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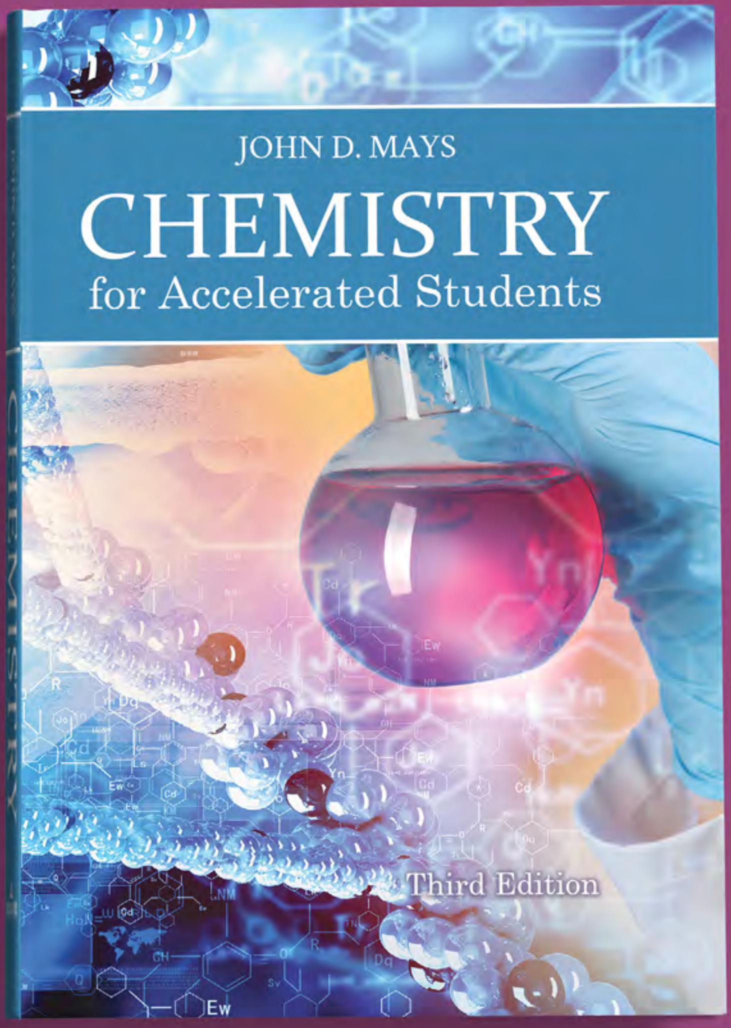

CHEMISTRY FOR ACCELERATED STUDENTS

10TH GRADE: ACCELERATED TRACK RECOMMENDATION

YEARLONG COURSE

NOVARE

Chemistry for Accelerated Students is designed for accelerated students in high school. This course is typically taught in 10th grade, while students are concurrently enrolled in Algebra 2 and after students have completed *Accelerated Studies in Physics and Chemistry* (9th). Here we highlight a few distinctive features of this text.

- Chemistry for Accelerated Students *supports our signature philosophy of science education based on wonder, integration, and mastery*. We always seek to build on and stimulate the student's innate sense of wonder at the marvels found in nature. Integration refers to the **epistemology**, **mathematics**, and **history** embedded in the text, and a curriculum designed to help develop the student's facility with using **language** to communicate scientific concepts. Finally, *Chemistry for Accelerated Students* is designed to be used in a mastery-learning environment, using the mastery teaching model John developed and describes in *From Wonder to Mastery: A Transformative Model for Science Education*. When teachers use this mastery-learning model, the result is high student achievement and exceptional long-term retention for *all students*.
- *The text includes a unique organizing introduction*. The introduction, entitled "What Is Chemistry All About?," sets forth five general organizing principles—chemistry is all about electrons, chemistry is all about electrical forces, chemistry is all about minimizing energy, chemistry is all about whole-number ratios of atoms, and chemistry is all about modeling. Throughout the balance of the text, students are repeatedly notified when a topic illustrates an instance of one of these five general principles.
- *The chapter exercises include plenty of content review*. Beginning with Chapter 2, the chapter exercises following each chapter include 6–10 review problems to help students keep the content from old chapters fresh.
- *The text treats advanced topics in detail*. Since this course is designed to follow the rigorous introduction to chemistry included in *Accelerated Studies in Physics and Chemistry* (*ASPC*), *Chemistry for Accelerated Students* skips the usual introductory material on units of measure, unit conversions, and the history of atomic models. Instead, the text dives right into more advanced topics and includes chapters on Thermochemistry and Kinetics as well as Chemical Equilibrium. For students who did not take *ASPC* but are otherwise qualified for this course, an introduction to unit conversions (dimensional analysis) is included in the appendices.
- *The text includes a bonus chapter*. Just for fun, we included a bonus chapter introducing interested students to organic chemistry. This chapter would not normally be taught as part of a one-year course, but some students are likely to be so interested in this subject that they want more!

SUPPORT RESOURCES

A number of support resources are available to accompany *Accelerated Chemistry.* They include:

The Student Lab Report Handbook
Students should begin writing their lab reports from scratch in 9th grade. This popular manual gives them everything they need. We recommend supplying this handbook to every freshman so they can refer to it throughout high school. Read more about this resource on page 10.

Solutions Manual to Accompany Accelerated Chemistry
This book contains complete written solutions for all the computations in the chapter exercises.

Chemistry Experiments for High School
This student manual includes 20 excellent chemistry experiments that illustrate concepts and foster real-world lab skills. Using this book requires a standard high school laboratory facility.

Chemistry Experiments for High School at Home
This manual was developed specifically for home school students. The experiments are very similar to the experiments in the classroom version described above, but numerous changes to apparatus and supplies were incorporated to make the experiments usable at home. This volume includes an extended introduction with detailed information pertaining to safety, chemical storage, preparation of standard solutions, and sourcing materials. Waste disposal procedures are itemized at the end of each experiment.

Novare Chemistry Supplement
As mentioned above, this text is designed to follow *ASPC* in 9th grade and skips some material normally found in the first two chapters of chemistry texts. To enable qualified students who have not had *ASPC* to take this course, this small book fills in the gap left by not having *ASPC* first. Students using this book should also complete the unit conversions tutorial found in Appendix A of the main text.

Digital Resources
The following materials are accessible exclusively through Novare Science:

- a full year of chapter exams
- two short quizzes for each chapter
- two semester exams
- a document containing all keys and sample answers to all verbal questions (text and exams)
- a document with recommendations for teaching the course
- a lesson list and example calendar

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About Novare Science

Novare Science is an imprint of Classical Academic Press that focuses on the highest-quality science curriculum for Christian schools and home schools. Founded by educator John D. Mays, Novare Science offers a completely unique approach to secondary science curriculum. For more information on our vision for secondary science education, please refer to the Overview section on pages 3-7 in this series of samples.

CONTACT US

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SAMPLE CHAPTERS

The following pages contain samples from the text. The Table of Contents is shown, as well as Chapters 1, 2, and 10. Note that the sample chapters shown are from the new edition planned for 2023. The new edition has been revised to accommodate the extensive changes to the metric system that went into effect in 2019. The edition currently in print looks exactly the same but uses the former definitions for the Avogadro constant, the mole, and other constants.

Chemistry *for Accelerated Students*

A Mastery-Oriented Curriculum

Third Edition

John D. Mays

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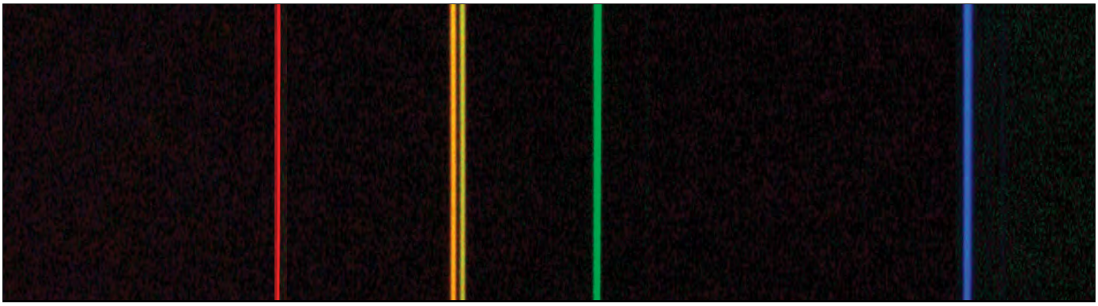
Atomic Structure



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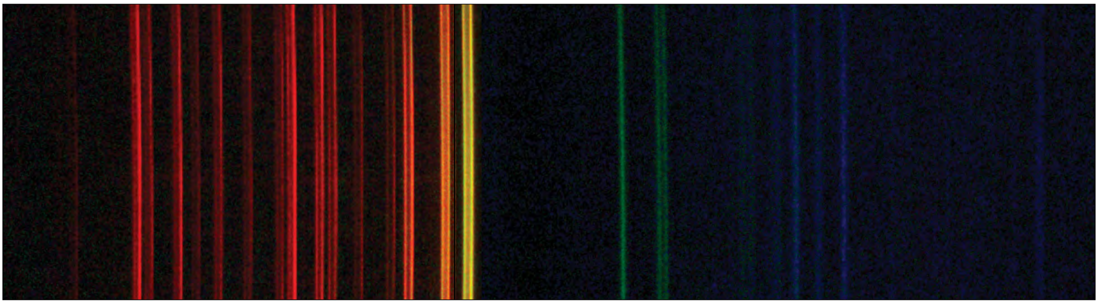

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When excited by heat or electricity, the atoms of each element emit a specific, unique set of wavelengths of light—the atomic spectrum for that element. The visible spectra emitted by mercury and neon are shown above. Atomic spectra were known and studied in the 19th century, but there was no theory at that time that could explain the source of the colors different elements emit. Then in 1913, Niels Bohr published his new model of the atom, locating the electrons in atoms in specific energy levels. Bohr theorized that when excited, electrons jump to higher energy levels, and that to drop back down to a lower energy level an electron emits a packet of electromagnetic energy—what we now call a photon. In 1901, Max Planck had published the equation relating specific amounts of energy to specific wavelengths (colors) of light. Bohr's successful explanation for atomic spectra opened the door for detailed study of the internal structure of atoms.

The two spectra shown above were imaged in the Laser Optics Lab at Regents School of Austin in Austin, Texas.

Objectives for Chapter 1

After studying this chapter and completing the exercises, you should be able to do each of the following tasks, using supporting terms and principles as necessary.

SECTION 1.1

1. Describe the electromagnetic spectrum and state approximate wavelengths for the ends of the visible spectrum.
2. Define *quantum* and explain what it means for energy to be quantized.
3. Given the Planck relation and Planck's constant, determine the energy of a photon of a given wavelength and vice versa.
4. Describe the two main ways that atoms can possess energy.

SECTION 1.2

5. Describe the Bohr model of the atom and relate how the model explained the phenomenon of atomic spectra.

SECTION 1.3

6. Distinguish qualitatively between the orbital energies in the hydrogen atom and those of other atoms.
7. State and describe the four quantum numbers required to describe the quantum state of an electron.
8. For the first three principle quantum numbers, describe the orbitals available for electrons.
9. State the Aufbau principle, the Madelung rule, and Hund's rule, and relate them to the way electrons are located in atoms.
10. State the Pauli exclusion principle and explain its relationship to the placement of electrons in atoms.

SECTION 1.4

11. Given the periodic table, write electron configurations (full and condensed) and draw orbital diagrams for all elements in the first five periods (including the nine *d*-block elements with anomalous configurations).

SECTION 1.5

12. Given the periodic table, determine the number of protons, electrons, and neutrons in the atoms of a given nuclide.
13. Given isotope mass and abundance data, calculate the atomic mass of an element.
14. Define the unified atomic mass unit, u, and state two definitions for the mole.
15. Calculate the molar mass of a compound or molecule, and calculate the mass in grams of a given mole quantity of a compound or molecule, or vice versa.
16. Calculate the number of atoms or molecules in a given quantity of substance.
17. Given mass data for an unknown compound, determine the percent composition and empirical formula of the compound.
18. Use the percent composition along with the molar mass or molecular mass of an unknown compound to determine the molecular formula for the compound.
19. Correctly use the rules for significant digits in computations, including the addition rule.

1.1 Atomic Spectra

1.1.1 The Electromagnetic Spectrum

Understanding our present theory of atomic structure and the story of how it unfolded requires a basic understanding of the electromagnetic spectrum. We thus begin this chapter with a brief review of this topic.

The spectrum of visible light is shown in Figure 1.1. The visible spectrum runs through the colors of the rainbow—red, orange, yellow, green, blue, violet—and includes wavelengths from about 750 nm (red) down to about 400 nm (violet).

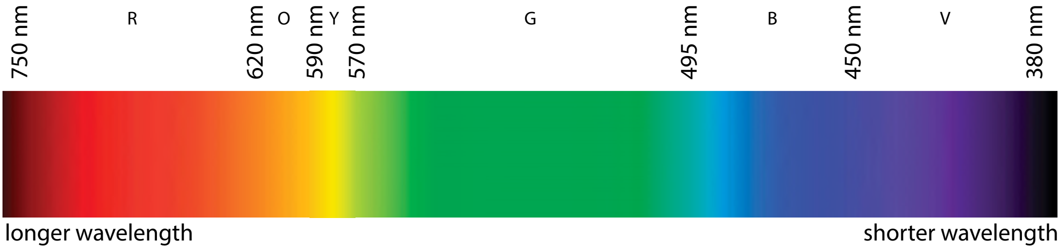

Figure 1.1. Colors and approximate wavelength ranges in the visible portion of the electromagnetic spectrum.

Visible light is just a small portion of a vast spectrum of electromagnetic radiation that occurs in nature. Figure 1.2 shows the most important regions of the electromagnetic spectrum, from radiation with wavelengths in the range of 1 km, the region of AM Radio waves, down to the high-energy Gamma Rays, with wavelengths in the range of 1 picometer (pm). (The metric prefix *pico*–, which may be new to you, means 10^{-12}. One picometer is one thousandth of a nanometer.) As you see from the figure, the solar emission spectrum runs from wavelengths of about 1 mm down to wavelengths of about 0.1 µm. The solar spectrum includes the infrared, visible, and ultraviolet regions, and is strongest in the middle of the visible spectrum.

The contemporary theory of light (a shorter term for electromagnetic radiation in general) holds that light exhibits both wave-like properties and particle-like properties. Since light behaves like waves, we can refer to the wavelengths of particular colors. But light also behaves like particles. We call these particles *photons*, and each photon represents a single packet of energy. The packet of energy in a photon is also called a *quantum* of energy. (The plural is *quanta*.)

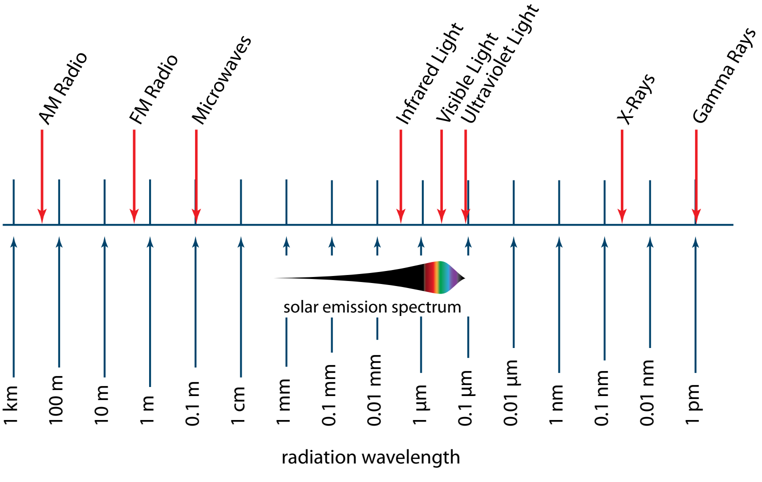

Figure 1.2. The electromagnetic spectrum.

When thinking of light as waves, we characterize those waves by the wavelength. When considering light as discrete packets of energy, we tend to think of the amount of energy in each packet (each photon). It turns out there is a simple equation relating these together.

Figure 1.3. German physicist Max Planck (1858–1947).

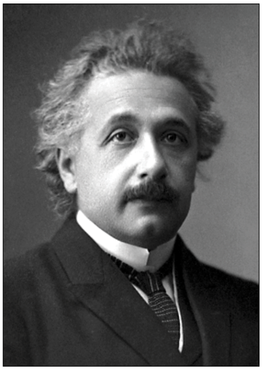

Figure 1.4. German physicist Albert Einstein (1879–1955).

It was in 1901 that German physicist Max Planck (Figure 1.3) conceived of treating energy as if it were quantized. He was working on a different problem at the time (the so-called blackbody radiation problem), and he did not imagine that energy really *is* quantized. However, he introduced what he thought was a mathematical trick—the quantization of energy—and in the process, quantum theory was born. Planck won the Nobel Prize in Physics for this work in 1918. (It's ironic, isn't it, to win the Nobel Prize for a major discovery that the scientist thinks is just a mathematical trick?) Four years later in 1905, German physicist Albert Einstein (Figure 1.4) proposed that energy really is quantized and used this idea to solve another problem (explaining the photoelectric effect). For this, Einstein won the Nobel Prize in Physics in 1921.

The equation Planck introduced is called the *Planck relation*. This important equation is:

$$E = hf \tag{1.1}$$

In this equation, E is the energy in the photon in joules (J). The next term in the equation, h, is a constant known as the *Planck constant*. The value of h is defined as exactly

$$h = 6.62607015 \times 10^{-34}\ \mathrm{J \cdot s} \tag{1.2}$$

The last term in the Planck relation, f, is the frequency of the wave. The frequency and wavelength of a wave are related by the equation

$$v = \lambda f \tag{1.3}$$

In this equation, v is the velocity of the wave, which is the speed of light in this case (2.9979×10^8 m/s). The wavelength is represented by the Greek letter λ (lambda, the Greek lower-case letter l). If we solve Equation (1.3) for the frequency and insert it into the Planck relation, we have

$$E = \frac{hv}{\lambda} \tag{1.4}$$

With this equation, we can compute the energy in a single photon of light at any wavelength, or vice versa. To illustrate such a calculation, we have our first example problem. As you see below, example problems in this text are set off by two red triangles. In presenting this example, I am assuming you are:

- familiar with the SI System of units and unit prefixes
- proficient at performing unit conversions
- proficient at applying the basic rules for the use of significant digits in measurements and computations (except for the addition rule, covered later in the chapter).

If you are lacking skills in any of these areas, please refer to Appendix A for a tutorial.

▼ Example 1.1

The bright blue line in the mercury vapor spectrum (see the upper image on the opening page of this chapter) has a wavelength of 435.8 nm. Determine the energy contained in a single photon of this blue light.

We begin by writing down the given information and the unknown we seek to find.

$$\lambda = 435.8 \text{ nm}$$
$$E = ?$$

Next, we convert the given wavelength into the MKS[1] length unit, meters.

$$\lambda = 435.8 \text{ nm} \cdot \frac{1 \text{ m}}{10^9 \text{ nm}} = 4.358 \times 10^{-7} \text{ m}$$

From this value, along with the Planck constant and the speed of light, we calculate the energy of a photon with this wavelength.

$$E = \frac{hv}{\lambda} = \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)\left(2.9979 \times 10^{8} \ \frac{\text{m}}{\text{s}}\right)}{4.358 \times 10^{-7} \text{ m}} = 4.558 \times 10^{-19} \text{ J}$$

This is an extremely small amount of energy, less than a billionth of a billionth of a joule. The given wavelength and the value for the Planck constant each have four significant digits. Thus, the result is stated with a precision of four significant digits.

▲

1.1.2 Energy in Atoms

As mentioned in the caption on the opening page of this chapter, the atoms of every element emit a specific set of colors when excited. In the context of atomic theory, the term *excitation* refers to the absorption of energy by atoms, either from electromagnetic radiation (light) or from collisions with other particles.

Let's spend a moment considering the ways an individual atom can possess energy. There are two basic mechanisms by which atoms can possess energy. First, all atoms possess *kinetic energy*, the energy associated with motion. Kinetic energy in atoms is illustrated in Figure 1.5. In solids, the atoms are fixed in place and are not free to move around, so the kinetic energy is manifest in the atoms' vibrations. In liquids and gases (fluids), atoms are free to move around, so the energy possessed by atoms in fluids is in their translational kinetic energy. Also, when atoms in fluids are bound together in molecules, the molecules can tumble and rotate, so some of their kinetic energy is in the energy of rotation. Atoms in molecules also vibrate, just as balls attached to one another by springs can wiggle back and forth. In all these cases, the kinetic energy in atoms and

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[1] MKS stands for meter-kilogram-second. The MKS system is a subset of the metric or SI System of units. Using MKS units for computations is always wise practice because the units of measure in the computation will all be consistent with each other, and the result of the computation always comes out in MKS units. For more on this, see Appendix A.

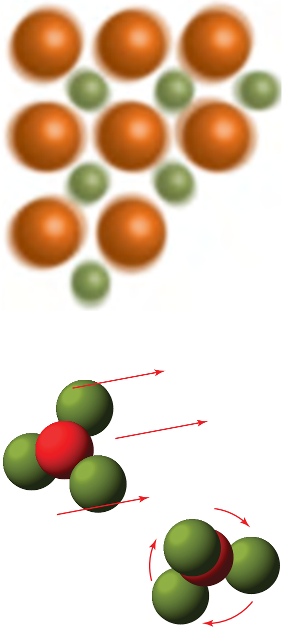

Figure 1.5. The atoms in the solid crystal at the top are blurred to illustrate their vibrations. The gas molecules at the bottom are translating and tumbling.

molecules correlates directly to their temperature. The hotter they are, the more vigorously they vibrate and the faster they move.

The second basic way an atom can possess energy is in the energies of the atom's electrons. As mentioned in the Introduction and Chapter 1 (and discussed in detail later in this chapter), the electrons in atoms are located in various orbitals, and different orbitals are associated with different amounts of electron energy. Atoms can absorb quanta of energy from the photons of electromagnetic radiation and from collisions with other particles, such as ions and free electrons. When an atom absorbs energy in this way, the quantum of energy absorbed by the atom is manifest in one or more of the atom's electrons moving into higher-energy orbitals. This is atomic excitation.

