# FACETS OF CHEMISTRY 8.2

# Irregularities in the Periodic Variations in Ionization Energy and Electron Affinity

The variation in first ionization energy across a period is not a smooth one, as seen in the graph in Figure 1 for the elements in Period 2. The first irregularity occurs between Be and B, where the IE increases from Li to Be but then decreases from Be to B. This happens because there is a change in the nature of the subshell from which the electron is being removed. For Li and Be, the electron is removed from the 2s subshell, but at boron the first electron comes from the higher-energy 2p subshell where it is not bound so tightly.

Another irregularity occurs between nitrogen and oxygen. For nitrogen, the electron that's removed comes from a singly occupied orbital. For oxygen, the electron is taken from an orbital that already contains an electron. We can diagram this as follows:

For oxygen, repulsions between the two electrons in the p orbital that's about to lose an electron help the electron leave. This "help" is absent for the electron that's about to leave the p orbital of nitrogen. As a result, it is not as difficult to remove one electron from an oxygen atom as it is to remove one electron from a nitrogen atom.

As with ionization energy, there are irregularities in the periodic trends for electron affinity. For example, the Group IIA elements have little tendency to acquire electrons because their outer shell s orbitals are filled. The incoming electron must enter a higher-energy p orbital. We also see that the EA for elements in Group VA are either endothermic or only slightly exothermic. This is because the incoming electron must enter an orbital already occupied by an electron.

One of the most interesting irregularities occurs between Periods 2 and 3 among the nonmetals. In any group, the element in Period 2 has a less exothermic electron affinity than the element below it. The reason seems to be the small size of the nonmetal atoms of Period 2, which are among the smallest elements in the periodic table. Repulsions between the many electrons in the small valence shells of these atoms leads to a lower-than-expected attraction for an incoming electron and a less exothermic electron affinity than the element below in Period 3.

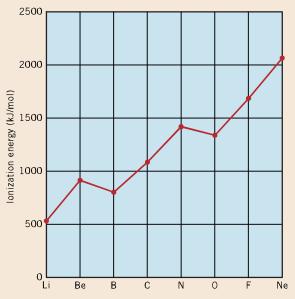


FIGURE 1 Variation in IE for the Period 2 elements Li through F.

# **Electron affinity**

The **electron affinity** (abbreviated **EA**) is the potential energy change associated with the addition of an electron to a gaseous atom or ion in its ground state. For an element X, it is the change in potential energy associated with the process

$$X(g) + e^{-} \longrightarrow X^{-}(g)$$

As with ionization energy, electron affinities are usually expressed in units of kilojoules per mole, so we can also view the IE as the energy change associated with adding 1 mol of electrons to 1 mol of gaseous atoms or ions.

For nearly all the elements, the addition of one electron to the neutral atom is exothermic, and the EA is given as a negative value. This is because the incoming electron experiences an attraction to the nucleus that causes the potential energy to be lowered as the electron approaches the atom. However, when a second elec-

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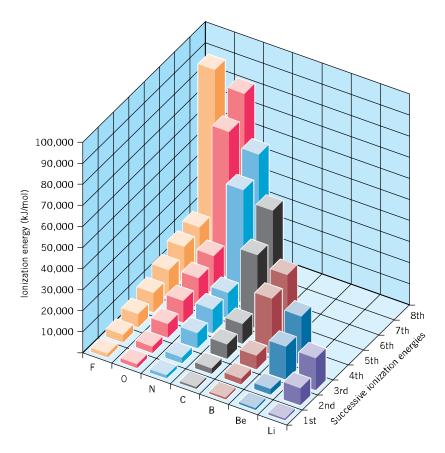


FIGURE 8.33 Variations in successive ionization energies for the elements lithium through fluorine.

tron must be added, as in the formation of the oxide ion, O<sup>2-</sup>, work must be done to force the electron into an already negative ion.

Change	EA (kJ/mol)
$O(g) + e^- \rightarrow O^-(g)$	-141
$O^-(g) + e^- \rightarrow O^{2-}(g)$	+844
$O(g) + 2e^- \rightarrow O^{2-}(g)$	+703 (net)

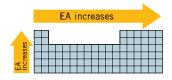


FIGURE 8.34 Variation of electron affinity (as an exothermic quantity) within the periodic table.



Periodic trends in electron affinity

Notice that more energy is absorbed adding an electron to the  $O^-$  ion than is released by adding an electron to the O atom. Overall, the formation of an isolated oxide ion leads to a net increase in potential energy (so we say its formation is *endothermic*). The same applies to the formation of *any* negative ion with a charge larger than 1-.

The electron affinities of the representative elements are given in Table 8.3, and we see that periodic trends in electron affinity roughly parallel those for ionization energy. (See Facets of Chemistry 8.2 for a discussion of some of the irregularities in the trends.)

