$

Seconds are in the numerator and the denominator, so they cancel, leaving us with joules, the unit of energy. So

$$E = 1.03 \times 10^{-23} \text{ J}$$

This is an extremely small amount of energy—but this is for only one light wave.

Test Yourself

What is the frequency of a light wave if its energy is 4.156×10^{-20} J?

Answer

 $6.27 \times 10^{13} \, \text{s}^{-1}$

Because a light wave behaves like a little particle of energy, light waves have a particle-type name: the **photon**. It is not uncommon to hear light described as photons.

photon

The name of a wave of light acting as a particle.

electromagnetic spectrum

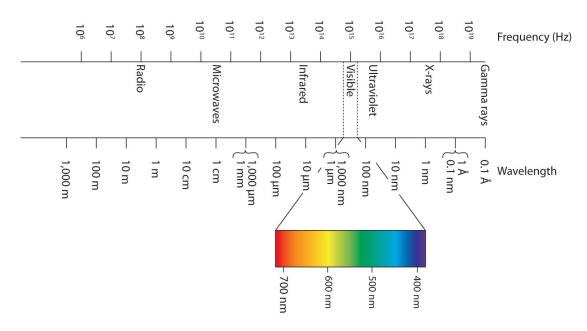
The full span of the possible wavelengths, frequencies, and energies of light.

Wavelengths, frequencies, and energies of light span a wide range; the entire range of possible values for light is called the **electromagnetic spectrum**. We are mostly familiar with visible light, which is light having a wavelength range between about 400 nm and 700 nm. Light can have much longer and much shorter wavelengths than this, with corresponding variations in frequency and energy. Figure 8.2 shows the entire electromagnetic spectrum and how certain regions of the spectrum are labeled. You may already be familiar with some of these regions; they are all light—with different frequencies, wavelengths, and energies.

FIGURE 8.2 The Electromagnetic Spectrum

The electromagnetic spectrum, with its various regions labeled. The borders of each region are approximate.

Electromagnetic Spectrum



KEY TAKEAWAYS

- Light acts like a wave, with a frequency and a wavelength.
- The frequency and wavelength of light are related by the speed of light, a constant.
- Light acts like a particle of energy, whose value is related to the frequency of light.

EXERCISES

- 1. Describe the characteristics of a light wave.
- 2. What is a characteristic of a particle of light?
- 3. What is the frequency of light if its wavelength is 7.33×10^{-5} m?
- 4. What is the frequency of light if its wavelength is 1.226 m?
- 5. What is the frequency of light if its wavelength is 733 nm?
- 6. What is the frequency of light if its wavelength is 8.528 cm?
- 7. What is the wavelength of light if its frequency is $8.19 \times 10^{14} \, \text{s}^{-1}$?

- 8. What is the wavelength of light if its frequency is $3.66 \times 10^6 \text{ s}^{-1}$?
- 9. What is the wavelength of light if its frequency is 1.009×10^6 Hz?
- 10. What is the wavelength of light if its frequency is 3.79×10^{-3} Hz?
- 11. What is the energy of a photon if its frequency is 5.55×10^{13} s⁻¹?
- 12. What is the energy of a photon if its frequency is $2.06 \times 10^{18} \, \text{s}^{-1}$?
- 13. What is the energy of a photon if its wavelength is 5.88×10^{-4} m?
- 14. What is the energy of a photon if its wavelength is 1.888×10^2 m?

ANSWERS

- 1. Light has a wavelength and a frequency.
- 3. $4.09 \times 10^{12} \, \text{s}^{-1}$
- 5. $4.09 \times 10^{14} \, \text{s}^{-1}$

- 7. 3.66×10^{-7} m
- 9. 297 m
- 11. $3.68 \times 10^{-20} \,\mathrm{J}$
- 13. 3.38×10^{-22} J

2. QUANTUM NUMBERS FOR ELECTRONS

LEARNING OBJECTIVES

- 1. Explain what spectra are.
- 2. Learn the quantum numbers that are assigned to electrons.

There are two fundamental ways of generating light: either heat an object up so hot it glows or pass an electrical current through a sample of matter (usually a gas). Incandescent lights and fluorescent lights generate light via these two methods, respectively.

A hot object gives off a continuum of light. We notice this when the visible portion of the electromagnetic spectrum is passed through a prism: the prism separates light into its constituent colors, and all colors are present in a continuous rainbow (part (a) in Figure 8.3). This image is known as a **continuous spectrum**. However, when electricity is passed through a gas and light is emitted and this light is passed though a prism, we see only certain lines of light in the image (part (b) in Figure 8.3). This image is called a **line spectrum**. It turns out that every element has its own unique, characteristic line spectrum.

FIGURE 8.3 Prisms and Light

(a) A glowing object gives off a full rainbow of colors, which are noticed only when light is passed through a prism to make a continuous spectrum. (b) However, when electricity is passed through a gas, only certain colors of light are emitted. Here are the colors of light in the line spectrum of Hg.



(a)



(b)

Why does the light emitted from an electrically excited gas have only certain colors, while light given off by hot objects has a continuous spectrum? For a long time, it was not well explained. Particularly simple was the spectrum of hydrogen gas, which could be described easily by an equation; no other element has a spectrum that is so predictable (Figure 8.4). Late-nineteenth-century scientists found that the positions of the lines obeyed a pattern given by the equation

$$\frac{1}{\lambda} = (109,700 \text{ cm}^{-1}) \left(\frac{1}{4} - \frac{1}{n^2} \right)$$

where n = 3, 4, 5, 6,..., but they could not explain why this was so.

continuous spectrum

An image that contains all colors of light.

line spectrum

An image that contains only certain colors of light.

FIGURE 8.4 Hydrogen Spectrum

The spectrum of hydrogen was particularly simple and could be predicted by a simple mathematical expression.



quantum number

An index that corresponds to a property of an electron, like its energy.

quantized

When a quantity is restricted to having only certain values.

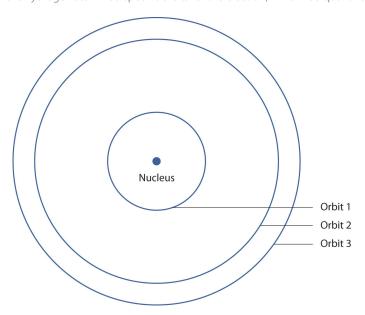
In 1913, the Danish scientist Niels Bohr suggested a reason why the hydrogen atom spectrum looked this way. He suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number n (the same n in the equation above and now called a **quantum number**). Quantities that have certain specific values are called **quantized** values. Bohr suggested that the energy of the electron in hydrogen was quantized because it was in a specific orbit. Because the energies of the electron can have only certain values, the changes in energies can have only certain values (somewhat similar to a staircase: not only are the stair steps set at specific heights but the height between steps is fixed). Finally, Bohr suggested that the energy of light emitted from electrified hydrogen gas was equal to the energy difference of the electron's energy states:

$$E_{\text{light}} = h\nu = \Delta E_{\text{electron}}$$

This means that only certain frequencies (and thus, certain wavelengths) of light are emitted. Figure 8.5 shows a model of the hydrogen atom based on Bohr's ideas.