When an atom's electrons are all in their lowest-energy orbitals, the atom is said to be in the *ground state*. Excitation occurs when an atom absorbs a quantum of energy causing an electron to move to a higher-energy orbital. When this happens, the atom is said to be in an *excited state*. Atoms tend not to remain in excited states. Instead, after becoming excited an atom typically heads straight back to the ground state, generally by emitting the energy it absorbed in the form of one or more new photons.[2]

A newly emitted photon may not have the same amount of energy as the original quantum of energy the atom absorbed. To explain this, we need to introduce a commonly used graphical representation of the different energies electrons can possess. For now, let's call these *energy levels*. We will relate these more carefully to the energies of electrons in atoms in the next few sections.

Figure 1.6 is a diagram representing four different energy levels actually available to an electron in a hydrogen atom, labeled in the figure $n = 1$, $n = 2$, and so on. I explain this diagram carefully below, but first we need to pause here to revisit one of the points made in the Introduction. In Section I.3, I note that when an electron is

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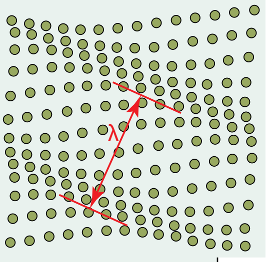
[2] In some substances, electrons in atoms can remain in excited states for an extended period of time. As the atoms in such a substance return to the ground state over time the substance gradually radiates the energy away. This is the way *phosphorescence* (glowing in the dark) works.

Hmm... Interesting. Neon signs and phonons

When excited atoms in gases return to the ground state they do so by emitting photons. Neon signs are tubes of gas excited by high-voltage electricity. Their glowing colors are caused by the atoms returning to the ground state. When excited atoms in solids (and some liquids) return to the ground state, they can do so by emitting photons as gases do, but they can also emit *phonons*, packets of vibrational energy. Phonons can travel as waves through the crystal lattice in a solid, displacing the atoms from their equilibrium positions. In the image on the right, the wavelength of the emitted energy is shown in red (and the displacement of the atoms is greatly exaggerated).



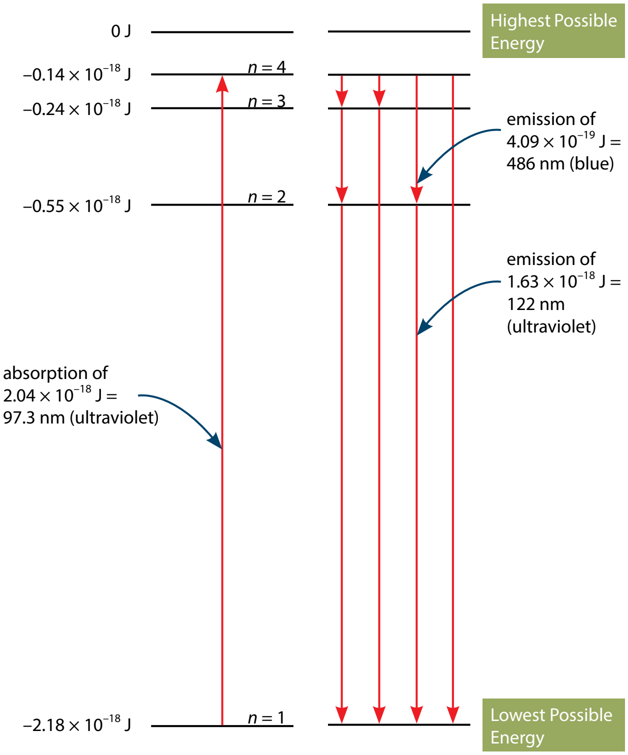


Figure 1.6. An energy-level diagram illustrating how quanta of energy are absorbed and released by electrons in hydrogen atoms.

held at a certain distance away from the positive nucleus, it has a high potential energy. As the electron is allowed to move closer to the nucleus, its potential energy decreases just as the gravitational potential energy of an object above the ground decreases with decreasing height. Since the electron's potential energy decreases as the electron moves closer to the nucleus, the electron releases energy as it gets closer and closer to the nucleus.

In discussions of the energies of electrons in atoms, it is customary to assign a reference value of 0 joules to the energy an electron has when it is completely free from the nucleus—in other words, when it is very far away. Then, since the electron's potential energy decreases as it gets closer to the nucleus, the energy an electron has is expressed as a negative value. This happens because instead of setting the potential energy to be zero at the nucleus, we set the zero energy reference to be when the electron is far away from the nucleus. So don't let the negative energy values bother you. It makes sense that the electron's energy is set to zero when it is far away from the nucleus because at that point the electron really has nothing to do with that nucleus. But to be consistent with what we know about potential energy, the electron's energy must decrease as it enters the area near the nucleus, so its energy takes on increasingly negative values relative to the zero-energy reference.

Going back now to Figure 1.6, let's assume that an electron in a hydrogen atom is in the ground state, which means it has the lowest possible energy. Since hydrogen atoms only have one electron, this places the electron at the bottom of the figure at the first energy level, $n = 1$. An energy of -2.18×10^{-18} J is the energy an electron has when it is in this first energy level. Assume now that this electron absorbs a quantum of energy equal to 2.04×10^{-18} J from an incoming photon, indicated by the arrow pointing upward on the left side of the figure. From the Planck relation, you can verify that this corresponds to a wavelength of 97.3 nm, placing this photon in the ultraviolet region of the electromagnetic spectrum. The electron is now in the fourth energy level. If you subtract the energy of $n = 1$ from that of $n = 4$, the difference is the amount of energy the electron absorbed, 2.04×10^{-18} J.

Remember, energy in atoms is quantized. Electrons can only have certain specific values of energy, and the permissible values of energy an electron in a hydrogen atom can have (for the first four energy levels) are the energies listed down the left side of Figure 1.6. Very quickly the atom emits this energy in the form of new photons and the electron drops back down to the ground state. But as you can see from the right side of the figure, the electron in the hydrogen atom has four different ways of doing this.

First, the electron can release the smallest permissible amount of energy each time it emits a photon. This causes it to drop down one energy level at a time, emitting three separate photons on its way back to the ground state, as shown by the sequence of three downward pointing arrows leading from $n = 4$ to $n = 1$. Second, the electron can first drop from $n = 4$ to $n = 3$ and then drop to $n = 1$. Third, the electron can first drop from $n = 4$ to $n = 2$ and then drop to $n = 1$. For this possibility, the emitted amounts of energy are shown in the figure. The energy emitted when dropping from $n = 4$ to $n = 2$ is 4.09×10^{-19} J. Using the Planck relation, you can calculate the wavelength of a photon with this energy. Doing so gives a wavelength of 486 nm, which is in the visible portion of the electromagnetic spectrum. A check of Figure 1.1 indicates that this wavelength corresponds to blue light. The drop from $n = 2$ to $n = 4$ is a much larger energy drop, 1.63×10^{-18} J. This energy corresponds to a wavelength of 122 nm, which is in the ultraviolet region and is not visible.

Finally, the electron can drop back to $n = 1$ by emitting 2.04×10^{-18} J, the same amount of energy it absorbed in the first place. This energy produces a new ultraviolet photon with the same wavelength as the photon originally absorbed by the atom.

Note from Equation (1.4) that energy and wavelength are inversely proportional. Longer wavelengths represent lower energies; shorter wavelengths represent higher energies. This relationship is illustrated in Figure 1.7.

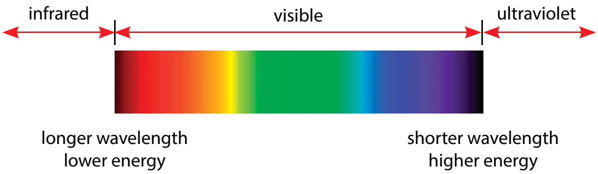


Figure 1.7. Wavelengths and energies in and near the visible spectrum.

The spectrum of wavelengths emitted by each element is unique, which means that light spectra can be used to identify the element's presence in a gas or solution. The science of such identifications is called *spectroscopy*.

1.1.3 The Hydrogen Atom

The hydrogen atom is the simplest atom, with only one electron, and thus it has been studied extensively. The wavelengths for the possible electron energy transitions in the first six energy levels of the hydrogen atom are shown in Figure 1.8. All the arrows in this diagram are shown pointing in both directions because the wavelengths shown can represent either the absorption or emission of energy. These are the energies hydrogen atoms can absorb and emit.

In 1885, Swiss mathematician and physicist Johann Balmer discovered the formula that predicts the lines in the visible hydrogen spectrum. This series of lines is now called the Balmer series. In 1888, Swedish physicist Johannes Rydberg worked out the more general formula for all the hydrogen wavelengths. The ultraviolet and infrared lines in the hydrogen spectrum were not known initially (because they are invisible). But in 1906, American physicist Theodore Lyman observed the ultraviolet series that bears his name, and in 1908, German physicist Friedrich Paschen observed the infrared series of lines in the hydrogen spectrum.

The Rydberg formula that predicts all these wavelengths has an interesting mathematical structure, and is worth showing here. Here it is:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.5}$$

The R in this equation is the so-called Rydberg constant (1.097×10^7 m^{-1}), and n_1 and n_2 represent the numbers for the two energy levels in question. Whenever I see mathematical patterns like this in nature, I am always reminded that the mathematical structure found everywhere in

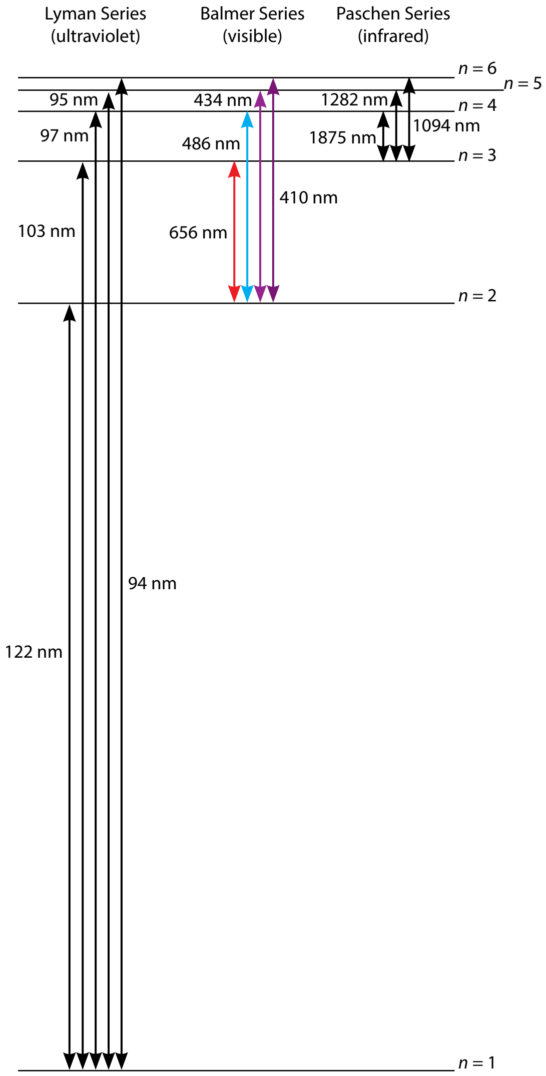


Figure 1.8. Wavelengths for electron transitions in the first six energy levels of the hydrogen atom.

nature could not have arisen apart from the hand of an intelligent Creator. The mathematics embedded in creation is strong evidence that the physical universe we are studying in our science courses is a great and beautiful gift, and as Nicolaus Copernicus said, was "built for us by the Best and most Orderly Workman of all."

1.2 The Bohr Model of the Atom

As mentioned on the opening page of this chapter, Danish physicist Niels Bohr introduced his new model of the atom in 1913. This new atomic model was of tremendous importance in the development of atomic theory. Rydberg's formula predicting the lines in the hydrogen spectrum had been known since 1888, but until Bohr's model there was no theoretical basis for the observed spectrum.

In Bohr's atomic model, the electrons orbit the nucleus like planets orbiting the sun. In the model, the electrons have fixed energies, the same energies as those shown in Figures 1.6 and 1.8. These different energy levels correspond to different orbits around the nucleus.

Bohr correctly described the cause of the specific lines in the emission spectra of atoms—electrons absorbing energy and moving to higher energy levels and then releasing photons at specific energies as they move back to lower energy levels.

Another significant feature of the Bohr model is the number of electrons that he permitted at each energy level. These numbers are shown in Figure 1.9. If you compare these numbers to the Periodic Table of the Elements shown on the inside back cover of this text, you see that the number of electrons in each energy level corresponds to the number of elements in each period (row) of the table: two in the first, eight in the second, eight in the third, and 18 in the fourth, etc.

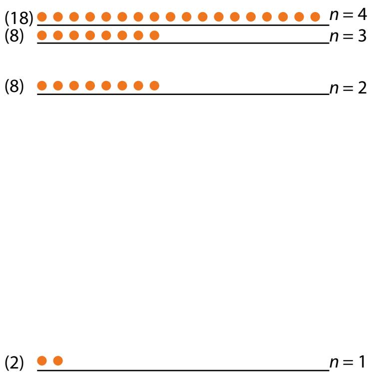


Figure 1.9. Number of permissible electrons in the first four energy levels of the Bohr model of the atom.

As powerful as it is, the Bohr model was known to have weaknesses from the start. For one thing, there is no explanation for why electrons are able to stay in their orbits. Electrons moving in circles radiate energy, so one would think electrons in orbits would gradually lose energy, slow down, and spiral in to the nucleus. Another issue is that for atoms other than hydrogen, the energies between the energy levels do not match up precisely with the observed wavelengths in the emission spectra of elements.

1.3 The Quantum Model of the Atom

1.3.1 Schrödinger and Pauli

In 1926, Austrian physicist Erwin Schrödinger (Figure 1.10) published what is now called the *Schrödinger equation*. This was a landmark achievement and one of the hallmarks of 20th-century physics. For this work, Schrödinger received the Nobel Prize in Physics in 1933.

Solutions to the Schrödinger equation are now understood to provide us with the details of the internal structure of energy levels in atoms. With the arrival of the Schrödinger equation, the *quantum model* of the atom began to unfold. The history of quantum physics is still being written. There are many mysteries associated with the behavior of electrons as described by the quantum model. But quantum theory has a colossally impressive string of achievements, and its success in predicting atomic behavior is undeniable. We know the quantum model will continue to evolve, and may some day even be replaced. But the details we consider in this section are now generally accepted as correct. Remember, chemistry is all about modeling—developing theories. Theories are explanations, and the quantum model is widely accepted as our best explanation of how atoms are structured.

Figure 1.10. Austrian physicist Erwin Schrödinger (1887–1961).

In addition to Schrödinger's equation, there is one other theoretical milestone that we need to have in hand to understand the details to follow. In 1925, while Schrödinger was working on his equation, another Austrian physicist, Wolfgang Pauli (Figure 1.11) formulated what is now known as the *Pauli exclusion principle*. In short, *the Pauli exclusion principle holds that no two electrons in the same atom can occupy the same quantum state*. We will unpack this further as we go along. For this important contribution to quantum theory, Pauli won the Nobel Prize in Physics in 1945.

Figure 1.11. Austrian physicist Wolfgang Pauli (1900–1958).

1.3.2 Shells, Subshells, and Orbitals

The quantum state of an electron in an atom—its unique address, we might say, within the atomic quantum realm—is specified by four different *quantum numbers*. According to the Pauli exclusion principle, every electron in an atom has a unique quantum state. This is one of the laws of nature governing the way atoms are structured. This situation in atoms is analogous to postal addresses. Every postal customer in the U.S. has a unique address. For a house, this unique address requires four pieces of information—the street number, street name, city, and state. For an apartment complex, an apartment number is also required. (The zip code doesn't have any additional location information in it; it just helps speed things up.)

The physics behind these quantum numbers is quite complicated, and as an introductory chemistry student you would not normally be required to get much into that. However, introductory chemistry classes do generally now require students to learn the arrangement of shells, subshells, and orbitals in atoms for "energy levels" $n = 1$ through $n = 4$ because knowing this structure allows us to specify where the electrons are in an atom. And as you recall from the Introduction, chemistry is all about electrons! So here we go. There is a lot of detail in this section, and it is all important.

The phrase *energy levels* is in quotes just above for an important reason. We are transitioning now from the energy levels in Bohr's atomic model to those of the far more accurate quantum model. In Bohr's model, and in the hydrogen atom as we still understand it, there is only one energy level for each value of n. The quantum model is quite different, as we will see.

Recall from Figure 1.9 that the numbers of electrons permitted in the first four levels of Bohr's model are 2, 8, 8, and 18. These numbers correspond to the number of elements in the first four periods of the periodic table. Bohr was on the right track, but did not initially perceive the correct pattern. We now refer to n as the *principle quantum number*, and in every atom except hydrogen there are multiple energy levels associated with each value of n. As explained in detail below, the number of electrons allowed for each value of n is actually $2n^2$. This gives us 2, 8, 18, and 32 electrons in the various energy levels associated with $n = 1$ through $n = 4$.

The clusters of energy levels associated with each value of n are commonly called *shells*. As I state just above, the quantum state of an electron in an atom, including its energy, is specified by four quantum numbers; the principle quantum number—the shell number—is the first of them. So beginning with the principle quantum number you are already familiar with, here is a list of the names and other details for the four quantum numbers:

1. Principle Quantum Number, n Values for n are the integers 1, 2, 3, 4, 5, ... These are the main clusters of energy levels in the atom, also called shells. So far as we know, there is no highest value for n.

2. Azimuthal Quantum Number, l Within each shell except the first one ($n = 1$), there are *subshells*. The number of subshells in a shell is equal to the principle quantum number. For example, for $n = 3$ there are three subshells. Values for l are integers ranging from 0 to $(n - 1)$. Typically, these subshells are referred to by the letters *s*, *p*, *d*, *f*, and *g* rather than by the values of l. These common letter designations are shown Table 1.1. The azimuthal quantum numbers describe specific types of subshell configurations. So for example, within any shell the *s* subshell is always structured the same way. Likewise, the *p* subshell has the same general structure in every shell except $n = 1$ (since $n = 1$ doesn't have a *p* subshell). Again, the number of subshells in a given shell is equal to the principle quantum number. So, in the first shell there is one subshell, denoted as 1*s*. In the $n = 2$ shell, there are two subshells, denoted as 2*s* and 2*p*, and so on. (Note: The azimuthal quantum number is also sometimes called the *angular momentum quantum number*.)

l value	Common Letter Designation
0	*s*
1	*p*
2	*d*
3	*f*
4	*g*

Table 1.1. Letters used to designate values of the azimuthal quantum number, l.

3. Magnetic Quantum Number, m_l Within each subshell (numbered l), the possible values for m_l are the integers ranging from $-l$ to l. So, in a subshell with $l = 2$, the values for m_l are −2, −1, 0, 1, and 2. The magnetic quantum number is associated with specific shapes and orientations of orbitals within a subshell. A important point to note is that *any orbital in an atom can hold at most two electrons.*

4. Spin Projection Quantum Number, m_s As you recall, the Pauli exclusion principle requires every electron in an atom to be in a unique quantum state. That is, each electron has a unique set of quantum numbers. And since each orbital can hold two electrons, we need one more piece of information to distinguish from one another the quantum states of the two electrons. This characteristic is called *spin*. Unfortunately, it's a very misleading term because electrons aren't really spinning. In fact, it's pretty hard to say exactly *what* they are doing. But anyway, accepting spin as a real property analogous in some way to spinning, any two electrons in the same orbital have opposite spins. The two possible values for electron spin are $m_s = +1/2$ and $m_s = -1/2$, and we call these "spin up" and "spin down." At this point in your career you really don't need to worry about what these strange names and numbers mean. The fact is, if there are two electrons in the same orbital (and there can be at most two) one has spin up and one has spin down. This final quantum specification allows each electron in every atom to inhabit a unique quantum state.

All this information pertaining to the first three quantum numbers is summarized in Table 1.2. Hopefully your understanding of all these shells, subshells and orbitals will be enhanced by looking at images of computer models of the orbitals. Let's be a bit clearer about what these orbitals are: they represent the solutions to the Schrödinger equation for electrons in atoms with different energies. Table 1.3 depicts the orbitals in the various subshells associated with the first three shells, $n = 1$ through $n = 3$. Note first that in each shell there is an *s* orbital. These are spherical in shape. The models shown depict the sphere cut in half so you can see the relative sizes. If you look carefully at the 2*s* orbital, you can see the tiny 1*s* orbital inside it. And inside the 3*s* orbital you can see both the 1*s* and 2*s* orbitals inside it. We are coming back to electron energy soon, but for now note that within any shell, the *s* orbital is the lowest energy orbital in that shell. Note also that for all these orbital arrangements, the atomic nucleus is at the center. All orbitals are symmetric about the nucleus.

Beginning with $n = 2$, there is a *p* subshell in each shell, and beginning with $n = 3$ there is also a *d* subshell in each shell. The orbitals in the *p* subshell are usually described as resembling "dumbbells" because of their twin lobes. There are three of these twin-lobed orbitals in each *p* subshell, each oriented at right angles to the other two. For this reason, they are designated the p_x, p_y, and p_z orbitals—they can be thought of as lined up along the *x*, *y*, and *z* axes in a three-dimensional Cartesian coordinate system as depicted in Figure 1.12. (I explain the elongated appearance of the orbitals shown in Figure 1.12 shortly.) In Table 1.3, in order to make the *s* orbitals large enough to see and still have room to fit the *p* and *d* orbitals on the page, the *p* and *d* orbitals are shown much smaller than their actual size relative to the *s* orbitals.

Looking now at the $n = 3$ orbitals in Table 1.3, note that the 3*p* orbitals are shown surrounding the 2*p* orbitals. The three 3*p* orbitals are superimposed on each other just as the 2*p* ones are

n	Possible Values of l	Subshell Name	Possible Values of m_l (Each value corresponds to one orbital.)	Number of Orbitals in the Subshell	Total Number of Orbitals in the Shell (= n^2)
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

Table 1.2. Subshells and orbitals for the $n = 1$ through $n = 4$ shells.