Although there are some irregularities, overall, the electron affinities of the elements become more *exothermic* going from left to right across a period and from bottom to top in a group (Figure 8.34).

This shouldn't be surprising, because a valence shell that loses electrons easily (low IE) will have little attraction for additional electrons (small EA). On the other hand, a valence shell that holds its electrons tightly will also tend to bind an additional electron tightly.

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TABI	E 8.3	ELECTRON ELEMENTS		OF THE REP	RESENTATIV	E
IA	IIA	IIIA	IVA	VA	VIA	VIIA
H -73						
Li	Be	B	C	N	O	F
-60	+238	-27	-122	~ +9	-141	-328
Na	Mg	Al	Si	P	S	Cl
-53	+230	-44	-134	-72	-200	-348
K	Ca	Ga	Ge	As	Se	Br
-48	+155	-30	-120	-77	-195	-325
Rb	Sr	In	Sn	Sb	Te	I
-47	+167	-30	-121	-101	-190	-295
Cs	Ba	TI	Pb	Bi	Po	At
-45	+50	-30	-110	-110	-183	-270

# SUMMARY

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**Electromagnetic Energy** Electromagnetic energy, or light energy, travels through space at a constant speed of  $3.00 \times 10^8$  m s<sup>-1</sup> in the form of waves. The **wavelength**,  $\lambda$ , and **frequency**,  $\nu$ , of the wave are related by the equation  $\lambda \nu = c$ , where c is the **speed of light**. The SI unit for frequency is the **hertz** (**Hz**, 1 Hz = 1 s<sup>-1</sup>). Light also behaves as if it consists of small packets of energy, called **photons** or **quanta**. The energy delivered by a photon is proportional to the frequency of the light and is given by the equation  $E = h\nu$ , where h is **Planck's constant**. White light is composed of all the frequencies visible to the eye and can be split into a **continuous spectrum**. Visible light represents only a small portion of the entire **electromagnetic spectrum**, which also includes **X rays**, **ultraviolet**, **infrared**, **radio**, and **TV** waves, and **microwaves**.

Atomic Spectra The occurrence of line spectra tells us that atoms can emit energy only in discrete amounts and suggests that the energy of the electron is quantized; that is, the electron is restricted to certain specific energy levels in an atom. Niels Bohr recognized this and, although his theory was later shown to be incorrect, he was the first to propose a model that was able to account for the Rydberg equation. Bohr was the first to introduce the idea of quantum numbers.

**Matter Waves** The wave behavior of electrons and other tiny particles, which can be demonstrated by **diffraction** experiments, was suggested by de Broglie. Schrödinger applied wave theory to the atom and launched the theory we call **wave mechanics** or **quantum mechanics**. This theory tells us that electron waves in atoms are **standing waves** whose crests and **nodes** are stationary. Each standing wave, or **orbital**, is characterized by three quantum numbers, n,  $\ell$ , and  $m_{\ell}$  (**principal, secondary**, and **magnetic quantum numbers**, repectively). **Shells** are designated by n (which can range from 1 to  $\infty$ ),

**subshells** by  $\ell$  (which can range from 0 to n-1), and orbitals within subshells by  $m_{\ell}$  (which can range from  $-\ell$  to  $+\ell$ ).

**Electron Configurations** The electron has magnetic properties that are explained in terms of spin. The spin quantum **number,**  $m_s$ , can have values of  $\pm \frac{1}{2}$  or  $-\frac{1}{2}$ . The **Pauli exclusion** principle limits orbitals to a maximum population of two electrons with paired spins. Substances with unpaired electrons are paramagnetic and are attracted weakly to a magnetic field. Substances with only paired electrons are diamagnetic and are slightly repelled by a magnetic field. The electron configuration of an element in its ground state is obtained by filling orbitals beginning with the 1s subshell and following the Pauli exclusion principle and Hund's rule (which states that electrons spread out as much as possible in orbitals of equal energy). The periodic table serves as a guide in predicting electron configurations. Abbreviated configurations show subshell populations outside a noble gas core. Valence shell configurations show the populations of subshells in the outer shell of an atom of the representative elements. Sometimes we represent electron configurations using orbital diagrams. Unexpected configurations occur for chromium and copper because of the extra stability of half-filled and filled subshells.

**Orbital Shapes** The **Heisenberg uncertainty principle** says we cannot know exactly the position and velocity of an electron both at the same instant. Consequently, wave mechanics describes the probable locations of electrons in atoms. In each orbital the electron is conveniently viewed as an **electron cloud** with a varying **electron density**. All s orbitals are spherical; each p orbital consists of two lobes with a **nodal plane** between them. A p subshell has three p orbitals whose axes are mutually perpendicular and point along the x, y, and z axes of an imaginary coordinate system centered at the nucleus. Four of the five d orbitals in a d subshell have the same shape, with

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four lobes of electron density each. The fifth has two lobes of electron density pointing in opposite directions along the z axis and a ring of electron density in the x-y plane.