FIGURE 8.5 Bohr's Model of the Hydrogen Atom

Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.



quantum mechanics

The theory of electrons that treats them as a wave.

Bohr's ideas were useful but were applied only to the hydrogen atom. However, later researchers generalized Bohr's ideas into a new theory called **quantum mechanics**, which explains the behavior of electrons as if they were acting as a wave, not as particles. Quantum mechanics predicts two major things: quantized energies for electrons of all atoms (not just hydrogen) and an organization of electrons within atoms. Electrons are no longer thought of as being randomly distributed around a nucleus or restricted to certain orbits (in that regard, Bohr was wrong). Instead, electrons are collected into groups and subgroups that explain much about the chemical behavior of the atom.

In the quantum-mechanical model of an atom, the state of an electron is described by four quantum numbers, not just the one predicted by Bohr. The first quantum number is called the **principal quantum number** (n). The principal quantum number largely determines the energy of an electron. Electrons in the same atom that have the same principal quantum number are said to occupy an electron **shell** of the atom. The principal quantum number can be any nonzero positive integer: 1, 2, 3, 4,....

Within a shell, there may be multiple possible values of the next quantum number, the **angular momentum quantum number** (ℓ). The ℓ quantum number has a minor effect on the energy of the electron but also affects the spatial distribution of the electron in three-dimensional space—that is, the shape of an electron's distribution in space. The value of the ℓ quantum number can be any integer between 0 and n-1:

$$\ell = 0, 1, 2, ..., n - 1$$

Thus, for a given value of n, there are different possible values of ℓ :

If <i>n</i> equals	ℓ can be
1	0
2	0 or 1
3	0, 1, or 2
4	0, 1, 2, or 3

and so forth. Electrons within a shell that have the same value of ℓ are said to occupy a **subshell** in the atom. Commonly, instead of referring to the numerical value of ℓ , a letter represents the value of ℓ (to help distinguish it from the principal quantum number):

If ℓ equals	The letter is
0	S
1	р
2	d
3	f

The next quantum number is called the **magnetic quantum number** (m_{ℓ}) . For any value of ℓ , there are $2\ell + 1$ possible values of m_{ℓ} , ranging from $-\ell$ to ℓ :

$$-\ell \leq m\ell \leq \ell$$

or

$$\mid m_{\ell} \mid \leq \ell$$

The following explicitly lists the possible values of m_{ℓ} for the possible values of ℓ :

If & equals	The m_ℓ values can be
0	0
1	-1, 0, or 1
2	-2, -1, 0, 1, or 2
3	-3, -2, -1, 0, 1, 2, or 3

The particular value of m_ℓ dictates the orientation of an electron's distribution in space. When ℓ is zero, m_ℓ can be only zero, so there is only one possible orientation. When ℓ is 1, there are three possible orientations for an electron's distribution. When ℓ is 2, there are five possible orientations of electron distribution. This goes on and on for other values of ℓ , but we need not consider any higher values of ℓ here. Each value of m_ℓ designates a certain **orbital**. Thus, there is only one orbital when ℓ is zero, three orbitals when ℓ is 1, five orbitals when ℓ is 2, and so forth. The m_ℓ quantum number has no effect on the energy of an electron unless the electrons are subjected to a magnetic field—hence its name.

The ℓ quantum number dictates the general shape of electron distribution in space (Figure 8.6). Any s orbital is spherically symmetric (part (a) in Figure 8.6), and there is only one orbital in any s subshell. Any p orbital has a two-lobed, dumbbell-like shape (part (b) in Figure 8.6); because there are

principal quantum number

The index that largely determines the energy of an electron in an atom.

Represented by n.

shell

A term used to describe electrons with the same principal quantum number.

angular momentum quantum number

An index that affects the energy and the spatial distribution of an electron in an atom. Represented by ℓ .

subshell

A term used to describe electrons in a shell that have the same angular momentum quantum number.

magnetic quantum number

The index that determines the orientation of the electron's spatial distribution.

Represented by m_ℓ .

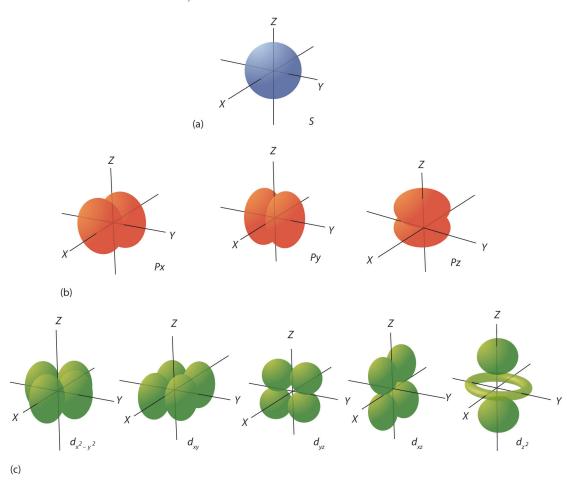
orbital

The specific set of principal, angular momentum, and magnetic quantum numbers for an electron.

three of them, we normally represent them as pointing along the x-, y-, and z-axes of Cartesian space. The d orbitals are four-lobed rosettes (part (c) in Figure 8.6); they are oriented differently in space (the one labeled d_z^2 has two lobes and a torus instead of four lobes, but it is equivalent to the other orbitals). When there is more than one possible value of m_ℓ , each orbital is labeled with one of the possible values. It should be noted that the diagrams in Figure 8.6 are estimates of the electron distribution in space, not surfaces electrons are fixed on.

FIGURE 8.6 Electron Orbitals

(a) The lone s orbital is spherical in distribution. (b) The three p orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five d orbitals are rosette in shape, except for the $d = \frac{d}{z^2}$ orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.



spin quantum number

The index that indicates one of two spin states for an electron. Represented by $m_{
m S}$.

The final quantum number is the **spin quantum number** (m_s). Electrons and other subatomic particles behave as if they are spinning (we cannot tell if they really are, but they behave as if they are). Electrons themselves have two possible spin states, and because of mathematics, they are assigned the quantum numbers +1/2 and -1/2. These are the only two possible choices for the spin quantum number of an electron.

EXAMPLE 3

Of the set of quantum numbers $\{n, \ell, m_\ell, m_s\}$, which are possible and which are not allowed?

