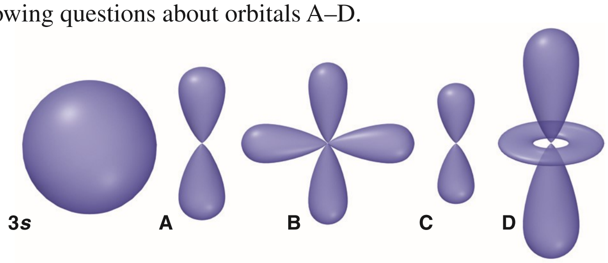
intermediate energy level, and a second to return to the ground state.
(a) What higher level did the electron reach?
(b) What intermediate level did the electron reach?
(c) What was the wavelength of the second photon emitted?

7.60 Use the relative size of the 3*s* orbital below to answer the following questions about orbitals A–D.



(a) Which orbital has the highest value of n? (b) Which orbital(s) have a value of $l = 1$? $l = 2$? (c) How many other orbitals with the same value of n have the same shape as orbital B? Orbital C? (d) Which orbital has the highest energy? Lowest energy?

7.61 Why do the spaces between spectral lines within a series decrease as wavelength becomes shorter?

7.62 Enormous numbers of microwave photons are needed to warm macroscopic samples of matter. A portion of soup containing 252 g of water is heated in a microwave oven from 20.°C to 98°C, with radiation of wavelength 1.55×10^{-2} m. How many photons are absorbed by the water in the soup?

7.63 The quantum-mechanical treatment of the hydrogen atom gives this expression for the wave function, ψ, of the 1*s* orbital:

$$\psi = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

where r is the distance from the nucleus and a_0 is 52.92 pm. The probability of finding the electron in a tiny volume at distance r from the nucleus is proportional to ψ^2. The total probability of finding the electron at all points at distance r from the nucleus is proportional to $4\pi r^2\psi^2$. Calculate the values (to three significant figures) of ψ, ψ^2, and $4\pi r^2\psi^2$ to fill in the following table and sketch a plot of each set of values versus r. Compare the latter two plots with those in Figure 7.16A (p. 237):

r (pm)	ψ (pm$^{-3/2}$)	ψ^2 (pm^{-3})	$4\pi r^2\psi^2$ (pm^{-1})
0			
50			
100			
200			

7.64 Photoelectron spectroscopy applies the principle of the photoelectric effect to study orbital energies of atoms and molecules. High-energy radiation (usually UV or x-ray) is absorbed by a sample and an electron is ejected. The orbital energy can be calculated from the known energy of the radiation and the measured energy of the electron lost. The following energy differences were determined for several electron transitions:

$\Delta E_{2\longrightarrow1} = 4.098\times10^{-17}$ J $\Delta E_{3\longrightarrow1} = 4.854\times10^{-17}$ J
$\Delta E_{5\longrightarrow1} = 5.242\times10^{-17}$ J $\Delta E_{4\longrightarrow2} = 1.024\times10^{-17}$ J

Calculate ΔE and λ of a photon emitted in the following transitions: (a) level 3 $\longrightarrow$ 2; (b) level 4 $\longrightarrow$ 1; (c) level 5 $\longrightarrow$ 4.

7.65 For any microscope, the smallest object observable is one-half the wavelength of the radiation used. For example, the smallest object observable with light of 400 nm is 2×10^{-7} m. (a) What is the smallest object observable with an electron microscope using electrons moving at 5.5×10^4 m/s? (b) At 3.0×10^7 m/s?

7.66 In fireworks, the heat of the reaction of an oxidizing agent, such as $KClO_4$, with an organic compound excites certain salts, which emit specific colors. Strontium salts have an intense emission at 641 nm, and barium salts have one at 493 nm. (a) What colors do these emissions produce? (b) What is the energy (in kJ) of these emissions for 5.00 g each of the chloride salts of Sr and Ba? (Assume that all the heat produced is converted to emitted light.)

7.67 Atomic hydrogen produces several series of spectral lines. Each series fits the Rydberg equation with its own particular n_1 value. Calculate the value of n_1 (by trial and error if necessary) that would produce a series of lines in which:
(a) The *highest* energy line has a wavelength of 3282 nm.
(b) The *lowest* energy line has a wavelength of 7460 nm.

7.68 Fish-liver oil is a good source of vitamin A, whose concentration is measured spectrometrically at a wavelength of 329 nm.
(a) Suggest a reason for using this wavelength.
(b) In what region of the spectrum does this wavelength lie?
(c) When 0.1232 g of fish-liver oil is dissolved in 500. mL of solvent, the absorbance is 0.724 units. When 1.67×10^{-3} g of vitamin A is dissolved in 250. mL of solvent, the absorbance is 1.018 units. Calculate the vitamin A concentration in the fish-liver oil.

7.69 Many calculators use photocells as their energy source. Find the maximum wavelength needed to remove an electron from silver ($\phi = 7.59\times10^{-19}$ J). Is silver a good choice for a photocell that uses visible light? [The concept of the work function (ϕ) is explained in Problem 7.55.]

7.70 In a game of "Clue," Ms. White is killed in the conservatory. A spectrometer in each room records who is present to help find the murderer. For example, if someone wearing yellow is in a room, light at 580 nm is reflected. The suspects are Col. Mustard, Prof. Plum, Mr. Green, Ms. Peacock (blue), and Ms. Scarlet. At the time of the murder, the spectrometer in the dining room shows a reflection at 520 nm, those in the lounge and study record lower frequencies, and the one in the library records the shortest possible wavelength. Who killed Ms. White? Explain.

7.71 Technetium (Tc; $Z = 43$) is a synthetic element used as a radioactive tracer in medical studies. A Tc atom emits a beta particle (electron) with a kinetic energy (E_k) of 4.71×10^{-15} J. What is the de Broglie wavelength of this electron ($E_k = \frac{1}{2}mv^2$)?

7.72 Electric power is measured in watts (1 W = 1 J/s). About 95% of the power output of an incandescent bulb is converted to heat and 5% to light. If 10% of that light shines on your chemistry text, how many photons per second shine on the book from a 75-W bulb? (Assume the photons have a wavelength of 550 nm.)

7.73 The net change during photosynthesis involves CO_2 and H_2O forming glucose ($C_6H_{12}O_6$) and O_2. Chlorophyll absorbs light in the 600–700 nm region.
(a) Write a balanced thermochemical equation for formation of 1.00 mol of glucose.
(b) What is the minimum number of photons with $\lambda = 680.$ nm needed to form 1.00 mol of glucose?

7.74 In contrast to the situation for an electron, calculate the uncertainty in the position of a 142-g baseball that was pitched in 2010 by a Cincinnati Reds reliever and traveled at 100.0 mi/h $\pm$ 1.00%.

Electron Configuration and Chemical Periodicity

8

Expanding Shells of Electrons A nautilus's shell, with its recurring and increasing chambers, is an analogy for the increasing numbers of electrons in the energy levels of an atom. Recurring patterns of electrons within atoms correlate with recurring chemical behavior of the elements.

Outline

Key Principles
to focus on while studying this chapter

- Arranging the elements by atomic number reveals a periodic recurrence of similar properties *(periodic law)*. ***(Introduction)***
- The *electron configuration* of an atom, the distribution of electrons into its energy levels and sublevels, ultimately determines the behavior of the element. ***(Section 8.1)***
- There are three new characteristics required to explain the behavior of atoms with more than one electron (all elements except hydrogen): a fourth quantum number (m_s) specifies *electron spin;* an orbital holds no more than two electrons *(exclusion principle)*; and interactions between electrons and between nucleus and electrons *(shielding* and *penetration)* cause energy levels to split into sublevels of different energy. ***(Section 8.1)***
- The periodic table is "*built up*" by adding one electron (and one proton and one or more neutrons) to each preceding atom. This method results in vertical groups of elements having *identical outer electron configurations* and, thus, similar behavior. The few seemingly *anomalous configurations* are explained by factors that affect the order of sublevel energies. ***(Section 8.2)***
- Three atomic properties—*atomic size, ionization energy* (energy involved in removing an electron from an atom), and *electron affinity* (energy involved in adding an electron to an atom)—exhibit recurring trends throughout the periodic table. ***(Section 8.3)***
- These atomic properties have a profound effect on many macroscopic properties, including *metallic behavior, acid-base behavior of oxides, ionic behavior,* and *magnetic behavior* of the elements and their compounds. ***(Section 8.4)***

CONCEPTS & SKILLS TO REVIEW before studying this chapter

- format of the periodic table (Section 2.6)
- characteristics of metals and nonmetals (Section 2.6)
- attractions, repulsions, and Coulomb's law (Section 2.7)
- characteristics of acids and bases (Section 4.4)
- rules for assigning quantum numbers (Section 7.4)

We often see recurring patterns in nature—day and night, the seasons, solar and lunar eclipses, the rhythm of a heartbeat. Elements exhibit recurring patterns in properties because their atoms do.

The outpouring of scientific creativity by early 20th-century physicists that led to the new quantum-mechanical model of the atom was preceded by countless hours of laboratory work by 19th-century chemists who were exploring the nature of electrolytes, the kinetic-molecular theory, and chemical thermodynamics. Condensed from all these efforts, an enormous body of facts about the elements became organized into the periodic table:

- *The original periodic table*. In 1870, the Russian chemist Dmitri Mendeleev arranged the 65 elements known at the time into a table and summarized their behavior in the **periodic law:** when arranged by *atomic mass,* the elements exhibit a periodic recurrence of similar properties. Mendeleev left blank spaces in his table and was even able to *predict* the properties of several elements, for example, germanium, that were not discovered until later.
- *The modern periodic table*. Today's table *(inside front cover)* includes 52 elements not known in 1870 and, most importantly, arranges the elements by *atomic number* (number of protons) *not* atomic mass.

The great test for the new atomic model, which relates directly to the order of elements in the table, was to answer a central question: *why* do the elements behave as they do? Or, rephrasing to fit the main topic of this chapter, how does the **electron configuration** of an element—*the distribution of electrons within the levels and sublevels of its atoms*—relate to its chemical and physical properties?

8.1 • CHARACTERISTICS OF MANY-ELECTRON ATOMS

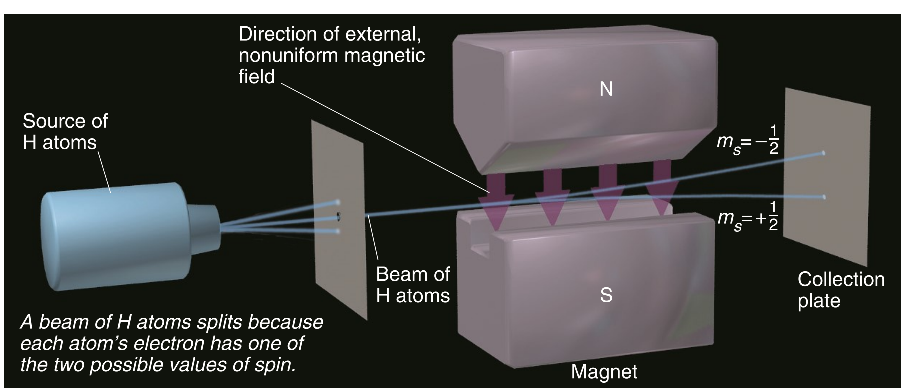
The Schrödinger equation (introduced in Chapter 7) does not give *exact* solutions for the energy levels of *many-electron atoms,* those with more than one electron—that is, all atoms except hydrogen. However, unlike the Bohr model, it gives excellent *approximate* solutions. Three additional features become important in many-electron atoms: (1) a fourth quantum number, (2) the number of electrons that can occupy an orbital, and (3) a splitting of energy levels into sublevels.

The Electron-Spin Quantum Number

The three quantum numbers *n, l,* and m_l describe the size (energy), shape, and orientation, respectively, of an atomic orbital. An additional quantum number describes a property called *spin,* which is a property of the electron and not the orbital.

When a beam of atoms that have one or more lone electrons passes through a nonuniform magnetic field (created by magnet faces with different shapes), it splits into two beams; Figure 8.1 shows this for a beam of H atoms. Each electron behaves like a

Figure 8.1 The effect of electron spin.



spinning charge and generates a tiny magnetic field, which can have one of two values of *spin*. The two electron fields have opposing directions, so half of the electrons are *attracted* by the large external magnetic field while the other half are *repelled* by it.

Corresponding to the two directions of the electron's field, the **spin quantum number (m_s)** has two possible values, $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus, *each electron in an atom is described completely by a set of **four** quantum numbers: the first three describe its orbital, and the fourth describes its spin.* The quantum numbers are summarized in Table 8.1.

Now we can write a set of four quantum numbers for any electron in the ground state of any atom. For example, the set of quantum numbers for the lone electron in hydrogen (H; $Z = 1$) is $n = 1$, $l = 0$, $m_l = 0$, and $m_s = +\frac{1}{2}$. (The spin quantum number could just as well have been $-\frac{1}{2}$, but by convention, we assign $+\frac{1}{2}$ to the first electron in an orbital.)

Table 8.1 Summary of Quantum Numbers of Electrons in Atoms

Name	Symbol	Permitted Values	Property
Principal	n	Positive integers (1, 2, 3, . . .)	Orbital energy (size)
Angular momentum	l	Integers from 0 to $n - 1$	Orbital shape (the l values 0, 1, 2, and 3 correspond to *s, p, d,* and *f* orbitals, respectively)
Magnetic	m_l	Integers from $-l$ to 0 to $+l$	Orbital orientation
Spin	m_s	$+\frac{1}{2}$ or $-\frac{1}{2}$	Direction of e^- spin

The Exclusion Principle and Orbital Occupancy

The element after hydrogen is helium (He; $Z = 2$), the first with atoms having more than one electron. The first electron in the He ground state has the same set of quantum numbers as the electron in the H atom, but the second He electron does not. Based on observations of excited states, the Austrian physicist Wolfgang Pauli formulated the **exclusion principle:** *no two electrons in the same atom can have the same four quantum numbers.* Therefore, the second He electron occupies the same orbital as the first but has an opposite spin: $n = 1$, $l = 0$, $m_l = 0$, and $m_s = -\frac{1}{2}$.

THINK OF IT THIS WAY
Baseball Quantum Numbers

The unique set of quantum numbers that describes an electron is analogous to the unique location of a box seat at a baseball game. The stadium (atom) is divided into section (n, level), box (l, sublevel), row (m_l, orbital), and seat (m_s, spin). Only one person (electron) can have this particular set of stadium "quantum numbers."

The major consequence of the exclusion principle involves orbital occupancy: *an atomic orbital can hold a maximum of two electrons and they must have opposing spins.* The 1*s* orbital in He is *filled,* and the electrons have *paired spins.* Thus, a beam of He atoms is not split in an experiment like that in Figure 8.1.

Electrostatic Effects and Energy-Level Splitting

Electrostatic effects—attraction of opposite charges and repulsion of like charges—play a major role in determining the energy states of many-electron atoms. Unlike the H atom, in which there is only the attraction between nucleus and electron and the energy state is determined *only* by the n value, the energy states of many-electron atoms are also affected by electron-electron repulsions. You'll see shortly how these additional interactions give rise to *the splitting of energy levels into sublevels of differing energies: the energy of an orbital in a many-electron atom depends mostly on its n value (size) and to a lesser extent on its l value (shape).*

Our first encounter with energy-level splitting occurs with lithium (Li; $Z = 3$). The first two electrons of Li fill its 1*s* orbital, so the third Li electron must go into the $n = 2$ level. But, this level has 2*s and* 2*p* sublevels: which does the third electron enter? For reasons we discuss below, the 2*s* is lower in energy than the 2*p,* so the ground state of Li has its third electron in the 2*s*.

The energy differences among sublevels arise from three factors—*nuclear attraction, electron repulsions,* and *orbital shape* (i.e., radial probability distribution). Their interplay leads to two phenomena—*shielding* and *penetration*—that occur in all atoms *except* hydrogen. [In the following discussion, keep in mind that more energy is needed to remove an electron from a more stable (lower energy) sublevel than from a less stable (higher energy) sublevel.]

The Effect of Nuclear Charge (*Z*) on Sublevel Energy Higher charges interact more strongly than lower charges (Coulomb's law, Section 2.7). Therefore, *a higher nuclear charge increases nucleus-electron attractions and, thus, lowers sublevel energy (stabilizes the atom).* We see this effect by comparing the 1*s* sublevel energies of three species with one electron—H atom ($Z = 1$), He^+ ion ($Z = 2$), and Li^{2+} ion ($Z = 3$): the 1*s* sublevel in H is the least stable (highest energy), and the 1*s* sublevel in Li^{2+} is the most stable.