**Atomic Properties** The amount of positive charge felt by the valence electrons of an atom is the **effective nuclear charge**. This is less than the actual nuclear charge because core electrons partially shield the valence electrons from the full positive charge of the nucleus. **Atomic radii** depend on the value of n of the valence shell orbitals and the effective nuclear charge experienced by the valence electrons. These radii are expressed in units of picometers or nanometers, or an older unit called the **angstrom** ( $\mathring{\mathbf{A}}$ );  $1\mathring{\mathbf{A}} = 100 \,\mathrm{pm} = 0.1 \,\mathrm{nm}$ . Atomic radii decrease from left to right in a period and from bottom to top in a group in the periodic table. Negative ions are larger than the atoms from which they are formed; positive ions are smaller than the atoms from which they are formed.

**Ionization energy (IE)** is the energy needed to remove an electron from an isolated gaseous atom, molecule, or ion in its ground state; it is endothermic. The first ionization energies of the elements increase from left to right in a group and from bottom to top in a period. (Irregularities occur in a period when the nature of the orbital from which the electron is removed changes and when the electron removed is first taken from a doubly occupied p orbital.) Successive ionization energies become larger, but there is a very large jump when the next electron must come from the noble gas core beneath the valence shell.

Electron affinity (EA) is the potential energy change associated with the addition of an electron to a gaseous atom or ion in its ground state. For atoms, the first EA is usually exothermic. When more than one electron is added to an atom, the overall potential energy change is endothermic. In general, electron affinity becomes more exothermic from left to right in a period and from bottom to top in a group. (However, the EA of second-period nonmetals is less exothermic than for the nonmetals of the third period. Irregularities across a period occur when the electron being added must enter the next higher-energy subshell and when it must enter a half-filled p subshell.)

# TOOLS YOU HAVE LEARNED

The table below lists the tools you have learned in this chapter. Notice that only two of them are related to numerical calculations. The others are conceptual tools that we use in analyzing properties of substances in terms of the underlying structure of matter. Review all these tools and refer to them, if necessary, when working on the Thinking-It-Through problems and the Review Exercises that follow.

Thinking it through problems and the neview Exercises that follow.				
<b>TOOL Wavelength-frequency relationship</b> (page 306)	HOW IT WORKS  We need this to convert between wavelength and frequency.			
Energy of a photon (page 310)	This equation is used to calculate the energy carried by a photon of frequency $\nu$ . Also, $\nu$ can be calculated if $E$ is known.			
Periodic table (page 328)	We will use the periodic table as a tool for many purposes. In this chapter, you learned to use the periodic table as an aid in writing electron configurations of the elements and as a tool to correlate an element's location in the table to properties such as atomic radius, ionization energy, and electron affinity.			
Periodic trends in atomic and ionic size (page 340)	We are able to compare the sizes of atoms and ions.			
Periodic trends in ionization energy (page 341)	We are able to compare the ease with which atoms of the elements lose electrons.			
Periodic trends in electron affinity (page 344)	We are able to compare the tendency of atoms or ions to gain electrons.			

# THINKING IT THROUGH

Need extra help? Visit the Brady/ Senese web site at www.wiley.com/ college/brady



The goal for the following problems is not to find the answers themselves, but rather to assemble the information needed to solve them and explain how you would use the information to find the answers. The problems in Level 2 are more challenging than those in Level 1 and may contain more data than are required, in which case you are also asked to identify the unnecessary data. Detailed answers to the Thinking-It-Through problems can be found on the web site.

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#### **Level 1 Problems**

- 1. An FM radio station broadcasts at a frequency of 101.9 MHz. What is the wavelength of these radio waves expressed in meters? How many peaks of these waves pass a given point each second? (Set up the calculation.)
- 2. The human ear does not respond to sounds with frequencies higher than 20 kHz. Sound is not electromagnetic radiation; it travels at a speed of about 330 m s<sup>-1</sup> through air. What is the distance between peaks of sound waves of this frequency, in meters? (Show how you would set up the calculation.)
- 3. Ultraviolet (UV) radiation can cause sunburn and has been implicated as a causative factor in the formation of certain skin cancers. A typical photon of UV light has a wavelength of 150 nm. How can you calculate the energy of a photon of this light? How many times larger is this than the energy of a photon emitted by a high-voltage wire carrying 60 Hz alternating current?
- **4.** For a hydrogen atom, explain how to calculate the frequency of the photon that is emitted when the electron drops from an energy level that has n = 6 to n = 2. Describe how you would calculate the wavelength of this light. How can you determine what color the light is?
- 5. Atoms of which of the following elements are paramagnetic? (a) Mg, (b) Zn, (c) As, (d) Ar, (e) Ag
- **6.** The atoms of which element have valence electrons that experience the greater effective nuclear charge, silicon or sulfur? Explain the reasoning required to answer this question.
- 7. State the specific relationship that allows you to determine
- (a) which element has the larger atoms, Ge or S.
- (b) which element is likely to have the larger first ionization energy, phosphorus or sulfur.
- (c) which element is likely to have the more exothermic electron affinity, phosphorus or sulfur.