- 1. {3, 2, 1, +1/2}
- 2. $\{2, 2, 0, -1/2\}$
- 3. $\{3, -1, 0, +1/2\}$

Solution

- 1. The principal quantum number n must be an integer, which it is here. The quantum number ℓ must be less than n, which it is. The m_{ℓ} quantum number must be between $-\ell$ and ℓ , which it is. The spin quantum number is +1/2, which is allowed. Because this set of quantum numbers follows all restrictions, it is possible.
- 2. The quantum number n is an integer, but the quantum number ℓ must be less than n, which it is not. Thus, this is not an allowed set of quantum numbers.
- 3. The principal quantum number n is an integer, but ℓ is not allowed to be negative. Therefore this is not an allowed set of quantum numbers.

Test Yourself

Of the set of quantum numbers $\{n, \ell, m_\ell, m_s\}$, which are possible and which are not allowed?

- 1. $\{4, 2, -2, 1\}$
- 2. $\{3, 1, 0, -1/2\}$

Answers

- 1. Spin must be either +1/2 or -1/2, so this set of quantum number is not allowed.
- 2. allowed

Chemistry Is Everywhere: Neon Lights

A neon light is basically an electrified tube with a small amount of gas in it. Electricity excites electrons in the gas atoms, which then give off light as the electrons go back into a lower energy state. However, many so-called "neon" lights don't contain neon!

Although we know now that a gas discharge gives off only certain colors of light, without a prism or other component to separate the individual light colors, we see a composite of all the colors emitted. It is not unusual for a certain color to predominate. True neon lights, with neon gas in them, have a reddish-orange light due to the large amount of red-, orange-, and yellow-colored light emitted. However, if you use krypton instead of neon, you get a whitish light, while using argon yields a blue-purple light. A light filled with nitrogen gas glows purple, as does a helium lamp. Other gases—and mixtures of gases—emit other colors of light. Ironically, despite its importance in the development of modern electronic theory, hydrogen lamps emit little visible light and are rarely used for illumination purposes.

The different colors of these "neon" lights are caused by gases other than neon in the discharge tubes.



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KEY TAKEAWAYS

- Electrons in atoms have quantized energies.
- The state of electrons in atoms is described by four quantum numbers.

EXERCISES

- 1. Differentiate between a continuous spectrum and a line spectrum.
- 2. Under what circumstances is a continuous spectrum formed? Under what circumstances is a line spectrum formed?
- 3. What is the wavelength of light from the hydrogen atom spectrum when n = 3?
- 4. What is the wavelength of light from the hydrogen atom spectrum when n = 5?
- 5. What are the restrictions on the principal quantum number?
- 6. What are the restrictions on the angular momentum quantum number?
- 7. What are the restrictions on the magnetic quantum number?
- 8. What are the restrictions on the spin quantum number?

- 9. What are the possible values for ℓ when n = 5?
- 10. What are the possible values for ℓ when n = 1?
- 11. What are the possible values for $m\ell$ when $\ell = 3$?
- 12. What are the possible values for $m\ell$ when $\ell = 6$?
- 13. Describe the shape of an s orbital.
- 14. Describe the shape of a *p* orbital.
- 15. Which of these sets of quantum numbers is allowed? If it is not, explain why.
 - a. $\{4, 1, -2, +1/2\}$
 - b. $\{2, 0, 0, -1/2\}$
- 16. Which of these sets of quantum numbers is allowed? If it is not, explain why.
 - a. $\{5, 2, -1, -1/2\}$
 - b. $\{3, -1, -1, -1/2\}$

ANSWERS

- A continuous spectrum is a range of light frequencies or wavelengths; a line spectrum shows only certain frequencies or wavelengths.
- 3. 6.56×10^{-7} m, or 656 nm
- The principal quantum number is restricted to being a positive whole number.

- 7. The absolute value of $m\ell$ must be less than or equal to ℓ : $|m\ell| \le \ell$.
- 9. l can be 0, 1, 2, 3, or 4.
- 11. $m\ell$ can be -3, -2, -1, 0, 1, 2, or 3.
- 13. An s orbital is spherical in shape.
- a. Because |mℓ| must be less than ℓ, this set of quantum numbers is not allowed.
 - b. allowed

3. ORGANIZATION OF ELECTRONS IN ATOMS

LEARNING OBJECTIVES

- 1. Learn how electrons are organized in atoms.
- 2. Represent the organization of electrons by an electron configuration.

Pauli exclusion principle

No two electrons in an atom can have the same set of four quantum numbers.

Now that you know that electrons have quantum numbers, how are they arranged in atoms? The key to understanding electronic arrangement is summarized in the **Pauli exclusion principle**: no two electrons in an atom can have the same set of four quantum numbers. This dramatically limits the number of electrons that can exist in a shell or a subshell.

Electrons are typically organized around an atom by starting at the lowest possible quantum numbers first, which are the shells-subshells with lower energies. Consider H, an atom with a single electron only. Under normal conditions, the single electron would go into the n = 1 shell, which has only a single s subshell with one orbital (because m_{ℓ} can equal only 0). The convention is to label the shell-subshell combination with the number of the shell and the letter that represents the subshell. Thus, the

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electron goes in the 1s shell-subshell combination. It is usually not necessary to specify the m_{ℓ} or $m_{\rm S}$ quantum numbers, but for the H atom, the electron has $m_{\ell} = 0$ (the only possible value) and an $m_{\rm S}$ of either +1/2 or -1/2.

The He atom has two electrons. The second electron can also go into the 1s shell-subshell combination but only if its spin quantum number is different from the first electron's spin quantum number. Thus, the sets of quantum numbers for the two electrons are $\{1, 0, 0, +1/2\}$ and $\{1, 0, 0, -1/2\}$. Notice that the overall set is different for the two electrons, as required by the Pauli exclusion principle.

The next atom is Li, with three electrons. However, now the Pauli exclusion principle implies that we cannot put that electron in the 1s shell-subshell because no matter how we try, this third electron would have the same set of four quantum numbers as one of the first two electrons. So this third electron must be assigned to a different shell-subshell combination. However, the n=1 shell doesn't have another subshell; it is restricted to having just $\ell=0$, or an s subshell. Therefore, this third electron has to be assigned to the n=2 shell, which has an s ($\ell=0$) subshell and a p ($\ell=1$) subshell. Again, we usually start with the lowest quantum number, so this third electron is assigned to the 2s shell-subshell combination of quantum numbers.

The Pauli exclusion principle has the net effect of limiting the number of electrons that can be assigned a shell-subshell combination of quantum numbers. For example, in any s subshell, no matter what the shell number, there can be a maximum of only two electrons. Once the s subshell is filled up, any additional electrons must go to another subshell in the shell (if it exists) or to higher-numbered shell. A similar analysis shows that a p subshell can hold a maximum of six electrons. A d subshell can hold a maximum of 10 electrons, while an f subshell can have a maximum of 14 electrons. By limiting subshells to these maxima, we can distribute the available electrons to their shells and subshells.