Shielding: The Effect of Electron Repulsions on Sublevel Energy In many-electron atoms, each electron "feels" not only the attraction to the nucleus but also repulsions from other electrons. Repulsions counteract the nuclear attraction somewhat, making each electron easier to remove by, in effect, helping to push it away. We speak of each electron "shielding" the other electrons to some extent from the nuclear charge. **Shielding** (also called *screening*) reduces the full nuclear charge to an **effective nuclear charge (Z_{eff}),** the nuclear charge an electron *actually experiences, and this lower nuclear charge makes the electron easier to remove.*

1. *Shielding by other electrons in a given energy level.* Electrons in the *same* energy level shield each other somewhat. Compare the He atom and He^+ ion: both have a 2+ nuclear charge, but He has two electrons in the 1*s* sublevel and He^+ has only one. It takes less than half as much energy to remove an electron from He (2372 kJ/mol) than from He^+ (5250 kJ/mol) because the second electron in He repels the first, in effect causing a lower Z_{eff}.

2. *Shielding by electrons in inner energy levels.* Because inner electrons spend nearly all their time *between* the outer electrons and the nucleus, they shield outer electrons *much more effectively* than do electrons in the same level. *Shielding by inner electrons greatly lowers Z_{eff} for outer electrons.*

Penetration: The Effect of Orbital Shape on Sublevel Energy To see why the third Li electron occupies the 2*s* sublevel rather than the 2*p*, we have to consider orbital shapes, that is, radial probability distributions (Figure 8.2). A 2*p* orbital *(orange curve)* is slightly closer to the nucleus, on average, than the major portion of the 2*s* orbital *(blue curve).* But a small portion of the 2*s* radial probability distribution peaks within the 1*s* region. Thus, an electron in the 2*s* orbital spends part of its time "penetrating" very close to the nucleus. **Penetration** has two effects:

- It *increases the nuclear attraction* for a 2*s* electron over that for a 2*p* electron.
- It *decreases the shielding* of a 2*s* electron by the 1*s* electrons.

Thus, since it takes more energy to remove a 2*s* electron (520 kJ/mol) than a 2*p* (341 kJ/mol), the 2*s* sublevel is lower in energy than the 2*p*.

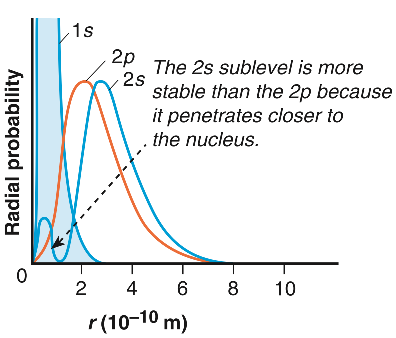


Figure 8.2 Penetration and sublevel energy.

Splitting of Levels into Sublevels In general, *penetration and the resulting effects on shielding cause an energy level to split into sublevels of differing energy.* The lower the *l* value of a sublevel, the more its electrons penetrate, and so the greater their attraction to the nucleus. Therefore, *for a given n value, a lower l value indicates a more stable (lower energy) sublevel:*

$$\text{Order of sublevel energies: } s < p < d < f \qquad (8.1)$$

Thus, the 2s ($l = 0$) is lower in energy than the 2p ($l = 1$), the 3p ($l = 1$) is lower than the 3d ($l = 2$), and so forth.

Figure 8.3 shows the general energy order of levels (n value) and how they are split into sublevels (l values) of differing energies. (Compare this with the H atom energy levels in Figure 7.20.) Next, we'll use this energy order to construct a periodic table of ground-state atoms.

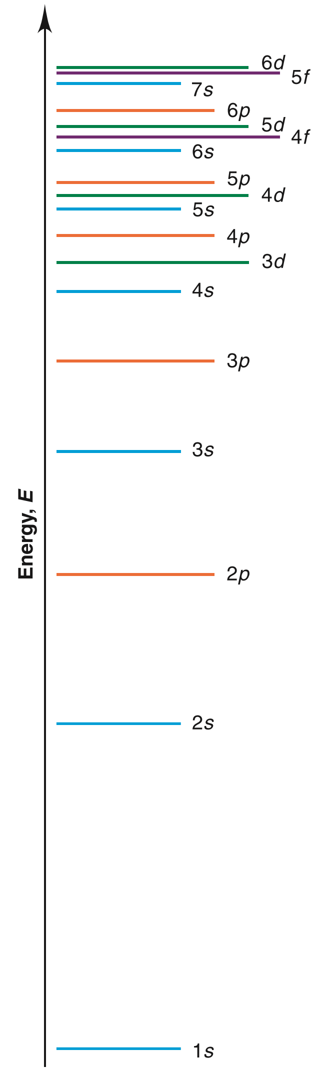


Figure 8.3 Order for filling energy sublevels with electrons. In general, energies of sublevels increase with the principal quantum number n ($1 < 2 < 3$, etc.) and the angular momentum quantum number l ($s < p < d < f$). As n increases, some sublevels overlap; for example, the 4s sublevel is lower in energy than the 3d. (Line color indicates sublevel type.)

Summary of Section 8.1

- Identifying electrons in many-electron atoms requires four quantum numbers: three (n, l, m_l) describe the orbital, and a fourth (m_s) describes electron spin.
- The exclusion principle requires each electron to have a unique set of four quantum numbers; therefore, an orbital can hold no more than two electrons, and their spins must be paired (opposite).
- Electrostatic interactions determine sublevel energies as follows:
  1. Greater nuclear charge lowers sublevel energy, making electrons harder to remove.
  2. Electron-electron repulsions raise sublevel energy, making electrons easier to remove. Repulsions shield electrons from the full nuclear charge, reducing it to an effective nuclear charge, Z_{eff}. Inner electrons shield outer electrons very effectively.
  3. Penetration makes an electron harder to remove because nuclear attraction increases and shielding decreases. As a result, an energy level is split into sublevels with the energy order $s < p < d < f$.

8.2 • THE QUANTUM-MECHANICAL MODEL AND THE PERIODIC TABLE

Quantum mechanics provides the theoretical foundation for the experimentally based periodic table. In this section, we fill the table by determining the ground-state electron configuration of each element—*the lowest-energy distribution of electrons in the sublevels of its atoms*. Note especially the *recurring pattern in electron configurations, which is the basis for recurring patterns in chemical behavior.*

A useful way to determine electron configurations is based on the **aufbau principle** (German *aufbauen,* "to build up"). We start at the beginning of the periodic table and add one proton to the nucleus and one electron to the *lowest energy sublevel available.* (Of course, one or more neutrons are also added to the nucleus.)

There are two common ways to indicate the distribution of electrons:

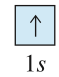
- *The electron configuration.* This shorthand notation consists of the principal energy level (n value), the letter designation of the sublevel (l value), and the number of electrons (#) in the sublevel, written as a superscript: $\boldsymbol{nl^{\#}}$.
- *The orbital diagram.* An **orbital diagram** consists of a box (or circle, or just a line) for each orbital in a given energy level, grouped by sublevel (with nl designation shown beneath), with an arrow representing an electron *and* its spin: ↑ is $+\frac{1}{2}$ and ↓ is $-\frac{1}{2}$. (Throughout the text, orbital occupancy is also indicated by color intensity: no color is empty, pale color is half-filled, and full color is filled.)

Building Up Period 1

Let's begin by applying the aufbau principle to Period 1, whose ground-state elements have only the $n = 1$ level and, thus, only the 1s sublevel, which consists of only the 1s orbital. We'll also assign a set of four quantum numbers to each element's *last added* electron.

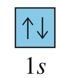
1. *Hydrogen.* For the electron in H, as you've seen, the set of quantum numbers is H ($Z = 1$): $n = 1$, $l = 0$, $m_l = 0$, $m_s = +\frac{1}{2}$. The electron configuration (spoken "one-ess-one") and orbital diagram are

H ($Z = 1$) $1s^1$



2. *Helium.* Recall that the first electron in He has the same quantum numbers as the electron in H, but the second He electron has opposing spin (exclusion principle) He ($Z = 2$): $n = 1$, $l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$. The electron configuration (spoken "one-ess-two," *not* "one-ess-squared") and orbital diagram are

He ($Z = 2$) $1s^2$

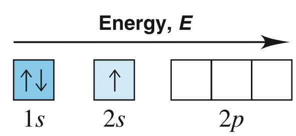


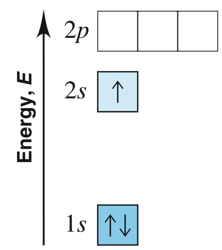
Building Up Period 2

The exclusion principle says an orbital can hold no more than two electrons. Therefore, with He, the 1*s* orbital, the 1*s* sublevel, the $n = 1$ level, and Period 1 are filled. Filling the $n = 2$ level builds up Period 2 and begins with the 2*s* sublevel, which is the next lowest in energy (see Figure 8.2) and consists of only the 2*s* orbital. When the 2*s* sublevel is filled, we proceed to fill the 2*p*.

1. *Lithium*. The first two electrons in Li fill the 1*s* sublevel, and the last added Li electron has quantum numbers $n = 2$, $l = 0$, $m_l = 0$, $m_s = +\frac{1}{2}$. The electron configuration and orbital diagram are

Li ($Z = 3$) $1s^2 2s^1$

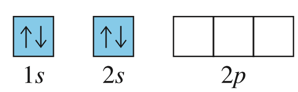




(Note that a complete orbital diagram shows all the orbitals for the given *n* value, whether or not they are occupied.) To save space on a page, orbital diagrams are written horizontally, with *the sublevel energy increasing left to right*. The orbital diagram to the right above shows the sublevels vertically.

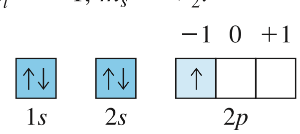
2. *Beryllium*. The 2*s* orbital is only half-filled in Li, and the fourth electron of beryllium fills it with the electron's spin paired: $n = 2$, $l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$.

Be ($Z = 4$) $1s^2 2s^2$



3. *Boron*. The next lowest energy sublevel is the 2*p*. A *p* sublevel has $l = 1$, so the m_l (orientation) value can be -1, 0, or $+1$. The three orbitals in the 2*p* sublevel have *equal energy* (same *n* and *l* values), which means that the fifth electron of boron can go into *any one of the 2p orbitals.* For convenience, let's label the boxes from left to right: -1, 0, $+1$. By convention, we start on the left and place the fifth electron in the $m_l = -1$ orbital: $n = 2$, $l = 1$, $m_l = -1$, $m_s = +\frac{1}{2}$.

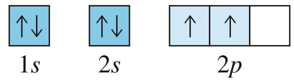
B ($Z = 5$) $1s^2 2s^2 2p^1$



4. *Carbon.* To minimize electron-electron repulsions, the sixth electron of carbon enters one of the *unoccupied* 2*p* orbitals; by convention, we place it in the $m_l = 0$ orbital. Experiment shows that the spin of this electron is *parallel* to (the same as) the spin of the other 2*p* electron. This result exemplifies **Hund's rule:** *when orbitals of equal energy are available, the electron configuration of lowest energy has the maximum number*

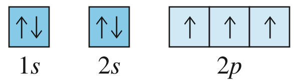
of unpaired electrons with parallel spins. Thus, the sixth electron has $n = 2$, $l = 1$, $m_l = 0$, and $m_s = +\frac{1}{2}$.

C ($Z = 6$) $1s^22s^22p^2$



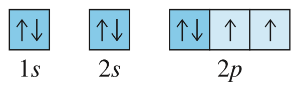
5. *Nitrogen.* Based on Hund's rule, nitrogen's seventh electron enters the last empty $2p$ orbital, with its spin parallel to the other two: $n = 2$, $l = 1$, $m_l = +1$, $m_s = +\frac{1}{2}$.

N ($Z = 7$) $1s^22s^22p^3$



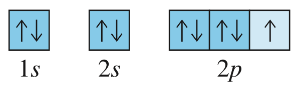
6. *Oxygen*. The eighth electron in oxygen must enter one of the three half-filled $2p$ orbitals and "pair up" with (oppose the spin of) the electron present. We place the electron in a half-filled $2p$ orbital: $n = 2$, $l = 1$, $m_l = -1$, $m_s = -\frac{1}{2}$.

O ($Z = 8$) $1s^22s^22p^4$



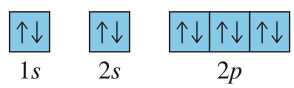
7. *Fluorine.* Fluorine's ninth electron enters the next of the two remaining half-filled $2p$ orbitals: $n = 2$, $l = 1$, $m_l = 0$, $m_s = -\frac{1}{2}$.

F ($Z = 9$) $1s^22s^22p^5$



8. *Neon.* Only one unfilled $2p$ orbital remains, so the tenth electron of neon occupies it: $n = 2$, $l = 1$, $m_l = +1$, $m_s = -\frac{1}{2}$. With neon, the $n = 2$ level is filled.

Ne ($Z = 10$) $1s^22s^22p^6$



Sample Problem 8.1 Determining Quantum Numbers from Orbital Diagrams

Problem Use the orbital diagram shown above to write the set of quantum numbers for the third electron and the set for the eighth electron of the F atom.

Plan Referring to the orbital diagram, we identify the electron of interest and note its level (n), sublevel (l), orbital (m_l), and spin (m_s).

Solution The third electron is in the $2s$ orbital. The upward arrow indicates a spin of $+\frac{1}{2}$:

$$n = 2, l = 0, m_l = 0, m_s = +\tfrac{1}{2}$$

The eighth electron is in the first $2p$ orbital, which is designated $m_l = -1$, and has a downward arrow:

$$n = 2, l = 1, m_l = -1, m_s = -\tfrac{1}{2}$$

FOLLOW-UP PROBLEM 8.1 Use the periodic table to identify the element with the electron configuration $1s^22s^22p^4$. Write its orbital diagram and the set of quantum numbers for its sixth electron.

Building Up Period 3

The Period 3 elements, Na through Ar, lie directly under the Period 2 elements, Li through Ne. That is, even though the $n = 3$ level splits into $3s$, $3p$, and $3d$ sublevels, Period 3 fills only $3s$ and $3p$; as you'll see shortly, the $3d$ is filled in Period 4. Table 8.2 introduces two ways to present electron distributions more concisely:

- *Partial orbital diagrams* show only the sublevels being filled, here the $3s$ and $3p$.
- *Condensed electron configurations (rightmost column)* have the element symbol of the previous noble gas in brackets, to stand for its configuration, followed by the electron configuration of filled inner sublevels and the energy level being filled. For example, the condensed electron configuration of sulfur is [Ne] $3s^23p^4$, where [Ne] stands for $1s^22s^22p^6$.

Table 8.2 Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 3

Atomic Number	Element	Partial Orbital Diagram (3*s* and 3*p* Sublevels Only): 3*s*	3*p*	Full Electron Configuration†	Condensed Electron Configuration
11	Na	[↑]	[ ][ ][ ]	$[1s^22s^22p^6]\ 3s^1$	$[Ne]\ 3s^1$
12	Mg	[↑↓]	[ ][ ][ ]	$[1s^22s^22p^6]\ 3s^2$	$[Ne]\ 3s^2$
13	Al	[↑↓]	[↑][ ][ ]	$[1s^22s^22p^6]\ 3s^23p^1$	$[Ne]\ 3s^23p^1$
14	Si	[↑↓]	[↑][↑][ ]	$[1s^22s^22p^6]\ 3s^23p^2$	$[Ne]\ 3s^23p^2$
15	P	[↑↓]	[↑][↑][↑]	$[1s^22s^22p^6]\ 3s^23p^3$	$[Ne]\ 3s^23p^3$
16	S	[↑↓]	[↑↓][↑][↑]	$[1s^22s^22p^6]\ 3s^23p^4$	$[Ne]\ 3s^23p^4$
17	Cl	[↑↓]	[↑↓][↑↓][↑]	$[1s^22s^22p^6]\ 3s^23p^5$	$[Ne]\ 3s^23p^5$
18	Ar	[↑↓]	[↑↓][↑↓][↑↓]	$[1s^22s^22p^6]\ 3s^23p^6$	$[Ne]\ 3s^23p^6$

*Colored type indicates the sublevel to which the last electron is added.
†The full configuration is not usually written with square brackets; they are included here to show how the [Ne] designation arises.

In Na (the second alkali metal) and Mg (the second alkaline earth metal), electrons are added to the 3*s* sublevel, which contains only the 3*s* orbital; this is directly comparable to the filling of the 2*s* sublevel in Li and Be in Period 2. Then, in the same way as the 2*p* orbitals of B, C, and N in Period 2 are half-filled, the last electrons added to Al, Si, and P in Period 3 half-fill successive 3*p* orbitals with spins parallel (Hund's rule). The last electrons added to S, Cl, and Ar then successively pair up to fill those 3*p* orbitals, which fills the 3*p* sublevel. Thus, Ag, the next noble gas after He and Ne, ends Period 3. (As you'll see shortly, the 3*d* orbitals are filled in Period 4.)