#### **Level 2 Problems**

- **8.** Explain in detail how to calculate the ionization energy of the hydrogen atom from information provided in this chapter.
- 9. Magnesium forms the ion  $\mathrm{Mg^{2+}}$  when a magnesium atom loses two electrons. Show how you would calculate the energy required to remove two electrons from a mole of magnesium atoms. How much water (in grams) could have its temperature raised from room temperature (25 °C) to the boiling point (100 °C) by the energy needed to remove two electrons from a mole of magnesium atoms? Set up the calculation.
- 10. Explain how one can easily determine the ionization energy of the fluoride ion,  $F^-$ . Is this ionization energy endothermic or exothermic?
- 11. How can you determine the electron affinity of an Al<sup>3+</sup> ion?
- 12. How can you show that Na(g) + Cl(g) is more stable (of lower energy) than  $Na^+(g) + Cl^-(g)$ , assuming infinite distance of separation between atoms or ions? The potential energy of the  $Na^+$  and  $Cl^-$  ions is inversely proportional to the distance between the ions and is given by the equation

$$E = \frac{z^+ z^-}{4\pi d\epsilon_0^2}$$

where  $z^+$  and  $z^-$  are the charges on the cation and anion, respectively, in units of coulombs, d is the distance between the ions in meters, and  $\epsilon_0$  is a constant which equals  $8.85 \times 10^{-12} \, \text{C}^2 \, \text{m}^{-1} \, \text{J}^{-1}$ . Describe how you would use this equation to determine the distance below which the energy of the Na<sup>+</sup> and Cl<sup>-</sup> ions is lower than the energy of the neutral atoms.

13. What wavelength of light would be required to eject an electron from an atom of sodium? Set up the calculation.

# **REVIEW QUESTIONS**

#### **Electromagnetic Radiation**

- **8.1** In general terms, why do we call light *electromagnetic radiation*?
- **8.2** In general, what does the term *frequency* imply? What is meant by the term *frequency of light*? What symbol is used for it, and what is the SI unit (and symbol) for frequency?
- **8.3** What is meant by the term wavelength of light? What symbol is used for it?
- **8.4** Sketch a picture of a wave and label its wavelength and its amplitude.
- **8.5** Which property of light waves affects the brightness of the light? Which affects the color of the light? Which affects the energy of the light?
- **8.6** Arrange the following regions of the electromagnetic spectrum in order of increasing wavelength (i.e., shortest wavelength → longest wavelength): microwave, TV, X-ray, ultraviolet, visible, infrared, gamma rays.
- **8.7** What wavelength range is covered by the *visible spectrum*?

- **8.8** Arrange the following colors of visible light in order of increasing wavelength: orange, green, blue, yellow, violet, red.
- **8.9** Write the equation that relates the wavelength and frequency of a light wave.
- **8.10** How is the frequency of a particular type of radiation related to the energy associated with it? (Give an equation, defining all symbols.)
- **8.11** What is a photon?
- **8.12** Show that the energy of a photon is given by the equation  $E = hc/\lambda$ .
- **8.13** Examine each of the following pairs and state which of the two has the higher *energy*:
- (a) microwaves and infrared
- (b) visible light and infrared
- (c) ultraviolet light and X rays
- (d) visible light and ultraviolet light
- **8.14** What is a quantum of energy?

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#### **Atomic Spectra**

- **8.15** What is an atomic spectrum? How does it differ from a continuous spectrum?
- **8.16** What fundamental fact is implied by the existence of atomic spectra?

#### **Bohr Atom and the Hydrogen Spectrum**

- **8.17** Describe Niels Bohr's model of the structure of the hydrogen atom.
- **8.18** In qualitative terms, how did Bohr's model account for the atomic spectrum of hydrogen?
- **8.19** What is the term used to describe the lowest energy state of an atom?
- **8.20** In what way was Bohr's theory a success? How was it a failure?