EXAMPLE 4

How would the six electrons for C be assigned to the n and ℓ quantum numbers?

Solution

The first two electrons go into the 1s shell-subshell combination. Two additional electrons can go into the 2s shell-subshell, but now this subshell is filled with the maximum number of electrons. The n=2 shell also has a p subshell, so the remaining two electrons can go into the 2p subshell. The 2p subshell is not completely filled because it can hold a maximum of six electrons.

Test Yourself

How would the 11 electrons for Na be assigned to the n and ℓ quantum numbers?

Answe

two 1s electrons, two 2s electrons, six 2p electrons, and one 3s electron

Now that we see how electrons are partitioned among the shells and subshells, we need a more concise way of communicating this partitioning. Chemists use an **electron configuration** to represent the organization of electrons in shells and subshells in an atom. An electron configuration simply lists the shell and subshell labels, with a right superscript giving the number of electrons in that subshell. The shells and subshells are listed in the order of filling.

For example, an H atom has a single electron in the 1s subshell. Its electron configuration is

H: $1s^1$

He has two electrons in the 1s subshell. Its electron configuration is

He: $1s^2$

The three electrons for Li are arranged in the 1s subshell (two electrons) and the 2s subshell (one electron). The electron configuration of Li is

Li: $1s^2 2s^1$

Be has four electrons, two in the 1s subshell and two in the 2s subshell. Its electron configuration is

Be: $1s^2 2s^2$

Now that the 2s subshell is filled, electrons in larger atoms must go into the 2p subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2p subshell:

electron configuration

The representation of the organization of electrons in shells and subshells in an atom.

B: $1s^2 2s^2 2p^1$

C: $1s^2 2s^2 2p^2$

N: $1s^2 2s^2 2p^3$

O: $1s^2 2s^2 2p^4$

F: $1s^2 2s^2 2p^5$

Ne: $1s^2 2s^2 2p^6$

Now that the 2p subshell is filled (all possible subshells in the n = 2 shell), the next electron for the next-larger atom must go into the n = 3 shell, s subshell.

EXAMPLE 5

What is the electron configuration for Na, which has 11 electrons?

Solution

The first two electrons occupy the 1s subshell. The next two occupy the 2s subshell, while the next six electrons occupy the 2p subshell. This gives us 10 electrons so far, with 1 electron left. This last electron goes into the n = 3 shell, s subshell. Thus, the electron configuration of Na is $1s^22s^22p^63s^1$.

Test Yourself

What is the electron configuration for Mg, which has 12 electrons?

Answer

 $1s^22s^22p^63s^2$

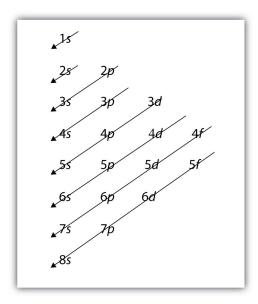
For larger atoms, the electron arrangement becomes more complicated. This is because after the 3p subshell is filled, filling the 4s subshell first actually leads to a lesser overall energy than filling the 3d subshell. Recall that while the principal quantum number largely dictates the energy of an electron, the angular momentum quantum number also has an impact on energy; by the time we get to the 3d and 4s subshells, we see overlap in the filling of the shells. Thus, after the 3p subshell is completely filled (which occurs for Ar), the next electron for K occupies the 4s subshell, not the 3d subshell:

$$\text{K: } 1s^22s^22p^63s^23p^64s^1, not \ 1s^22s^22p^63s^23p^63d^1$$

For larger and larger atoms, the order of filling the shells and subshells seems to become even more complicated. There are some useful ways to remember the order, like that shown in Figure 8.7. If you follow the arrows in order, they pass through the subshells in the order that they are filled with electrons in larger atoms. Initially, the order is the same as the expected shell-subshell order, but for larger atoms, there is some shifting around of the principal quantum numbers. However, Figure 8.7 gives a valid ordering of filling subshells with electrons for most atoms.

FIGURE 8.7 Electron Shell Filling Order

Starting with the top arrow, follow each arrow. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms. The n = 5 and higher shells have more subshells, but only those subshells that are needed to accommodate the electrons of the known elements are given.



EXAMPLE 6

What is the predicted electron configuration for Sn, which has 50 electrons?

Solution

We will follow the chart in Figure 8.7 until we can accommodate 50 electrons in the subshells in the proper order:

Sn:
$$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^2$$

Verify by adding the superscripts, which indicate the number of electrons: 2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 10 + 2 = 50, so we have placed all 50 electrons in subshells in the proper order.

Test Yourself

What is the electron configuration for Ba, which has 56 electrons?

Answe

 $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^2$

As the previous example demonstrated, electron configurations can get fairly long. An **abbreviated electron configuration** uses one of the elements from the last column of the periodic table, which contains what are called the *noble gases*, to represent the core of electrons up to that element. Then the remaining electrons are listed explicitly. For example, the abbreviated electron configuration for Li, which has three electrons, would be

where [He] represents the two-electron core that is equivalent to He's electron configuration. The square brackets represent the electron configuration of a noble gas. This is not much of an abbreviation. However, consider the abbreviated electron configuration for W, which has 74 electrons:

W:
$$[Xe]6s^24f^{14}5d^4$$

This is a significant simplification over an explicit listing of all 74 electrons. So for larger elements, the abbreviated electron configuration can be a very useful shorthand.

abbreviated electron configuration

An electron configuration that uses one of the noble gases to represent the core of electrons up to that element.

EXAMPLE 7

What is the abbreviated electron configuration for P, which has 15 electrons?

Solution

With 15 electrons, the electron configuration of P is

P:
$$1s^22s^22p^63s^23p^3$$

The first immediate noble gas is Ne, which has an electron configuration of $1s^22s^22p^6$. Using the electron configuration of Ne to represent the first 10 electrons, the abbreviated electron configuration of P is

P: [Ne]
$$3s^23p^3$$

Test Yourself

What is the abbreviated electron configuration for Rb, which has 37 electrons?

Answer

 $[Kr]5s^1$

There are some exceptions to the rigorous filling of subshells by electrons. In many cases, an electron goes from a higher-numbered shell to a lower-numbered but later-filled subshell to fill the later-filled subshell. One example is Ag. With 47 electrons, its electron configuration is predicted to be

Ag:
$$[Kr]5s^24d^9$$

However, experiments have shown that the electron configuration is actually

Ag:
$$[Kr]5s^14d^{10}$$

This, then, qualifies as an exception to our expectations. At this point, you do not need to memorize the exceptions; but if you come across one, understand that it is an exception to the normal rules of filling subshells with electrons, which can happen.