(Figure 1.12). Finally, you can see that shapes of the five 3*d* orbitals are pretty bizarre. These orbitals are also superimposed on each other, and the whole bunch of them is superimposed on top of all the other orbitals in the table. Then, of course, there are all the orbitals for higher principle quantum numbers superimposed on top of them. Beginning with the $n = 4$ shell (not shown in the table) there is an *f* subshell in each shell. There are seven orbitals in each *f* subshell,

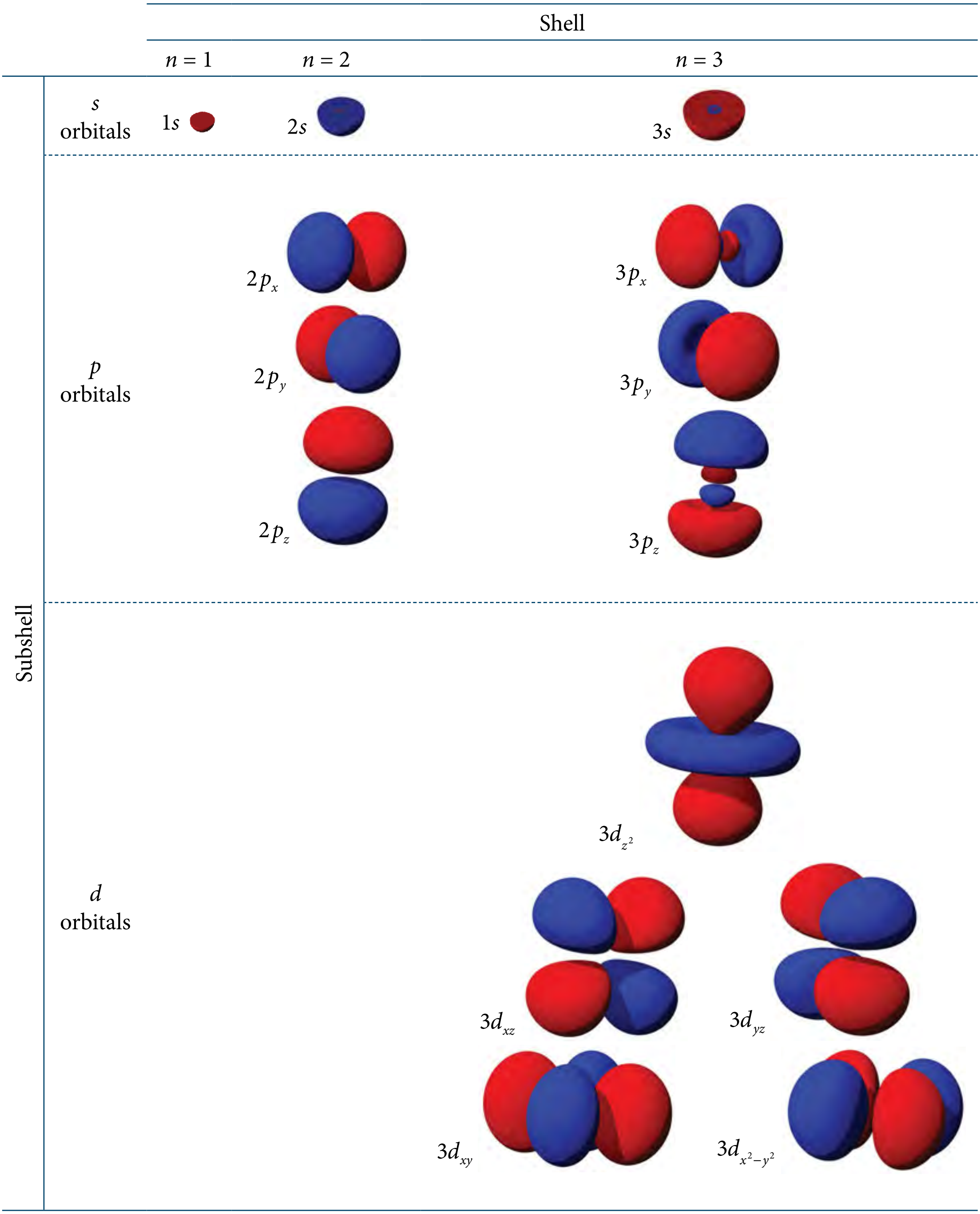


Table 1.3. Shapes of *s*, *p*, and *d* orbitals for the $n = 1$, $n = 2$, and $n = 3$ shells.

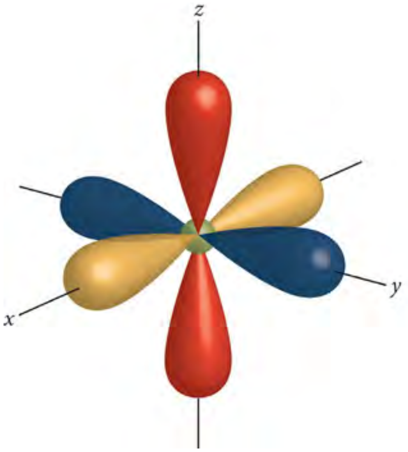


Figure 1.12. The elongated "probability distributions" of the 2*s* and 2*p* orbitals shown together. (2*s* = green; $2p_x$ = yellow, $2p_y$ = blue, $2p_z$ = red)

and they sort of resemble the *d* orbitals, only with six or eight lobes instead of four.

Recall that each orbital can house a maximum of two electrons (with opposite spins). For example, just to be clear, the $2p_x$ orbital with its two lobes is a single orbital (even though Table 1.3 shows the two lobes in different colors). Likewise, the $3d_{z^2}$ orbital with its two lobes and doughnut around the middle is also a single orbital. With a maximum of two electrons in each orbital, you can see that the first shell, $n = 1$, can hold at most two electrons, both in the 1*s* orbital. The $n = 2$ shell can hold a maximum of eight electrons: two in the 2*s* orbital, and two in each of the three 2*p* orbitals. The $n = 3$ shell can hold up to 18 electrons: two in the 3*s* orbital, six in the 3*p* orbitals, and a total of 10 in the 3*d* orbitals.

Before we move on and get back to talking about energy, one more important point should be made about orbitals. As noted above, the orbitals shown in Table 1.3 are the solutions to the Schrödinger equation. However, it is not correct to think of these shapes as locating where the electrons *are*. (Remember, the world of quantum mechanics is weird.) But it turns out that if we *square* the solutions to the Schrödinger equation we get shapes indicating *probabilities* of where the electrons are. This is what is depicted in Figure 1.12. Squaring the 2*p* solutions elongates the shapes of the orbitals. These orbitals that come from squaring solutions to the Schrödinger equation are called *probability distributions*. They should be envisioned as fuzzy at the edges and denser in the middle, indicating a lower probability that an electron is at the edge of the orbital and a higher probability that an electron is in the center part of the orbital.

Note just one more feature of the orbital arrangements: just because an orbital has more than one part—like the two lobes of a *p* orbital—does not mean that one electron is in one lobe and the other electron is in the other lobe. Instead, both electrons inhabit both lobes. Even stranger, to pass from one lobe to the other the electron somehow passes right through the atomic nucleus. (Don't hurt your brain by trying too hard to understand this. No one else understands it either! Electrons are very strange.)

1.3.3 The Aufbau Principle, the Madelung Rule, and Hund's Rule

Now that you know how the orbitals are arranged, we return to the topic of electron energies. Let's begin by recalling how one knows how many electrons an atom has. Unless it has ionized, an atom has the same number of electrons as protons, and the number of protons is given by the *atomic number* (*Z*). For example, if you check the periodic table inside the back cover of the book, you see that iron is element 26. This means an atom of iron has 26 protons and 26 electrons. The protons are all in the nucleus with the neutrons. The electrons are distributed around in various orbitals.

Figure 1.13 is another type of energy level diagram and illustrates the energies associated with the different orbitals. In this diagram, each little square represents an orbital, and each string of connected squares represents a subshell. On the left are the orbital energies for the hydrogen atom. As you see, all orbitals associated with a given principle quantum number have the same energy. These are the energies shown in Figures 1.6 and 1.8.

On the right side of Figure 1.13 is a general arrangement depicting the energies for atoms other than hydrogen. Here the energies go up with each subshell. For example, subshell 4*f* has

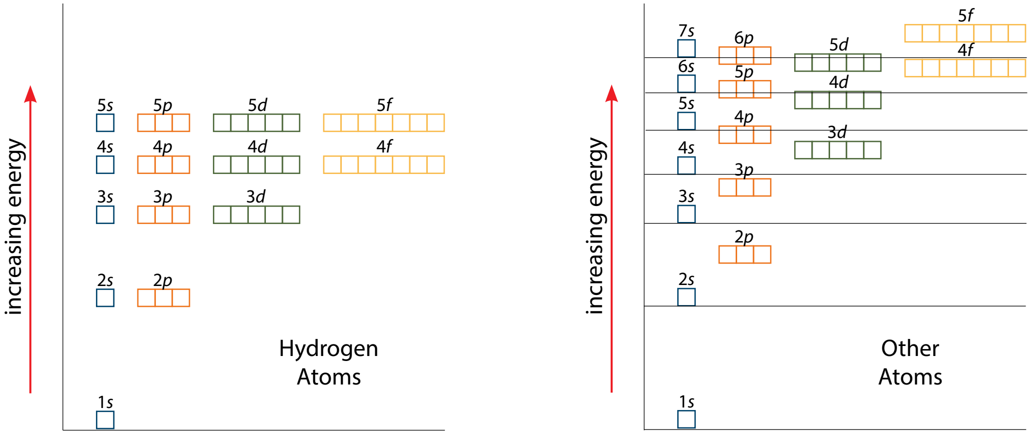


Figure 1.13. In hydrogen atoms, all orbitals within a given shell are at the same energy level. In atoms of other elements, orbital energy increases with increasing azimuthal quantum number, and the sequence of energies follows the Madelung rule.

a higher energy than 4*d*, which has a higher energy than 4*p*, which has a higher energy than 4*s*. Also, note especially that the energies associated with different principle quantum numbers (shells) overlap. Thus, subshell 4*s* has a lower energy than subshell 3*d*.

An important point to note about the right side of Figure 1.13 is that the exact energies associated with various subshells are different for every atom. With only one electron, the orbitals in an energy level of a hydrogen atom are basically all the same. But with multiple electrons repelling each other in an atom, the subshells begin spreading upward and each subshell is at a different energy. The amount of spread—and thus the exact energy associated with each subshell—is different for every atom. The important consequence of this for what we have covered so far in this chapter pertains to atomic spectra. The energy released by an electron transition from, say, a 5*d* orbital to a 4*p* orbital depends on the atom—that is, the element—involved. As you know, the energy in an emitted photon determines its wavelength and color (the Planck relation). The fact that the energies for the different orbitals depend on the element is the reason why spectroscopy can be used to identify the presence of elements in a sample. Each atom emits its own spectrum of wavelengths corresponding to the unique energy differences between the orbitals in that particular kind of atom.


Figure 1.14. Lithium (top) and copper flame tests.

The colors emitted by excited atoms in two metals are illustrated in Figure 1.14. The images show lithium and copper wires heated in a stove-top gas flame, causing electrons in the metal atoms to absorb photons of heat energy (electromagnetic radiation in the infrared region). As the electrons return to the ground state, they emit photons of visible light, and the colors produced depend on the energies of the subshells in the atoms of the respective metals. If the flames are observed through a prism, the colors in the flames are separated into a line spectrum and the individual color wavelengths can be identified. A test like this that uses flame as the energy source for exciting the metal is called a *flame test*.

With the energy picture under our belts, we are finally ready to describe how electrons are arranged in atoms. We are describing here the electron positions when atoms are in the ground state. You already know that when atoms are excited, electrons jump from ground state energies up to higher energies.

There are three principles involved in determining electron arrangement in ground state atoms. The first is the *Aufbau principle*, named after a German word meaning "building up." The Aufbau principle states that *electrons fill places in orbitals in order of increasing energy, starting from the lowest energy orbital and going up from there*. Remember: chemistry is all about minimizing energy. Electrons in a ground-state atom go into the lowest energy orbitals available.

The second principle is the *Madelung rule*. This principle specifies the order of the shells and orbitals for increasing energy. On the right side of Figure 1.13, the sequence the orbitals are in as energy increases follows the Madelung rule. Another common way of depicting the sequence of energies according to the Madelung rule is shown in Figure 1.15. If you start at the top and follow the arrows in descending order, you get the same sequence of orbitals as shown on the right side of Figure 1.13. The mathematical principle involved is that each arrow in Figure 1.15 represents a particular value of the sum of the principle quantum number and the azimuthal quantum number, $n + l$.

For example, look at the arrow starting at the 3*d* orbital. For 3*d*, $n = 3$ and $l = 2$, so $n + l = 5$. (The values of l are shown in Table 1.1.) For 4*p*, $n = 4$ and $l = 1$, and $n + l = 5$. For 5*s*, $n = 5$ and $l = 0$, so $n + l = 5$. So the subshells fill up in the sequence shown in Figure 1.15.

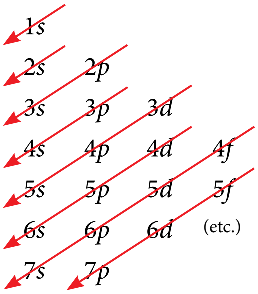


Figure 1.15. Since each red arrow represents a particular value of $n + l$, this diagram shows the order in which the subshells fill with electrons, according to the Madelung rule.

The third principle involved in electron arrangements is *Hund's rule*, which applies to the case of subshells that are only partially filled. Hund's rule states that *if orbitals of equal energy are available within a subshell, electrons fill them all up singly before they begin doubling up in orbitals*. For example, as you can see from the right side of Figure 1.13, the 3*d* subshell contains five orbitals of equal energy. According to Hund's rule, if there are electrons in this subshell, but not enough electrons to fill the subshell, the electrons go into the orbitals as one electron per orbital until each of the five orbitals has one electron in it. After that, any remaining electrons go in as the second electron in each orbital until each electron has a place. And again, remember that all orbitals can hold at most two electrons.

The principle at work behind Hund's rule is again energy minimization. Spreading single electrons in the orbitals of unfilled subshells is a lower energy configuration than putting pairs of electrons together when other orbitals remain empty. Minimizing the energy this way also makes the atom more stable, just as the cone on its side in Figure I.6 is more stable than the cone on its point.

1.4 Electron Configurations

1.4.1 Electron Configurations and Orbital Diagrams

You may be pleased to know that the ocean of information described in the previous section will be a lot easier to remember after you have had a bit of practice writing *electron configurations* to indicate where all the electrons are in an atom of a given element. The electron configuration for a given element is a list, written in a particular format, of all the subshells in use in an atom and how many electrons are in each one. As an example, consider iron, atomic number 26

($Z = 26$). There are 26 electrons in an atom of iron. The subshells required to hold them all, in order of increasing energy according to the Madelung rule, are as follows:

1*s*	2*s*	2*p*	3*s*	3*p*	4*s*	3*d*
holds 2 electrons	holds 2 electrons	holds 6 electrons	holds 2 electrons	holds 6 electrons	holds 2 electrons	holds 6 electrons in 10 places

The electron configuration is formed simply by chaining these together, placing the numbers of electrons as superscripts on the subshells they go with, without any punctuation. In front of the electron configuration, it is customary to place the element's chemical symbol followed by a colon. So, the electron configuration for iron is written as follows:

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Electron configurations only indicate subshells; they do not indicate which orbitals electrons are in inside the subshells. But we can use an *orbital diagram* similar to Figure 1.13 to show more precisely where the electrons are. Remember, Hund's rule comes into play, requiring that orbitals of equal energy each receive one spin-up electron before any of them take a second spin-down electron. A great metaphor for this was first used by Wolfgang Pauli, who formulated the Pauli exclusion principle. Pauli said that when filling up the orbitals in a subshell, electrons are like passengers filling a bus. Each takes a seat by himself until every seat has one person in it. After that, people start doubling up.

Figure 1.16 shows the electron arrangement for phosphorus, $Z = 15$. Each of the little arrows represents one electron, with upward arrows representing spin up and downward arrows representing spin down. Notice that the three electrons in the 3*p* subshell are placed so that each orbital contains one spin-up electron, as Hund's rule requires.

To make an orbital diagram, you simply show the orbitals in order, side by side, and put in the arrows representing the electrons. Thus, the orbital diagram and electron configuration for phosphorus are as follows:

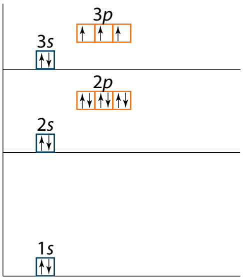
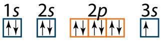
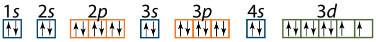


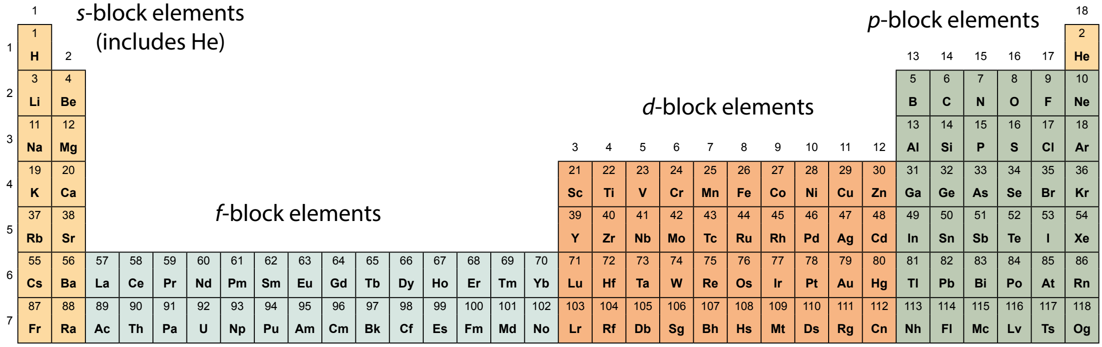
Figure 1.16. The electron arrangement for phosphorus, with 15 electrons.

Orbital Diagram	Electron Configuration
	P: $1s^2 2s^2 2p^6 3s^2 3p^3$

Here are three more examples: sodium (Na) with 11 electrons, chlorine (Cl) with 17 electrons, and nickel (Ni) with 28 electrons:

Z	Orbital Diagram	Electron Configuration
11		Na: $1s^2 2s^2 2p^6 3s^1$
17		Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$
28		Ni: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$

Note in each case that the superscripts add up to the number of electrons being represented in the notation, 11, 17, and 28 in the three examples above.



	1	2															3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																															2 He
2	3 Li	4 Be																									5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg																									13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca															21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr															39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Figure 1.17. Common terms applied to groups of elements based on the type of suborbital that is being filled as we move through the block in a given period (row). Group numbers shown are the numbers typically shown on the standard table with the *f*-block elements taken out.

To write an electron configuration, you need to know the atomic number (*Z*) to get the number of electrons, the number of electrons that can reside in each of the types of subshells (*s*, *p*, *d*, and *f*; we won't deal with *g* subshells), and the energy sequence according to the Madelung rule. The periodic table itself is the best aid to writing an electron configuration. Figure 1.17 is a depiction of the periodic table in its full, long form. The rare-earth elements, normally shown separated out beneath the main table, are shown in their rightful place.[3] Notice the captions on the different blocks of elements in the table. There are two groups (columns) in the *s* block, because *s* subshells can only hold two electrons. The *p* subshells can hold six electrons because there are three orbitals in each *p* subshell, and the *p* block is six groups wide. In the same way, the *d* block is 10 groups wide, and the *f* block is 14 groups wide. (See Table 1.2 to confirm the number of orbitals in a subshell, keeping in mind that each orbital can hold up to two electrons.)

Now look what happens as we move in order through elements in the table:

- Hydrogen (H) has one electron, helium (He) has two. In the element at the end of the 1st period (row)—helium—the 1*s* subshell is full.
- Lithium (Li) has three electrons, beryllium (Be) has four. With Be, the 1*s* and 2*s* subshells are full. The 5th electron possessed by boron (B) goes into the 2*p* subshell. So do all the additional electrons added in elements 6 through 10. Neon (Ne) has 10 electrons, so in the element at the end of the 2nd period (neon), subshells 1*s*, 2*s*, and 2*p* are all full.
- Sodium (Na) has 11 electrons, and the 11th one goes in the 3*s* subshell. Magnesium (Mg) has 12, and the 12th one fills the 3*s* subshell. Aluminum (Al) has 13, and the 13th one goes in the 3*p* subshell. In the element at the end of the third period—argon (Ar)—the 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* subshells are full.
- The 4th period begins with potassium (K) and calcium (Ca), in which new electrons are placed in the 4*s* subshell. Then look what happens next: the next element, scandium (Sc), has 21 electrons and the 21st one goes into a *d* subshell, the 3*d* subshell, in fact. Each new electron for elements 21 through 30 goes into the 3*d* subshell. Then the 31st electron in gallium (Ga) is placed in the 4*p* subshell. In the element at the end of the 4th period—krypton (Kr)—the 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, and 4*p* subshells are full.

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[3] The *f*-block elements shown are also called the *inner transition metals* or *rare-earth elements*. They are usually removed from the table and shown beneath it for the simple reason that with them in place, the table is inconveniently wide. Since most of our work in chemistry is with *s*-, *p*-, and *d*-block elements, the removal of the *f*-block elements in the standard representation of the periodic table doesn't cause much trouble.

This pattern continues, and the order of new shells coming into use continues to follow the Madelung rule. Now you can see why the blocks of elements in Figure 1.16 are identified the way they are. Moving from left to right across any period in the table, the additional electron for atoms of the next element goes into a subshell of the type indicated by the name of the block the element is in.

Be careful when writing electron configurations for elements at the beginning of the *d* and *f* blocks. The first *d* subshell that occurs in the sequence of shell filling is the 3*d* subshell, even though the elements that fill it are in the 4th period. Table 1.2 and Figure 1.15 will help remind you that the number of subshells for a particular principle quantum number *n* is equal to *n*.

1.4.2 Condensed Electron Configurations

You may already know that the elements in Group 18, the noble gases, are very unreactive. In fact, these elements eluded discovery by researchers for a long time. Since they don't form compounds, scientists didn't even know they existed!

The reason the noble gases are so nonreactive is that their electron arrangements are very stable, low-energy configurations. Obviously, each of the noble gases is at the end of a period in the periodic table (Group 18). Figure 1.18 illustrates the pattern that occurs in the orbital filling of these elements. In each case, all orbitals are filled up to but not including the *s* orbital of the next principle quantum number.

Since the noble gases are so stable, occurring as they do at the end of each period, the chemical symbols of the noble gases are used to form the so-called *condensed electron configurations*. The condensed electron configuration is a shorter, more convenient form.