Similar Electron Configurations Within Groups

One of the central points in chemistry is that *similar outer electron configurations correlate with similar chemical behavior.* Figure 8.4 shows the condensed electron configurations of the first 18 elements. Note the similarity within each group. Here are examples from three of the groups:

- In Group 1A(1), Li and Na have the outer electron configuration ns^1 (where n is the quantum number of the highest energy level), as do the other alkali metals (K, Rb, Cs, and Fr). All are highly reactive metals whose atoms lose the outer electron when they form ionic compounds with nonmetals, and all react vigorously with water to displace H_2.
- In Group 7A(17), F and Cl have the outer electron configuration ns^2np^5, as do the other halogens (Br, I, and At). All are reactive nonmetals that occur as diatomic molecules (X_2), and all form ionic compounds with metals (KX, MgX_2), covalent compounds with hydrogen (HX) that yield acidic solutions in water, and covalent compounds with carbon (CX_4).
- In Group 8A(18), He has the electron configuration ns^2, and all the other elements in the group have the outer configuration ns^2np^6. Consistent with their *filled* energy levels, all members of this group are very unreactive monatomic gases.

To summarize the major connection between quantum mechanics and chemical periodicity: *sublevels are filled in order of increasing energy, which leads to outer electron configurations that recur periodically, which leads to chemical properties that recur periodically*.

Period	1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 **H** $1s^1$							2 **He** $1s^2$
2	3 **Li** [He] $2s^1$	4 **Be** [He] $2s^2$	5 **B** [He] $2s^22p^1$	6 **C** [He] $2s^22p^2$	7 **N** [He] $2s^22p^3$	8 **O** [He] $2s^22p^4$	9 **F** [He] $2s^22p^5$	10 **Ne** [He] $2s^22p^6$
3	11 **Na** [Ne] $3s^1$	12 **Mg** [Ne] $3s^2$	13 **Al** [Ne] $3s^23p^1$	14 **Si** [Ne] $3s^23p^2$	15 **P** [Ne] $3s^23p^3$	16 **S** [Ne] $3s^23p^4$	17 **Cl** [Ne] $3s^23p^5$	18 **Ar** [Ne] $3s^23p^6$

Figure 8.4 **Condensed electron configurations in the first three periods.** Elements in a group have similar outer electron configurations *(color).*

Building Up Period 4: The First Transition Series

Period 4 contains the first series of **transition elements,** those in which *d* orbitals are being filled. Let's examine three factors that affect the filling pattern in a period with a transition series. (We'll return to the first in Section 8.4.)

1. *Effects of shielding and penetration on sublevel energy*. The 3*d* sublevel is filled in Period 4, but *the 4s sublevel is filled first.* This switch in filling order is due to shielding and penetration effects. Based on the 3*d* radial probability distribution (see Figure 7.18), a 3*d* electron spends most of the time outside the filled inner $n = 1$ and $n = 2$ levels, so it is shielded very effectively from the nuclear charge. However, the outermost 4*s* electron penetrates close to the nucleus part of the time, so it is subject to a greater attraction. As a result, the 4*s* orbital is slightly *lower* in energy than the 3*d* and fills first. In any period, *the ns sublevel fills before the* $(n - 1)d$ *sublevel.* Other variations in the filling pattern occur at higher values of *n* because sublevel energies become very close together (see Figure 8.3).

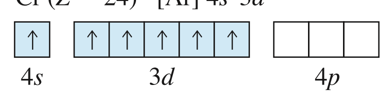
2. *Filling the 4s and 3d sublevels.* Table 8.3 *(next page)* shows the partial orbital diagrams and full and condensed electron configurations for the 18 elements in Period 4. The first two elements, K and Ca, are the next alkali and alkaline earth metals, respectively; the last electron of K half-fills and that of Ca fills the 4*s* sublevel. The last electron of scandium (Sc; $Z = 21$), the first transition element, occupies any one of the five 3*d* orbitals because they are equal in energy; Sc has the electron configuration [Ar] $4s^23d^1$. Filling of the 3*d* orbitals proceeds one electron at a time, as with the *p* orbitals, except in two cases, chromium (Cr; $Z = 24$) and copper (Cu; $Z = 29$), discussed next.

3. *Stability of half-filled and filled sublevels.* Vanadium (V; $Z = 23$) has three half-filled *d* orbitals ([Ar] $4s^23d^3$). However, the last electron of the next element, Cr, does not enter a fourth empty *d* orbital to give [Ar] $4s^23d^4$; instead, Cr has one electron in the 4*s* sublevel and five in the 3*d* sublevel, making both sublevels half filled: [Ar] $4s^13d^5$ *(see margin).* In the next element, manganese (Mn; $Z = 25$), the 4*s* sublevel is filled again ([Ar] $4s^23d^5$).

Because it follows nickel (Ni; [Ar] $4s^23d^8$), copper would be expected to have the configuration [Ar] $4s^23d^9$. Instead, the 4*s* sublevel of Cu is *half-filled* with 1 electron, and the 3*d* sublevel is *filled* with 10 *(see margin).* From these two exceptions, Cr and Cu, we conclude that *half-filled and filled sublevels are unexpectedly stable (low in energy);* we see this pattern with many other elements.

With zinc (Zn; $Z = 30$), the 4*s* sublevel is filled ([Ar] $4s^23d^{10}$), and the first transition series ends. The 4*p* sublevel is filled by the next six elements, and Period 4 ends with the noble gas krypton (Kr; $Z = 36$).

Cr ($Z = 24$) [Ar] $4s^13d^5$



Cu ($Z = 29$) [Ar] $4s^13d^{10}$

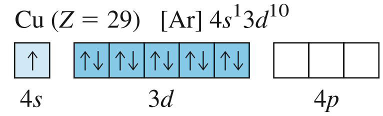


Table 8.3 Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 4

Atomic Number	Element	Partial Orbital Diagram (4*s*, 3*d*, and 4*p* Sublevels Only): 4*s*	3*d*	4*p*	Full Electron Configuration	Condensed Electron Configuration
19	K	[↑]	[ ][ ][ ][ ][ ]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^1$	[Ar] $4s^1$
20	Ca	[↑↓]	[ ][ ][ ][ ][ ]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^2$	[Ar] $4s^2$
21	Sc	[↑↓]	[↑][ ][ ][ ][ ]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^1$	[Ar] $4s^23d^1$
22	Ti	[↑↓]	[↑][↑][ ][ ][ ]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^2$	[Ar] $4s^23d^2$
23	V	[↑↓]	[↑][↑][↑][ ][ ]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^3$	[Ar] $4s^23d^3$
24	Cr	[↑]	[↑][↑][↑][↑][↑]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^13d^5$	[Ar] $4s^13d^5$
25	Mn	[↑↓]	[↑][↑][↑][↑][↑]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^5$	[Ar] $4s^23d^5$
26	Fe	[↑↓]	[↑↓][↑][↑][↑][↑]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^6$	[Ar] $4s^23d^6$
27	Co	[↑↓]	[↑↓][↑↓][↑][↑][↑]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^7$	[Ar] $4s^23d^7$
28	Ni	[↑↓]	[↑↓][↑↓][↑↓][↑][↑]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^8$	[Ar] $4s^23d^8$
29	Cu	[↑]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^13d^{10}$	[Ar] $4s^13d^{10}$
30	Zn	[↑↓]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^{10}$	[Ar] $4s^23d^{10}$
31	Ga	[↑↓]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^1$	[Ar] $4s^23d^{10}4p^1$
32	Ge	[↑↓]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑][↑][ ]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^2$	[Ar] $4s^23d^{10}4p^2$
33	As	[↑↓]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑][↑][↑]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^3$	[Ar] $4s^23d^{10}4p^3$
34	Se	[↑↓]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓][↑][↑]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^4$	[Ar] $4s^23d^{10}4p^4$
35	Br	[↑↓]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓][↑↓][↑]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^5$	[Ar] $4s^23d^{10}4p^5$
36	Kr	[↑↓]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓][↑↓][↑↓]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^6$	[Ar] $4s^23d^{10}4p^6$

*Colored type indicates sublevel(s) whose occupancy changes when the last electron is added.

General Principles of Electron Configurations

Figure 8.5 shows the partial (highest energy sublevels being filled) ground-state electron configurations of the known elements. Let's highlight some key relationships among them.

Similar Outer Electron Configurations Within a Group Among the main-group elements (A groups)—the *s*-block and *p*-block elements—outer electron configurations within a group are identical. Some variations in the transition elements (B groups, *d* block) and inner transition elements (*f* block) occur, as we'll see.

Orbital Filling Order When the elements are "built up" by filling levels and sublevels in order of increasing energy, we obtain the sequence in the periodic table. Reading the table from left to right, like words on a page, gives the energy order of levels and sublevels (Figure 8.6); the following is a memory aid for sublevel filling order when a periodic table is not available.

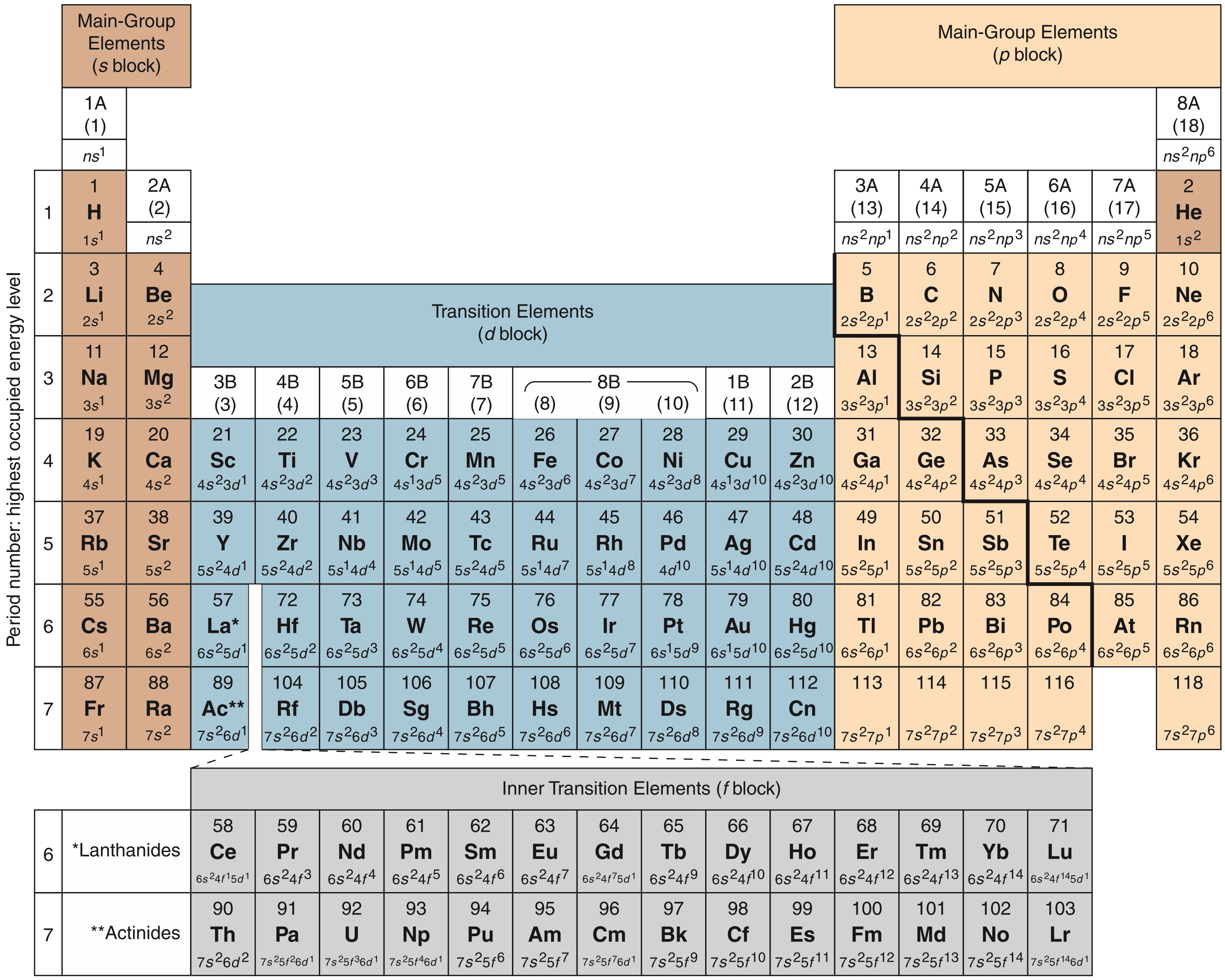


Figure 8.5 A periodic table of partial ground-state electron configurations.

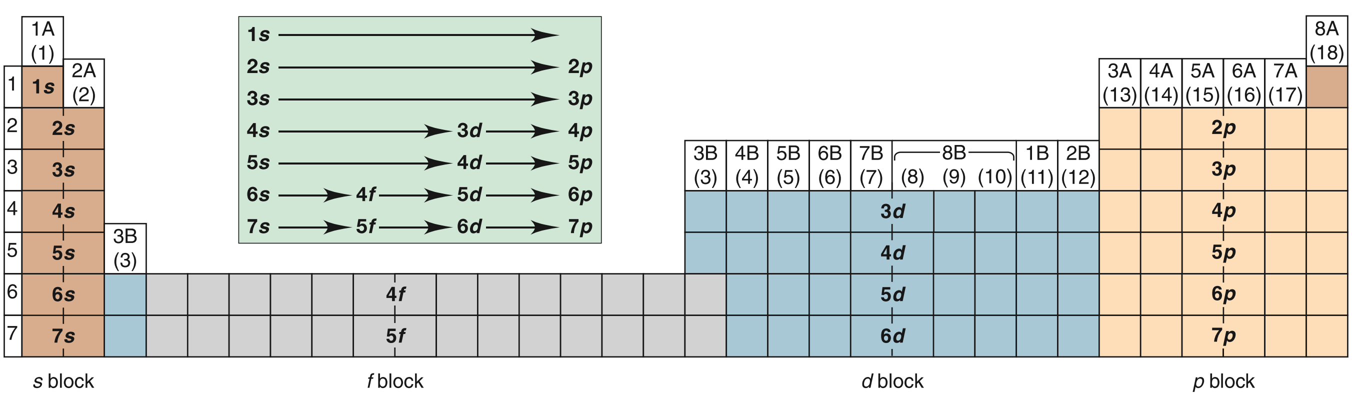
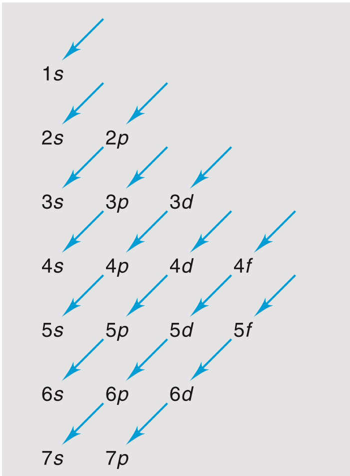


Figure 8.6 **Orbital filling and the periodic table.** This form of the periodic table shows the sublevel blocks. *Pale green inset:* A summary of the sublevel filling order.

THINK OF IT THIS WAY

The Filling Order of the Periodic Table



If you list the sublevels as shown at right and follow the direction of the arrows, starting from 1*s*, you obtain the sublevels in order of increasing energy. Note that
- the n value is constant horizontally,
- the l value is constant vertically, and
- the sum $n + l$ is constant diagonally.

Categories of Electrons We can describe three categories of electrons:

1. **Inner (core) electrons** are those an atom has in common with the previous noble gas and any *completed* transition series. They fill all the *lower energy levels* of an atom.
2. **Outer electrons** are those in the *highest energy level* (highest n value). They spend most of their time farthest from the nucleus.
3. **Valence electrons** are those involved in forming compounds:
   - For main-group elements, the *valence electrons* ***are*** *the outer electrons*.
   - For transition elements, in addition to the outer ns electrons, the $(n - 1)d$ electrons are also valence electrons, though the metals Fe ($Z = 26$) through Zn ($Z = 30$) may use only a few, if any, of their d electrons in bonding.

Group and Period Numbers Key information is embedded in the periodic table:

- Among the main-group elements (A groups), *the A number equals the number of outer electrons* (those with the highest n); thus, chlorine (Cl; Group **7**A) has 7 outer electrons, and so forth.
- *The period number is the n value of the highest energy level.*
- For an energy level, the n value squared (n^2) is the number of *orbitals,* and $2n^2$ is the maximum number of *electrons* (or elements). For example, consider the $n = 3$ level. The number of orbitals is $n^2 = 9$: one 3*s*, three 3*p*, and five 3*d*. The number of electrons is $2n^2 = 18$: two 3*s* and six 3*p* electrons for the eight elements of Period 3, and ten 3*d* electrons for the ten transition elements of Period 4.

Intervening Series: Transition and Inner Transition Elements

The *d* block and *f* block occur between the main-group *s* and *p* blocks (see Figure 8.6).

1. *Transition series.* Periods 4, 5, 6, and 7 incorporate the 3*d,* 4*d,* 5*d,* and 6*d* sublevels, respectively. As you've seen, the general pattern is that the $(n - 1)d$ sublevel is filled between the ns and np sublevels. Thus, in Period 5, the filling order is 5*s,* then 4*d,* and then 5*p.*

2. *Inner transition series.* Period 6 holds the first of two series of **inner transition elements,** those in which *f* orbitals are being filled (Figure 8.6). The *f* orbitals have $l = 3$, so the possible m_l values are $-3, -2, -1, 0, +1, +2,$ and $+3$; that is, there are seven *f* orbitals, for a total of 14 elements in *each* of the two inner transition series:
- The Period 6 inner transition series, called the **lanthanides** (or **rare earths**), occurs after lanthanum (La; $Z = 57$), and the 4*f* orbitals are filled.
- The Period 7 inner transition series, called the **actinides,** occurs after actinium (Ac; $Z = 89$), and the 5*f* orbitals are filled.