KEY TAKEAWAYS

- The Pauli exclusion principle limits the number of electrons in the subshells and shells.
- Electrons in larger atoms fill shells and subshells in a regular pattern that we can follow.
- Electron configurations are a shorthand method of indicating what subshells electrons occupy in atoms.
- Abbreviated electron configurations are a simpler way of representing electron configurations for larger atoms.
- Exceptions to the strict filling of subshells with electrons occur.

EXERCISES

- 1. Give two possible sets of four quantum numbers for the electron in an H atom.
- 2. Give the possible sets of four quantum numbers for the electrons in a Li atom.
- 3. How many subshells are completely filled with electrons for Na? How many subshells are unfilled?
- 4. How many subshells are completely filled with electrons for Mg? How many subshells are unfilled?
- 5. What is the maximum number of electrons in the entire n = 2 shell?

- 6. What is the maximum number of electrons in the entire *n* = 4 shell?
- 7. Write the complete electron configuration for each atom.
 - a. Si, 14 electrons
 - b. Sc, 21 electrons
- 8. Write the complete electron configuration for each atom.
 - a. Br, 35 electrons
 - b. Be, 4 electrons
- 9. Write the complete electron configuration for each atom.
 - a. Cd, 48 electrons
 - b. Mg, 12 electrons

- 10. Write the complete electron configuration for each atom.
 - a. Cs, 55 electrons
 - b. Ar, 18 electrons
- 11. Write the abbreviated electron configuration for each atom in Exercise 7.
- 12. Write the abbreviated electron configuration for each atom in Exercise 8.
- 13. Write the abbreviated electron configuration for each atom in Exercise 9.
- 14. Write the abbreviated electron configuration for each atom in Exercise 10.

ANSWERS

- 1. {1, 0, 0, 1/2} and [1, 0, 0, -1/2}
- 3. Three subshells (1s, 2s, 2p) are completely filled, and one shell (3s) is partially filled.
- 5. 8 electrons
- 7. a. $1s^2 2s^2 2p^6 3s^2 3p^2$
 - b. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

- 9. a. $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}$
 - b. $1s^2 2s^2 2p^6 3s^2$
- 11. a. [Ne] $3s^23p^2$
 - b. [Ar]4s²3d¹
- 13. a. $[Kr]5s^24d^{10}$
 - b. [Ne]3s²

4. ELECTRONIC STRUCTURE AND THE PERIODIC TABLE

LEARNING OBJECTIVES

- 1. Relate the electron configurations of the elements to the shape of the periodic table.
- 2. Determine the expected electron configuration of an element by its place on the periodic table.

In Chapter 3, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure 8.8. The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.

FIGURE 8.8 The Periodic Table

1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be _{9.012182}											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne ^{20.1797}
11 Na 22.989770	12 Mg _{24.3050}											13 A I _{26.581538}	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc _{44.955910}	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge _{72.61}	33 As 74.92160	34 Se _{78.96}	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 TC (98)	Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 r 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 TI 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db	106 Sg (263)	107 Bh	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112		114 (289) (287)		116 (289)		118

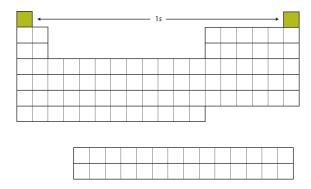
58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.116	140.50765	144.24	(145)	150.36	151.964	157.25	158.92534	162.50	164.93032	167.26	168.93421	173.04	174.967
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.0381	^{231.035888}	238.0289	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)

Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations: *the shape of the periodic table mimics the filling of the subshells with electrons*.

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the n = 1 shell is filled. These two elements make up the first row of the periodic table (see Figure 8.9).

FIGURE 8.9 The 1s Subshell

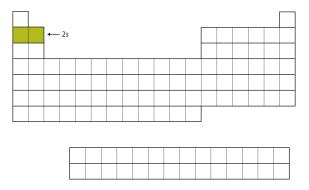
H and He represent the filling of the 1s subshell.



The next two electrons, for Li and Be, would go into the 2s subshell. Figure 8.10 shows that these two elements are adjacent on the periodic table.

FIGURE 8.10 The 2s Subshell

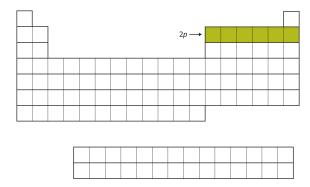
In Li and Be, the 2s subshell is being filled.



For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 8.11).

FIGURE 8.11 The 2p Subshell

For B through Ne, the 2p subshell is being occupied.

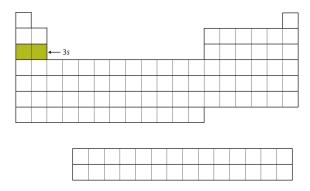


The next subshell to be filled is the 3s subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 8.12).

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FIGURE 8.12 The 3s Subshell

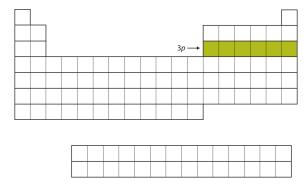
Now the 3s subshell is being occupied.



Next, the 3*p* subshell is filled with the next six elements (Figure 8.13).

FIGURE 8.13 The 3p Subshell

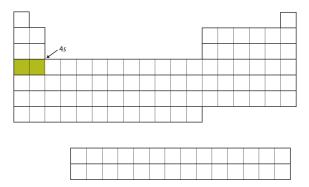
Next, the 3p subshell is filled with electrons.



Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 8.14).

FIGURE 8.14 The 4s Subshell

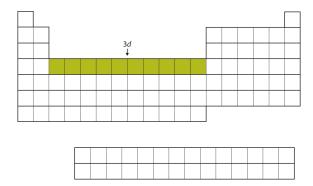
The 4s subshell is filled before the 3d subshell. This is reflected in the structure of the periodic table.



After the 4s subshell is filled, the 3d subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure 8.15).

FIGURE 8.15 The 3d Subshell

The 3d subshell is filled in the middle section of the periodic table.

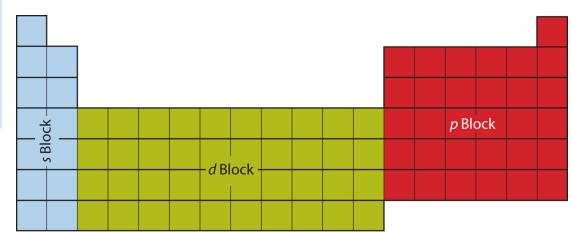


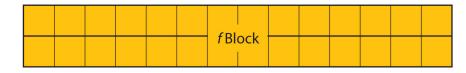
And so forth. As we go across the rows of the periodic table, the overall shape of the table outlines how the electrons are occupying the shells and subshells.

The first two columns on the left side of the periodic table are where the s subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the s block. Similarly, the p block are the right-most six columns of the periodic table, the d block is the middle 10 columns of the periodic table, while the f block is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 8.16 shows the blocks of the periodic table.