Here's an example to show how this works. A glance at the periodic table shows that the only difference in the electron configurations of, say, titanium (Ti, $Z = 22$) and argon (Ar, $Z = 18$), is that titanium has four extra electrons. The electron configurations for argon and titanium are:

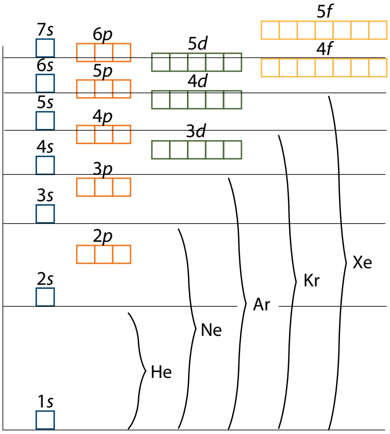


Figure 1.18. The orbital filling pattern of the noble gases.

Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$

Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

The condensed electron configuration for any element is written by using the chemical symbol of the noble gas in the previous period to represent all the filled orbitals up to that point, and then just adding on the orbitals in the period where the element is. The noble gas chemical symbol is always written in square brackets. The condensed electron configuration for titanium is written as

Ti: $[\mathrm{Ar}]4s^2 3d^2$

As one more example, the condensed electron configuration for phosphorus ($Z = 15$) is written as

P: $[\mathrm{Ne}]3s^2 3p^3$

In the condensed electron configuration, the inner-shell electrons lumped together under the noble gas symbol are called the *core electrons*.

1.4.3 Anomalous Electron Configurations

There are a few elements with electron configurations that are notable exceptions to the ordinary rules. All these exceptions are *d*-block or *f*-block elements, as shown in Figure 1.19.

We would expect the condensed electron configuration for chromium ($Z = 24$) to be

Cr: $[\mathrm{Ar}]4s^2 3d^4$

However, it is not! One of the 4*s* electrons goes into the 3*d* subshell instead, giving

Cr: $[\mathrm{Ar}]4s^1 3d^5$

Copper ($Z = 29$), does the same thing. We would expect the condensed electron configuration to be

Cu: $[\mathrm{Ar}]4s^2 3d^9$

Instead, it is

Cu: $[\mathrm{Ar}]4s^1 3d^{10}$

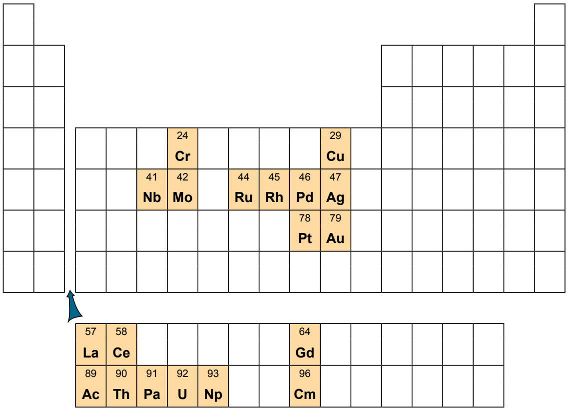


Figure 1.19. Elements with anomalous electron configurations.

Element	Atomic Number, Z	Symbol	Condensed Configuration
chromium	24	Cr	Cr: $[\mathrm{Ar}]4s^1 3d^5$
copper	29	Cu	Cu: $[\mathrm{Ar}]4s^1 3d^{10}$
niobium	41	Nb	Nb: $[\mathrm{Kr}]5s^1 4d^4$
molybdenum	42	Mo	Mo: $[\mathrm{Kr}]5s^1 4d^5$
ruthenium	44	Ru	Ru: $[\mathrm{Kr}]5s^1 4d^7$
rhodium	45	Rh	Rh: $[\mathrm{Kr}]5s^1 4d^8$
palladium	46	Pd	Pd: $[\mathrm{Kr}]4d^{10}$
silver	47	Ag	Ag: $[\mathrm{Kr}]5s^1 4d^{10}$
lanthanum	57	La	La: $[\mathrm{Xe}]6\mathrm{s}^2 5d^1$
cerium	58	Ce	Ce: $[\mathrm{Xe}]6\mathrm{s}^2 4f^1 5d^1$
gadolinium	64	Gd	Gd: $[\mathrm{Xe}]6\mathrm{s}^2 4f^7 5d^1$
platinum	78	Pt	Pt: $[\mathrm{Xe}]6\mathrm{s}^1 4f^{14} 5d^9$
gold	79	Au	Au: $[\mathrm{Xe}]6\mathrm{s}^1 4f^{14} 5d^{10}$
actinium	89	Ac	Ac: $[\mathrm{Rn}]7\mathrm{s}^2 6d^1$
thorium	90	Th	Th: $[\mathrm{Rn}]7\mathrm{s}^2 6d^2$
protactinium	91	Pa	Pa: $[\mathrm{Rn}]7\mathrm{s}^2 5f^2 6d^1$
uranium	92	U	U: $[\mathrm{Rn}]7\mathrm{s}^2 5f^3 6d^1$
neptunium	93	Np	Np: $[\mathrm{Rn}]7\mathrm{s}^2 5f^4 6d^1$
curium	96	Cm	Np: $[\mathrm{Rn}]7\mathrm{s}^2 5f^7 6d^1$

Table 1.4. Elements with anomalous electron configurations.

The electron configurations for all the anomalous elements are shown in Table 1.4. Notice that palladium ($Z = 46$) is so anxious to get electrons into the 4*d* subshell that it steals both the electrons that ordinarily would be in the 5*s* subshell and places them in the 4*d* subshell to fill it up.

The electron configurations for these elements are not difficult to remember. For the *d*-block exceptions, except for palladium, they move one *s*-subshell electron into a *d* subshell at the highest energy in the atom. Palladium is the exception among exceptions: it moves two.

The *f*-block exceptions move one *f* subshell electron into a *d* subshell at the highest energy in the atom. As with the *d*-block exceptions, there is one exception among the *f*-block anomalies: thorium moves two *f*-subshell electrons into the *d* subshell.

Although the details are complex, the bottom line for these exceptions to the normal rules is that there are other factors coming into play in their atomic structure. At high energy levels, the orbital energies are very close together. The anomalous configurations represent the arrangement of electrons that minimizes the energy in the atom.

1.5 Isotopes and Atomic Masses

1.5.1 Isotopes

As you know, the atomic number (Z) of an element designates the number of protons in the nucleus of an atom of that element. For a given element, the atomic number is fixed: if an atom has a different number of protons, it is an atom of a different element. But the number of neutrons that may be present in the nucleus is not fixed. For most elements, there are variations in the number of neutrons that can be present in the nucleus. The varieties are called *isotopes*. For most elements, there is one isotope that is the most abundant in nature and several other isotopes that are also present but in smaller quantities. The general term for any isotope of any element is *nuclide*.

Isotopes are designated by writing the name of the element followed by the number of nucleons (protons and neutrons) in the isotope. The number of nucleons in a nucleus is called the *mass number*. For example, the most common isotope of carbon is carbon-12, accounting for about 98.9% of all the naturally occurring carbon. In the nucleus of an atom of carbon-12 there are six protons and six neutrons. There are two other naturally occurring carbon isotopes. Carbon-13 with seven neutrons accounts for about 1.1% of natural carbon. Atoms of carbon-14, of which only a trace exists in nature, have eight neutrons in the nucleus.

1.5.2 The Unified Atomic Mass Unit

The mass of a single atom is an extremely small number. But so much of our work in chemistry depends on atomic masses that scientists having been using units of *relative* atomic mass for a long time—all the way back to John Dalton, before actual masses of atoms were even known. Prior to the discovery of isotopes in 1912, the so-called *atomic mass unit* (amu) was defined as 1/16 the mass of an oxygen atom. After the discovery of isotopes, physicists defined the amu as 1/16 the mass of an atom of oxygen-16, but the definition used by chemists was 1/16 the average mass of naturally occurring oxygen, which is composed of several isotopes. To eliminate the confusion resulting from these conflicting definitions, the new *unified atomic mass unit* (u) was adopted in 1961 to replace them. Many texts continue to use the amu as a unit, but they define it as the u is defined. Strictly speaking, the amu is an obsolete unit that has been replaced by the u, now also called the dalton (Da). The u and the Da are alternative names (and symbols) for the same unit. The use of the dalton has increased in recent years, particularly in molecular biology.

The unified atomic mass unit, u, *is defined as exactly 1/12 the mass of an atom of carbon-12.* Table 1.5 lists a few nuclides and their atomic masses using the u as a unit of mass. All the elements listed exist as other isotopes in addition to those shown, but as you see from the percentage abundances, the ones shown are the major ones for the elements represented in the table.

1.5.3 Atomic Masses

In addition to the atomic number, the Periodic Table of the Elements lists the atomic mass in unified atomic mass units (u) for each element. But since there are multiple isotopes for just about every element, *the atomic mass values in the periodic table represent the weighted average of the masses of naturally occurring isotopes.*

An example of a weighted average is the average age of the students in the sophomore class at your school. Let's say there are 47 sophomores, 40 of whom are 15 years old and 7 of whom are 16 years old at the beginning of the school year. To determine the average age of these students, let's first determine the proportion of the students at each age.

$$\frac{40}{47}=0.851\ \ (85.1\%)$$

$$\frac{7}{47}=0.149\ \ (14.9\%)$$

To calculate the average age, we first multiply each student age by the proportion of students of that age to find the contribution to the average from each age group. Then we add the contributions together to find the weighted average age for the sophomore class.

$$\begin{array}{r} 15\text{ years}\cdot 0.851=12.8\text{ years} \\ +16\text{ years}\cdot 0.149=2.38\text{ years} \\ \hline =15.2\text{ years} \end{array}$$

We perform a similar calculation when computing the average atomic mass of an element from the masses of its isotopes, as shown in the following example.

Z	Nuclide	Mass (u)	Abundance (%)
1	hydrogen-1	1.0078	99.9885
1	hydrogen-2	2.0141	0.0115
6	carbon-12	12.0000	98.93
6	carbon-13	13.0034	1.078
14	silicon-28	27.9769	92.223
14	silicon-29	28.9765	4.685
14	silicon-30	29.9738	3.092
17	chlorine-35	34.9689	75.76
17	chlorine-37	36.9659	24.24
20	calcium-40	39.9626	96.941
20	calcium-42	41.9586	0.647
26	iron-54	53.9396	5.845
26	iron-56	55.9349	91.754
26	iron-57	56.9354	2.119
26	iron-58	57.9333	0.282
29	copper-63	62.9296	69.15
29	copper-65	64.9278	30.85
92	uranium-235	235.0439	0.7204
92	uranium-238	238.0508	99.2742

Table 1.5. Major isotopes for a few elements.

Example 1.2

Given the isotope masses and abundances for copper-63 and copper-65 in Table 1.5, determine the atomic mass for naturally occurring copper.

Multiply each isotope's mass by its abundance to get the isotope's contribution to the average atomic mass of the element. Then add together the contributions from each isotope. The data from the table are:

copper-63: mass = 62.9296 u, abundance = 69.15%

copper-65: mass = 64.9278 u, abundance = 30.85%

$$\begin{array}{r} 62.9296\text{ u}\cdot 0.6915=43.51\text{ u} \\ +\ \ 64.9278\text{ u}\cdot 0.3085=20.03\text{ u} \\ \hline =63.55\text{ u} \end{array}$$

Compare this value to the value shown in the periodic table inside the back cover of the text.

The unified atomic mass unit, u, is defined as 1/12 the mass of an atom of carbon-12. Although the value of this mass is quite close to the masses of the proton and neutron, it is not exact because of the mass of the electrons in atoms of carbon-12, and also because of the mass-en-

Particle	Mass
proton	1.007277 u
neutron	1.008665 u
electron	0.0005486 u

Table 1.6. Masses in u of the three basic subatomic particles.

ergy involved in binding the nucleus of the atom together. (The mass of nucleons bound together in a nucleus does not equal the sum of their individual masses.) Table 1.6 shows the masses of the three basic subatomic particles in unified atomic mass units.

Still, the proton and neutron masses are very close to unity (one) and the electron mass is extremely small. This means that for elements with a very large abundance of one isotope we can use the atomic mass and atomic number in the periodic table to determine the numbers of protons and neutrons in the nucleus of the most common isotope. For example, from Table 1.5, the mass of uranium-238 is very close to 238 u. Since an atom of uranium-238 has 92 protons, the balance of the mass is essentially all neutrons. Thus, there are 238 – 92 = 146 neutrons in uranium-238.

1.5.4 The Mole and the Avogadro Constant

When solving problems in chemistry, we are generally working with chemical reactions in which huge numbers of atoms are involved, including all the naturally occurring isotopes, so performing reaction calculations with the masses of individual atoms is not practical. However, the average mass of a given multiple of some kind of atom is simply that multiple times the atomic mass. The mass of one million atoms of aluminum is 1,000,000 times the atomic mass of aluminum.

In chemistry, the standard bulk quantity of substance used in calculations is the *mole* (mol). The mole is a particular number of particles of a substance, just as the terms *dozen*, *score*, and *gross* refer to specific numbers of things (12, 20, and 144, respectively). A mole is exactly $6.02214076 \times 10^{23}$ particles of a substance.

This value is known today as the *Avogadro constant*, N_A. More formally, the Avogadro constant is defined as exactly:

$$N_A = 6.02214076 \times 10^{23}\ \text{mol}^{-1} \tag{1.6}$$

Usually, we just round this value to $6.022 \times 10^{23}\ \text{mol}^{-1}$. In the next section, I'll describe why this value is what it is, instead of being a more convenient round number. For the moment, let's focus on what it means. Now, don't freak out over the unit of measure. Allow me to explain. Raising a unit of measure to the power –1 is mathematically equivalent to placing the unit in a denominator because $x^{-1} = \frac{1}{x}$. In other words, Equation (1.6) is the same thing as saying "$6.02214076 \times 10^{23}$ per mole." To make things even clearer, it's okay to say it this way: "N_A is about 6.022×10^{23} particles per mole." This is the way I like to think of it when performing unit conversions, as we do quite a lot in coming chapters. Without the units of measure, the value $6.02214076 \times 10^{23}$ is called *Avogadro's number*. With the units, it is called the Avogadro constant. Using this terminology, the mole can be defined this way:

A mole is the amount of a pure substance (element or compound) that contains Avogadro's number of particles of the substance.

Let's now consider what we mean when we refer to *particles* of a substance. For substances that exist as molecules, the particles are the molecules. For substances that exist as individual atoms, the particles are the individual atoms. Metals are like this, since a pure metal is composed of individual atoms of the same element joined together in a crystal lattice. The noble gases are also like this. The noble gases are located in the far right-hand column of the Periodic Table of the Elements. As I discuss more in coming chapters, atoms of noble gases are almost completely unreactive—they don't bond with other atoms at all. At ordinary temperature and pressure, the noble gases are gases composed of individual atoms.

For crystalline compounds, the "particles" in a mole of the substance are the *formula units* in the crystal lattice. A formula unit is one set of the atoms represented by the chemical formula of the compound. For example, the chemical formula for calcium carbonate is $CaCO_3$. One formula unit of calcium carbonate includes one calcium atom, one carbon atom, and three oxygen atoms.

The value of the Avogadro constant was determined approximately by French Physicist Jean Perrin (Figure 1.20) in the early 20th century. Perrin determined the value of the constant through several different experimental methods. In the 19th century, many scientists did not yet accept the existence of atoms as a scientific fact and Perrin's research put the atomic nature of matter beyond dispute. For this work, he received the Nobel Prize in Physics in 1926. Perrin proposed naming the constant after Amedeo Avogadro, a 19th-century Italian scientist who was the first to propose that the volume of a gas at a given temperature and pressure is proportional to the number of particles of the gas (atoms or molecules), regardless of the identity of the gas. In fact, at 0°C and atmospheric pressure, one mole of any gas occupies a volume of 22.4 L.

Figure 1.20. French physicist Jean Perrin (1870–1942).

1.5.5 Molar Mass and Formula Mass

Since 2019, the value of the Avogadro constant in Equation (2.2) is exact by definition. But the number has the value it does because it was originally chosen so that the average atomic mass in u of a molecule of a compound, as computed from the mass values in the periodic table, would be numerically equivalent to the mass of one mole of the compound in grams per mole. (We address these calculations below.) Now, recall that the definition of the unified atomic mass unit (or dalton) is such that an atom of carbon-12 has a mass of exactly 12 u. According to the original definition of Avogadro's number, there were also exactly 12 grams of carbon-12 in one mole of carbon-12. So according to these definitions, an atom of carbon-12 has a mass of exactly 12 u, and a mole of carbon-12 had a mass of exactly 12 grams. This quantity, the mass of one mole of a substance, is called the *molar mass*. Because of the way the molar and atomic masses were defined, the molar mass for an atom was numerically equivalent to the atomic mass. As a result of the 2019 redefinition of Avogadro's number, the atomic mass in u and the molecular mass in g/mol are no longer exactly equivalent. However, they are extremely close and may still be treated as equal for practical purposes. (The difference is a factor of only about 4×10^{-10}.)

Even though the exact equivalence ended in 2019, these are still very handy definitions! For example, from the periodic table we find that the average mass of one atom of silicon ($Z = 14$) is 28.0855 u. This also tells us that the mass of one mole of silicon is 28.0855 g, so the molar mass of silicon is 28.0855 g/mol. Likewise, from the periodic table we find that the average mass of one atom of copper ($Z = 29$) is 63.546 u. This also tells us that the mass of one mole of copper is 63.546 g, so the molar mass of copper is 63.546 g/mol. For the elements that exist as single atoms, the molar mass in g/mol and the atomic mass in u are numerically equivalent (almost).

From the periodic table, we can also determine the molar mass of compounds—the mass of a mole of the compound. We simply add up the molar masses for the elements in the chemical formula, taking into account any subscripts present in the formula, and we have the molar mass for the compound in g/mol. If we add up the element atomic masses in unified atomic mass

Quantity	Units	Definition
molar mass	g/mol	The mass of one mole of a substance, approximately equal to the sum of the atomic masses of the elements in a chemical formula, taking into account the subscripts indicating atomic ratios in the compound.
formula mass	u	The mass of one formula unit of a substance. Numerically nearly equivalent to the molar mass.
molecular mass	u	The average mass of a single molecule of a molecular substance. Numerically equivalent to the formula mass. (May also be converted to grams and expressed in grams, see Section 2.4.4.)

Table 1.7. Definitions and units for molar mass, formula mass, and molecular mass.

units we obtain what is called the *formula mass* of the compound in u. If the compound is molecular, then the formula mass may also be referred to as the *molecular mass*, the average mass of a single molecule of the substance.

The details of these three different mass terms are summarized in Table 1.7.

▼ Example 1.3

Determine the formula mass and molar mass for water, H_2O. We note that since water is composed of molecules, the formula mass may also be called the molecular mass.

From the periodic table, the atomic masses of hydrogen (H) and oxygen (O) are:

H: 1.0079 u
O: 15.9994 u

There are two hydrogen atoms and one oxygen atom in each water molecule, so we multiply these numbers by the element atomic masses and add them up to get the formula mass of H_2O.

$$(2\times1.0079\text{ u})+(1\times15.9994\text{ u})=18.0152\text{ u}$$

Thus, the formula mass for water is 18.0152 u. This is also the molecular mass. The calculation of the molar mass is identical, except we use units of g/mol instead of u.

From the periodic table, the molar masses of hydrogen (H) and oxygen (O) are:

H: $1.0079\ \frac{\text{g}}{\text{mol}}$
O: $15.9994\ \frac{\text{g}}{\text{mol}}$

There are two hydrogen atoms and one oxygen atom in each water molecule, so we multiply these numbers by the element masses and add them up to get the molar mass of H_2O.

$$\left(2\times1.0079\ \frac{\text{g}}{\text{mol}}\right)+\left(1\times15.9994\ \frac{\text{g}}{\text{mol}}\right)=18.0152\ \frac{\text{g}}{\text{mol}}$$

▲

▼ Example 1.4

Determine the molar mass for nitrogen gas, N_2.

From the periodic table, the atomic mass of nitrogen (N) is:

$$\text{N: } 14.0067\ \frac{\text{g}}{\text{mol}}$$

There are two nitrogen atoms in each molecule, so we multiply the atomic mass by two to get the molar mass of N_2.

$$\left(2\times 14.0067\ \frac{\text{g}}{\text{mol}}\right)=28.0134\ \frac{\text{g}}{\text{mol}}$$

▲

▼ Example 1.5

Determine the mass in grams of 2.5 mol sodium bicarbonate, $NaHCO_3$ (baking soda).

In any problem like this, we first find the molar mass of the given compound. Then we simply use that molar mass to compute the mass of the given quantity. From the periodic table, the atomic masses of the elements in the compound are:

$$\text{Na: } 22.9898\ \frac{\text{g}}{\text{mol}}$$

$$\text{H: } 1.0079\ \frac{\text{g}}{\text{mol}}$$

$$\text{C: } 12.011\ \frac{\text{g}}{\text{mol}}$$

$$\text{O: } 15.9994\ \frac{\text{g}}{\text{mol}}$$

The oxygen appears three times in the formula, so its mass must be multiplied by three and added to the others.

$$22.9898\ \frac{\text{g}}{\text{mol}}+1.0079\ \frac{\text{g}}{\text{mol}}+12.011\ \frac{\text{g}}{\text{mol}}+\left(3\times 15.9994\ \frac{\text{g}}{\text{mol}}\right)=84.007\ \frac{\text{g}}{\text{mol}}$$

This value is the molar mass for $NaHCO_3$. To find the mass of 2.5 mol we multiply:

$$2.5\ \text{mol}\cdot 84.007\ \frac{\text{g}}{\text{mol}}=210\ \text{g}$$

▲

▼ Example 1.6

A scientist measures out 125 g of potassium chloride (KCl). How many moles of KCl does this quantity represent?

First, determine the molar mass of KCl. From the periodic table:

$$\text{K: } 39.098\ \frac{\text{g}}{\text{mol}}$$

$$\text{Cl: } 35.4527\ \frac{\text{g}}{\text{mol}}$$

The formula includes one atom of each, so we add them to obtain the molar mass:

$$39.098\ \frac{\text{g}}{\text{mol}} + 35.4527\ \frac{\text{g}}{\text{mol}} = 74.551\ \frac{\text{g}}{\text{mol}}$$

Beginning now, always think of the molar mass of any substance as a conversion factor that can be written right side up or upside down to convert grams to moles or vice versa. For KCl, 74.551 g is equivalent to 1 mol, so these quantities can be written as conversion factors, like this:

$$\frac{74.551\ \text{g}}{1\ \text{mol}} = \frac{1\ \text{mol}}{74.551\ \text{g}}$$

This makes the last step of this problem easy. Just select the way of writing the molar mass conversion factor that cancels out the given units (g) and gives the units required (mol). This is nothing but a unit conversion.

$$125\ \text{g} \cdot \frac{1\ \text{mol}}{74.551\ \text{g}} = 1.68\ \text{mol}$$

▲

The photograph in Figure 1.21 shows one mole of each of four substances. The first is one mole of copper, equal to 63.5 g. The second is a 250-mL beaker containing one mole of water. As you can see, this is not much water—only 18 mL. In the upper right is a weigh tray containing one mole of sodium chloride, 40.0 g. (This is just under 1/4 cup.) Finally, one mole of baking soda, 84.1 g. (This is right at 1/3 cup.)