  Thus, in Periods 6 and 7, the filling sequence is

$$ns\text{, first of the } (n-1)d\text{, all } (n-2)f\text{, remainder of the } (n-1)d\text{, and } np$$

Period 6 ends with the 6*p* sublevel. Period 7 is incomplete because only five elements with 7*p* electrons are known at this time; element 117 has not yet been synthesized.

3. *Irregular filling patterns.* Irregularities in the filling pattern, such as those for Cr and Cu in Period 4, occur in the *d* and *f* blocks because the sublevel energies in these larger atoms differ very little. Even though occasional deviations occur in the *d* block, the sum of ns electrons and $(n - 1)d$ electrons always equals the new group number (in parentheses). For instance, despite variations in Group 6B(**6**)—Cr, Mo, W, and Sg—the sum of ns and $(n - 1)d$ electrons is 6; for Group 8B(**10**)—Ni, Pd, Pt, and Ds—the sum is 10. (We discuss the electron configurations of transition elements further in Chapter 22.)

Sample Problem 8.2 Determining Electron Configurations

Problem Using the periodic table (not Table 8.3 or Figure 8.5) and assuming a regular filling pattern, give the full and condensed electron configurations, partial orbital diagrams showing valence electrons only, and number of inner electrons for the following elements:
(a) Potassium (K; $Z = 19$) **(b)** Technetium (Tc; $Z = 43$) **(c)** Lead (Pb; $Z = 82$)

Plan The atomic number tells us the number of electrons, and the periodic table shows the order for filling sublevels. In the partial orbital diagrams, we include all electrons added after the previous noble gas *except* those in *filled* inner sublevels. The number of inner electrons is the sum of those in the previous noble gas and in filled *d* and *f* sublevels.

Solution **(a)** For K ($Z = 19$), the full electron configuration is $1s^22s^22p^63s^23p^64s^1$.
The condensed configuration is [Ar] $4s^1$.
The partial orbital diagram showing valence electrons is

4s	3d					4p		
↑								

K is a main-group element in Group 1A(1) and Period 4, so there are 18 inner electrons.
(b) For Tc ($Z = 43$), assuming the expected pattern, the full electron configuration is $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^5$.
The condensed electron configuration is [Kr] $5s^24d^5$.
The partial orbital diagram showing valence electrons is

5s	4d					5p		
↑↓	↑	↑	↑	↑	↑			

Tc is a transition element in Group 7B(7) and Period 5, so there are 36 inner electrons.
(c) For Pb ($Z = 82$), the full electron configuration is
$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^2$.
The condensed electron configuration is [Xe] $6s^24f^{14}5d^{10}6p^2$.
The partial orbital diagram showing valence electrons (no filled inner sublevels) is

6s	6p		
↑↓	↑	↑	

Pb is a main-group element in Group 4A(14) and Period 6, so there are 54 (in Xe) + 14 (in the 4*f* sublevel) + 10 (in the 5*d* sublevel) = 78 inner electrons.

Check Be sure that the sum of the superscripts (numbers of electrons) in the full electron configuration equals the atomic number and that the number of *valence* electrons in the condensed configuration equals the number of electrons in the partial orbital diagram.

FOLLOW-UP PROBLEM 8.2 Without referring to Table 8.3 or Figure 8.5, give full and condensed electron configurations, partial orbital diagrams showing valence electrons only, and the number of inner electrons for the following elements:
(a) Ni ($Z = 28$) **(b)** Sr ($Z = 38$) **(c)** Po ($Z = 84$)

Summary of Section 8.2

- By the aufbau principle, one electron is added to an atom of each successive element in accord with the exclusion principle (no two electrons can have the same set of quantum numbers) and Hund's rule (orbitals of equal energy become half-filled, with electron spins parallel, before any pairing of spins occurs).
- The elements of a group have similar outer electron configurations and similar chemical behavior.
- For the main-group elements, valence electrons (those involved in reactions) are in the outer (highest energy) level only. For transition elements, $(n - 1)d$ electrons are also considered valence electrons.
- Because of shielding of *d* electrons by electrons in inner sublevels and penetration by the *ns* electron, the $(n - 1)d$ sublevel fills after the *ns* and before the *np* sublevels.
- In Periods 6 and 7, $(n - 2)f$ orbitals fill between the first and second $(n - 1)d$ orbitals.

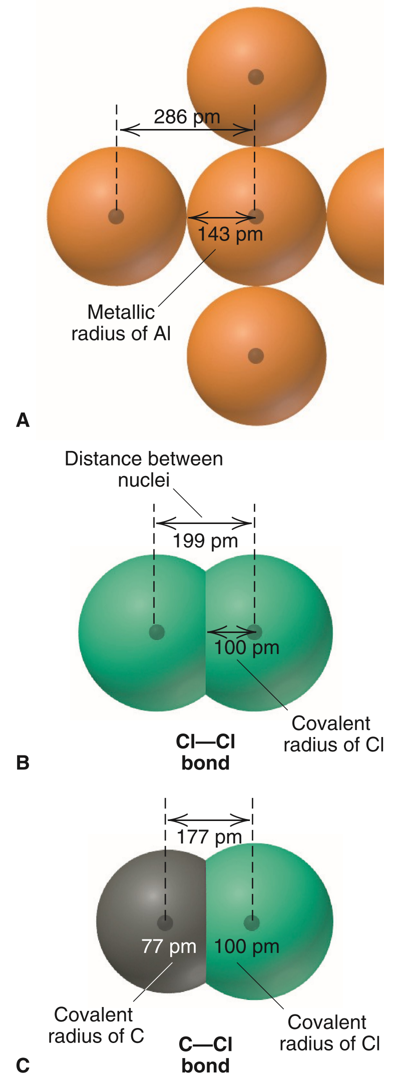


Figure 8.7 Defining atomic size. **A,** The metallic radius of aluminum. **B,** The covalent radius of chlorine. **C,** Known covalent radii and distances between nuclei can be used to find unknown radii.

8.3 • TRENDS IN THREE ATOMIC PROPERTIES

In this section, we focus on three atomic properties that reflect the central importance of electron configuration and effective nuclear charge: atomic size, ionization energy, and electron affinity. Most notably, these properties are *periodic,* which means they generally exhibit consistent changes, or *trends,* within a group or period.

Trends in Atomic Size

Recall from Chapter 7 that we often represent atoms with spherical contours in which the electrons spend 90% of their time. We *define* **atomic size** (the extent of the contour) in terms of how closely one atom lies next to another. But, in practice, as we discuss in Chapter 12, we measure the distance between atomic nuclei in a sample of an element and divide that distance in half. Because atoms do not have hard surfaces, the size of an atom in a compound depends somewhat on the atoms near it. In other words, *an element's atomic size varies slightly from substance to substance.*

Figure 8.7 shows two common definitions of atomic size:

1. **Metallic radius.** Used mostly for *metals,* it is one-half the shortest distance between nuclei of adjacent, individual atoms in a crystal of the element (Figure 8.7A).
2. **Covalent radius.** Used for elements occurring as molecules, mostly *nonmetals,* it is one-half the shortest distance between nuclei of bonded atoms (Figure 8.7B).

Radii measured for some elements are used to determine the radii of other elements from distances between atoms in compounds. For instance, in a carbon-chlorine compound, the distance between nuclei in a C—Cl bond is 177 pm. Using the known covalent radius of Cl (100 pm), we find the covalent radius of C (177 pm − 100 pm = 77 pm) (Figure 8.7C).

Main-Group Elements Figure 8.8 shows the atomic radii of the main-group elements and most of the transition elements. Among the main-group elements, atomic size varies within both groups and periods as a result of two opposing influences:

1. *Changes in n.* As the principal quantum number (n) increases, the probability that outer electrons spend most of their time farther from the nucleus increases as well; thus, atomic size increases.
2. *Changes in* Z_{eff}. As the effective nuclear charge (Z_{eff}) increases, outer electrons are pulled closer to the nucleus; thus, atomic size decreases.

The net effect of these influences depends on how effectively the inner electrons shield the increasing nuclear charge:

1. *Down a group, n dominates.* As we move down a main group, each member has *one more level of inner electrons that shield the outer electrons very effectively*. Even though additional protons do moderately increase Z_{eff} for the outer electrons, the atoms get larger as a result of the increasing n value:

Atomic radius generally ***increases*** *down a group.*

2. *Across a period,* Z_{eff} *dominates.* Across a period from left to right, electrons are added to the *same* outer level, so the shielding by inner electrons does not change. Despite greater electron repulsions, outer electrons shield each other only slightly, so Z_{eff} rises significantly, and the outer electrons are pulled closer to the nucleus:

Atomic radius generally ***decreases*** *across a period.*

Transition Elements As Figure 8.8 shows, size trends are *not* as consistent for the transition elements:

1. *Down a transition group, n* increases, but shielding by an additional level of inner electrons results in only a small size increase from Period 4 to 5 and none from 5 to 6.

2. *Across a transition series*, atomic size shrinks through the first two or three elements because of the increasing nuclear charge. But, from then on, *size remains relatively constant* because shielding by the inner *d* electrons counteracts the increase in Z_{eff}. Thus, for example, in Period 4, the third transition element, vanadium (V;

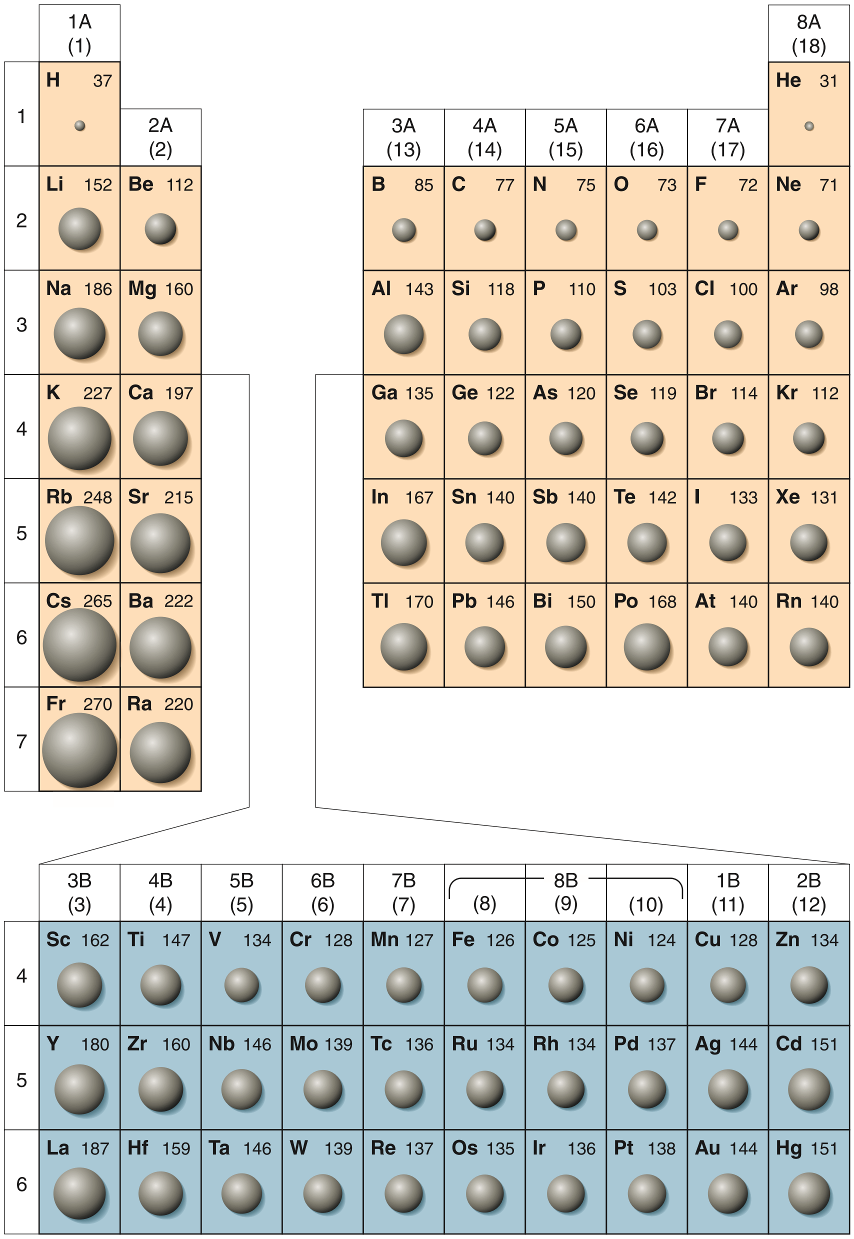


Figure 8.8 **Atomic radii of the main-group and transition elements.** Atomic radii (in picometers) are shown for the main-group elements *(tan)* and the transition elements *(blue)*. (Values for the noble gases are calculated.)

Z = 23), has the same radius as the last, zinc (Zn; Z = 30). This pattern also appears in Periods 5 and 6 in the transition and both inner transition series.

3. *A transition series affects atomic size in neighboring main groups*. Shielding by d electrons causes a *major size decrease from Group 2A(2) to Group 3A(13)* in Periods 4 through 6. Because the np sublevel has more penetration than the $(n - 1)d$, the first np electron [added in Group 3A(13)] "feels" a much greater Z_{eff}, due to all the protons added in the intervening transition elements. The greatest decrease occurs in Period 4: calcium (Ca; Z = 20) in Group 2A(2) is nearly 50% larger than gallium (Ga; Z = 31) in 3A(13). In fact, d-orbital shielding causes gallium to be slightly *smaller* than aluminum (Al; Z = 13), the element above it!

Sample Problem 8.3 Ranking Elements by Atomic Size

Problem Using only the periodic table (not Figure 8.8), rank each set of main-group elements in order of *decreasing* atomic size:
(a) Ca, Mg, Sr **(b)** K, Ga, Ca **(c)** Br, Rb, Kr **(d)** Sr, Ca, Rb

Plan To rank the elements by atomic size, we find them in the periodic table. They are main-group elements, so size increases down a group and decreases across a period.

Solution **(a)** Sr > Ca > Mg. These three elements are in Group 2A(2), and size decreases up the group.
(b) K > Ca > Ga. These three elements are in Period 4, and size decreases across a period.
(c) Rb > Br > Kr. Rb is largest because it has one more energy level (Period 5) and is farthest to the left. Kr is smaller than Br because Kr is farther to the right in Period 4.
(d) Rb > Sr > Ca. Ca is smallest because it has one fewer energy level. Sr is smaller than Rb because it is farther to the right.

Check From Figure 8.8, we see that the rankings are correct.

FOLLOW-UP PROBLEM 8.3 Using only the periodic table, rank the elements in each set in order of *increasing* size: **(a)** Se, Br, Cl; **(b)** I, Xe, Ba.

Periodicity of Atomic Size Figure 8.9 shows the variation in atomic size with atomic number. Note the up-and-down pattern as size drops across a period to the noble gas *(purple)* and then leaps up to the alkali metal *(brown)* that begins the next period. Also note the deviations from the smooth size decrease in each transition *(blue)* and inner transition *(green)* series.

Trends in Ionization Energy

The **ionization energy (IE)** is the energy required for the *complete removal* of 1 mol of electrons from 1 mol of gaseous atoms or ions. Pulling an electron away from a nucleus *requires* energy to overcome their electrostatic attraction. Because energy flows *into* the system, the ionization energy is always positive (like ΔH of an endothermic reaction). (Chapter 7 presented the ionization energy of the H atom as the energy difference between $n = 1$ and $n = \infty$, where the electron is completely removed.) The ionization energy is a key factor in an element's reactivity:

- *Atoms with a low IE tend to form cations during reactions.*
- *Atoms with a high IE (except the noble gases) tend to form anions.*

Many-electron atoms can lose more than one electron. The *first* ionization energy (IE_1) removes an outermost electron (highest energy sublevel) from a gaseous atom:

$$\text{Atom}(g) \longrightarrow \text{ion}^+(g) + e^- \qquad \Delta E = IE_1 > 0 \tag{8.2}$$

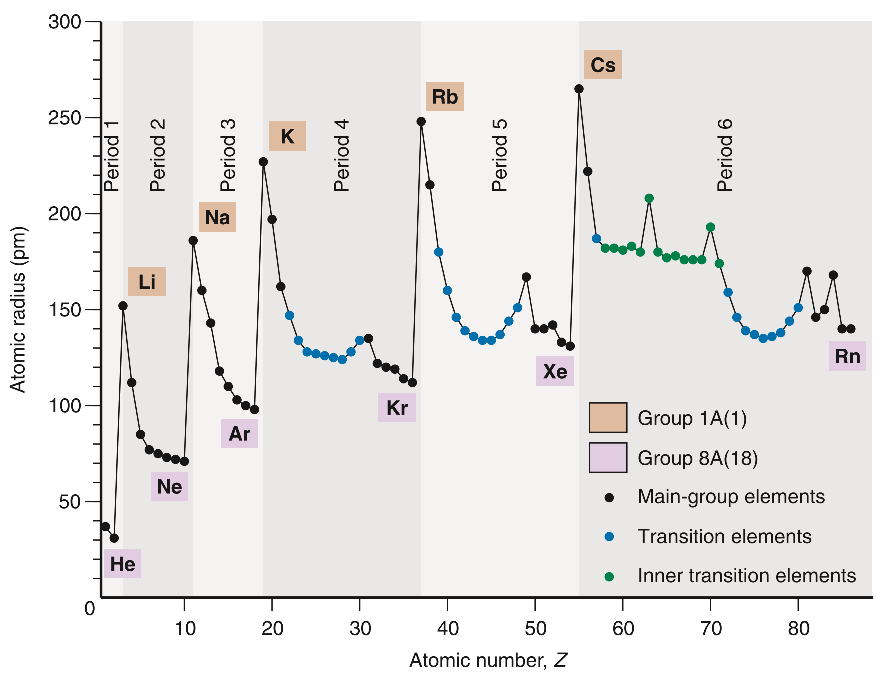


Figure 8.9 Periodicity of atomic radius.