FIGURE 8.16 Blocks on the Periodic Table

The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.





s block

The columns of the periodic table in which ^{\$\mathbf{S}\$} subshells are being occupied.

p block

The columns of the periodic table in which ${\cal P}$ subshells are being occupied.

d block

The columns of the periodic table in which d subshells are being occupied.

f block

The columns of the periodic table in which f subshells are being occupied.

valence electrons

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell.

valence shell

The highest-numbered shell in an atom that contains electrons.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

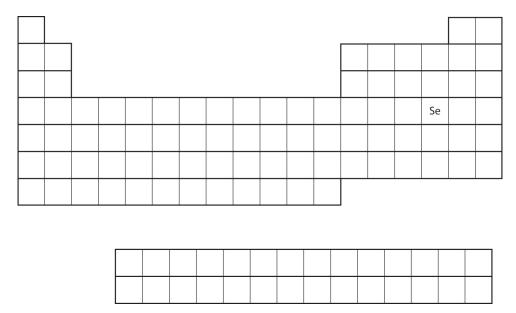
H:	1s ¹
Li:	1s ² 2s ¹
Na:	[Ne]3s ¹
K:	[Ar] 4s 1
Rb:	[Kr] 5s 1
Cs:	[Xe] 6s 1

They all have a similar electron configuration in their valence shells: a single *s* electron. Because much of the chemistry of an element is influenced by valence electrons, we would expect that these elements would have similar chemistry—*and they do*. The organization of electrons in atoms explains not only the shape of the periodic table but also the fact that elements in the same column of the periodic table have similar chemistry.

The same concept applies to the other columns of the periodic table. Elements in each column have the same valence shell electron configurations, and the elements have some similar chemical properties. This is strictly true for all elements in the s and p blocks. In the d and f blocks, because there are exceptions to the order of filling of subshells with electrons, similar valence shells are not absolute in these blocks. However, many similarities do exist in these blocks, so a similarity in chemical properties is expected.

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 8.17. It is in the fourth column of the p block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^23d^{10}4p^4$, as expected.

FIGURE 8.17 Selenium on the Periodic Table



EXAMPLE 8

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. See Figure 8.18.

- 1. Ca
- 2. Sn

Solution

- 1. Ca is located in the second column of the s block. We would expect that its electron configuration should end with s^2 . Calcium's electron configuration is $[Ar]4s^2$.
- 2. Sn is located in the second column of the p block, so we expect that its electron configuration would end in p^2 . Tin's electron configuration is [Kr]5 $s^24d^{10}5p^2$.

Test Yourself

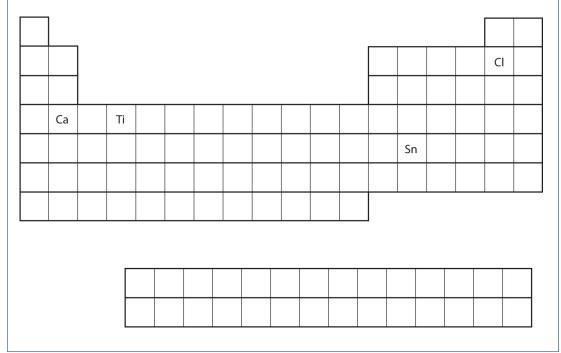
From the element's position on the periodic table, predict the valence shell electron configuration for each atom. See Figure 8.18.

- 1. Ti
- 2. Cl

Answer

- 1. $[Ar]4s^23d^2$
- 2. [Ne] $3s^23p^5$

Various Elements on the Periodic Table



Food and Drink App: Artificial Colors

The color of objects comes from a different mechanism than the colors of neon and other discharge lights. Although colored lights produce their colors, objects are colored because they preferentially reflect a certain color from the white light that shines on them. A red tomato, for example, is bright red because it reflects red light while absorbing all the other colors of the rainbow.

Many foods, such as tomatoes, are highly colored; in fact, the common statement "you eat with your eyes first" is an implicit recognition that the visual appeal of food is just as important as its taste. But what about processed foods?

Many processed foods have food colorings added to them. There are two types of food colorings: natural and artificial. Natural food colorings include caramelized sugar for brown; annatto, turmeric, and saffron for various shades of orange or yellow; betanin from beets for purple; and even carmine, a deep red dye that is extracted from the cochineal, a small insect that is a parasite on cacti in Central and South America. (That's right: you may be eating bug juice!)

Some colorings are artificial. In the United States, the Food and Drug Administration currently approves only seven compounds as artificial colorings in food, beverages, and cosmetics:

- 1. FD&C Blue #1: Brilliant Blue FCF
- 2. FD&C Blue #2: Indigotine
- 3. FD&C Green #3: Fast Green FCF
- 4. RD&C Red #3: Erythrosine
- 5. FD&C Red #40: Allura Red AC
- 6. FD&C Yellow #5: Tartrazine
- 7. FD&C Yellow #6: Sunset Yellow FCF

Lower-numbered colors are no longer on the market or have been removed for various reasons. Typically, these artificial colorings are large molecules that absorb certain colors of light very strongly, making them useful even at very low concentrations in foods and cosmetics. Even at such low amounts, some critics claim that a small portion of the population (especially children) is sensitive to artificial colorings and urge that their use be curtailed or halted. However, formal studies of artificial colorings and their effects on behavior have been inconclusive or contradictory. Despite this, most people continue to enjoy processed foods with artificial coloring (like those shown in the accompanying figure).

Artificial food colorings are found in a variety of food products, such as processed foods, candies, and egg dyes. Even pet foods have artificial food coloring in them, although it's likely that the animal doesn't care!



Source: Photo courtesy of Matthew Bland, http://www.flickr.com/photos/matthewbland/3111904731.

KEY TAKEAWAYS

- The arrangement of electrons in atoms is responsible for the shape of the periodic table.
- Electron configurations can be predicted by the position of an atom on the periodic table.

EXERCISES

- 1. Where on the periodic table are s subshells being occupied by electrons?
- 2. Where on the periodic table are *d* subshells being occupied by electrons?
- 3. In what block is Ra found?
- 4. In what block is Br found?
- 5. What are the valence shell electron configurations of the elements in the second column of the periodic table?
- 6. What are the valence shell electron configurations of the elements in the nextto-last column of the periodic table?
- 7. What are the valence shell electron configurations of the elements in the first column of the *p* block?
- 8. What are the valence shell electron configurations of the elements in the last column of the *p* block?
- 9. From the element's position on the periodic table, predict the electron configuration of each atom.
 - a. Sr
 - b. S

- 10. From the element's position on the periodic table, predict the electron configuration of each atom.
 - a. Fe
 - b. Ba
- 11. From the element's position on the periodic table, predict the electron configuration of each atom.
 - a. V
 - b. Ar
- 12. From the element's position on the periodic table, predict the electron configuration of each atom.
 - a. Cl
 - b. K
- 13. From the element's position on the periodic table, predict the electron configuration of each atom.
 - a. Ge
 - b. C
- 14. From the element's position on the periodic table, predict the electron configuration of each atom.
 - a. Mg
 - b. I

ANSWERS

- 1. the first two columns
- 3. the s block
- 5. ns²
- 7. ns^2np^1

- 9. a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$
 - b. $1s^2 2s^2 2p^6 3s^2 3p^4$
- 11. a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
 - b. $1s^2 2s^2 2p^6 3s^2 3p^6$
- 13. a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$
 - b. $1s^2 2s^2 2p^2$

5. PERIODIC TRENDS

LEARNING OBJECTIVE

1. Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

periodic trends

Variation of properties versus position on the periodic table.

atomic radius

An indication of the size of the atom.