#### **Wave Nature of Matter**

- **8.21** How does the behavior of very small particles differ from that of the larger, more massive objects that we meet in everyday life? Why don't we notice this same behavior for the larger, more massive objects?
- **8.22** Describe the phenomenon called *diffraction*. How can this be used to demonstrate that de Broglie's theory was correct?
- **8.23** What experiment could you perform to determine whether a beam was behaving as a wave or as a stream of particles?
- **8.24** What is wave/particle duality?
- **8.25** What is the difference between a *traveling wave* and a *standing wave*?
- **8.26** What is the collapsing atom paradox?
- **8.27** How does quantum mechanics resolve the collapsing atom paradox?

## **Electron Waves in Atoms**

- **8.28** What are the names used to refer to the theories that apply the matter-wave concept to electrons in atoms?
- **8.29** What is the term used to describe a particular waveform of a standing wave for an electron?
- **8.30** What are the two properties of orbitals in which we are most interested? Why?

## **Quantum Numbers**

- **8.31** What are the allowed values of the principal quantum number?
- **8.32** What is the value for n for (a) the K shell and (b) the M shell?
- **8.33** Why does every shell contain an s subshell?
- **8.34** How many orbitals are found in (a) an s subshell, (b) a p subshell, (c) a d subshell, and (d) an f subshell?
- **8.35** If the value of  $m_{\ell}$  for an electron in an atom is 2, could another electron in the same subshell have  $m_{\ell} = -3$ ?

**8.36** Suppose an electron in an atom has the following set of quantum numbers: n = 2,  $\ell = 1$ ,  $m_{\ell} = 1$ ,  $m_s = +\frac{1}{2}$ . What set of quantum numbers is impossible for another electron in this same atom?

#### **Electron Spin**

- **8.37** What physical property of electrons leads us to propose that they spin like a toy top?
- **8.38** What is the name of the magnetic property exhibited by atoms that contain unpaired electrons?
- **8.39** What is the Pauli exclusion principle? What effect does it have on the populating of orbitals by electrons?
- **8.40** What are the possible values of the spin quantum number?

#### **Electron Configuration of Atoms**

- **8.41** What do we mean by the term *electronic structure*?
- **8.42** Within any given shell, how do the energies of the *s*, *p*, *d*, and *f* subshells compare?
- **8.43** What facts about the energies of subshells was responsible for the apparent success of Bohr's theory about electronic structure?
- **8.44** How do the energies of the orbitals belonging to a given subshell compare?
- **8.45** Give the electron configurations of the elements in Period 2 of the periodic table.
- **8.46** Give the correct electron configurations of (a) Cr and (b) Cu.
- **8.47** What is the correct electron configuration of silver?
- **8.48** How are the electron configurations of the elements in a given group similar? Illustrate your answer by writing shorthand configurations for the elements in Group VIA.
- 8.49 Define the terms valence shell and valence electrons.

#### **Shapes of Atomic Orbitals**

- **8.50** Why do we use probabilities when we discuss the position of an electron in the space surrounding the nucleus of an atom?
- **8.51** Sketch the approximate shape of (a) a 1s orbital and (b) a 2p orbital.
- **8.52** How does the size of a given type of orbital vary with n?
- **8.53** How are the p orbitals of a given p subshell oriented relative to each other?
- **8.54** What is a nodal plane?
- 8.55 How do nodes affect the energy of an orbital?
- **8.56** How many nodal planes does a p orbital have? How many does a d orbital have?
- **8.57** On appropriate coordinate axes, sketch the shape of the following d orbitals: (a)  $d_{xy}$ , (b)  $d_{x^2-y^2}$ , (c)  $d_{z^2}$ .

#### **Atomic and Ionic Size**

**8.58** What is the meaning of *effective nuclear charge?* How does the effective nuclear charge felt by the outer electrons

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vary going down a group? How does it change as we go from left to right across a period?

- **8.59** In what region of the periodic table are the largest atoms found? Where are the smallest atoms found?
- **8.60** Going from left to right in the periodic table, why are the size changes among the transition elements more gradual than those among the representative elements?

#### **Ionization Energy**

- **8.61** Define *ionization energy.* Why are ionization energies of atoms and positive ions endothermic quantities?
- **8.62** For oxygen, write an equation for the change associated with (a) its first ionization energy and (b) its third ionization energy.
- **8.63** Explain why ionization energy increases from left to right in a period and decreases from top to bottom in a group.
- **8.64** Why is an atom's second ionization energy always larger than its first ionization energy?
- **8.65** Why is the fifth ionization energy of carbon so much larger than its fourth?

- **8.66** Why is the first ionization energy of aluminum less than the first ionization energy of magnesium?
- **8.67** Why does phosphorus have a larger first ionization energy than sulfur?