The *second* ionization energy (IE_2) removes a second electron. Since this electron is pulled away from a positive ion, IE_2 is always larger than IE_1:

$$\text{Ion}^+(g) \longrightarrow \text{ion}^{2+}(g) + e^- \qquad \Delta E = IE_2 \text{ (always} > IE_1)$$

Periodicity of First Ionization Energy Figure 8.10 shows the variation in first ionization energy with atomic number. This up-and-down pattern—IE_1 rising across a period to the noble gas *(purple)* and then dropping down to the next alkali metal *(brown)*—is the *inverse* of the variation in atomic size (Figure 8.9): *as size decreases, it takes more energy to remove an electron because the nucleus is closer, so* IE_1 *increases.*

Let's examine the group and period trends and their exceptions:

1. *Down a group.* As we move *down* a main group, the *n* value increases, so atomic size does as well. As the distance from nucleus to outer electron increases, their attraction lessens, so the electron is easier to remove (Figure 8.11, *next page*):

Ionization energy generally ***decreases*** *down a group.*

The only significant exception occurs in Group 3A(13): IE_1 decreases from boron (B) to aluminum (Al), but not for the rest of the group. Filling the transition series in Periods 4, 5, and 6 causes a much higher Z_{eff} and an unusually small change in size, so outer electrons in the larger Group 3A members are held tighter.

2. *Across a period.* As we move left to right across a period, Z_{eff} increases and atomic size decreases. The attraction between nucleus and outer electron increases, so the electron is harder to remove:

Ionization energy generally ***increases*** *across a period.*

There are two exceptions to the otherwise smooth increase in IE_1 across periods:

- In Periods 2 and 3, there are dips at the Group 3A(13) elements, B and Al. These elements have the first *np* electrons, which are removed more easily because the resulting ion has a filled (stable) *ns* sublevel.
- In Periods 2 and 3, once again, there are dips at the Group 6A(16) elements, O and S. These elements have a fourth *np* electron, the first to pair up with another *np* electron, and electron-electron repulsions raise the orbital energy. The fourth *np* electron is easier to remove because doing so relieves the repulsions and leaves a half-filled (stable) *np* sublevel.

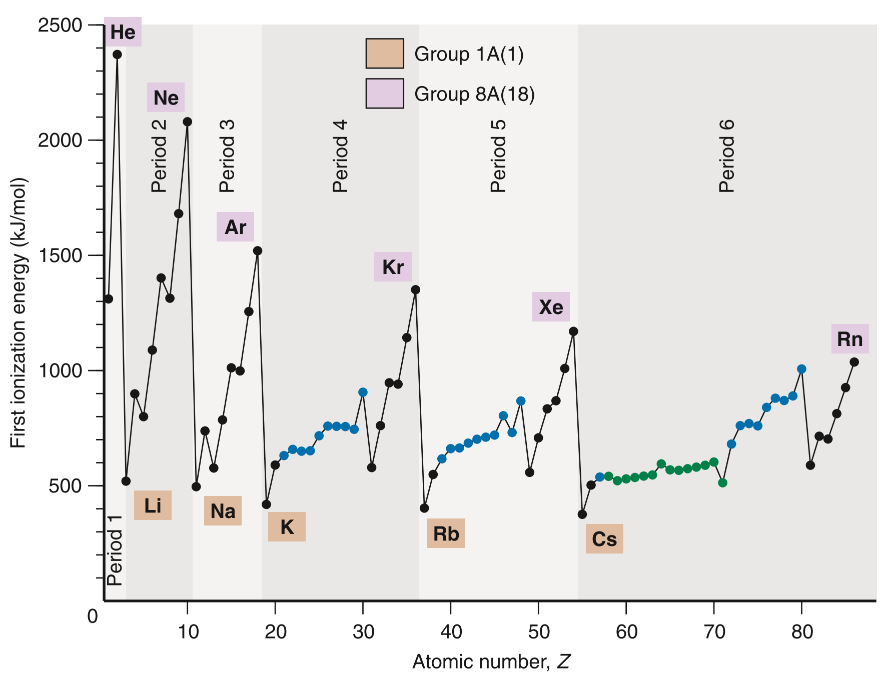


Figure 8.10 Periodicity of first ionization energy (IE_1). This trend is the *inverse* of the trend in atomic size (see Figure 8.9).

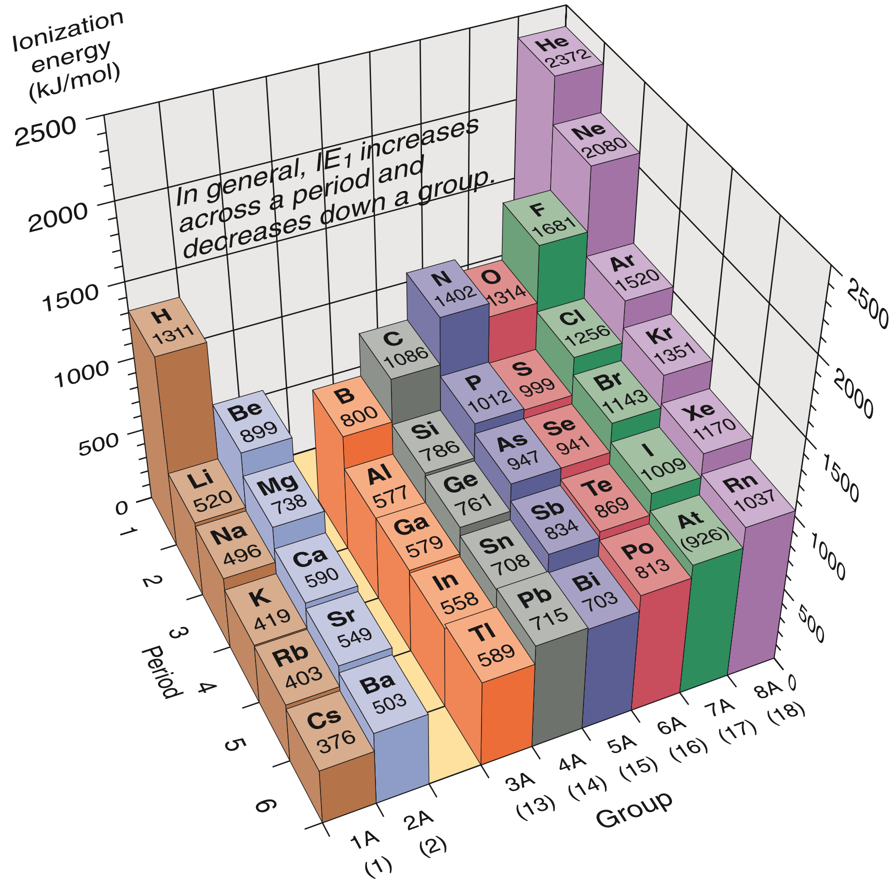


Figure 8.11 First ionization energies of the main-group elements.

Sample Problem 8.4 Ranking Elements by First Ionization Energy

Problem Using the periodic table only, rank the elements in each set in order of *decreasing* IE_1: **(a)** Kr, He, Ar; **(b)** Sb, Te, Sn; **(c)** K, Ca, Rb; **(d)** I, Xe, Cs.

Plan We find the elements in the periodic table and then apply the general trends of decreasing IE_1 down a group and increasing IE_1 across a period.

Solution **(a)** He > Ar > Kr. These are in Group 8A(18), and IE_1 decreases down a group.

(b) Te > Sb > Sn. These are in Period 5, and IE_1 increases across a period.

(c) Ca > K > Rb. IE_1 of K is larger than IE_1 of Rb because K is higher in Group 1A(1). IE_1 of Ca is larger than IE_1 of K because Ca is farther to the right in Period 4.

(d) Xe > I > Cs. IE_1 of I is smaller than IE_1 of Xe because I is farther to the left. IE_1 of I is larger than IE_1 of Cs because I is farther to the right and in the previous period.

Check Because trends in IE_1 are generally the opposite of the trends in size, you can rank the elements by size and check that you obtain the reverse order.

FOLLOW-UP PROBLEM 8.4 Rank the elements in each set in order of *increasing* IE_1: **(a)** Sb, Sn, I; **(b)** Sr, Ca, Ba.

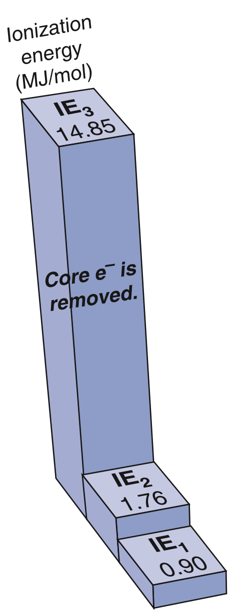


Figure 8.12 The first three ionization energies of beryllium. Beryllium has two valence electrons, so IE_3 is much larger than IE_2.

Successive Ionization Energies For a given element, IE_1, IE_2, and so on, increase because each electron is pulled away from a species with a higher positive charge. This increase includes an enormous jump *after* the outer (valence) electrons have been removed because *much* more energy is needed to remove an inner (core) electron (Figure 8.12).

Table 8.4 shows successive ionization energies for Period 2 and the first element in Period 3. Move across the values for any element, and you reach a point that separates relatively low from relatively high IE values *(shaded area)*. For example, follow the values for boron (B): IE_1 (0.80 MJ) is lower than IE_2 (2.43 MJ), which is lower

Table 8.4 Successive Ionization Energies of the Elements Lithium Through Sodium

Z	Element	Number of Valence Electrons	Ionization Energy (MJ/mol)* IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8	IE_9	IE_{10}
3	Li	1	0.52	7.30	11.81							
4	Be	2	0.90	1.76	14.85	21.01			CORE ELECTRONS			
5	B	3	0.80	2.43	3.66	25.02	32.82					
6	C	4	1.09	2.35	4.62	6.22	37.83	47.28				
7	N	5	1.40	2.86	4.58	7.48	9.44	53.27	64.36			
8	O	6	1.31	3.39	5.30	7.47	10.98	13.33	71.33	84.08		
9	F	7	1.68	3.37	6.05	8.41	11.02	15.16	17.87	92.04	106.43	
10	Ne	8	2.08	3.95	6.12	9.37	12.18	15.24	20.00	23.07	115.38	131.43
11	Na	1	0.50	4.56	6.91	9.54	13.35	16.61	20.11	25.49	28.93	141.37

*MJ/mol, or megajoules per mole = 10^3 kJ/mol.

than IE_3 (3.66 MJ), which is *much* lower than IE_4 (25.02 MJ). From this jump, we know that boron has three electrons in the highest energy level ($1s^22s^22p^1$). Because they are so difficult to remove, *core electrons are not involved in reactions*.

Sample Problem 8.5 Identifying an Element from Its Ionization Energies

Problem Name the Period 3 element with the following ionization energies (kJ/mol), and write its full electron configuration:

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
1012	1903	2910	4956	6278	22,230

Plan We look for a large jump in the IE values, which occurs after all valence electrons have been removed. Then we refer to the periodic table to find the Period 3 element with this number of valence electrons and write its electron configuration.

Solution The large jump occurs after IE_5, indicating that the element has five valence electrons and, thus, is in Group 5A(15). This Period 3 element is phosphorus (P; Z = 15). Its electron configuration is $1s^22s^22p^63s^23p^3$.

FOLLOW-UP PROBLEM 8.5 Element Q is in Period 3 and has the following ionization energies (in kJ/mol):

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
577	1816	2744	11,576	14,829	18,375

Name element Q, and write its full electron configuration.

Trends in Electron Affinity

The **electron affinity (EA)** is the energy change (kJ/mol) accompanying the *addition* of 1 mol of electrons to 1 mol of gaseous atoms or ions. The *first electron affinity* (EA_1) refers to the formation of 1 mol of monovalent (1−) gaseous anions:

$$\text{Atom}(g) + e^- \longrightarrow \text{ion}^-(g) \qquad \Delta E = EA_1$$

As with ionization energy, there is a first electron affinity, a second, and so forth. The first electron is *attracted* by the atom's nucleus, so in most cases, *EA_1 is negative* (energy is released), analogous to the negative ΔH for an exothermic reaction.* But the second electron affinity (EA_2) is always positive because energy must be *absorbed* to overcome electrostatic repulsions and add another electron to a negative ion.

*Some tables of EA_1 list them as positive values because energy would be *absorbed* to remove an electron from the anion.

Figure 8.13 Electron affinities of the main-group elements (in kJ/mol). Values for Group 8A(18) are estimates, which is indicated by parentheses.

1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
H −72.8							**He** (0.0)
Li −59.6	**Be** ≤0	**B** −26.7	**C** −122	**N** +7	**O** −141	**F** −328	**Ne** (+29)
Na −52.9	**Mg** ≤0	**Al** −42.5	**Si** −134	**P** −72.0	**S** −200	**Cl** −349	**Ar** (+35)
K −48.4	**Ca** −2.37	**Ga** −28.9	**Ge** −119	**As** −78.2	**Se** −195	**Br** −325	**Kr** (+39)
Rb −46.9	**Sr** −5.03	**In** −28.9	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** (+41)
Cs −45.5	**Ba** −13.95	**Tl** −19.3	**Pb** −35.1	**Bi** −91.3	**Po** −183	**At** −270	**Rn** (+41)

Factors other than Z_{eff} and atomic size affect electron affinities, so trends are not regular, as are those for size and IE_1. The many exceptions arise from changes in sublevel energy and electron-electron repulsion:

- *Down a group.* We might expect a smooth decrease (smaller negative number) down a group because size increases, and the nucleus is farther away from an electron being added. But only Group 1A(1) exhibits this behavior (Figure 8.13).
- *Across a period.* We might expect a regular increase (larger negative number) across a period because size decreases, and higher Z_{eff} should attract the electron being added more strongly. There is an overall left-to-right increase, but it is not at all regular.

Despite irregularities, relative values of IE and EA show three general patterns:

1. *Reactive nonmetals.* Members of Group 6A(16) and especially Group 7A(17) (the halogens) have high IEs and highly negative (exothermic) EAs: these elements lose electrons with difficulty but attract them strongly. Therefore, *in their ionic compounds, they form negative ions.*
2. *Reactive metals.* Members of Groups 1A(1) and 2A(2) have low IEs and slightly negative (exothermic) EAs: they lose electrons easily but attract them weakly, if at all. Therefore, *in their ionic compounds, they form positive ions.*
3. *Noble gases.* Members of Group 8A(18) have very high IEs and slightly positive (endothermic) EAs: *they tend **not** to lose or gain electrons.* In fact, only the larger members of the group (Kr, Xe, and Rn) form compounds at all.

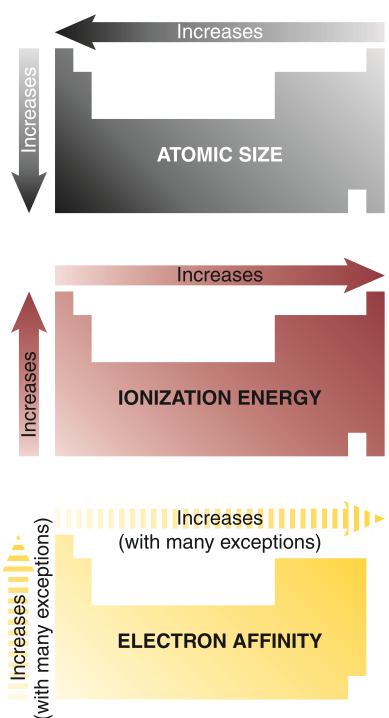


Figure 8.14 Trends in three atomic properties. For electron affinity, the dashed arrows indicate that there are numerous exceptions to expected trends.