One of the reasons the periodic table is so useful is because its structure allows us to qualitatively determine how some properties of the elements vary versus their position on the periodic table. The variation of properties versus position on the periodic table is called **periodic trends**. There is no other tool in science that allows us to judge relative properties of a class of objects like this, which makes the periodic table a very useful tool. Many periodic trends are general. There may be a few points where an opposite trend is seen, but there is an overall trend when considered across a whole row or down a whole column of the periodic table.

The first periodic trend we will consider atomic radius. The **atomic radius** is an indication of the size of an atom. Although the concept of a definite radius of an atom is a bit fuzzy, atoms behave as if they have a certain radius. Such radii can be estimated from various experimental techniques, such as the x-ray crystallography of crystals.

As you go down a column of the periodic table, the atomic radii increase. This is because the valence electron shell is getting a larger and there is a larger principal quantum number, so the valence shell lies physically farther away from the nucleus. This trend can be summarized as follows:

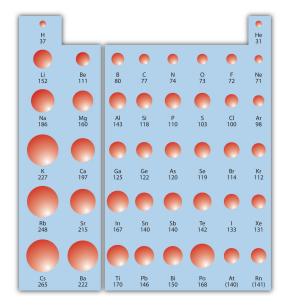
where PT stands for periodic table. Going across a row on the periodic table, left to right, the trend is different. This is because although the valence shell maintains the same principal quantum number, the number of protons—and hence the nuclear charge—is increasing as you go across the row. The increasing positive charge casts a tighter grip on the valence electrons, so as you go across the periodic table, the atomic radii decrease. Again, we can summarize this trend as follows:

as
$$\Rightarrow$$
 PT, atomic radius \downarrow

Figure 8.19 shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

FIGURE 8.19 Atomic Radii Trends on the Periodic Table

Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.



EXAMPLE 9

Referring only to a periodic table and not to Figure 8.19, which atom is larger in each pair?

- 1. Si or S
- 2. S or Te

Solution

- 1. Si is to the left of S on the periodic table, so it is larger because as you go across the row, the atoms get smaller.
- 2. S is above Te on the periodic table, so Te is larger because as you go down the column, the atoms get larger.

Test Yourself

Referring only to a periodic table and not to Figure 8.19, which atom is smaller, Ca or Br?

Answer

Br

ionization energy (IE)

The amount of energy required to remove an electron from an atom in the gas phase.

Ionization energy (IE) is the amount of energy required to remove an electron from an atom in the gas phase:

$$A(g) \rightarrow A^+(g) + e^ \Delta H \equiv IE$$

IE is usually expressed in kJ/mol of atoms. It is always positive because the removal of an electron always requires that energy be put in (i.e., it is endothermic). IE also shows periodic trends. As you go down the periodic table, it becomes easier to remove an electron from an atom (i.e., IE decreases) because the valence electron is farther away from the nucleus. Thus,

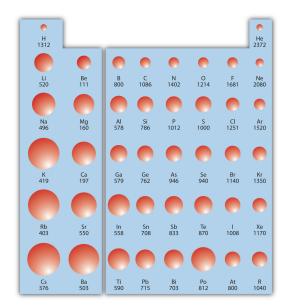
However, as you go across the periodic table and the electrons get drawn closer in, it takes more energy to remove an electron; as a result, IE increases:

as
$$\rightarrow$$
 PT, IE \uparrow

Figure 8.20 shows values of IE versus position on the periodic table. Again, the trend isn't absolute, but the general trends going across and down the periodic table should be obvious.

FIGURE 8.20 Ionization Energy on the Periodic Table

Values are in kJ/mol.



IE also shows an interesting trend within a given atom. This is because more than one IE can be defined by removing successive electrons (if the atom has them to begin with):

$$A(g) \rightarrow A^{+}(g) + e^{-} IE_{1}$$

 $A^{+}(g) \rightarrow A^{2+}(g) + e^{-} IE_{2}$
 $A^{2+}(g) \rightarrow A^{3+}(g) + e^{-} IE_{3}$

and so forth.

Each successive IE is larger than the previous because an electron is being removed from an atom with a progressively larger positive charge. However, IE takes a large jump when a successive ionization goes down into a new shell. For example, the following are the first three IEs for Mg, whose electron configuration is $1s^22s^22p^63s^2$:

$$Mg(g) \rightarrow Mg^{+}(g) + e^{-} IE_{1} = 738 \text{ kJ/mol}$$

 $Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-} IE_{2} = 1,450 \text{ kJ/mol}$
 $Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^{-} IE_{3} = 7,734 \text{ kJ/mol}$

The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first two electrons are removed from the 3s subshell, but the third electron has to be removed from the n=2 shell (specifically, the 2p subshell, which is lower in energy than the n=3 shell). Thus, it takes much more energy than just overcoming a larger ionic charge would suggest. It is trends like this that demonstrate that electrons are organized in atoms in groups.

EXAMPLE 10

Which atom in each pair has the larger IE?

- 1. Ca or Sr
- 2. K or K⁺

Solution

- 1. Because Sr is below Ca on the periodic table, it is easier to remove an electron from it; thus, Ca has the higher IE.
- 2. Because K⁺ has a positive charge, it will be harder to remove another electron from it, so its IE is larger than that of K. Indeed, it will be significantly larger because the next electron in K⁺ to be removed comes from another shell.

Test Yourself

Which atom has the lower ionization energy, C or F?

Answer

 C

The opposite of IE is described by **electron affinity** (EA), which is the energy change when a gasphase atom accepts an electron:

$$A(g) + e^{-} \rightarrow A^{-}(g)$$
 $\Delta H \equiv EA$

EA is also usually expressed in kJ/mol. EA also demonstrates some periodic trends, although they are less obvious than the other periodic trends discussed previously. Generally, as you go across the periodic table, EA increases its magnitude:

as
$$\Rightarrow$$
 PT, EA \uparrow

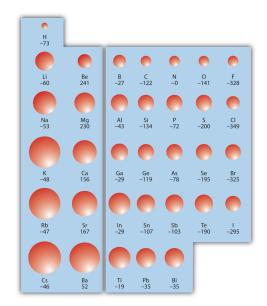
There is not a definitive trend as you go down the periodic table; sometimes EA increases, sometimes it decreases. Figure 8.21 shows EA values versus position on the periodic table for the *s*- and *p*-block elements. The trend isn't absolute, especially considering the large positive EA values for the second column. However, the general trend going across the periodic table should be obvious.

electron affinity (EA)

The energy change when a gas-phase atom accepts an electron.