#### **Electron Affinity**

- 8.68 Define electron affinity.
- **8.69** For sulfur, write an equation for the change associated with (a) its first electron affinity and (b) its second electron affinity. How should they compare?
- **8.70** Why does CI have a more exothermic electron affinity than F? Why does Br have a less exothermic electron affinity than CI?
- **8.71** Why is the second electron affinity of an atom always endothermic?
- **8.72** How is electron affinity related to effective nuclear charge? On this basis, explain the relative magnitudes of the electron affinities of oxygen and fluorine.

# REVIEW PROBLEMS

Answers to problems whose numbers are printed in color are given in Appendix B. More challenging problems are marked with asterisks. **ILW** = Interactive LearningWare solution is available at *www.wiley.com/college/brady*.

# **Electromagnetic Radiation**

- **8.73** What is the frequency in hertz of blue light having a wavelength of 430 nm?
- **8.74** Ultraviolet light with a wavelength of more than 280 nm has little germicidal value. What is the frequency that corresponds to this wavelength?
- 8.75 A certain substance strongly absorbs infrared light having a wavelength of 6.85  $\mu$ m. What is the frequency of this light in hertz?
- **8.76** The sun emits many wavelengths of light. The brightest light is emitted at about 0.48  $\mu$ m. What frequency does this correspond to?
- **8.77** Ozone protects Earth's inhabitants from the harmful effects of ultraviolet light arriving from the sun. This shielding is a maximum for UV light having a wavelength of 295 nm. What is the frequency in hertz of this light?
- **8.78** The meter is defined as the length of the path light travels in a vacuum during the time interval of 1/299,792,458 of a second. The standards body recommends use of light from a helium—neon laser for realizing the meter. The light from the laser has a wavelength of 632.99139822 nm. What is the frequency of this light, in hertz?
- **8.79** In New York City, radio station WCBS broadcasts its FM signal at a frequency of 101.1 megahertz (MHz). What is the wavelength of this signal in meters?
- **8.80** Sodium vapor lamps are often used in residential street lighting. They give off a yellow light having a fre-

- quency of  $5.09 \times 10^{14}$  Hz. What is the wavelength of this light in nanometers?
- **8.81** There has been some concern in recent times about possible hazards to people who live very close to high-voltage electric power lines. The electricity in these wires oscillates at a frequency of 60 Hz, which is the frequency of any electromagnetic radiation that they emit. What is the wavelength of this radiation in meters? What is it in kilometers?
- **8.82** An X-ray beam has a frequency of  $1.50 \times 10^{18}$  Hz. What is the wavelength of this light in nanometers and in picometers?
- **8.83** Calculate the energy in joules of a photon of red light having a frequency of  $4.0 \times 10^{14}$  Hz. What is the energy of 1 mol of these photons?
- **8.84** Calculate the energy in joules of a photon of green light having a wavelength of 560 nm.

#### **Atomic Spectra**

- **8.85** In the spectrum of hydrogen, there is a line with a wavelength of 410.3 nm. (a) What color is this line? (b) What is its frequency? (c) What is the energy of each of its photons?
- **8.86** In the spectrum of sodium, there is a line with a wavelength of 589 nm. (a) What color is this line? (b) What is its frequency? (c) What is the energy of each of its photons?
- **8.87** Use the Rydberg equation to calculate the wavelength in nanometers of the spectral line of hydrogen for which  $n_2 = 6$  and  $n_1 = 3$ . Would we be expected to see the light corresponding to this spectral line? Explain your answer.

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- **8.88** Use the Rydberg equation to calculate the wavelength in nanometers of the spectral line of hydrogen for which  $n_2 = 5$  and  $n_1 = 2$ . Would we be expected to see the light corresponding to this spectral line? Explain your answer.
- **8.89** Calculate the wavelength of the spectral line produced in the hydrogen spectrum when an electron falls from the tenth Bohr orbit to the fourth. In which region of the electromagnetic spectrum (UV, visible, or infrared) is the line?
- **8.90** Calculate the energy in joules and the wavelength in nanometers of the spectral line produced in the hydrogen spectrum when an electron falls from the fourth Bohr orbit to the first. In which region of the electromagnetic spectrum (UV, visible, or infrared) is the line?