Summary of Section 8.3

- Trends in three atomic properties are summarized in Figure 8.14.
- Atomic size (half the distance between nuclei of adjacent atoms) increases down a main group and decreases across a period. In a transition series, size remains relatively constant.
- First ionization energy (the energy required to remove the outermost electron from a mole of gaseous atoms) is inversely related to atomic size: IE_1 decreases down a main group and increases across a period.
- Successive ionization energies of an element show a very large increase after all valence electrons have been removed, because the first inner (core) electron is in an orbital of much lower energy and so is held very tightly.
- Electron affinity (the energy involved in adding an electron to a mole of gaseous atoms) shows many variations from expected trends.
- Based on the relative sizes of IEs and EAs, Group 1A(1) and 2A(2) elements tend to form cations and Group 6A(16) and 7A(17) elements tend to form anions in ionic compounds. Group 8A(18) elements are very unreactive.

8.4 • ATOMIC PROPERTIES AND CHEMICAL REACTIVITY

All physical and chemical behaviors of the elements and their compounds are based on electron configuration and effective nuclear charge. In this section, you'll see how atomic properties determine metallic behavior and the properties of ions.

Trends in Metallic Behavior

The three general classes of elements have distinguishing properties:

- *Metals,* found in the left and lower three-quarters of the periodic table, are typically shiny solids, have moderate to high melting points, are good conductors of heat and electricity, can be machined into wires and sheets, and lose electrons to nonmetals.
- *Nonmetals,* found in the upper right quarter of the table, are typically not shiny, have relatively low melting points, are poor conductors, are mostly crumbly solids or gases, and tend to gain electrons from metals.
- *Metalloids,* found between the other two classes, have intermediate properties.

Thus, *metallic behavior decreases left-to-right across a period and increases down a group in the periodic table* (Figure 8.15).

Remember, though, that some elements don't fit these categories: as graphite, nonmetallic carbon is a good electrical conductor; the nonmetal iodine is shiny; metallic gallium melts in your hand; mercury is a liquid; and iron is brittle. Despite such exceptions, in this discussion, we'll make several generalizations about metallic behavior and its application to the acid-base behavior of oxides.

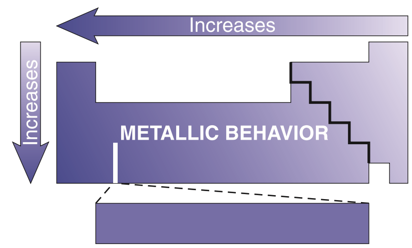


Figure 8.15 Trends in metallic behavior. (Hydrogen appears next to helium.)

Relative Tendency to Lose or Gain Electrons Metals tend to lose electrons to nonmetals during reactions:

1. *Down a main group*. The increase in metallic behavior down a group is consistent with an increase in size and a decrease in IE and is most obvious in groups with more than one class of element, such as Group 5A(15): *elements at the top can form anions, and those at the bottom can form cations.* Nitrogen (N) is a gaseous nonmetal, and phosphorus (P) is a soft nonmetal; both occur occasionally as 3− anions in their compounds. Arsenic (As) and antimony (Sb) are metalloids, with Sb the more metallic, and neither forms ions readily. Bismuth (Bi) is a typical metal, forming a 3+ cation in its mostly ionic compounds. Groups 3A(13), 4A(14), and 6A(16) show a similar trend. But even in Group 2A(2), which contains only metals, the tendency to form cations increases down the group: beryllium (Be) forms covalent compounds with nonmetals, whereas all compounds of barium (Ba) are ionic.

2. *Across a period*. The decrease in metallic behavior across a period is consistent with a decrease in size, an increase in IE, and a more favorable (more negative) EA. Consider Period 3: *elements at the left tend to form cations, and those at the right tend to form anions.* Sodium and magnesium are metals that occur as Na^+ and Mg^{2+} in seawater, minerals, and organisms. Aluminum is a metallic element and occurs as Al^{3+} in some compounds, but it bonds covalently in most others. Silicon (Si) is a shiny metalloid that does not occur as a monatomic ion. Phosphorus is a white, waxy nonmetal that occurs rarely as P^{3-}, whereas crumbly, yellow sulfur forms S^{2-} in many compounds, and gaseous, yellow-green chlorine occurs in nature almost always as Cl^-.

Acid-Base Behavior of Oxides Metals are also distinguished from nonmetals by the acid-base behavior of their oxides in water:

- Most main-group metals *transfer* electrons to oxygen, so their *oxides are ionic. In water, these oxides act as bases,* producing OH^- ions from O^{2-} and reacting with acids.
- Nonmetals *share* electrons with oxygen, so *nonmetal oxides are covalent. In water, these oxides act as acids,* producing H^+ ions and reacting with bases.

Some metals and many metalloids form oxides that are **amphoteric:** they can act as acids *or* bases in water.

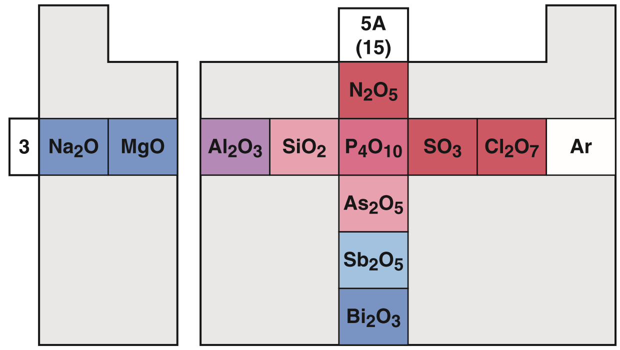


Figure 8.16 Acid-base behavior of some element oxides.

In Figure 8.16, the acid-base behavior of some common oxides of elements in Group 5A(15) and Period 3 is shown with a gradient from blue (basic) to red (acidic):

1. *As elements become more metallic down a group (larger size and smaller IE), their oxides become more basic.* In Group 5A(15), dinitrogen pentoxide, N_2O_5, forms the strong acid HNO_3:

$$N_2O_5(s) + H_2O(l) \longrightarrow 2HNO_3(aq)$$

Tetraphosphorus decoxide, P_4O_{10}, forms the weaker acid H_3PO_4:

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

The oxide of the metalloid arsenic is weakly acidic, whereas that of the metalloid antimony is weakly basic. Bismuth, the most metallic of the group, forms a basic oxide that is insoluble in water but reacts with acid to yield a salt and water:

$$Bi_2O_3(s) + 6HNO_3(aq) \longrightarrow 2Bi(NO_3)_3(aq) + 3H_2O(l)$$

2. *As the elements become less metallic across a period (smaller size and higher IE), their oxides become more acidic.* In Period 3, Na_2O and MgO are strongly basic, and amphoteric aluminum oxide (Al_2O_3) reacts with acid or with base:

$$Al_2O_3(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O(l)$$
$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2NaAl(OH)_4(aq)$$

Silicon dioxide is weakly acidic, forming a salt and water with base:

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

The common oxides of phosphorus, sulfur, and chlorine form acids of increasing strength: H_3PO_4, H_2SO_4, and $HClO_4$.

Properties of Monatomic Ions

So far we have focused on the reactants—the atoms—in the process of electron loss and gain. Now we focus on the products—the ions—considering their electron configurations, magnetic properties, and sizes.

Electron Configurations of Main-Group Ions Why does an ion have a particular charge: Na^+ not Na^{2+}, or F^- not F^{2-}? Why do some metals form two ions, such as Sn^{2+} and Sn^{4+}? The answer relates to the location of the element in the periodic table and the energy associated with losing or gaining electrons:

1. *Ions with a noble gas configuration.* Atoms of the noble gases have very low reactivity because their highest energy level is *filled* (ns^2np^6). Thus, *when elements at either end of a period form ions, they attain a filled outer level—a noble gas configuration.* These elements lie on either side of Group 8A(18), and their ions are **isoelectronic** (Greek *iso*, "same") with the nearest noble gas (Figure 8.17).

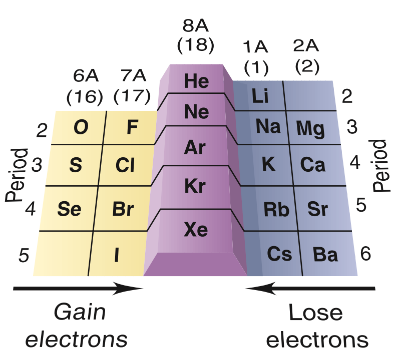


Figure 8.17 Main-group elements whose ions have noble gas electron configurations.

- Elements in Groups 1A(1) and 2A(2) *lose* electrons and become isoelectronic with the *previous* noble gas. The Na^+ ion, for example, is isoelectronic with neon (Ne):

$$Na\ (1s^22s^22p^63s^1) \longrightarrow e^- + Na^+\ ([He]\ 2s^22p^6)\ [\text{isoelectronic with Ne } ([He]\ 2s^22p^6)]$$

- Elements in Groups 6A(16) and 7A(17) *gain* electrons and become isoelectronic with the *next* noble gas. The Br^- ion, for example, is isoelectronic with krypton (Kr):

$$Br\ ([Ar]\ 4s^23d^{10}4p^5) + e^- \longrightarrow Br^-\ ([Ar]\ 4s^23d^{10}4p^6)$$
$$[\text{isoelectronic with Kr } ([Ar]\ 4s^23d^{10}4p^6)]$$

The energy needed to remove electrons from metals or add them to nonmetals determines the charges of the resulting ions:

- *Cations*. Removing another electron from Na^+ or from Mg^{2+} means removing a core electron, which requires too much energy: thus, $NaCl_2$ and MgF_3 do *not* exist.
- *Anions*. Similarly, adding another electron to F^- or to O^{2-} means putting it into the next higher energy level ($n = 3$). With 10 electrons ($1s^22s^22p^6$) acting as inner electrons, the nuclear charge would be shielded very effectively, and adding an outer electron would require too much energy: thus, we never see Na_2F or Mg_3O_2.

2. *Ions without a noble gas configuration*. Except for aluminum, the metals of Groups 3A(13) to 5A(15) do not form ions with noble gas configurations. Instead, they form cations with two different stable configurations:

- *Pseudo–noble gas configuration.* If the metal atom empties its highest energy level, it attains the stability of empty *ns* and *np* sublevels and filled inner $(n - 1)d$ sublevel. This $(n - 1)d^{10}$ configuration is called a **pseudo–noble gas configuration.** For example, tin (Sn; $Z = 50$) loses four electrons to form the tin(IV) ion (Sn^{4+}), which has empty 5*s* and 5*p* sublevels and a filled inner 4*d* sublevel:

$$Sn\ ([Kr]\ 5s^24d^{10}5p^2) \longrightarrow Sn^{4+}\ ([Kr]\ 4d^{10}) + 4e^-$$

- *Inert pair configuration*. Alternatively, the metal atom loses just its *np* electrons and attains a stable configuration with filled *ns* and $(n - 1)d$ sublevels. The retained ns^2 electrons are sometimes called an *inert pair*. For example, in the more common tin(II) ion (Sn^{2+}), the atom loses the two 5*p* electrons and has filled 5*s* and 4*d* sublevels:

$$Sn\ ([Kr]\ 5s^24d^{10}5p^2) \longrightarrow Sn^{2+}\ ([Kr]\ 5s^24d^{10}) + 2e^-$$

Thallium, lead, and bismuth, the largest and, thus, most metallic members of Groups 3A(13) to 5A(15), form ions that retain the ns^2 pair: Tl^+, Pb^{2+}, and Bi^{3+}.

Once again, energy considerations explain these configurations. It would be energetically impossible for metals in Groups 3A(13) to 5A(15) to achieve noble gas configurations: tin, for example, would have to lose 14 electrons—ten 4*d* in addition to the two 5*p* and two 5*s*—to be isoelectronic with krypton (Kr; $Z = 36$), the previous noble gas.

Sample Problem 8.6 Writing Electron Configurations of Main-Group Ions

Problem Using condensed electron configurations, write equations representing the formation of the ion(s) of the following elements:
(a) Iodine ($Z = 53$) **(b)** Potassium ($Z = 19$) **(c)** Indium ($Z = 49$)

Plan We identify the element's position in the periodic table and recall that

- Ions of elements in Groups 1A(1), 2A(2), 6A(16), and 7A(17) are isoelectronic with the nearest noble gas.
- Metals in Groups 3A(13) to 5A(15) lose the *ns* and *np* electrons or just the *np*.

Solution **(a)** Iodine is in Group 7A(17), so it gains one electron, and I^- is isoelectronic with xenon:

$$I\ ([Kr]\ 5s^24d^{10}5p^5) + e^- \longrightarrow I^-\ ([Kr]\ 5s^24d^{10}5p^6) \qquad \text{(same as Xe)}$$

(b) Potassium is in Group 1A(1), so it loses one electron; K^+ is isoelectronic with argon:

$$K\ ([Ar]\ 4s^1) \longrightarrow K^+\ ([Ar]) + e^-$$

(c) Indium is in Group 3A(13), so it loses either three electrons to form In^{3+} (with a pseudo–noble gas configuration) or one to form In^{+} (with an inert pair):

$$\text{In}\ ([\text{Kr}]\ 5s^2 4d^{10} 5p^1) \longrightarrow \text{In}^{3+}\ ([\text{Kr}]\ 4d^{10}) + 3\text{e}^-$$

$$\text{In}\ ([\text{Kr}]\ 5s^2 4d^{10} 5p^1) \longrightarrow \text{In}^{+}\ ([\text{Kr}]\ 5s^2 4d^{10}) + \text{e}^-$$

Check Be sure that the number of electrons in the ion's electron configuration, plus the number gained or lost to form the ion, equals *Z*.

FOLLOW-UP PROBLEM 8.6 Using condensed electron configurations, write equations representing the formation of the ion(s) of the following elements:
(a) Ba (Z = 56) **(b)** O (Z = 8) **(c)** Pb (Z = 82)

Electron Configurations of Transition Metal Ions In contrast to many main-group ions, *transition metal ions rarely attain a noble gas configuration.* Aside from the Period 4 elements scandium, which forms Sc^{3+}, and titanium, which occasionally forms Ti^{4+}, *a transition element typically forms more than one cation by losing all of its ns and some of its (n − 1)d electrons.*

The reason, once again, is that energy costs are too high. Let's consider again the filling of Period 4. At the beginning of Period 4 (the same point holds in other periods), penetration makes the 4*s* sublevel *more stable* than the 3*d*. Therefore, the first and second electrons added enter the 4*s*, which is the outer sublevel. But, the 3*d* is an *inner* sublevel, so as it begins to fill, its electrons are not well shielded from the increasing nuclear charge.

A *crossover in sublevel energy* results: the 3*d* becomes *more stable* than the 4*s* in the transition series (Figure 8.18). This crossover has a major effect on the formation of Period 4 transition metal ions: because the 3*d* electrons are held tightly and shield those in the outer sublevel, *the 4s electrons of a transition metal are lost* ***before*** *the 3d electrons.* Thus, 4*s* electrons are added before 3*d* electrons to form the *atom* and are lost before them to form the *ion,* the so-called "first-in, first-out" rule.

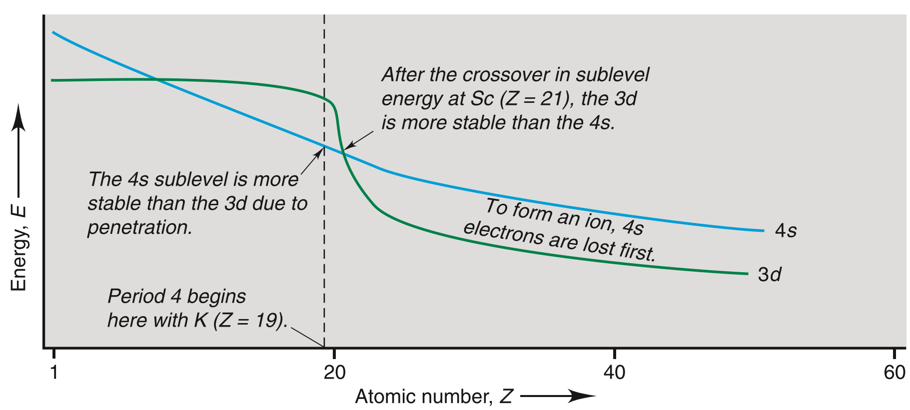


Figure 8.18 The crossover of sublevel energies in Period 4.

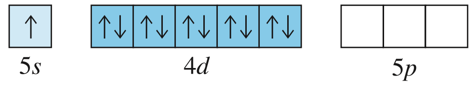
Ion Formation: A Summary of Electron Loss or Gain The various ways that cations form have one point in common—*outer electrons are removed first.* Here is a summary of the rules for formation of any main-group or transition metal ion:

- Main-group *s*-block metals lose all electrons with the highest *n* value.
- Main-group *p*-block metals lose *np* electrons before *ns* electrons.
- Transition (*d*-block) metals lose *ns* electrons before (*n* − 1)*d* electrons.
- Nonmetals gain electrons in the *p* orbitals of highest *n* value.

Magnetic Properties of Transition Metal Ions We learn a great deal about an element's electron configuration from atomic spectra, and magnetic studies provide additional evidence.