Figure 1.21. Clockwise from left are shown 1 mole of copper, 1 mole of water, 1 mole of table salt, and 1 mole of baking soda.

▼ Example 1.7

Calculate the number of water molecules in a 1.00-liter bottle of water.

The logic of this problem, in reverse, is as follows: To calculate a number of molecules, we must use the Avogadro constant. To use the Avogadro constant, we need to know the number of moles of water we have. To determine the number of moles, we need to know both the molar mass and the mass of the water. To determine the mass from a volume, we use the density equation.

So we begin with the given information and the density equation to determine the mass of water we have. The given information and unit conversions are as follows:

$$V = 1.00\ \text{L} \cdot \frac{1000\ \text{cm}^3}{1\ \text{L}} = 1.00 \times 10^3\ \text{cm}^3$$

$$\rho = 0.998\ \frac{\text{g}}{\text{cm}^3}$$

$$m = ?$$

Now we write down the density equation and solve for the mass:

$$\rho = \frac{m}{V}$$

$$m = \rho \cdot V = 0.998\ \frac{\text{g}}{\text{cm}^3} \cdot 1.00 \times 10^3\ \text{cm}^3 = 998\ \text{g}$$

Next we need the molar mass of water. We calculated this in Example 1.3 and obtained 18.0152 g/mol. We use this molar mass as a conversion factor to convert the mass of water into a number of moles of water:

$$998\ \text{g} \cdot \frac{1\ \text{mol}}{18.0152\ \text{g}} = 55.40\ \text{mol}$$

This intermediate result has four significant digits—one more than we need in the final result. Finally, with the number of moles in hand we use the Avogadro constant to determine how many particles of water this is, which is identical to the number of water molecules.

$$55.40\ \text{mol} \cdot \frac{6.022 \times 10^{23}\ \text{particles}}{\text{mol}} = 3.34 \times 10^{25}\ \text{particles}$$

▲

1.5.6 Gram Masses of Atoms and Molecules

The molar mass from the periodic table and the Avogadro constant can be used to calculate the mass in grams of an individual atom. Recall that the atomic mass value in the periodic table gives both the average atomic mass in u, and the molar mass in g/mol. Knowing the molar mass in g/mol we can simply divide by the number of atoms there are in one mole to find the mass of one atom in grams. Although this kind of calculation is quite simple, I have found that it is *very* easy for students to get confused and not be able to determine whether one should multiply or divide or what. So here's a problem solving tip: let the units of measure help you figure out what to do. If you include the units of measure in your work and pay attention to how the units cancel out or don't cancel out, these calculations are pretty straightforward. *Keep this principle firmly in mind throughout your study of chemistry!* Units of measure are not an annoying burden; they are the student's friend.

▼ Example 1.8

Determine the average mass in grams of an atom of boron.

From the periodic table we find that the molar mass of boron is 10.811 g/mol. One mole consists of Avogadro's number of atoms of boron, so if we divide the molar mass by the Avogadro constant, we will have the mass of a single atom of boron. Let's begin by setting up the division I just described, and then use the old invert-and-multiply trick for fraction division to help with the unit cancellations.

$$\frac{10.811\ \frac{\text{g}}{\text{mol}}}{6.0221\times 10^{23}\ \frac{\text{particles}}{\text{mol}}} = 10.811\ \frac{\text{g}}{\text{mol}} \cdot \frac{1}{6.0221\times 10^{23}}\ \frac{\text{mol}}{\text{particles}}$$

$$= \frac{10.811}{6.0221\times 10^{23}}\ \frac{\text{g}}{\text{particle}} = 1.7952\times 10^{-23}\ \frac{\text{g}}{\text{particle}}$$

So the average mass of one boron atom is 1.7952×10^{-23} g. Note that I use five digits in the value of the Avogadro constant to preserve the precision we have in the molar mass.

▲

For molecular substances, the molar mass can be used to compute the molecular mass in grams, the average mass of one molecule. This is done by first computing the molar mass of the compound, just as we did before. Then we simply divide by the Avogadro constant to obtain the mass of one molecule.

Like the atomic mass, the molecular mass is an average mass, since the atomic masses used in calculating the molar mass are all based on the average mass of different isotopes with their abundances taken into account. The molecular mass for a *specific* molecule would have to be calculated based on the specific masses of the nuclides in the molecule.

▼ Example 1.9

Determine the mass in grams of one molecule of carbon tetrachloride, CCl_4.

From the periodic table we find that the molar masses of carbon and chlorine are 12.011 g/mol and 35.4527 g/mol, respectively. From this we calculate the molar mass of CCl_4:

$$\left(1\times 12.011\ \frac{\text{g}}{\text{mol}}\right) + \left(4\times 35.4527\ \frac{\text{g}}{\text{mol}}\right) = 153.822\ \frac{\text{g}}{\text{mol}}$$

With this molar mass we use the Avogadro constant to get the molecular mass in grams. This time, instead of writing the Avogadro constant in the denominator of a big fraction, I simply treat it as a conversion factor and write it in the equation such that the mole units cancel out. (This is the way I always perform such calculations.) I also use six digits in the Avogadro constant to preserve the precision we have in the molar mass.

$$153.822\ \frac{\text{g}}{\text{mol}} \cdot \frac{1\ \text{mol}}{6.02214\times 10^{23}\ \text{particles}} = 2.55427\times 10^{-22}\ \frac{\text{g}}{\text{particle}}$$

▲

1.5.7 Percent Composition and Empirical Formulas

Laboratory chemical analysis of a substance enables a chemist to determine the *percent composition* of the substance. When a new compound is discovered, chemists place a high priority on determining the percentages, by mass, of each element in the substance. This is the percent composition. From the percent composition a so-called *empirical formula* for the substance can be worked out—a formula that represents the ratios of the elements in the substance.

For example, suppose laboratory analysis of a 221.6-g sample of ascorbic acid (vitamin C) results in the following mass data:

H: 10.15 g
C: 90.68 g
O: 120.8 g

If we divide each of the mass values by the total mass of the sample we have the percent composition of the sample:

$$\text{H: } \frac{10.15\text{ g}}{221.6\text{ g}} = 0.04580$$

$$\text{C: } \frac{90.68\text{ g}}{221.6\text{ g}} = 0.4092$$

$$\text{O: } \frac{120.8\text{ g}}{221.6\text{ g}} = 0.5451$$

Thus, the percent composition is 4.58% hydrogen, 40.92% carbon, and 54.51% oxygen. Note that we expect these percentages to add up to 100%, but due to limits on the precision of the data they add to 100.01%.

Given either the percent composition or the actual masses from a sample we can determine the empirical formula for a substance. The empirical formula may differ from the actual *molecular formula* of the substance. An empirical formula represents the smallest whole number ratios of the elements in the substance, while the molecular formula represents the actual numbers of each element in the molecule.

For example, hydrogen peroxide, H_2O_2, is a common household disinfectant. Molecules of hydrogen peroxide contain two atoms of hydrogen and two atoms of oxygen, so the molecular formula for this substance is H_2O_2. But the empirical formula is HO, because the empirical formula contains the smallest whole number values that can represent the ratios in the compound. Since each molecule of H_2O_2 contains two atoms of H and two atoms of O, the ratio of H to O in the molecule is 1 : 1, giving an empirical formula of HO.

In many cases, the empirical and molecular formulas are identical. The molecular formula for methane, for example, is CH_4. This formula indicates a ratio of carbon to hydrogen atoms in the molecule of 1 : 4. This same formula is the empirical formula, because 1 and 4 are the smallest whole numbers that can represent this ratio.

To determine the empirical formula from percent composition, assume you have a sample of the substance with a mass of exactly 100 g. Use the percent composition to determine the masses of each element in the 100-g sample, then use the mass data from the periodic table to convert each of these masses to numbers of moles. Finally, divide each of the mole values by the smallest number of moles to determine the whole number ratios in the formula. An example illustrates the calculation.

▼ Example 1.10

Given percent composition data for ascorbic acid (see above), determine the empirical formula for this substance.

We assume a sample with a mass of exactly 100 g. We begin by using the percent composition to obtain masses in grams for each element in the substance. Assuming a 100-g sample just makes this easy. Since hydrogen is 4.58% of the 100-g sample, the mass of the hydrogen in the sample is 4.58 g. Similarly, the masses of the carbon and oxygen are 40.92 g and 54.51 g, respectively.

Next, we use the molar masses for each element to convert each of these masses to number of moles. We use the molar mass as a conversion factor, just as we have before.

$$4.58\text{ g H}\cdot\frac{1\text{ mol}}{1.0079\text{ g}}=4.54\text{ mol H}$$

$$40.92\text{ g C}\cdot\frac{1\text{ mol}}{12.011\text{ g}}=3.407\text{ mol C}$$

$$54.51\text{ g O}\cdot\frac{1\text{ mol}}{15.9994\text{ g}}=3.408\text{ mol O}$$

Next, to determine the ratios of elements in the substance, divide each of these mole amounts by the smallest of them.

$$\frac{4.54\text{ mol}}{3.407\text{ mol}}=1.33$$

$$\frac{3.407\text{ mol}}{3.407\text{ mol}}=1.00$$

$$\frac{3.408\text{ mol}}{3.407\text{ mol}}=1.00$$

These values tell us that the ratio of hydrogen to carbon to oxygen in ascorbic acid is 1.33 : 1.00 : 1.00. Now, we need the smallest whole numbers that preserve this same ratio. Noting that the value 1.33 is very close to 4/3, we multiply all the values by 3 to get whole number ratios of 4 : 3 : 3 for hydrogen : carbon : oxygen. Finally, we use these ratios to write the empirical formula. In formulas containing these three elements it is traditional to write the elements in the formula in the order C—H—O. Doing so gives us

$C_3H_4O_3$.

1.5.8 Determining a Molecular Formula from an Empirical Formula

The empirical formula determined in the previous example relates to the molecular formula by some simple multiple. Recall that the subscripts in the molecular formula of hydrogen peroxide, H_2O_2, are simply double the subscripts in the empirical formula, HO. We can determine the molecular formula for a compound from the empirical formula if we have access to the molecular mass of the compound. We do this by computing the formula mass for the empirical formula and comparing this to the molecular mass to see what the multiple is between the empirical formula mass and the molecular mass. Then we can multiply the subscripts in the empirical formula by the same multiple to get the molecular formula. In other words,

$$\text{whole number multiple} = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

This calculation is illustrated in the following example. Note that although this example uses atomic masses and molecular mass in u, the same computation can be performed using molar masses in g/mol.

▼ Example 1.11

The experimentally determined molecular mass for ascorbic acid is 176.1 u. Use this value and the empirical formula from Example 1.9 to determine the molecular formula for ascorbic acid.

We begin by determining the formula mass for the empirical formula, $C_3H_4O_3$.

C: 12.011 u
H: 1.0079 u
O: 15.9994 u

$$(3\times12.011\text{ u})+(4\times1.0079\text{ u})+(3\times15.9994\text{ u})=88.063\text{ u}$$

Next we calculate the whole number ratio by dividing the molecular mass by the empirical formula mass:

$$\text{whole number multiple} = \frac{176.1\text{ u}}{88.063\text{ u}} = 2.000$$

Finally, we multiply all the subscripts in the empirical formula by this multiple to obtain the molecular formula:

$C_6H_8O_6$.

▲

1.5.9 Significant Digit Rules for Addition

As noted just before Example 1.1, I have been assuming in this chapter that students using this text are already familiar with the use of significant digits in scientific measurements and computations. If you are not, then now is the time to study the tutorial on the subject in Appendix A.

If you have used the significant digits rules prior to this course, your experience with the use of significant digits may be limited to computations involving multiplication and division. The rule for these kinds of computations is based on the number of significant digits in the values used in the computation: the result must have the same number of significant digits as the least precise value in the computation. With this rule, the limitation on the result is the *number of significant digits* in the least precise value used in the computation.

For addition, a completely different rule applies. If you pay attention to the significant digits in Example 1.3, you notice that our result contains six significant digits, even though one of the values used in the computation has only five significant digits. This is a result of the addition rule.

When performing addition, it is not the number of significant digits that governs the precision of the result. Instead, it is the *place value of the last digit that is farthest to the left in the numbers being added* that governs the precision of the result. To illustrate, consider the following addition example:

$$\begin{array}{r} 13.65 \\ 1.9017 \\ \underline{+\ 1{,}387.069} \\ 1{,}402.62 \end{array}$$

Of the three values being added, 13.65 has digits out to the hundredths place, the second number goes out to the ten thousandths place, and the last number goes out to the thousandths place. Looking at the final digits of these three, you can see that the final digit farthest to the left is the 5 in 13.65, which is in the hundredths place. This is the digit that governs the final digit of the result. There can be no digits to the right of the hundredths place in the result. The justification for this rule is that one of our measurements is precise only to the nearest hundredth, even though the other two are precise to the nearest thousandth or ten thousandth. Since one of our values is precise only to the nearest hundredth, it makes no sense to have a result that is precise to a place more precise than that, so hundredths are the limit.

Correctly performing addition problems in science (where nearly everything is a measurement) requires that you determine the place value governing the precision of your result, perform the addition, then round the result. In the above example, the sum is 1,4602.6207. Rounding this value to the hundredths place gives 1,4602.62.

Going back to Example 1.3, performing the multiplications gives the following addition problem:

$$\begin{array}{r} 2.0158 \\ \underline{+\ 15.9994} \\ 18.0152 \end{array}$$

Both values are precise to the nearest ten thousandth, and so is the result. In this case, we gain precision because now we have a value with six significant digits. The same thing occurs in the illustration above. One of the values in the addition has only four significant digits, but the result has six.

Chapter 1 Exercises

SECTION 1.1

1. Determine the energy in a photon of light from a green laser with a wavelength of 543 nm.
2. An atom absorbs a photon, causing one of its electrons to move to an orbital associated with 2.2718×10^{-19} J higher energy. Determine the wavelength of the absorbed photon and state what region of the electromagnetic spectrum it is in.
3. For a single photon to ionize a ground-state hydrogen atom, its energy has to raise the energy of the atom's electron to 0 J. What wavelength of light does this and what part of the electromagnetic spectrum is it in?
4. Calculate the energies for the four lines in the visible spectrum of the hydrogen atom.

SECTION 1.2

5. What are two of the limitations of the Bohr model of the atom?
6. In the Bohr model, how many electrons would you expect the 5th energy level to be able to hold? Explain your response.

SECTION 1.3

7. A certain atom is in the ground state. The 3*p* subshell of this atom is 2/3 full.
   a. Identify the element this atom represents.
   b. How many unpaired electrons are there in the atom? (A paired electron is one in an orbital with another one possessing opposite spin.)
8. In a certain ground-state atom, the 4*d* subshell has two electrons in it.
   a. Identify the element this atom represents.
   b. How many unpaired electrons are there in the atom?
9. How do the values of the azimuthal quantum number and magnetic quantum number relate to the principle quantum number?
10. Demonstrate mathematically that the 4*f* subshell can accommodate 14 electrons.
11. Generally speaking, what is the explanation for an atom's electron configuration not following the sequence described by the Madelung rule?

SECTION 1.4

12. For each of the following elements, draw the orbital diagram and write the full-length electron configuration.

    a. chlorine
    b. oxygen
    c. ruthenium
    d. potassium
    e. vanadium
    f. bromine

13. For each of the following elements, write the condensed electron configuration.

    a. chlorine
    b. nitrogen
    c. aluminum
    d. yttrium
    e. strontium
    f. tungsten
    g. cesium
    h. iodine
    i. neodymium

14. Compare the electron configurations for beryllium, magnesium, and calcium. Formulate a general rule for the condensed electron configuration of a Group 2 element.
15. For which group of elements does the electron configuration always end with np^2? Explain how you know.
16. Write the condensed electron configurations for ytterbium, einsteinium, and nobelium.

SECTION 1.5

17. Which two nuclides in Table 1.5 have 20 neutrons?
18. In Table 1.5, how many neutrons are there in the heaviest nuclide listed? How many neutrons are there in the lightest nuclide listed?
19. Determine the number of atoms in each of the following.

    a. 73.2 g Cu
    b. 1.35 mol Na
    c. 1.5000 kg W

20. Determine the mass in grams for each of the following.

    a. 6.022×10^{23} atoms K
    b. 100 atoms Au
    c. 0.00100 mol Xe
    d. 2.0 mol Li
    e. 4.2120 mol Br
    f. 7.422×10^{22} atoms Pt

21. Determine the number of moles present in each of the following.

a. 25 g $Ca(OH)_2$
b. 286.25 g $Al_2(CrO_4)_3$
c. 2.111 kg KCl
d. 47.50 g $LiClO_3$
e. 10.0 g O_2
f. 1.00 mg $C_{14}H_{18}N_2O_5$

22. As mentioned in the text, the sum of the masses of the particles in an atom does not equal the mass of the atom. Some of the mass of the individual particles is converted to energy, and the atom weighs less than the sum of the weights of its parts. How much mass is converted into energy when the individual protons, neutrons, and electrons are assembled to form an atom of uranium-238?

23. Referring to Table 1.5, calculate the atomic mass for silicon, calcium, iron, and uranium. Compare your results to the values shown in the periodic table.

24. Calculate the molar mass for each of the following compounds or molecules.

a. ammonia, NH_3
b. carbon dioxide, CO_2
c. chlorine gas, Cl_2
d. copper(II) sulfate, $CuSO_4$
e. calcium nitrite, $Ca(NO_2)_2$
f. sucrose, $C_{12}H_{22}O_{11}$
g. ethanol, C_2H_5OH
h. propane, C_3H_8
i. glass, SiO_2

25. Determine the formula masses for these compounds:

a. $MgCl_2$
b. $Ca(NO_3)_2$
c. $(SO_4)^{2-}$ (The 2– indicates this is an ion with an electrical charge of –2. The charge does not affect your calculation.)
d. $CuSO_4$
e. BF_3
f. CCl_4

26. Determine the mass in grams of 2.25 mol silver nitrate, $AgNO_3$.

27. Given 2.25 kg CCl_4, answer these questions:

   a. How many moles CCl_4 are present?
   b. How many carbon atoms are present?
   c. Approximately how many carbon-13 atoms are present?

28. Given 1.00 gal H_2O at 4°C, answer the questions below. (Hint: You must use the appropriate volume conversion and the density of water to determine the mass of 1.00 gal H_2O. See the information in Tables B.3 and B.5 in Appendix B.)

   a. How many moles H_2O are present?
   b. How many hydrogen atoms are present?
   c. Approximately how many deuterium (hydrogen-2) atoms are present?

29. Automobile antifreeze is composed of ethylene glycol. This green liquid is 38.7% C, 9.7% H, and 51.6% O by mass. The molecular mass is 62.1 u. Determine the empirical formula and the molecular formula for ethylene glycol.

30. A scientist isolates 47.593 g of a new, unidentified substance. The scientist also determines the following masses for the elements in the substance: carbon: 43.910 g; hydrogen: 3.683 g. Finally, the scientist is also able to determine the molecular mass of the substance to be 78.11 u. From these data, determine:

   a. the percent composition
   b. the empirical formula
   c. the molecular formula

31. Hydrogen chlorate, $HClO_3$, is a molecular substance that becomes chloric acid when dissolved in water. Determine the number molecules present in 125.0 g $HClO_3$.

32. Determine the percentage composition of these compounds:
    a. sodium bicarbonate, $NaHCO_3$
    b. sodium oxide, Na_2O
    c. iron(III) oxide, Fe_2O_3
    d. silver nitrate, $AgNO_3$
    e. calcium acetate, $Ca(CH_3COO)_2$
    f. aspirin, $C_9H_8O_4$

33. A *hydrate* is a compound with water molecules trapped in the crystal lattice. Determine the mass percentage of water in zinc sulfate septahydrate, $ZnSO_4{\cdot}7H_2O$. (The coefficient on the H_2O indicates the number of water molecules present for each unit of $ZnSO_4$.)

34. The results of quantitative analysis show that a compound contains 22.65% sulfur, 32.38% sodium, and 44.99% oxygen. Determine the empirical formula for this compound.

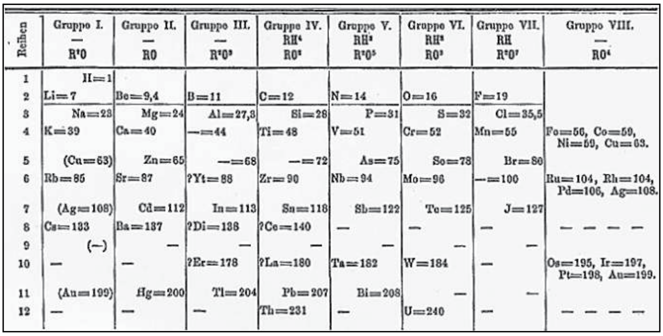
35. A compound has an empirical formula of CH_2O and a molar mass of 120.12 g/mol. Determine the molecular formula for this compound.

36. Determine the empirical and molecular formulas for each of the following:
    a. caffeine, which contains 49.5% C, 5.15% H, 28.9% N, and 16.5% O by mass, and has a molecular mass of 195 u.
    b. ibuprofen, which contains 75.69% C, 8.80% H, and 15.51% O by mass, and has a molar mass of 206 g/mol.
    c. propane, which contains 81.71% C and 18.29% H by mass, and has a molar mass of 44.096 g/mol.
    d. aspartame, a sugar-free sweetener, which contains 57.14% C, 6.16% H, 9.52% N, and 27.18% O, and has a molecular mass of 294.302 u.
    e. acetylene, a gas used in cutting torches, which contains 92.26% C and 7.74% H, and has a molar mass of 26.038 g/mol.