#### **Quantum Numbers**

- **8.91** What is the letter code for a subshell with (a)  $\ell = 1$  and (b)  $\ell = 3$ ?
- **8.92** What is the value of  $\ell$  for (a) an f orbital and (b) a d orbital?
- **8.93** Give the values of n and  $\ell$  for the following subshells: (a) 3s, (b) 5d.
- **8.94** Give the values of n and  $\ell$  for the following subshells: (a) 4p, (b) 6f.
- **8.95** For the shell with n = 6, what are the possible values of  $\ell$ ?
- **8.96** In a particular shell, the largest value of  $\ell$  is 7. What is the value of n for this shell?
- **8.97** What are the possible values of  $m_{\ell}$  for a subshell with (a)  $\ell = 1$  and (b)  $\ell = 3$ ?
- **8.98** If the value of  $\ell$  for an electron in an atom is 5, what are the possible values of  $m_{\ell}$  that this electron could have?
- **8.99** If the value of  $m_{\ell}$  for an electron in an atom is -4, what is the smallest value of  $\ell$  that the electron could have? What is the smallest value of n that the electron could have?
- **8.100** How many orbitals are there in an h subshell  $(\ell = 5)$ ? What are their values of  $m_{\ell}$ ?
- **8.101** Give the complete set of quantum numbers for all of the electrons that could populate the 2*p* subshell of an atom.
- **8.102** Give the complete set of quantum numbers for all of the electrons that could populate the 3d subshell of an atom.
- **8.103** In an antimony atom, how many electrons have  $\ell = 1$ ? How many electrons have  $\ell = 2$  in an antimony atom?
- **8.104** In an atom of barium, how many electrons have (a)  $\ell = 0$  and (b)  $m_{\ell} = 1$ ?

#### **Electron Configuration of Atoms**

- **8.105** Predict the electron configurations of (a) S, (b) K, (c) Ti, and (d) Sn.
- **8.106** Predict the electron configurations of (a) As, (b) Cl, (c) Ni, and (d) Si.
- **8.107** Which of the following atoms in their ground states are expected to be paramagnetic: (a) Mn, (b) As, (c) S, (d) Sr, (e) Ar?

- **8.108** Which of the following atoms in their ground states are expected to be diamagnetic: (a) Ba, (b) Se, (c) Zn, (d) Si?
- **ILW 8.109** How many unpaired electrons would be found in the ground state of (a) Mg, (b) P, and (c) V?
  - **8.110** How many unpaired electrons would be found in the ground state of (a) Cs, (b) S, and (c) Ni?
  - **8.111** Write the shorthand electron configurations for (a) Ni, (b) Cs, (c) Ge, (d) Br, and (e) Bi.
  - **8.112** Write the shorthand electron configurations for (a) AI, (b) Se, (c) Ba, (d) Sb, and (e) Gd.
  - **8.113** Draw complete orbital diagrams for (a) Mg and (b) Ti.
  - 8.114 Draw complete orbital diagrams for (a) As and (b) Ni.
  - **8.115** Draw orbital diagrams for the shorthand configurations of (a) Ni, (b) Cs, (c) Ge, and (d) Br.
  - **8.116** Draw orbital diagrams for the shorthand configurations of (a) Al, (b) Se, (c) Ba, and (d) Sb.
  - **8.117** What is the value of *n* for the valence shells of (a) Sn, (b) K, (c) Br, and (d) Bi?
  - **8.118** What is the value of *n* for the valence shells of (a) Al, (b) Se, (c) Ba, and (d) Sb?
  - **8.119** Give the configuration of the valence shell for (a) Na, (b) Al, (c) Ge, and (d) P.
  - **8.120** Give the configuration of the valence shell for (a) Mg, (b) Br, (c) Ga, and (d) Pb.
  - **8.121** Draw the orbital diagram for the valence shell for (a) Na, (b) Al, (c) Ge, and (d) P.
  - **8.122** Draw the orbital diagram for the valence shell of (a) Mg, (b) Br, (c) Ga, and (d) Pb.

# **Atomic Properties**

- **8.123** If the core electrons were 100% effective at shielding the valence electrons from the nuclear charge and the valence electrons provided no shielding for each other, what would be the effective nuclear charge felt by a valence electron in (a) Na, (b) S, (c) CI?
- **8.124** If the core electrons were 100% effective at shielding the valence electrons from the nuclear charge and the valence electrons provided no shielding for each other, what would be the effective nuclear charge felt by a valence electron in (a) Mg, (b) Si, (c) Br?
- **8.125** Choose the larger atom in each pair: (a) Na or Si; (b) P or Sb.
- **8.126** Choose the larger atom in each pair: (a) Al or Cl; (b) Al or In.
- **8.127** Choose the largest atom among the following: Ge, As, Sn, Sb.
- **8.128** Place the following in order of increasing size:  $N^{3-}$ ,  $Mg^{2+}$ ,  $Na^+$ , Ne,  $F^-$ ,  $O^{2-}$ .
- **8.129** Choose the larger particle in each pair: (a) Na or Na $^+$ ; (b) Co $^{3+}$  or Co $^{2+}$ ; (c) Cl or Cl $^-$ .
- **8.130** Choose the larger particle in each pair: (a) S or  $S^{2-}$ ; (b)  $AI^{3+}$  or AI; (c)  $Au^+$  or  $Au^{3+}$ .