Recall that electron spin generates a tiny magnetic field, which causes a beam of H atoms to split in an external magnetic field (see Figure 8.1). Only a beam of a species (atoms, ions, or molecules) with one or more *unpaired* electrons will split. A beam of silver atoms (Ag; $Z = 47$) was used in the original 1921 experiment:

Ag ($Z = 47$) [Kr] $5s^1 4d^{10}$



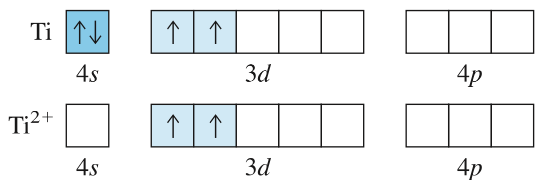
Note the unpaired $5s$ electron. A beam of cadmium atoms (Cd; $Z = 48$) is not split because their $5s$ electrons are *paired* ([Kr] $5s^2 4d^{10}$).

A species with unpaired electrons exhibits **paramagnetism:** it is attracted by an external field. A species with all of its electrons paired exhibits **diamagnetism:** it is not attracted (and is slightly repelled) by the field (Figure 8.19). Many transition metals and their compounds are paramagnetic because their atoms and ions have unpaired electrons.

Let's see how magnetic studies might provide evidence for a proposed electron configuration. Spectral analysis of titanium metal yields the electron configuration [Ar] $4s^2 3d^2$, and experiment shows that the metal is paramagnetic, which indicates the presence of unpaired electrons. Spectral analysis shows that the Ti^{2+} ion is [Ar] $3d^2$, indicating loss of the $4s$ electrons. In support of the spectra, magnetic studies show that Ti^{2+} compounds are paramagnetic. If Ti had lost its $3d$ electrons to form Ti^{2+}, its compounds would be diamagnetic:

$$\text{Ti ([Ar] } 4s^2 3d^2) \longrightarrow \text{Ti}^{2+} \text{ ([Ar] } 3d^2) + 2e^-$$

The partial orbital diagrams are



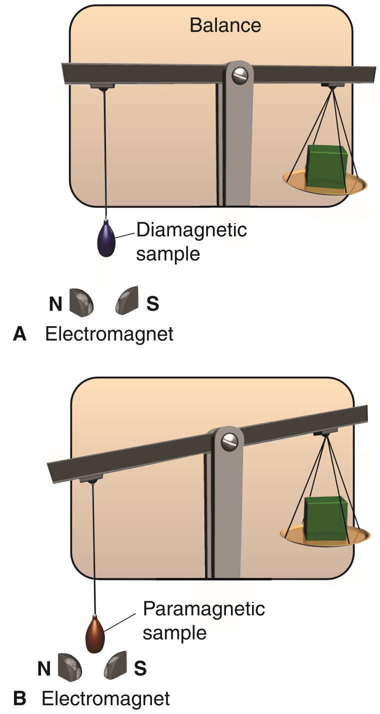


Figure 8.19 Measuring the magnetic behavior of a sample. The substance is weighed with the external magnetic field "off." **A,** If the substance is diamagnetic (has all *paired* electrons), its apparent mass is unaffected (or slightly reduced) with the field "on." **B,** If the substance is paramagnetic (has *unpaired* electrons), its apparent mass increases.

Sample Problem 8.7 Writing Electron Configurations and Predicting Magnetic Behavior of Transition Metal Ions

Problem Use condensed electron configurations to write an equation for the formation of each transition metal ion, and predict whether it is paramagnetic:
(a) Mn^{2+} ($Z = 25$) **(b)** Cr^{3+} ($Z = 24$) **(c)** Hg^{2+} ($Z = 80$)

Plan We first write the condensed electron configuration of the atom, recalling the irregularity for Cr. Then we remove electrons, beginning with *ns* electrons, to attain the ion charge. If unpaired electrons are present, the ion is paramagnetic.

Solution **(a)** Mn ([Ar] $4s^2 3d^5$) $\longrightarrow$ Mn^{2+} ([Ar] $3d^5$) + $2e^-$
There are five unpaired e^-, so Mn^{2+} is paramagnetic.
(b) Cr ([Ar] $4s^1 3d^5$) $\longrightarrow$ Cr^{3+} ([Ar] $3d^3$) + $3e^-$
There are three unpaired e^-, so Cr^{3+} is paramagnetic.
(c) Hg ([Xe] $6s^2 4f^{14} 5d^{10}$) $\longrightarrow$ Hg^{2+} ([Xe] $4f^{14} 5d^{10}$) + $2e^-$
The $4f$ and $5d$ sublevels are filled, so there are no unpaired e^-: Hg^{2+} is *not* paramagnetic.

Check We removed the *ns* electrons first, and the sum of the lost electrons and those in the electron configuration of the ion equals Z.

FOLLOW-UP PROBLEM 8.7 Write the condensed electron configuration of each transition metal ion, and predict whether it is paramagnetic:
(a) V^{3+} ($Z = 23$) **(b)** Ni^{2+} ($Z = 28$) **(c)** La^{3+} ($Z = 57$)

Ionic Size vs. Atomic Size The **ionic radius** is a measure of the size of an ion and is obtained from the distance between the nuclei of adjacent ions in a crystalline ionic compound (Figure 8.20). From the relation between effective nuclear charge (Z_{eff}) and atomic size, we can predict the size of an ion relative to its parent atom:

- *Cations are smaller than parent atoms.* When a cation forms, electrons are *removed from* the outer level. The resulting decrease in shielding due to fewer electron repulsions allows the nucleus to pull the remaining electrons closer.

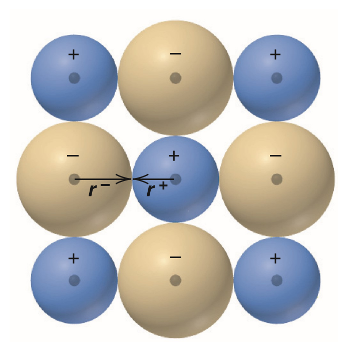


Figure 8.20 Ionic radius. Cation radius (r^+) and anion radius (r^-) together make up the distance between nuclei.

- *Anions are larger than parent atoms.* When an anion forms, electrons are *added to* the outer level. The increase in shielding due to greater electron repulsions means the electrons occupy more space.

Figure 8.21 shows the radii of some main-group ions and their parent atoms:

1. *Down a group, ionic size increases* because n increases.
2. *Across a period,* for instance, Period 3, the pattern is complex:
   - *Among cations,* the increase in Z_{eff} from left to right makes Na^+ larger than Mg^{2+}, which is larger than Al^{3+}.
   - *From last cation to first anion,* a great jump in size occurs: we are *adding* electrons rather than removing them, so repulsions increase sharply. For instance, P^{3-} has eight more electrons than Al^{3+}.
   - *Among anions,* the increase in Z_{eff} from left to right makes P^{3-} larger than S^{2-}, which is larger than Cl^-.
   - *Within an isoelectronic series,* these factors have striking results. Within the dashed outline in Figure 8.21, the ions are isoelectronic with neon. Period 2 anions are much larger than Period 3 cations because the same number of electrons are attracted by an increasing nuclear charge. The pattern is

$$3- > 2- > 1- > 1+ > 2+ > 3+$$

3. *Cation size decreases with charge*. When a metal forms more than one cation, *the greater the ionic charge, the smaller the ionic radius.* Of the two ions of iron, for example, Fe^{3+} has one fewer electron, so shielding is reduced somewhat, and the same nucleus is attracting fewer electrons. As a result, Z_{eff} increases, so Fe^{3+} (65 pm) is smaller than Fe^{2+} (78 pm).

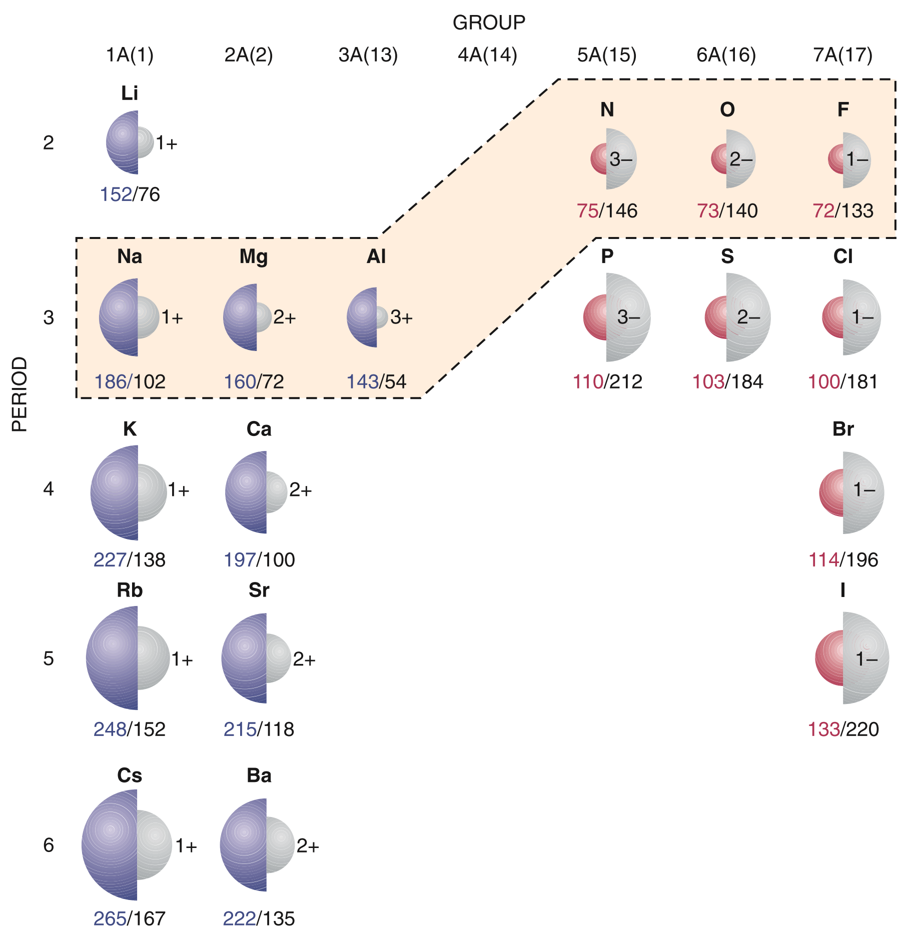


Figure 8.21 Ionic vs. atomic radii. Atomic radii *(color)* and ionic radii *(gray)* are given in picometers. Metal atoms *(blue)* form *smaller* positive ions, and nonmetal atoms *(red)* form *larger* negative ions. Ions in the dashed outline are *isoelectronic* with neon.

Sample Problem 8.8 Ranking Ions by Size

Problem Rank each set of ions in order of *decreasing* size, and explain your ranking:
(a) Ca^{2+}, Sr^{2+}, Mg^{2+} **(b)** K^+, S^{2-}, Cl^- **(c)** Au^+, Au^{3+}

Plan We find the position of each element in the periodic table and apply the ideas presented in the text.

Solution **(a)** Mg^{2+}, Ca^{2+}, and Sr^{2+} are all from Group 2A(2), so their sizes decrease up the group: $Sr^{2+} > Ca^{2+} > Mg^{2+}$.
(b) The ions K^+, S^{2-}, and Cl^- are isoelectronic. S^{2-} has a lower Z_{eff} than Cl^-, so it is larger. K^+ is a cation and has the highest Z_{eff}, so it is smallest: $S^{2-} > Cl^- > K^+$.
(c) Au^+ has a lower charge than Au^{3+}, so it is larger: $Au^+ > Au^{3+}$.

FOLLOW-UP PROBLEM 8.8 Rank the ions in each set in order of *increasing* size:
(a) Cl^-, Br^-, F^- **(b)** Na^+, Mg^{2+}, F^- **(c)** Cr^{2+}, Cr^{3+}

Summary of Section 8.4

- Metallic behavior correlates with large atomic size and low ionization energy. Thus, metallic behavior increases down a group and decreases across a period.
- Within the main groups, metal oxides are basic and nonmetal oxides acidic. Thus, oxides become more acidic across a period and more basic down a group.
- Many main-group elements form ions that are isoelectronic with the nearest noble gas. Removing (or adding) more electrons than needed to attain the noble gas configuration requires a prohibitive amount of energy.
- Metals in Groups 3A(13) to 5A(15) lose either their *np* electrons or both their *ns* and *np* electrons.
- Transition metals lose *ns* electrons before $(n - 1)d$ electrons and commonly form more than one ion.
- Many transition metals and their compounds are paramagnetic because their atoms (or ions) have unpaired electrons.
- Cations are smaller and anions larger than their parent atoms. Ionic radius increases down a group. Across a period, ionic radii generally decrease, but a large increase occurs from the last cation to the first anion.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills to review after studying this chapter.

Related section (§), sample problem (SP), and upcoming end-of-chapter problem (EP) numbers are listed in parentheses.

1. Understand the periodic law and the arrangement of elements by atomic number (Introduction) (EPs 8.1–8.3)
2. Describe the importance of the spin quantum number (m_s) and the exclusion principle for populating an orbital; understand how shielding and penetration lead to the splitting of energy levels into sublevels (§8.1) (EPs 8.4–8.13)
3. Understand orbital filling order, how outer configuration correlates with chemical behavior, and the distinction among inner, outer, and valence electrons; write the set of quantum numbers for any electron in an atom as well as full and condensed electron configurations and orbital diagrams for the atoms of any element (§8.2) (SPs 8.1, 8.2) (EPs 8.14–8.32)
4. Describe atomic size, ionization energy, and electron affinity and their periodic trends; explain patterns in successive ionization energies and identify which electrons are involved in ion formation (to yield a noble gas or pseudo–noble gas electron configuration) (§8.3) (SPs 8.3–8.5) (EPs 8.33–8.47)
5. Describe the general properties of metals and nonmetals and understand how trends in metallic behavior relate to ion formation, oxide acidity, and magnetic behavior; understand the relation between atomic and ionic size and write ion electron configurations (§8.4) (SPs 8.6–8.8) (EPs 8.48–8.64)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

Introduction
periodic law (246)
electron configuration (246)

Section 8.1
spin quantum number (m_s) (247)
exclusion principle (247)
shielding (248)
effective nuclear charge (Z_{eff}) (248)
penetration (248)

Section 8.2
aufbau principle (249)
orbital diagram (249)
Hund's rule (250)
transition elements (253)
inner (core) electrons (256)
outer electrons (256)
valence electrons (256)
inner transition elements (256)
lanthanides (rare earths) (256)
actinides (256)

Section 8.3
atomic size (258)
metallic radius (258)
covalent radius (258)
ionization energy (IE) (260)
electron affinity (EA) (263)

Section 8.4
amphoteric (265)
isoelectronic (266)
pseudo–noble gas configuration (267)
paramagnetism (269)
diamagnetism (269)
ionic radius (269)

Key Equations and Relationships

Numbered and screened concepts are listed for you to refer to or memorize.

8.1 Defining the energy order of sublevels in terms of the angular momentum quantum number (l value) (249):

Order of sublevel energies: $s < p < d < f$

8.2 Meaning of the first ionization energy (260):

$$\text{Atom}(g) \longrightarrow \text{ion}^{+}(g) + e^{-} \qquad \Delta E = \text{IE}_1 > 0$$

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS

Compare your own solutions to these calculation steps and answers.

8.1 The element has eight electrons, so $Z = 8$: oxygen.

1s	2s	2p		
↑↓	↑↓	↑↓	↑	↑

Sixth electron: $n = 2$, $l = 1$, $m_l = 0$, $+\frac{1}{2}$

8.2 (a) For Ni, $1s^22s^22p^63s^23p^64s^23d^8$; [Ar] $4s^23d^8$

4s	3d					4p		
↑↓	↑↓	↑↓	↑↓	↑	↑			

Ni has 18 inner electrons.

(b) For Sr, $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$; [Kr] $5s^2$

5s	4d					5p		
↑↓								

Sr has 36 inner electrons.

(c) For Po, $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^4$; [Xe] $6s^24f^{14}5d^{10}6p^4$

6s	6p		
↑↓	↑↓	↑	↑

Po has 78 inner electrons.

8.3 (a) Cl < Br < Se; (b) Xe < I < Ba

8.4 (a) Sn < Sb < I; (b) Ba < Sr < Ca

8.5 Q is aluminum: $1s^22s^22p^63s^23p^1$

8.6 (a) Ba ([Xe] $6s^2$) $\longrightarrow$ Ba^{2+} ([Xe]) + $2e^-$

(b) O ([He] $2s^22p^4$) + $2e^-$ $\longrightarrow$ O^{2-} ([He] $2s^22p^6$) (same as Ne)

(c) Pb ([Xe] $6s^24f^{14}5d^{10}6p^2$) $\longrightarrow$ Pb^{2+} ([Xe] $6s^24f^{14}5d^{10}$) + $2e^-$

Pb ([Xe] $6s^24f^{14}5d^{10}\,6p^2$) $\longrightarrow$ Pb^{4+} ([Xe] $4f^{14}5d^{10}$) + $4e^-$

8.7 (a) V^{3+}: [Ar] $3d^2$; paramagnetic

(b) Ni^{2+}: [Ar] $3d^8$; paramagnetic

(c) La^{3+}: [Xe]; not paramagnetic (diamagnetic)

8.8 (a) $F^- < Cl^- < Br^-$

(b) $Mg^{2+} < Na^+ < F^-$

(c) $Cr^{3+} < Cr^{2+}$

PROBLEMS

Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

Introduction

8.1 What would be your reaction to a claim that a new element had been discovered and it fit between tin (Sn) and antimony (Sb) in the periodic table?