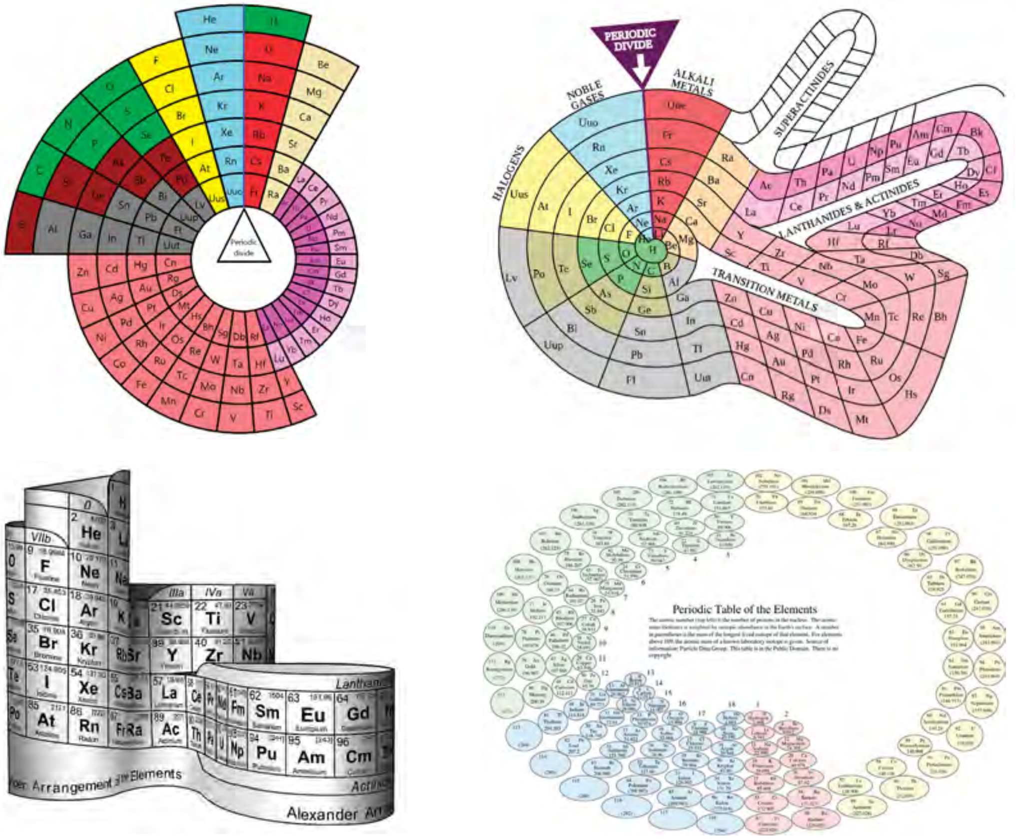
37. Toluene is a solvent commonly found in chemistry labs. An analysis of a 10.5-g sample shows that the sample contains 9.581 g carbon and 0.919 g hydrogen. If the molar mass of toluene is 92.140 g/mol, determine the percent composition, empirical formula, and molecular formula.

Chapter 2

The Periodic Law



Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —



The patterns among the elements have tempted many scientists to try their hands at developing different forms of the Periodic Table of the Elements. At the top is the original periodic table, published by Russian scientist Dmitri Mendeleev in 1869.

Objectives for Chapter 2

After studying this chapter and completing the exercises, you should be able to do each of the following tasks, using supporting terms and principles as necessary.

SECTION 2.1

1. Describe the general structure and arrangement of the Periodic Table of the Elements.

SECTION 2.2

2. Identify the names and locations of the major regions in the periodic table.
3. Identify the names and locations of the elements in Groups 1, 2, 3–12, 16, 17, and 18. Also identify the groups known as the rare-earth elements and the names of the two rows of these elements.
4. State the two collective names for Groups 1–2 and 13–18.
5. State the chief chemical property that distinguishes the metals from the nonmetals.

SECTION 2.3

6. Define the length unit known as the *angstrom* (Å).
7. Use diatomic bond length and atomic radius data to estimate bond lengths in molecules.
8. Describe the trends in atomic radii in the periodic table across periods and down groups.
9. Explain three factors influencing the trends in atomic radii in the periodic table.
10. Compare ionic radii to atomic radii for metals and nonmetals.
11. Use your knowledge of atomic and ionic size trends in the periodic table to arrange lists of elements and ions in order by size.

SECTION 2.4

12. Distinguish between core electrons and valence electrons.
13. Estimate effective nuclear charge, Z_{eff}.
14. Define *ionization energy*, describe the trends for ionization energy across periods and down groups in the periodic table, and use Z_{eff} and other factors to account for these trends.
15. Write regular and condensed electron configurations for an ion in a given oxidation state.
16. Use Z_{eff} to explain the large difference in ionization energy between an atom's core electrons and its valence electrons.
17. Predict oxidation states for metals in Groups 1–4 and nonmetals in Groups 15–17.
18. Define *electron affinity*, use Z_{eff} to account for the high electron affinity of elements in Groups 16 and 17, and explain why electron affinity values are not available for the noble gases.
19. Define *electronegativity*.
20. Describe the trends for electronegativity across periods and down groups in the periodic table. Name the elements with the lowest and highest electronegativity values.
21. Use Z_{eff} to account for the trend in electronegativity across periods.

SECTION 2.5

22. Explain why hydrogen is located in Group 1 and why it acts like the Group 17 elements.

2.1 The Periodic Table of the Elements

The contemporary Periodic Table of the Elements is shown again in Figure 2.1 and in the inside the rear cover of the text. Discovering new elements and figuring how they relate to one another was one of the hottest issues in science in the 19th century. By the 1860s, several scientists had noticed *periodicities* in the properties of the known elements. A periodicity is a regular, cyclic variation of some kind. These scientists noticed, for example, that when elements were listed in order according to atomic weight, the physical property of density increased and decreased in a cyclic fashion. In 1864, German chemist Lothar Meyer published a paper describing cyclic variation in the chemical property known as *valence*, an important property related to the number of bonds an atom makes with other atoms to form compounds.

Credit for the discovery of the *periodic law* and the development of the first Periodic Table of the Elements is generally given to Russian scientist Dmitri Mendeleev, who published his table of the elements in 1869. Mendeleev (Figure 2.2) had not only noticed the periodicities, but he also arranged some 67 elements into a table and predicted the existence of several unknown elements based on gaps in the table as he had organized it. The elements Mendeleev predicted included those now known as gallium, germanium, technetium, and others. The properties Mendeleev predicted for these elements included valence, density, atomic weight, and color. His predictions of not only the existence of these elements but also their properties is the reason for the general credit Mendeleev gets for discovering the periodic law.

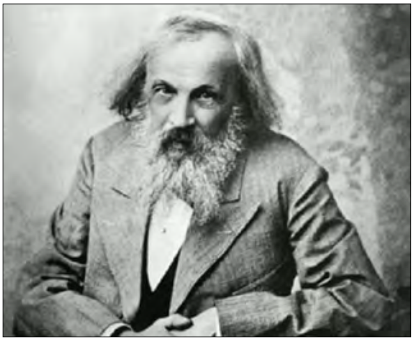


Figure 2.2. Russian scientist Dmitri Mendeleev (1834–1907).

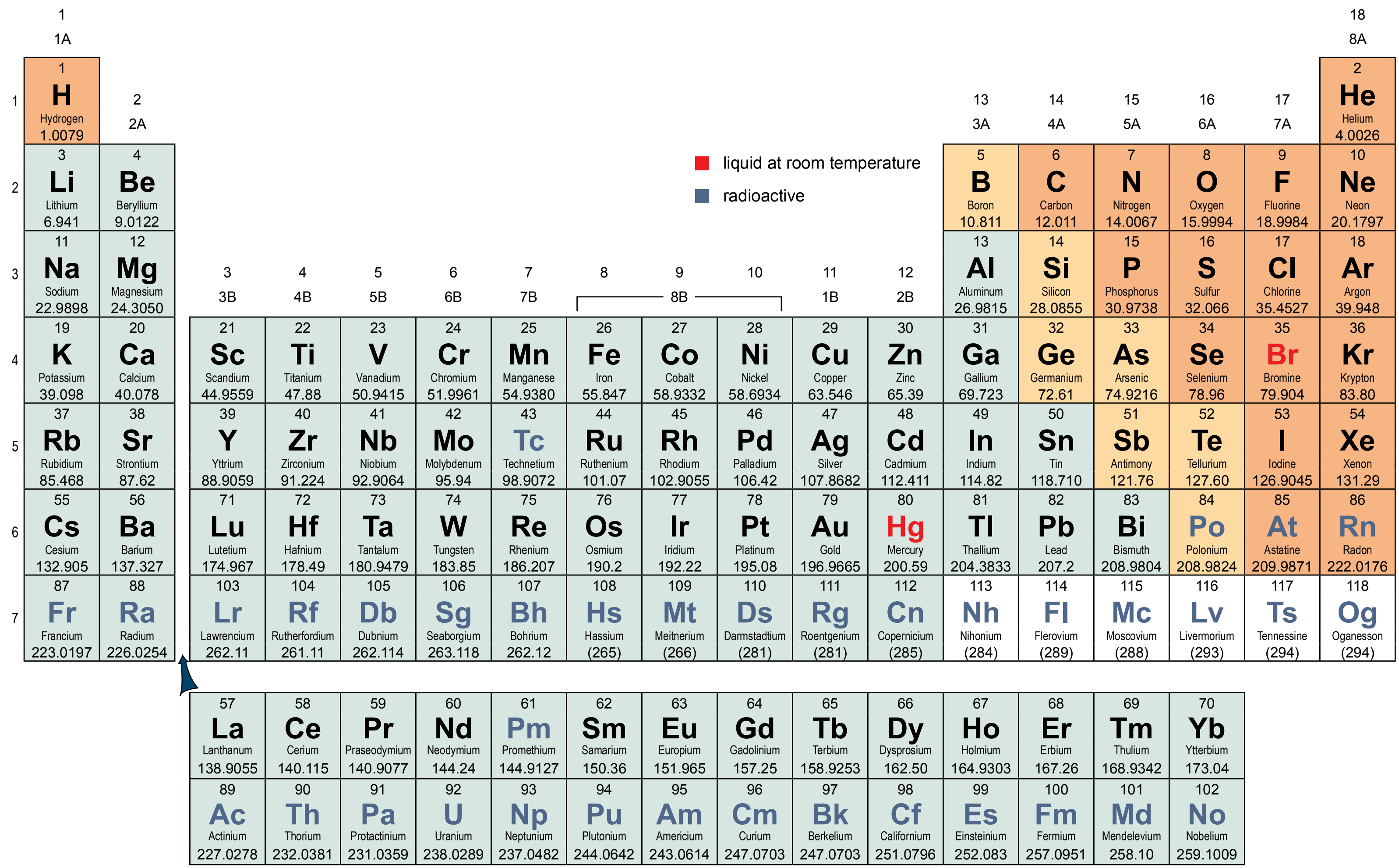
As Mendeleev organized the elements, he ordered them by atomic weight and aligned them into rows and columns based on their chemical and physical properties. Today, just as back then, one of the most important things to know about the periodic table is that *elements in the same group (column) exhibit very similar chemical properties.*

Mendeleev's original table is shown on the opening page of this chapter. In that image, just above the center and a bit to the left you can see gaps at the atomic mass values 68 and 72. These are the positions now occupied by gallium and germanium, discovered in 1875 and 1886, respectively. Mendeleev was a brilliant scientist. His fields of expertise included physics, chemistry, and a host of areas of technology. Mendeleev taught in St. Petersburg at several different institutions, and because of his work there St. Petersburg became internationally known for prominence in chemical research.

There were some debates in the 19th century regarding proper placement for four of the elements. If you look at tellurium ($Z = 52$) and iodine ($Z = 53$) in the periodic table to the right, you see that the atomic mass of tellurium is the larger of the two. Because of this, many scientists felt that iodine should come before tellurium in the table. But iodine exhibits all the properties of the Group 17 elements and Mendeleev argued that it should come after tellurium. This problem was resolved when scientists realized that the atomic number was the correct parameter to use for ordering the elements in the table. Mendeleev had ordered them by atomic mass (known then as atomic weight); today the atomic number governs the order. A similar debate over placement surrounded the elements cobalt ($Z = 27$) and nickel ($Z = 28$).

The noble gases were not known in Mendeleev's time and he provided no place for them in his table. Interestingly, when they were eventually discovered Mendeleev was resistant to accept the discovery because the new elements didn't fit into his table. The solution to this little problem was simply to add another column for them, now known as Group 18.

Figure 2.1. The Periodic Table of the Elements.



🟥 liquid at room temperature

🟦 radioactive

	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.0079																	2 **He** Helium 4.0026
2	3 **Li** Lithium 6.941	4 **Be** Beryllium 9.0122											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.0067	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984	10 **Ne** Neon 20.1797
3	11 **Na** Sodium 22.9898	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.9815	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.9738	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
4	19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.9559	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.9380	26 **Fe** Iron 55.847	27 **Co** Cobalt 58.9332	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.9216	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.9059	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.9064	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium 98.9072	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.9055	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.82	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.76	52 **Te** Tellurium 127.60	53 **I** Iodine 126.9045	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.905	56 **Ba** Barium 137.327	71 **Lu** Lutetium 174.967	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.85	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.2	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.9665	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.9804	84 **Po** Polonium 208.9824	85 **At** Astatine 209.9871	86 **Rn** Radon 222.0176
7	87 **Fr** Francium 223.0197	88 **Ra** Radium 226.0254	103 **Lr** Lawrencium 262.11	104 **Rf** Rutherfordium 261.11	105 **Db** Dubnium 262.114	106 **Sg** Seaborgium 263.118	107 **Bh** Bohrium 262.12	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 **Ds** Darmstadtium (281)	111 **Rg** Roentgenium (281)	112 **Cn** Copernicium (285)	113 **Nh** Nihonium (284)	114 **Fl** Flerovium (289)	115 **Mc** Moscovium (288)	116 **Lv** Livermorium (293)	117 **Ts** Tennessine (294)	118 **Og** Oganesson (294)

57 **La** Lanthanum 138.9055	58 **Ce** Cerium 140.115	59 **Pr** Praseodymium 140.9077	60 **Nd** Neodymium 144.24	61 **Pm** Promethium 144.9127	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.965	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.9253	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.9303	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.9342	70 **Yb** Ytterbium 173.04
89 **Ac** Actinium 227.0278	90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.0359	92 **U** Uranium 238.0289	93 **Np** Neptunium 237.0482	94 **Pu** Plutonium 244.0642	95 **Am** Americium 243.0614	96 **Cm** Curium 247.0703	97 **Bk** Berkelium 247.0703	98 **Cf** Californium 251.0796	99 **Es** Einsteinium 252.083	100 **Fm** Fermium 257.0951	101 **Md** Mendelevium 258.10	102 **No** Nobelium 259.1009

Note: The upper set of group numbers has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) and is now in wide use. The lower set of numbers is still in common use in America.

The first 92 elements in the periodic table are found in nature; elements 93–118 have been synthesized in laboratories. The "discovery" (by synthesis) of elements 114 and 116 was confirmed in 2011, and in January 2016 official confirmation of elements 113, 115, 117, and 118 was announced. The reason confirmations for the last few elements took so long is that once the nucleus of one of these heavy elements is assembled it doesn't stay around very long—far less than one second.

2.2 Periodic Table Nomenclature

The columns in the periodic table are called *groups* and the rows are called *periods*. The images in Figures 2.3 and 2.4 identify several different specific regions of elements in the periodic table. In the long form of the table shown in Figure 2.3, the elements are classified as *metals*, *nonmetals*, and *metalloids*. Note that hydrogen (H) is classified as a nonmetal, even though it is positioned with the metals in Group 1. Hydrogen's location in Group 1 is due to the fact that hydrogen has one valence electron, which I address in more detail later in the chapter.

As you probably know, metals possess a number of properties in common. Common physical properties include high electrical and thermal conductivity, malleability, ductility, and shininess or *luster*. Chemically, the metals are known for ionizing by losing electrons to form positive ions, known as *cations* (pronounced cat-ion). As positive ions, they bond with negative ions to form ionic compounds. (Again, we address compounds in detail later.) People commonly think of metals as shiny conductors of electricity. Chemists think of them as elements that form positive ions.

The metalloids possess properties that are neither clearly metallic nor clearly nonmetallic. For example, under some conditions they conduct electricity and under other conditions they don't. This property is the reason why some of the metalloids are the elements used to manufacture computer "semiconductors."

The nonmetals have their own distinguishing properties, such as ionization by gaining electrons to form negative ions, called *anions*. They also bond with each other—something metals almost never do.

In the standard form periodic table of Figure 2.4 are shown the common names for several specific groups (columns) of elements. All these names are used frequently in scientific discourse and you need to commit them to memory. Groups 1–2 and 13–18 are also collectively referred to as the *main group elements* or *representative elements*.

You probably noticed that in both the figures elements 113–118 are not included with the rest of the elements in the different classes or groups. This is due to the fact that they have only existed for extremely short periods of time in laboratories and little is known about their properties. By the way, you don't need to feel sorry for Groups 13–15 not having nicknames. They do,

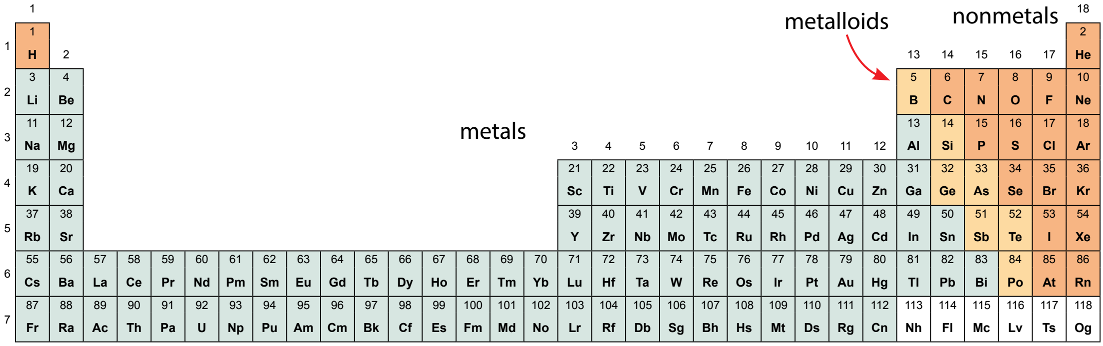
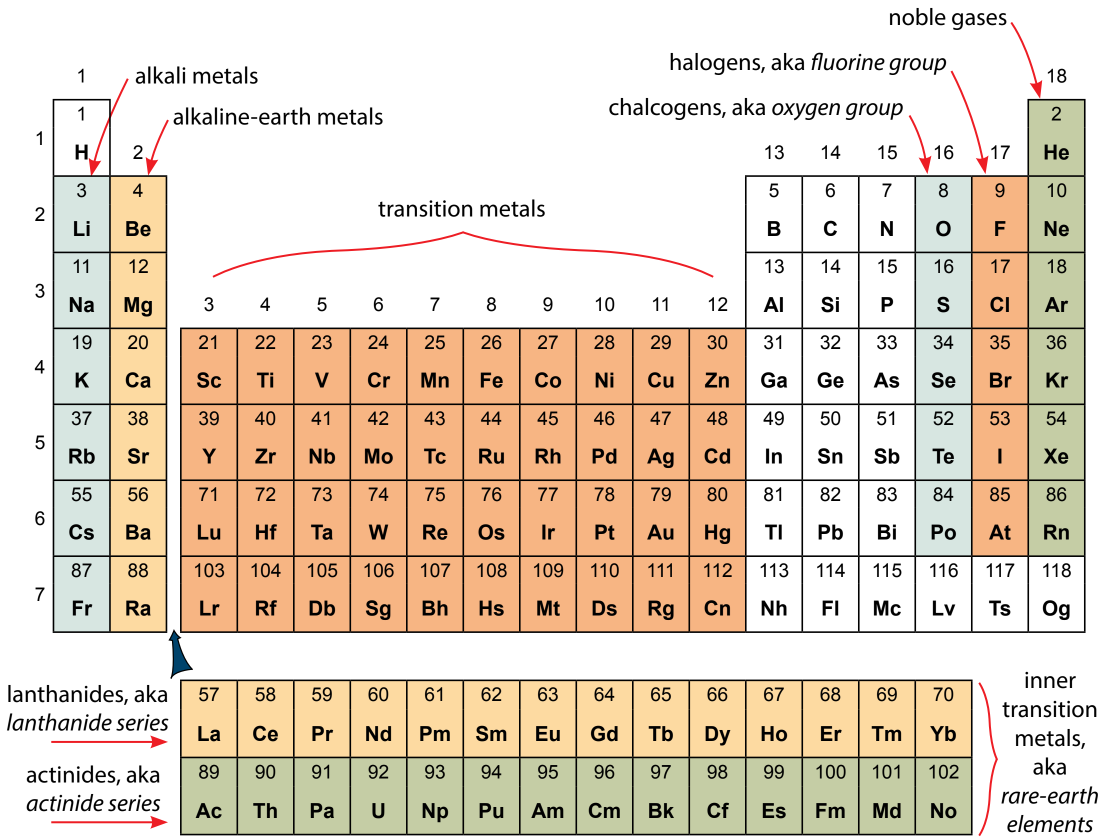


Figure 2.3. The long form of the periodic table indicating the three major classes of elements.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H**																	2 **He**
2	3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
3	11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
4	19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
5	37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
6	55 **Cs**	56 **Ba**	71 **Lu**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
7	87 **Fr**	88 **Ra**	103 **Lr**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112 **Cn**	113 **Nh**	114 **Fl**	115 **Mc**	116 **Lv**	117 **Ts**	118 **Og**

57 **La**	58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**
89 **Ac**	90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**

Figure 2.4. The standard form table indicating many of the common names for particular groups of elements.

but the names are seldom used. (Okay, Group 13 is called the *icosagens*, Group 14 the *crystallogens*, and Group 15 the *pnictogens*. See? Well, now you know.)

2.3 Periodic Physical Properties

Physical properties of substances are properties such as color, density, boiling point, electrical conductivity, malleability, and many others. Many of these properties exhibit strong periodicity—cyclic rises and falls with cycles that correspond to the periods in the periodic table. In this section, we look at one of the most important of these—atomic size. As we look at periodic trends in this section and the next, you should closely compare the charts presented with the periodic table in Figure 2.1.