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- **8.131** Choose the atom with the larger ionization energy in each pair: (a) B or C; (b) O or S; (c) Cl or As.
- **8.132** Choose the atom with the larger ionization energy in each pair: (a) Li or Cs; (b) Al or Si; (c) F or O.
- **8.133** Choose the atom with the more exothermic electron affinity in each pair: (a) Cl or Br; (b) Se or Br.
- **8.134** Choose the atom with the more exothermic electron affinity in each pair: (a) P or As; (b) Si or Ga.
- **8.135** Use the periodic table to select the element in the following list for which there is the largest difference between the second and third ionization energies: Na, Mg, Al, Si, P, Se, Cl.
- **8.136** Use the periodic table to select the element in the following list for which there is the largest difference between the fourth and fifth ionization energies: Na, Mg, Al, Si, P, Se, Cl.

# **ADDITIONAL EXERCISES**

- **8.137** The human ear is sensitive to sound ranging from 20 to 20,000 Hz. The speed of sound is 330 m/s in air and 1500 m/s under water. What is the longest and the shortest wavelength that can be heard (a) in air and (b) under water?
- **8.138** Microwaves are used to heat food in microwave ovens. The microwave radiation is absorbed by moisture in the food. This heats the water, and as the water becomes hot, so does the food. How many photons having a wavelength of 3.00 mm would have to be absorbed by 1.00 g of water to raise its temperature by  $1.00\,^{\circ}\text{C}$ ?
- **8.139** In the spectrum of hydrogen, there is a line with a wavelength of 410.3 nm. Use the Rydberg equation to calculate the value of n for the higher-energy Bohr orbit involved in the emission of this light. Assume the value of n for the lower energy orbit equals 2.
- **8.140** Calculate the wavelength in nanometers of the shortest wavelength of light emitted by a hydrogen atom.
- **8.141** Which of the following electronic transitions could lead to the emission of light from an atom?

$$1s \longrightarrow 4p \longrightarrow 3d \longrightarrow 5f \longrightarrow 4d \longrightarrow 2p$$

- **8.142** A neon sign is a gas discharge tube in which electrons traveling from the cathode to the anode collide with neon atoms in the tube and knock electrons off of them. As electrons return to the neon ions and drop to lower energy levels, light is given off. How fast would an electron have to be moving to eject an electron from an atom of neon, which has a first ionization energy equal to 2080 kJ mol<sup>-1</sup>?
- \*8.143 How many grams of water could have its temperature raised by 5.0 °C by a mole of photons that have a wavelength of (a) 600 nm and (b) 300 nm?
- \*8.144 It has been found that when the chemical bond between chlorine atoms in Cl<sub>2</sub> is formed, 328 kJ is released per mole of Cl<sub>2</sub> formed. What is the wavelength of light that would be required to break chemical bonds between chlorine atoms?
- **8.145** Calculate the wavelengths of the lines in the spec-

trum of hydrogen that result when an electron falls from a Bohr orbit with (a) n = 5 to n = 1, (b) n = 4 to n = 2, and (c) n = 6 to n = 4. In which regions of the electromagnetic spectrum are these lines?

- **8.146** What, if anything, is wrong with the following electron configurations for atoms in their ground states?
- (a)  $1s^22s^12p^3$
- (c)  $1s^22s^22p^4$
- (b)  $[Kr]3d^74s^2$
- (d) [Xe] $4f^{14}5d^86s^1$
- **8.147** Suppose students gave the following orbital diagrams for the 2s and 2p subshells in the ground state of an atom. What, if anything, is wrong with them? Are any of these electron distributions impossible?
- (a) ( ) ( ) ( )
- (c) ① ①①①
- (b) ① ①
- (d) ① ① ①
- **8.148** How many electrons are in p orbitals in an atom of germanium?
- **8.149** What are the quantum numbers of the electrons that are lost by an atom of iron when it forms the ion  $Fe^{2+}$ ?
- \*8.150 The removal of an electron from the hydrogen atom corresponds to raising the electron to the Bohr orbit that has  $n_471845$ On the basis of this statement, calculate the ionization energy of hydrogen in units of (a) joules per atom and (b) kilojoules per mole.
- **8.151** Use orbital diagrams to illustrate what happens when an oxygen atom gains two electrons. On the basis of what you have learned about electron affinities and electron configurations, why is it extremely difficult to place a third electron on the oxygen atom?
- **8.152** From the data available in this chapter, determine the ionization energy of (a) F<sup>-</sup>, (b) O<sup>-</sup>, and (c) O<sup>2-</sup>. Are any of these energies exothermic?
- **8.153** For an oxygen atom, which requires more energy, the addition of two electrons or the removal of one electron?