8.2 In an early 20th century study of atomic x-ray spectra, British physicist Henry Moseley discovered a relationship that replaced atomic mass as the criterion for ordering the elements. By what criterion are the elements now ordered in the periodic table? Give an example of a sequence of element order that was confirmed by Moseley's findings.

8.3 Before Mendeleev published his periodic table, German chemist Johann Döbereiner grouped elements with similar properties into "triads," in which the unknown properties of one member

could be predicted by averaging known values of the properties of the others. To test this idea, predict the values of the following quantities:
(a) The atomic mass of K from the atomic masses of Na and Rb
(b) The melting point of Br_2 from the melting points of Cl_2 (-101.0°C) and I_2 (113.6°C) (actual value $= -7.2$°C)

Characteristics of Many-Electron Atoms

8.4 Summarize the rules for the allowable values of the four quantum numbers of an electron in an atom.

8.5 Which of the quantum numbers relate(s) to the electron only? Which relate(s) to the orbital?

8.6 State the exclusion principle. What does it imply about the number and spin of electrons in an atomic orbital?

8.7 What is the key distinction between sublevel energies in one-electron species, such as the H atom, and those in many-electron species, such as the C atom? What factors lead to this distinction? Would you expect the pattern of sublevel energies in Be^{3+} to be more like that in H or that in C? Explain.

8.8 Define *shielding* and *effective nuclear charge*. What is the connection between the two?

8.9 What is penetration? How is it related to shielding? Use the penetration effect to explain the difference in relative orbital energies of a 3*p* and a 3*d* electron in the same atom.

8.10 How many electrons in an atom can have each of the following quantum number or sublevel designations?
(a) $n = 2, l = 1$ (b) 3*d* (c) 4*s*

8.11 How many electrons in an atom can have each of the following quantum number or sublevel designations?
(a) $n = 2, l = 1, m_l = 0$ (b) 5*p* (c) $n = 4, l = 3$

8.12 How many electrons in an atom can have each of the following quantum number or sublevel designations?
(a) 4*p* (b) $n = 3, l = 1, m_l = +1$ (c) $n = 5, l = 3$

8.13 How many electrons in an atom can have each of the following quantum number or sublevel designations?
(a) 2*s* (b) $n = 3, l = 2$ (c) 6*d*

The Quantum-Mechanical Model and the Periodic Table

(Sample Problems 8.1 and 8.2)

8.14 State the periodic law, and explain its relation to electron configuration. (Use Na and K in your explanation.)

8.15 State Hund's rule in your own words, and show its application in the orbital diagram of the nitrogen atom.

8.16 How does the aufbau principle, in connection with the periodic law, lead to the format of the periodic table?

8.17 For main-group elements, are outer electron configurations similar or different within a group? Within a period? Explain.

8.18 Write a full set of quantum numbers for the following:
(a) The outermost electron in an Rb atom
(b) The electron gained when an S^- ion becomes an S^{2-} ion
(c) The electron lost when an Ag atom ionizes
(d) The electron gained when an F^- ion forms from an F atom

8.19 Write a full set of quantum numbers for the following:
(a) The outermost electron in an Li atom
(b) The electron gained when a Br atom becomes a Br^- ion
(c) The electron lost when a Cs atom ionizes
(d) The highest energy electron in the ground-state B atom

8.20 Write the full ground-state electron configuration for each:
(a) Rb (b) Ge (c) Ar

8.21 Write the full ground-state electron configuration for each:
(a) Br (b) Mg (c) Se

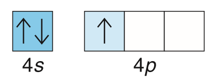
8.22 Draw a partial (valence-level) orbital diagram, and write the condensed ground-state electron configuration for each:
(a) Ti (b) Cl (c) V

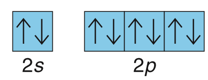
8.23 Draw a partial (valence-level) orbital diagram, and write the condensed ground-state electron configuration for each:
(a) Ba (b) Co (c) Ag

8.24 Draw the partial (valence-level) orbital diagram, and write the symbol, group number, and period number of the element:
(a) [He] $2s^22p^4$ (b) [Ne] $3s^23p^3$

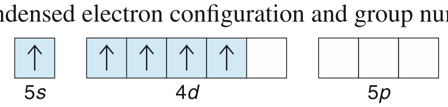
8.25 Draw the partial (valence-level) orbital diagram, and write the symbol, group number, and period number of the element:
(a) [Kr] $5s^24d^{10}$ (b) [Ar] $4s^23d^8$

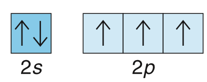
8.26 From each partial (valence-level) orbital diagram, write the condensed electron configuration and group number:

(a) 

(b) 

8.27 From each partial (valence-level) orbital diagram, write the condensed electron configuration and group number:

(a) 

(b) 

8.28 How many inner, outer, and valence electrons are present in an atom of each of the following elements?
(a) O (b) Sn (c) Ca (d) Fe (e) Se

8.29 How many inner, outer, and valence electrons are present in an atom of each of the following elements?
(a) Br (b) Cs (c) Cr (d) Sr (e) F

8.30 Identify each element below, and give the symbols of the other elements in its group:
(a) [He] $2s^22p^1$ (b) [Ne] $3s^23p^4$ (c) [Xe] $6s^25d^1$

8.31 Identify each element below, and give the symbols of the other elements in its group:
(a) [Ar] $4s^23d^{10}4p^4$ (b) [Xe] $6s^24f^{14}5d^2$ (c) [Ar] $4s^23d^5$

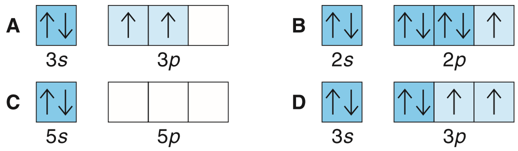
8.32 One reason spectroscopists study excited states is to gain information about the energies of orbitals that are unoccupied in an atom's ground state. Each of the following electron configurations represents an atom in an excited state. Identify the element, and write its condensed ground-state configuration:
(a) $1s^22s^22p^63s^13p^1$ (b) $1s^22s^22p^63s^23p^44s^1$
(c) $1s^22s^22p^63s^23p^64s^23d^44p^1$ (d) $1s^22s^22p^53s^1$

Trends in Three Atomic Properties

(Sample Problems 8.3 to 8.5)

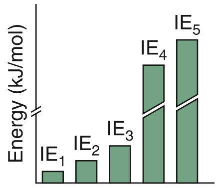
8.33 Explain the relationship between the trends in atomic size and in ionization energy within the main groups.

8.34 Given the following partial (valence-level) electron configurations, (a) identify each element, (b) rank the four elements in order of increasing atomic size, and (c) rank them in order of increasing ionization energy:



8.35 In what region of the periodic table will you find elements with relatively high IEs? With relatively low IEs?

8.36 (a) Why do successive IEs of a given element always increase? (b) When the difference between successive IEs of a given element is exceptionally large (for example, between IE_1 and IE_2 of K), what do we learn about its electron configuration? (c) The bars represent the relative magnitudes of the first five ionization energies of an atom:



Identify the element and write its complete electron configuration, assuming it comes from (a) Period 2; (b) Period 3; (c) Period 4.

8.37 In a plot of IE_1 for the Period 3 elements (see Figure 8.10, p. 261), why do the values for elements in Groups 3A(13) and 6A(16) drop slightly below the generally increasing trend?

8.38 Which group in the periodic table has elements with high (endothermic) IE_1 and very negative (exothermic) first electron affinities (EA_1)? Give the charge on the ions these atoms form.

8.39 How does *d*-electron shielding influence atomic size among the Period 4 transition elements?

8.40 Arrange each set in order of *increasing* atomic size:
(a) Rb, K, Cs (b) C, O, Be (c) Cl, K, S (d) Mg, K, Ca

8.41 Arrange each set in order of *decreasing* atomic size:
(a) Ge, Pb, Sn (b) Sn, Te, Sr (c) F, Ne, Na (d) Be, Mg, Na

8.42 Arrange each set of atoms in order of *increasing* IE_1:
(a) Sr, Ca, Ba (b) N, B, Ne (c) Br, Rb, Se (d) As, Sb, Sn

8.43 Arrange each set of atoms in order of *decreasing* IE_1:
(a) Na, Li, K (b) Be, F, C (c) Cl, Ar, Na (d) Cl, Br, Se

8.44 Write the full electron configuration of the Period 2 element with the following successive IEs (in kJ/mol):

$IE_1 = 801$ $IE_2 = 2427$ $IE_3 = 3659$
$IE_4 = 25{,}022$ $IE_5 = 32{,}822$

8.45 Write the full electron configuration of the Period 3 element with the following successive IEs (in kJ/mol):

$IE_1 = 738$ $IE_2 = 1450$ $IE_3 = 7732$
$IE_4 = 10{,}539$ $IE_5 = 13{,}628$

8.46 Which element in each of the following sets would you expect to have the *highest* IE_2?
(a) Na, Mg, Al (b) Na, K, Fe (c) Sc, Be, Mg

8.47 Which element in each of the following sets would you expect to have the *lowest* IE_3?
(a) Na, Mg, Al (b) K, Ca, Sc (c) Li, Al, B

Atomic Properties and Chemical Reactivity

(Sample Problems 8.6 to 8.8)

8.48 List three ways in which metals and nonmetals differ.

8.49 Summarize the trend in metallic character as a function of position in the periodic table. Is it the same as the trend in atomic size? The trend in ionization energy?

8.50 Summarize the acid-base behavior of the main-group metal and nonmetal oxides in water. How does oxide acidity in water change down a group and across a period?

8.51 What is a pseudo–noble gas configuration? Give an example of one ion from Group 3A(13) that has it.

8.52 The charges of a set of isoelectronic ions vary from 3+ to 3−. Place the ions in order of increasing size.

8.53 Which element would you expect to be *more* metallic?
(a) Ca or Rb (b) Mg or Ra (c) Br or I

8.54 Which element would you expect to be *more* metallic?
(a) S or Cl (b) In or Al (c) As or Br

8.55 Write the charge and full ground-state electron configuration of the monatomic ion most likely to be formed by each:
(a) Cl (b) Na (c) Ca

8.56 Write the charge and full ground-state electron configuration of the monatomic ion most likely to be formed by each:
(a) Rb (b) N (c) Br

8.57 How many unpaired electrons are present in a ground-state atom from each of the following groups?
(a) 2A(2) (b) 5A(15) (c) 8A(18) (d) 3A(13)

8.58 How many unpaired electrons are present in a ground-state atom from each of the following groups?
(a) 4A(14) (b) 7A(17) (c) 1A(1) (d) 6A(16)

8.59 Write the condensed ground-state electron configurations of these transition metal ions, and state which are paramagnetic:
(a) V^{3+} (b) Cd^{2+} (c) Co^{3+} (d) Ag^+

8.60 Write the condensed ground-state electron configurations of these transition metal ions, and state which are paramagnetic:
(a) Mo^{3+} (b) Au^+ (c) Mn^{2+} (d) Hf^{2+}

8.61 Palladium (Pd; $Z = 46$) is diamagnetic. Draw partial orbital diagrams to show which of the following electron configurations is consistent with this fact:
(a) [Kr] $5s^24d^8$ (b) [Kr] $4d^{10}$ (c) [Kr] $5s^14d^9$

8.62 Niobium (Nb; $Z = 41$) has an anomalous ground-state electron configuration for a Group 5B(5) element: [Kr] $5s^14d^4$. What is the expected electron configuration for elements in this group? Draw partial orbital diagrams to show how paramagnetic measurements could support niobium's actual configuration.

8.63 Rank the ions in each set in order of *increasing* size, and explain your ranking:
(a) Li^+, K^+, Na^+ (b) Se^{2-}, Rb^+, Br^- (c) O^{2-}, F^-, N^{3-}

8.64 Rank the ions in each set in order of *decreasing* size, and explain your ranking:
(a) Se^{2-}, S^{2-}, O^{2-} (b) Te^{2-}, Cs^+, I^- (c) Sr^{2+}, Ba^{2+}, Cs^+

Comprehensive Problems

8.65 Name the element described in each of the following:
(a) Smallest atomic radius in Group 6A(16)
(b) Largest atomic radius in Period 6
(c) Smallest metal in Period 3
(d) Highest IE_1 in Group 4A(14)
(e) Lowest IE_1 in Period 5
(f) Most metallic in Group 5A(15)
(g) Group 3A(13) element that forms the most basic oxide
(h) Period 4 element with highest energy level filled
(i) Condensed ground-state electron configuration of [Ne] $3s^23p^2$
(j) Condensed ground-state electron configuration of [Kr] $5s^24d^6$
(k) Forms 2+ ion with electron configuration [Ar] $3d^3$
(l) Period 5 element that forms 3+ ion with pseudo–noble gas configuration
(m) Period 4 transition element that forms 3+ diamagnetic ion
(n) Period 4 transition element that forms 2+ ion with a half-filled *d* sublevel
(o) Heaviest lanthanide
(p) Period 3 element whose 2− ion is isoelectronic with Ar
(q) Alkaline earth metal whose cation is isoelectronic with Kr
(r) Group 5A(15) metalloid with the most acidic oxide

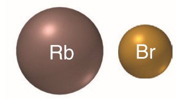
8.66 When a nonmetal oxide reacts with water, it forms an oxoacid with the same oxidation number as the nonmetal. Give the name and formula of the oxide used to prepare each of these oxoacids: (a) hypochlorous acid; (b) chlorous acid; (c) chloric acid; (d) perchloric acid; (e) sulfuric acid; (f) sulfurous acid; (g) nitric acid; (h) nitrous acid; (i) carbonic acid; (j) phosphoric acid.

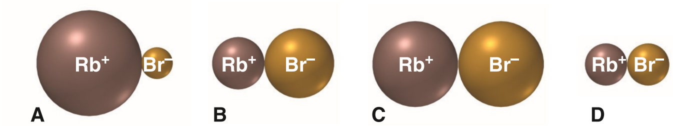
8.67 The energy difference between the 5*d* and 6*s* sublevels in gold accounts for its color. Assuming this energy difference is about 2.7 eV (electron volt; $1\ \text{eV} = 1.602\times10^{-19}$ J), explain why gold has a warm yellow color.

8.68 Write the formula and name of the compound formed from the following ionic interactions: (a) The 2+ ion and the 1− ion are both isoelectronic with the atoms of a chemically unreactive Period 4 element. (b) The 2+ ion and the 2− ion are both isoelectronic with the Period 3 noble gas. (c) The 2+ ion is the smallest with a filled *d* sublevel; the anion forms from the smallest halogen. (d) The ions form from the largest and smallest ionizable atoms in Period 2.

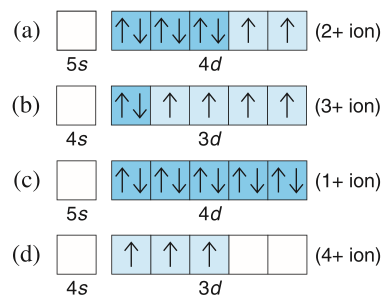
8.69 The hot glowing gases around the Sun, the *corona*, can reach millions of degrees Celsius, high enough to remove many electrons from gaseous atoms. Iron ions with charges as high as 14+ have been observed in the corona. Which ions from Fe^{+} to Fe^{14+} are paramagnetic? Which would be most strongly attracted to a magnetic field?

8.70 Rubidium and bromine atoms are depicted at right. (a) What monatomic ions do they form? (b) What electronic feature characterizes this pair of ions, and which noble gas are they related to? (c) Which pair best represents the relative ionic sizes?



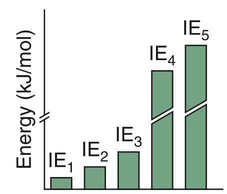


8.71 Partial (valence-level) electron configurations for four different ions are shown below:



Identify the elements from which the ions are derived, and write the formula of the oxide each ion forms.

8.72 The bars in the graph at right represent the relative magnitudes of the first five ionization energies of an atom. Identify the element and write its complete electron configuration, assuming it comes from (a) Period 2; (b) Period 3; (c) Period 4.



8.73 Data from the planet Zog for some main-group elements are shown below (Zoggian units are linearly related to Earth units but are not shown). Radio signals from Zog reveal that balloonium is a monatomic gas with two positive nuclear charges. Use the data to deduce the names that Earthlings give to these elements:

Name	Atomic Radius	IE_1	EA_1
Balloonium	10	339	0
Inertium	24	297	+4.1
Allotropium	34	143	−28.6
Brinium	63	70.9	−7.6
Canium	47	101	−15.3
Fertilium	25	200	0
Liquidium	38	163	−46.4
Utilium	48	82.4	−6.1
Crimsonium	72	78.4	−2.9