2.3.1 Atomic Radius and Bonding Atomic Radius

Defining the size of atoms is a bit tricky. The nucleus of the atom is extremely small, and virtually all the space an atom takes up is defined by the electrons in their orbitals surrounding the nucleus. The size of the orbitals themselves is defined by the probability distribution of where electrons may be found, and this probability does not drop cleanly to zero at the edge of the orbital. Instead, it fades toward zero, making the atomic radius fuzzy. Still, the electrons in the orbitals create a negatively charged shell around the atom that strongly resists penetration by the shells around other atoms. Thus scientists can measure atomic radius by firing two atoms at one another and examining how closely the two atoms come together before bouncing apart.

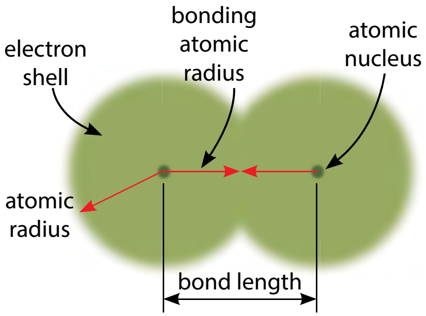


Figure 2.5. Comparison of atomic radius and bonding atomic radius.

The electron clouds repel each other so stiffly that atoms bounce apart as if they were steel spheres.

Figure 2.5 shows two atoms bonded together in a molecule, such as the diatomic oxygen molecule, O_2. As you see, when atoms are bonded together this way the electron shells do interpenetrate one another. The *bond length*, defined as the distance between nuclei, is less than twice the atomic radius. Accordingly, we define the *bonding atomic radius* as half the bond length and use this value to estimate the bond length in various molecules.

When discussing atomic size, a convenient length unit is the *angstrom* (Å), which is equal to 10^{-10} m, a tenth of a nanometer (0.1 nm or 100 pm). The following example illustrates the approximation of bond length in a molecule.

▼ Example 2.1

Figure 2.6 depicts a molecule of sulfur dioxide, SO_2, one of the compounds emitted into the atmosphere by burning fossil fuels. The atomic radii of oxygen and sulfur atoms are 0.64 Å and 1.04 Å, respectively. The bond lengths in O_2 and S_2 molecules are 1.21 Å and 1.89 Å, respectively. Estimate the S—O bond length in the SO_2 molecule.

We expect the bonding atomic radius of oxygen to be half the O_2 bond length, or about 0.61 Å. Similarly, we expect the bonding atomic radius of sulfur to be half the S_2 bond length, or about 0.95 Å. Adding these two bonding atomic radii gives 1.56 Å. This figure compares pretty well with the actual bond length in the SO_2 molecule of 1.43 Å (about 9% difference).

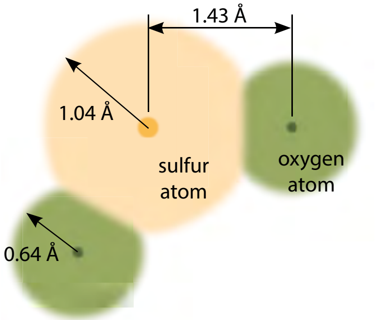


Figure 2.6. Comparison of atomic radius and bonding atomic radius in an SO_2 molecule.

▲

Figure 2.7 shows the presently accepted values for the atomic radii of the first 100 elements. As you see, typical radii are in the range of 1–2 Å, or 0.1–0.2 nm. This means that typical atomic diameters are in the range of 0.2–0.4 nm.

The most striking things about the graph are the strong peak that occurs at the beginning of each new period and the gradual decrease in atomic size from one element to the next within the period. There are at least three different effects present governing the size of atoms and leading to these patterns.

The first is the number of subshells in use holding the atoms' electrons. At the beginning of each period, an electron appears with a new, higher principle quantum number, *n*, and a new *s* subshell associated with that principle quantum number. This new shell allows for electrons to be much farther from the nucleus and is the major cause of the peak in atomic radius at the beginning of each period, as well as the overall upward trend in atomic size.

The second effect is the increasing attraction between the nucleus and the electrons as we move from left to right across the periodic table in any given period, or from top to bottom in a given group. Moving left to right across the periodic table, with each new element comes a new proton in the nucleus. The increasing positive electrical charge at the center of the atom tends to pull the atom's electrons in tighter and tighter. Thus, with a few exceptions, atomic size decreases

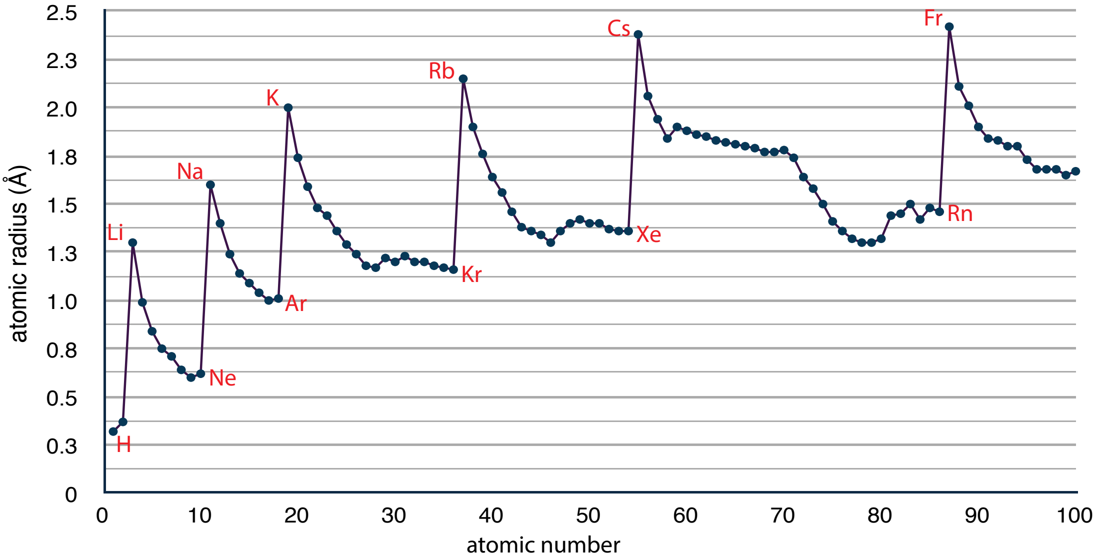


Figure 2.7. Atomic radius values. The six peaks are the alkali metals in Periods 2–7.

from left to right in a period. In the chart of Figure 2.7, this decrease in size after the start of a new period is quite pronounced.

The third effect is called the *shield effect* or *atomic shielding*. The electrons in shells with lower values of *n* effectively form an electrical screen around the nucleus and to some extent shield off the attraction of the positive nucleus for electrons in higher shells. To quantify this screening effect, chemists use a parameter called the *effective nuclear charge* (Z_{eff}). The details of the effective nuclear charge are easier to explain a bit later, so we return to it in Section 2.4.2.

A second feature to note from Figure 2.7 is that the radius of each of the alkali metals is larger than the one just above it in the periodic table. The same holds for each of the noble gases. In fact, this same trend is present in every group in the table. Down every group, the atomic radius of each element is greater than that of the element above it, and this results in the overall upward trend in atomic size shown in the chart. In summary, atomic size generally decreases from left to right in a period and always increases from top to bottom in a group.

2.3.2 Ionic Radius

Figure 2.8 depicts the sizes of atoms and their ions in four of the groups of the representative elements. The blue disks are the atomic sizes and the yellow disks are the ionic sizes, both in angstroms.

Metals ionize by losing electrons to form cations (positive ions). The loss of an electron leaves an atom with more protons than electrons, and thus the atom possesses a net positive charge. As we will discuss more in Section 2.4, Group 1 metals always ionize by losing one electron to become ions with a charge of +1. With sodium, for example, we write this ion as Na^+. Group 2 metals always ionize by losing two electrons to become ions with a charge of +2. Thus, for the calcium ion we write Ca^{2+}.[1] Nonmetals ionize by gaining electrons to become anions (negative ions). Group 17 elements ionize by gaining one electron to become ions with a net charge of −1. Group 16 elements ionize by gaining two electrons to become ions with a net charge of −2.

The blue circles in Figure 2.8 represent the atomic sizes, and yellow circles represent ionic sizes. Since the metals always ionize by losing the electrons in their highest *s* orbital, their di-

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[1] The most common convention is to write the sign of the charge after the value of the charge on the chemical symbol for an ion.

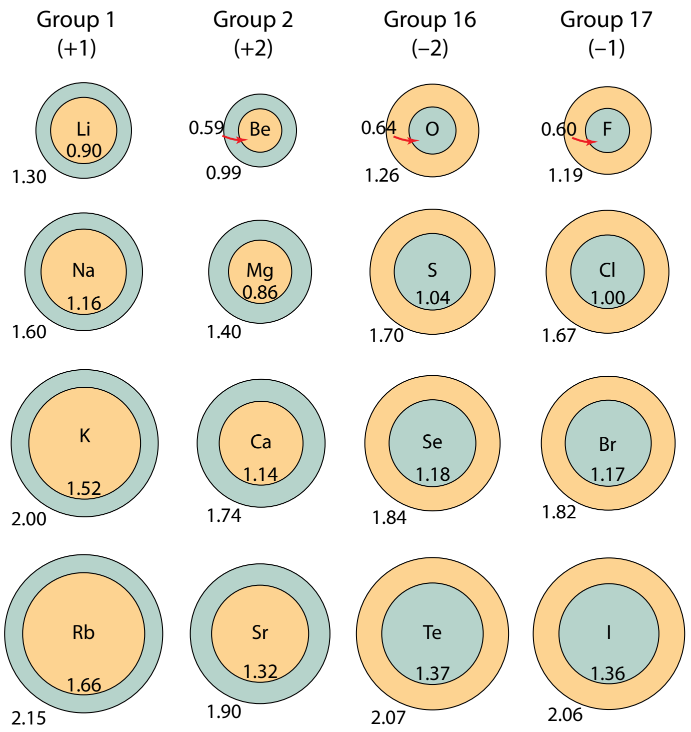


Figure 2.8. Atomic radii (blue) and ionic radii (yellow) for the Group 1 and 2 positive ions and Group 16 and 17 negative ions. All values are in angstroms.

ameters decrease considerably when they ionize. The opposite happens to the nonmetals. Gaining electrons adds to the mutual electron repulsion in the highest-energy orbitals, increasing atomic size.

Just as with neutral atoms, ionic sizes decrease in a period from left to right in the periodic table and increase going down a group. Further, we can summarize the paragraphs above by saying that cations are smaller than their neutral atoms and anions are larger than their neutral atoms.

One final ionic trend needs to be mentioned: among neutral atoms or ions with the same number of electrons, atomic size always decreases as the number of protons increases. Based on what we have seen so far, this should make perfect sense. Among atoms with the same number of electrons—a so-called *isoelectronic series*—there are no new shells to consider and there are no variations in the amount of shielding produced by changing electron configurations. Thus, the only variation is in the positive charge in the nucleus, and as this goes up, the attraction of the nucleus for the electrons goes up, pulling the electrons in tighter and making the atom smaller.

▼ Example 2.2

Based on your knowledge of trends in the periodic table, place the following atoms and ions in order of decreasing size: S, Se^{2-}, O, and S^{2-}.

Anions are larger than their neutral atoms, so $S^{2-} > S$. Elements and ions farther down in a group are larger than those above, so S > O. Also, Se^{2-} is larger than S^{2-}, so

$Se^{2-} > S^{2-} > S > O$.

▲

▼ Example 2.3

Arrange the following ions in order of size from largest to smallest: O^{2-}, Na^{+}, F^{-}, and Mg^{2+}.

We can address this question without any published data on atomic size. Referring to the periodic table, you see that each of the ions listed has 10 electrons. For example, magnesium (Mg) is element 12 and has 12 electrons before ionizing. But the charge on the ion is +2, which means the magnesium atom has lost two electrons and now has 10. Therefore, the order from largest to smallest follows the atomic number order from smallest to greatest, giving the sequence O^{2-}, F^{-}, Na^{+}, Mg^{2+}.

▲

2.4 Periodic Chemical Properties

2.4.1 Core and Valence Electrons

Chemistry is all about electrons, and when it comes to the chemical bonding that occurs in chemical reactions, the *valence electrons* of the elements involved determine what kinds of compounds form. To illustrate, consider the elements sulfur ($Z = 16$) and cobalt ($Z = 27$) located in the partial periodic tables of Figure 2.9.

The electron configurations for these elements are as follows:

Z	Electron Configuration	Condensed Electron Configuration
16	S: $1s^2 2s^2 2p^6 3s^2 3p^4$	S: $[Ne]3s^2 3p^4$
27	Co: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	Co: $[Ar]4s^2 3d^7$

As we saw in the previous chapter, when moving from one element to the next in the periodic table, we add one electron and one proton for each new element. As we look at an element's position in the periodic table, we can think of each of the elements before it as representing the position of one of the element's electrons, arranged according to the Madelung rule and Hund's rule.

Now consider Figure 2.9 and the electron configuration for sulfur. The first 10 electrons in a sulfur atom go to completely filling the $n = 1$ and $n = 2$ shells. The next six electrons go into the

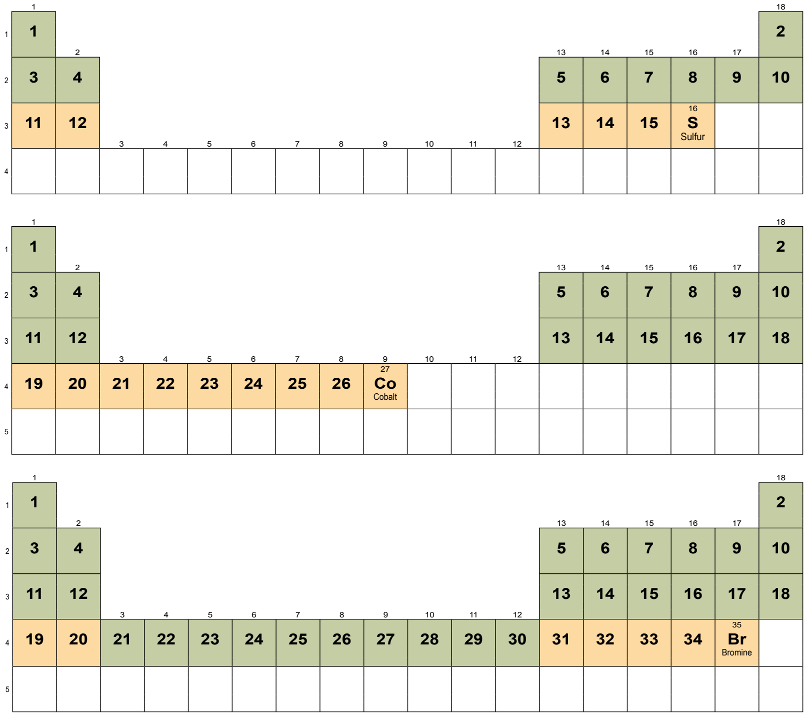


Figure 2.9. Core electrons (green) and valence electrons (yellow) for sulfur, cobalt, and bromine.

$n = 3$ shell. This shell can hold eight electrons, so it is only partially full. The electrons in the full shells are called *core electrons*. The electrons in the partially filled shell are called *valence electrons*, and the shell they are in is called the *valence shell*. The core electrons are the ones involved in screening the nucleus from the outer electrons in the valence shell. These core electrons have more negative energies than the valence electrons, which means they are more tightly bound to the nucleus. As a result, the core electrons are not involved in the electron swapping and sharing that takes place in chemical reactions. That involvement is limited to the valence electrons.

When you look at sulfur's position in the periodic table, just a quick glance indicates that sulfur has six valence electrons, all of them in the third shell, $n = 3$. It's as simple as observing that sulfur is in the third period and counting columns from the left over to where sulfur is. Notice that in the condensed electron configuration notation, all of sulfur's core electrons are represented by [Ne]. The valence electrons are still shown explicitly as $3s^2 3p^4$.

Looking now at cobalt, the element positions colored in green represent cobalt's core electrons. The first 18 electrons are the core electrons, represented by [Ar] in the condensed electron configuration. The next nine electrons are the valence electrons, easily seen from the fact that cobalt is in the fourth period and the ninth column from the left side of the periodic table.

Finally, note that for *p*-block elements in Periods 4–7, the electrons in filled, lower *d* subshells do not act as valence electrons. The only valence electrons in these atoms are those in the *s* and *p* subshells of the unfilled shell. This is illustrated by the diagram for bromine at the bottom of Figure 2.9.

2.4.2 Effective Nuclear Charge

Now we return to the idea of *effective nuclear charge*, Z_{eff}, mentioned a few pages back in Section 2.3.1. Effective nuclear charge is a useful concept when it comes to explaining some of the atomic size variations we see in the periodic table. Z_{eff} is calculated as

$$Z_{\text{eff}} = Z - S$$

where Z is the atomic number and S is a value called the *screening constant*. The idea here is that to a large extent the core electrons screen off the positive charge of the nucleus, reducing the actual electrical pull on the valence electrons. For a rough approximation of the effect of this screening, the screening constant can be taken to be the number of core electrons in the atom.

As examples, let's consider again sulfur and cobalt. For sulfur (Figure 2.10), $Z_{\text{eff}} = Z - S \approx 16 - 10 \approx +6$, and for Cobalt, $Z_{\text{eff}} = Z - S \approx 27 - 18 \approx +9$. Compare these two values to the values for the Group 1 metals in the same periods. For sodium, $Z_{\text{eff}} = Z - S \approx 11 - 10 \approx +1$ and for potassium, $Z_{\text{eff}} = Z - S \approx 19 - 18 \approx +1$. The alkali metals only have one valence electron, so Z_{eff} comes out to +1. Moving to the right across the period, additional protons are accrued in the nucleus but the number of core electrons remains the same as it is for the Group 1 metal at the beginning of the period. The increase in Z_{eff} from left to right in a period explains the fact that atomic radii decrease from left to right. The value of Z_{eff} can also be used to explain the trends in ionization energy we look at next.

A word of caution is in order here. The calculation outlined above for Z_{eff} is quite simplified, and the results it gives

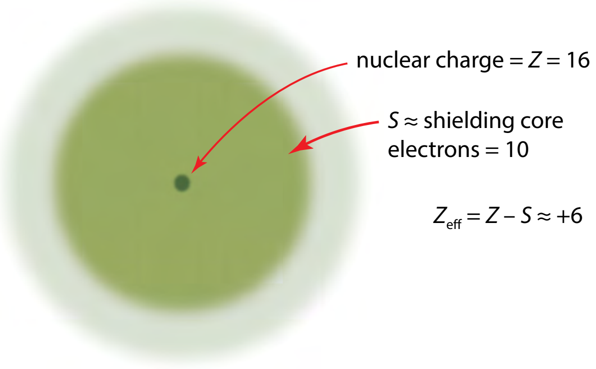


Figure 2.10. Effective nuclear charge for sulfur.

are only approximate. Simply using the number of core electrons for S gives $Z_{\text{eff}} = +1$ for each of the alkali metals. In fact, the values of Z_{eff} obtained from more sophisticated calculation methods for the first three alkali metals, lithium ($Z = 3$), sodium ($Z = 11$), and potassium ($Z = 19$), are +1.3, +2.5, and +3.5, respectively.

2.4.3 Ionization Energy

Ionization energy is defined as the amount of energy required to remove a ground-state electron from an isolated, gaseous atom. Recall from our discussion in the previous chapters that adding an electron to an atom releases energy because the electron is going into a lower energy state. Conversely, removing an electron from an atom requires an input of energy, which is the work required to pull the electron from its negative energy state up to zero energy, where it is free from the nuclear attraction of the atom.

Using hydrogen as an example, the removal of the electron from an atom of hydrogen is modeled by the following *ionization equation*:

$$\mathrm{H}(g) \rightarrow \mathrm{H}^+ + e^- \qquad \Delta E = 2.18\times 10^{-18}\ \mathrm{J} \tag{2.1}$$

This expression shows the neutral hydrogen atom on the left, with (g) indicating that the atom is in the gaseous state. On the right, H^+ indicates a hydrogen ion with a charge of +1, and e^- indicates a free electron. In an equation like this, it is customary to write the energy change (ΔE) that occurred in the atomic system (the atom and its electron) during the process. Notice that ΔE is positive, meaning that a certain amount of energy has to be added in order to accomplish the ionization. This amount of energy is the ionization energy.

Because the amounts of energy involved are so small, it is more convenient in discussions of this sort to use an energy unit called the *electron volt* (eV). The electron volt is defined as

$$1\ \mathrm{eV} = 1.60218 \times 10^{-19}\ \mathrm{J} \tag{2.2}$$

For the ionization of hydrogen, converting the energy above into eV gives

$$\Delta E = 2.18\times 10^{-18}\ \mathrm{J}\cdot\frac{1\ \mathrm{eV}}{1.602\times 10^{-19}\ \mathrm{J}} = 13.6\ \mathrm{eV}$$

The energy required to remove one electron from a neutral atom is called the *first ionization energy*. The additional energy required to remove a second electron is called the *second ionization energy*, and so on.

Figure 2.11 charts the first ionization energies of the elements. The strong upward trend in each period is easily accounted for by the increasing value of Z_{eff} moving from left to right in the period. The higher Z_{eff} is, the stronger the nucleus attracts the outermost electrons and the greater the energy required to remove one of them. Notice from the Group 1 and Group 18 elements labeled in the figure that the trend down a group is for the ionization energy to decrease, even though Z_{eff} actually increases down the group, as we saw previously. This is accounted for by the fact that the elements in each new period have their valence electrons in a shell with a higher principle quantum number. These electrons are thus farther from the nucleus, have a less negative energy, and are easier to remove.