FIGURE 8.21 Electron Affinity on the Periodic Table

Values are in kJ/mol.



EXAMPLE 11

Predict which atom in each pair will have the highest magnitude of EA.

- 1. CorF
- 2. Na or S

Solution

- 1. C and F are in the same row on the periodic table, but F is farther to the right. Therefore, F should have the larger magnitude of EA.
- 2. Na and S are in the same row on the periodic table, but S is farther to the right. Therefore, S should have the larger magnitude of EA.

Test Yourself

Predict which atom will have the highest magnitude of EA, As or Br.

Answer

Br

KEY TAKEAWAY

 Certain properties—notably atomic radius, IE, and EA—can be qualitatively understood by the positions of the elements on the periodic table.

EXERCISES

- 1. Write a chemical equation with an IE energy change.
- 2. Write a chemical equation with an EA energy change.
- 3. State the trends in atomic radii as you go across and down the periodic table.
- 4. State the trends in IE as you go across and down the periodic table.

- 5. Which atom of each pair is larger?
 - a. Na or Cs
 - b. Nor Bi
- 6. Which atom of each pair is larger?
 - a. C or Ge
 - b. Be or Ba
- 7. Which atom of each pair is larger?
 - a. Kor Cl
 - b. Ba or Bi

- 8. Which atom of each pair is larger?
 - a. Si or S
 - b. H or He
- 9. Which atom has the higher IE?
 - a. Na or S
 - b. Ge or Br
- 10. Which atom has the higher IE?
 - a. C or Ne
 - b. Rb or I
- 11. Which atom has the higher IE?
 - a. Li or Cs
 - b. Se or O
- 12. Which atom has the higher IE?
 - a. Al or Ga
 - b. For I
- 13. A third-row element has the following successive IEs: 738; 1,450; 7,734; and 10,550 kJ/mol. Identify the element.

- 14. A third-row element has the following successive IEs: 1,012; 1,903; 2,912; 4,940; 6,270; and 21,300 kJ/mol. Identify the element.
- 15. For which successive IE is there a large jump in IE for Ca?
- 16. For which successive IE is there a large jump in IE for Al?
- 17. Which atom has the greater magnitude of EA?
 - a. C or F
 - b. Al or Cl
- 18. Which atom has the greater magnitude of EA?
 - a. K or Br
 - b. Mg or S

ANSWERS

- 1. Na(g) \rightarrow Na⁺(g) + e⁻ ΔH = IE (answers will vary)
- 3. As you go across, atomic radii decrease; as you go down, atomic radii increase.
- 5. a. Cs
 - b. Bi
- 7. a. K
 - b. Ba

- 9. a. S
 - b. Br
- 11. a. Li
 - b. O
- 13. Mg
- 15. The third IE shows a large jump in Ca.
- 17. a. F
 - b. Cl

6. END-OF-CHAPTER MATERIAL

ADDITIONAL EXERCISES

- 1. What is the frequency of light if its wavelength is 1.00 m?
- 2. What is the wavelength of light if its frequency is $1.00 \, \text{s}^{-1}$?
- 3. What is the energy of a photon if its wavelength is 1.00 meter?
- 4. What is the energy of a photon if its frequency is 1.00 s⁻¹?
- 5. If visible light is defined by the wavelength limits of 400 nm and 700 nm, what is the energy range for visible light photons?
- 6. Domestic microwave ovens use microwaves that have a wavelength of 122 mm. What is the energy of one photon of this microwave?

- 7. Use the equation for the wavelengths of the lines of light in the H atom spectrum to calculate the wavelength of light emitted when *n* is 7 and 8.
- 8. Use the equation for the wavelengths of the lines of light in the H atom spectrum to calculate the wavelengths of light emitted when *n* is 5 and 6.
- Make a table of all the possible values of the four quantum numbers when the principal quantum number n = 5.
- 10. Make a table of all the possible values of $m\ell$ and m_S when $\ell=4$. What is the lowest value of the principal quantum number for this to occur?

- 11. a. Predict the electron configurations of Sc through Zn.
 - b. From a source of actual electron configurations, determine how many exceptions there are from your predictions in part a.
- 12. a. Predict the electron configurations of Ga through Kr.
 - b. From a source of actual electron configurations, determine how many exceptions there are from your predictions in part a.
- 13. Recently, Russian chemists reported experimental evidence of element 117. Use the periodic table to predict its valence shell electron configuration.
- 14. Bi (atomic number 83) is used in some stomach discomfort relievers. Using its place on the periodic table, predict its valence shell electron configuration.

- 15. Which atom has a higher ionization energy (IE), O or P?
- 16. Which atom has a higher IE, F or As?
- 17. Which atom has a smaller radius, As or CI?
- 18. Which atom has a smaller radius, K or F?
- 19. How many IEs does an H atom have? Write the chemical reactions for the successive ionizations.
- 20. How many IEs does a Be atom have? Write the chemical reactions for the successive ionizations.
- 21. Based on what you know of electrical charges, do you expect Na⁺ to be larger or smaller than Na?
- 22. Based on what you know of electrical charges, do you expect CI⁻ to be larger or smaller than CI?

ANSWERS

- 1. $3.00 \times 10^8 \,\mathrm{s}^{-1}$
- 3. $1.99 \times 10^{-22} \text{ J}$
- 5. 4.97×10^{-19} J to 2.84×10^{-19} J
- 7. 3.97×10^{-7} m and 3.89×10^{-7} m, respectively

9.	n	P	m e	m _S
	5	0	0	1/2 or -1/2
	5	1	-1, 0, 1	1/2 or -1/2
	5	2	-2, -1, 0, 1, 2	1/2 or -1/2
	5	3	-3, -2, -1, 0, 1, 2, 3	1/2 or -1/2
	5	4	-4, -3, -2, -1, 0, 1, 2, 3, 4	1/2 or -1/2

- 11. a. The electron configurations are predicted to end in 3d¹, 3d², 3d³, 3d⁴, 3d⁵, 3d⁶, 3d⁷, 3d⁸, 3d⁹, and 3d¹⁰.
 - b. Cr and Cu are exceptions.
- 13. Element 117's valence shell electron configuration should be $7s^27p^5$.
- 15. O
- 17. CI
- 19. H has only one IE: $H \rightarrow H^+ + e^-$
- 21. smaller