Writing electron configurations for ions requires you to keep a somewhat surprising rule in mind: *the electrons an element loses during ionization come from the orbital with the highest principle quantum number, n*. Further, *among the orbitals associated with the highest principle quantum number, the electrons come from the orbitals with the highest value of the azimuthal quantum number, l*. This means, for example, that sodium ionizes (as we would expect) by losing

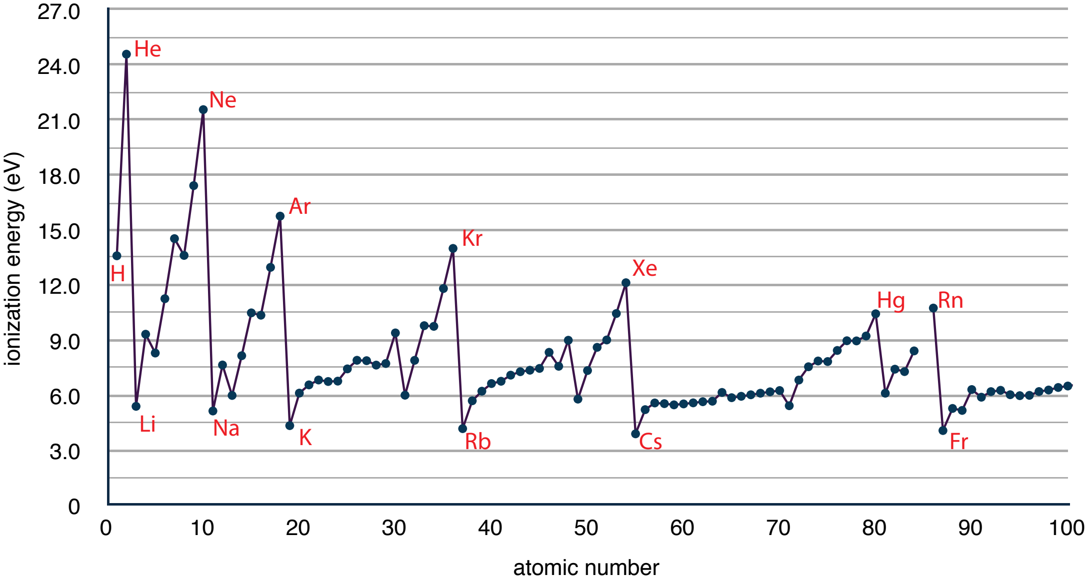


Figure 2.11. First ionization energies.

its $3s$ electron. However, scandium ionizes by losing a $4s$ electron, not a $3d$ electron. The following example illustrates further.

Example 2.4

Write the electron configurations for Sn^{4+} and Cr^{3+}.

Sn is a p-block metal in Period 5 and Group 14 with configuration

Sn: $[Kr]5s^2 4d^{10} 5p^2$

Its valence electrons are therefore in the $5s$ and $5p$ subshells. It first loses its two $5p$ electrons, because these have $n = 5$ and $l = 1$. The next two to go are the $5s$ electrons which have $n = 5$ and $l = 0$. The electron configuration of the ion is:

Sn^{4+}: $[Kr]4d^{10}$

Cr is a transition metal with the anomalous electron configuration:

Element	1st	2nd	3rd	4th	5th	6th	7th
Li	5.38	75.64	122.45				
Be	9.32	18.21	153.90	217.72			
B	8.30	25.15	37.93	259.38	340.23		
C	11.26	24.38	47.89	64.49	392.09	489.99	
N	14.53	29.60	47.45	77.47	97.89	552.07	667.05
O	13.62	35.12	54.94	77.41	113.90	138.12	739.29
F	17.42	34.97	62.71	87.14	114.24	157.17	185.19
Ne	21.56	40.96	63.45	97.12	126.21	157.93	207.28

Table 2.1. Ionization energies (eV) for Period 2 elements.

Cr: [Ar]$4s^1 3d^5$

To ionize to Cr^{3+}, the atom first loses the 4*s* electron, which has $n = 4$ and $l = 0$. Then it loses two of its 3*d* electrons, which have $n = 3$ and $l = 2$. Thus, the configuration of the ion is:

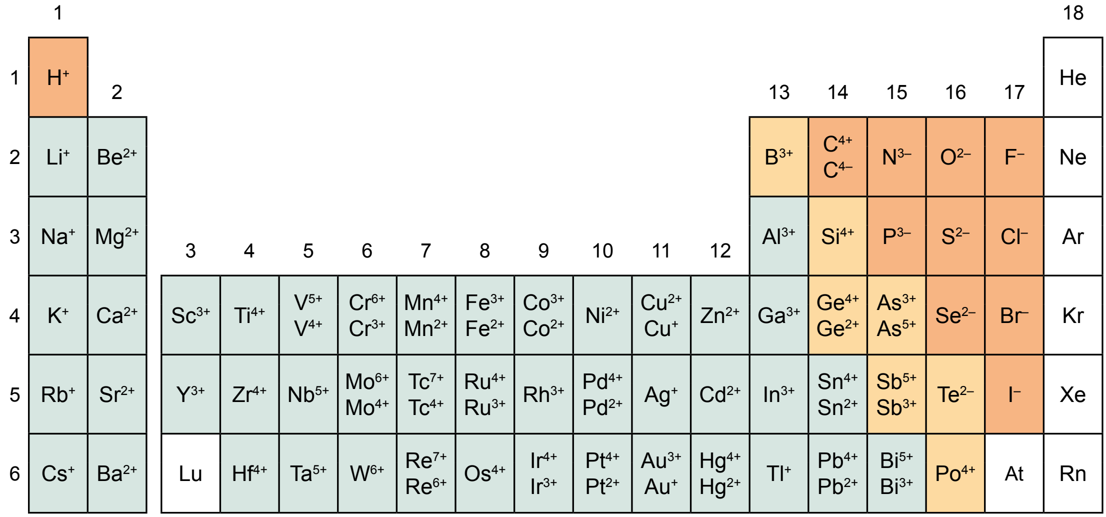
Cr^{3+}: [Ar]$3d^3$

▲

Table 2.1 lists the ionization energies up through the 7th ionization energy for the Period 2 elements. Values without shading represent the energies required to remove valence electrons. The yellow shading indicates where core electrons are being removed. Notice the whopping increase in the ionization energy once we start getting into an atom's core electrons. This is explained by the shield effect we discussed previously. Core electrons shield the nucleus from exerting its full attraction on the valence electrons, an effect quantified by the value of Z_{eff}. But inside the core, the full attraction of the nucleus is felt and the energy required to remove an electron is dramatically greater.

This discussion about ionization is an appropriate time to show representative values for ionizations exhibited by the main group elements and transition metals. These values, displayed in Figure 2.12, are called *oxidation states*. I address the origin and use of the term "oxidation" in a later chapter. In this context, it just means that when atoms of a given element ionize, these are the values of charge they typically acquire. The first and most important thing to notice is that on both ends of the periodic table, elements ionize so as to end up with either an empty valence shell or a full one, depending on whether the valence shell was closer to being full or empty to start with. All Group 1 metals and hydrogen ionize by losing their only valence electron and retaining their core electrons. After this ionization, the Group 1 metals are left with one more proton than electron, so they are cations with a charge of +1. Similarly, Group 2 metals lose two electrons and Group 3 metals lose three electrons to end up as cations with charges of +2 or +3, respectively.

On the other end of the table, the noble gases don't readily ionize, so no oxidation states are shown. The nonmetals ionize by taking on electrons to become anions. The halogens all have *p* subshells containing five electrons, so they ionize by gaining one electron to fill up the *p* sub-



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H^+																	He
2	Li^+	Be^{2+}											B^{3+}	C^{4+} C^{4-}	N^{3-}	O^{2-}	F^-	Ne
3	Na^+	Mg^{2+}											Al^{3+}	Si^{4+}	P^{3-}	S^{2-}	Cl^-	Ar
4	K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}	V^{5+} V^{4+}	Cr^{6+} Cr^{3+}	Mn^{4+} Mn^{2+}	Fe^{3+} Fe^{2+}	Co^{3+} Co^{2+}	Ni^{2+}	Cu^{2+} Cu^+	Zn^{2+}	Ga^{3+}	Ge^{4+} Ge^{2+}	As^{3+} As^{5+}	Se^{2-}	Br^-	Kr
5	Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{6+} Mo^{4+}	Tc^{7+} Tc^{4+}	Ru^{4+} Ru^{3+}	Rh^{3+}	Pd^{4+} Pd^{2+}	Ag^+	Cd^{2+}	In^{3+}	Sn^{4+} Sn^{2+}	Sb^{5+} Sb^{3+}	Te^{2-}	I^-	Xe
6	Cs^+	Ba^{2+}	Lu	Hf^{4+}	Ta^{5+}	W^{6+}	Re^{7+} Re^{6+}	Os^{4+}	Ir^{4+} Ir^{3+}	Pt^{4+} Pt^{2+}	Au^{3+} Au^+	Hg^{4+} Hg^{2+}	Tl^+	Pb^{4+} Pb^{2+}	Bi^{5+} Bi^{3+}	Po^{4+}	At	Rn

Figure 2.12. Representative oxidation states.

shell, becoming anions with a charge of −1 in the process. Similarly, Group 16 nonmetals gain two electrons and Group 15 nonmetals gain three electrons to become anions with charges of −2 or −3, respectively.

All the transition metals have multiple oxidation states, and the oxidation state they assume depends on what other elements are around to swap electrons with. The values shown are the most common states. This chart makes it easy to visualize the metalloids as the boundary between the cations and the anions. In the cases of lutetium (Lu) and astatine (At), these elements have multiple oxidation states with none preferred, and for this reason none are shown.

It should be clear now that although ionization energy is defined as the energy required to *remove* an electron from an atom, which is what happens to metals when they ionize, the nonmetals ionize by *gaining* electrons to form anions. The energy involved in a neutral atom gaining an electron is called the *electron affinity*, and is our next topic.

2.4.4 Electron Affinity

Electron affinity is defined as the amount of energy *released* when adding an electron to a ground-state, isolated, gaseous atom. The term “affinity” indicates that electron affinity is a measure of how eager the atoms of a given element are to take on another electron, an important measure when trying to understand or predict chemical reactions.

Here is yet another instance in which energy relationships are crucial for understanding chemical behavior. Most atoms release energy when an electron is added, and accept the additional electron into an orbital to become an anion with a charge of −1. The major exceptions to know about are the noble gases. These elements do not release energy when an electron is added. Instead, energy is required to attach the electron and as a result the atom is not stable. Such an ion immediately rejects the electron and returns to its neutral state. This is because the valence shells in the noble gas atoms are full—the most stable electron configuration there is.

Using sulfur as an example, the gaining of an electron is modeled with an ionization equation as follows:

$$\mathrm{S}(g) + e^{-} \rightarrow \mathrm{S}^{-}(g) \qquad \Delta E = 2.077 \text{ eV} \tag{2.3}$$

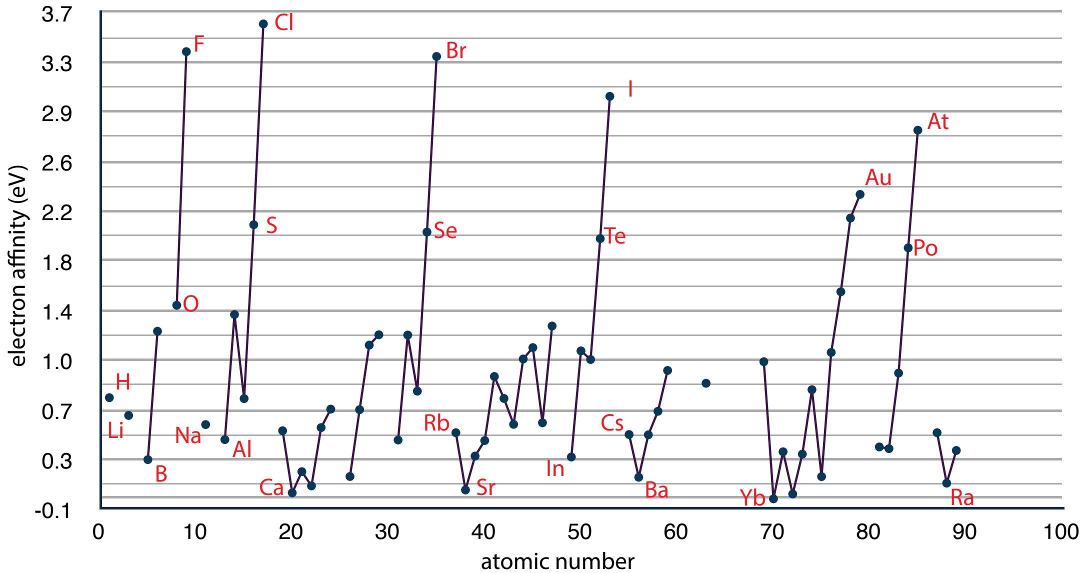


Figure 2.13. Electron affinities.

As with ionization Equation (2.1), the (*g*) indicates that the sulfur is in the gaseous state, and the energy change is stated to the right of the equation.

It is important for you to distinguish clearly in your mind between ionization energy and electron affinity. Ionization energy is the energy required to *remove* an electron from a neutral atom (creating a cation). This energy is positive for every element. Electron affinity is the energy released when an electron is *added* to a neutral atom (creating an anion). Defined this way, this energy is also positive for every element except for the noble gases and a few other elements.

Figure 2.13 shows the electron affinities for the stable atoms. As with other properties we have addressed, there is an obvious periodicity in the affinity values corresponding to the periods in the periodic table. We can again explain the large values associated with the Group 16 and Group 17 elements in terms of the effective nuclear charge, Z_{eff}. In these two groups, the value of Z_{eff} is as high as it gets, so the nuclei of these elements exert the highest possible attraction on a free electron, causing the atom/electron system to release as much energy as possible when the electron drops down into the lower energy state in one of the atom's orbitals.

The breaks between connected dots in Figure 2.13 indicate that several other elements are missing besides the noble gases. These are Be, N, Mg, Mn, and Zn. All these elements exhibit the same unstable behavior the noble gases do when an electron is added to them. Most of these can be at least partially explained by referring to the periodic table. Beryllium has two electrons in the 2*s* subshell. An added electron would go into the 2*p* subshell, where its energy is too high for the small nucleus to hold it. The same is the case for magnesium. Nitrogen has three electrons in the 2*p* subshell—a stable, low-energy state. Adding a fourth electron results in repulsion between two electrons in the p_x orbital, and once again the small nucleus does not have a strong enough attraction to wrangle those electrons and keep them both there. Similar considerations apply for manganese and zinc. Manganese has five electrons in the 3*d* subshell, so the 3*d* subshell is exactly half full with one electron in each orbital. This puts manganese in a situation similar to that of nitrogen. Zinc has 10 electrons in the 3*d* subshell and none in the 4*p* subshell, so zinc is in a situation similar to that of beryllium and magnesium.

There is one element with a very slightly negative value for electron affinity that will still accept an electron. This element is ytterbium (Yb, $Z = 70$). Ytterbium is at the far right of the

Term	Definition Used In This Text	If the energy quantity ΔE is positive, it means:
ionization energy	energy *required* to *remove* an electron	energy flows *into* the atomic system from outside
electron affinity	energy *released* when *adding* an electron	energy flows *out of* the atomic system

Term	Alternative Definition	If the energy quantity ΔE is positive, it means:
ionization energy	energy *involved* when removing an electron	energy flows *into* the atomic system from outside
electron affinity	energy *involved* when adding an electron	energy flows *into* the atomic system from outside (thus, ΔE and the electron affinity values are nearly always negative)

Table 2.2. Definitions used here and elsewhere for ionization energy and electron affinity.

rare-earth elements, in Period 6. Its 4*f* subshell is full and an additional electron goes into the 5*d* subshell.

There is one final point to make before we move on. I have used care in defining ionization energy and electron affinity so that it is clear which way the energy is going when energy values are positive or negative. But you should be aware that some texts and other sources use definitions that may not be as clear, possibly leading to confusion. Instead of using the terms *required* or *released* to define the direction of positive energy flow, some sources use the term *involved*, and define positive energy flow in terms of energy going into or out of the atomic system. Both definitions are valid, as long as one specifies the direction of energy flow that constitutes a positive value of energy.

The definitions we have seen in the last two sections are fairly standard. But to help you avoid confusion, Table 2.2 spells out my definitions and the alternative definitions side by side.

2.4.5 Electronegativity

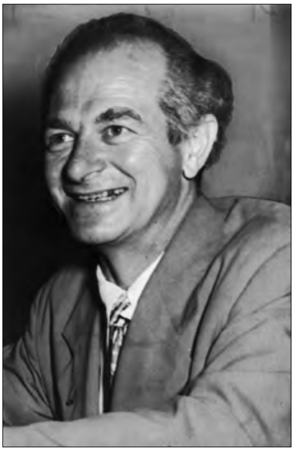


Figure 2.14. American chemist Linus Pauling (1901–1994).

American chemist Linus Pauling (Figure 2.14) was one of the most important chemists of the 20th century. His work in the 1930s, 1940s, and 1950s on the nature of chemical bonds remains foundational for our understanding of chemistry to this day. For his work, Pauling won the Nobel Prize in Chemistry in 1954. Beginning in the mid-1940s, Pauling showed a deep concern for the negative health effects due to nuclear fallout from nuclear weapons testing, and he presented a petition signed by 11,000 scientists to the United Nations in 1958 to urge a ban on nuclear weapons testing. A scientific study that came out in 1961 showed that radioactivity contamination was indeed widespread in the population, leading to nuclear test ban treaties with the Soviet Union. All this led to Pauling winning the Nobel Peace Prize in 1962. To this day, Pauling remains the only person ever to win two unshared Nobel Prizes.

In 1932, as part of his efforts to understand chemical bonding, Pauling introduced what is now called the *Pauling electronegativity scale*. The electronegativity scale uses a dimensionless quantity called *electronegativity*, with values running from 0.7 (francium) to 3.98 (fluorine). Electronegativity is a measure of how strongly atoms attract the electrons shared between atoms inside molecules. The higher an element's electronegativity relative to the other elements in a molecule, the more an atom attracts the shared electrons in the molecule toward itself.

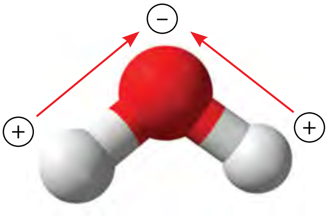


Figure 2.15. The higher electronegativity of oxygen atoms compared to hydrogen atoms results in the polar water molecule.

Once again, the importance of electrical attraction in the atomic world is crucial. Recall from the Introduction that many of the important properties of water are due to the difference between the electronegativities of oxygen (3.44) and hydrogen (2.20) in the water molecule. The oxygen atom attracts shared electrons more strongly than the hydrogen atoms do, and as a result the four bonding electrons in the molecule crowd over toward the oxygen atom. The result is that the oxygen region of the water molecule is more electrically negative and the hydrogen regions are more electrically positive, so water molecules are *polar*—negative at the elbow and positive at the ends, as shown in Figure 2.15. In this diagram, the arrows point from the positive region of the molecule toward the negative region of the molecule. We consider electronegativity further in the next chapter in the context of covalent bonding.

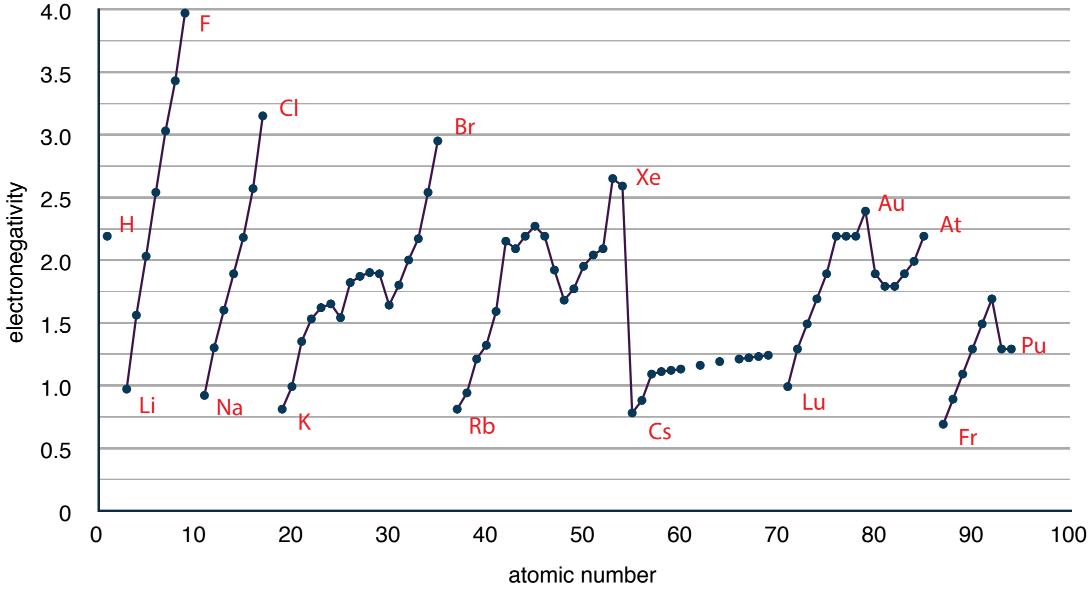


Figure 2.16. Electronegativity values, according to the Pauling electronegativity scale.

Figure 2.16 shows the periodicity of electronegativity and the trend of increasing electronegativity from left to right in the periodic table. There are gaps between the halogens and the alkali metals because the noble gases are not included. This is because electronegativity measures atomic attraction within molecules, and the noble gases don't form bonds with other elements, molecular or otherwise, except under the extreme and unusual conditions that can be produced in a specialized laboratory.

As with electron affinity and ionization energy, the trends in electronegativity can be understood in terms of the effective nuclear charge, Z_{eff}, which increases from left to right as the number of protons in the nucleus increases while the number of core electrons screening the nucleus remains constant. A larger value of Z_{eff} means not only that an atom attracts its own valence electrons more tightly. It also means the atom attracts the valence electrons shared with neighboring atoms more strongly relative to the attraction of neighboring atoms.

The diagram in Figure 2.17 summarizes the general trend of electronegativity values over the periodic table from the lowest value held by francium, to the highest value held by fluorine. You may need various electronegativity values for exercises in this and later chapters, so they are all shown in Figure 2.18 and inside the back cover. If you look at the values toward the right end of the transition metals, you see that around Groups 10–13 there is a small decline in the electronegativities, going against the general upward trend in values from lower left to upper right.

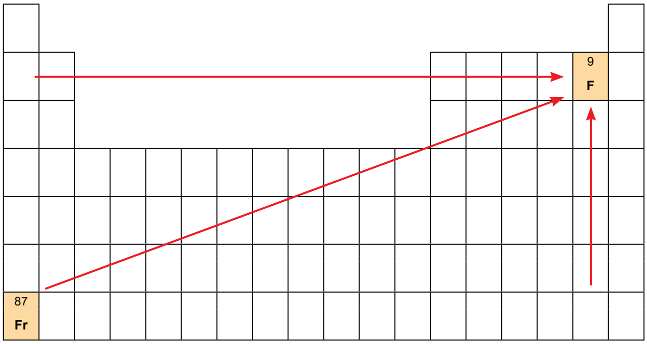
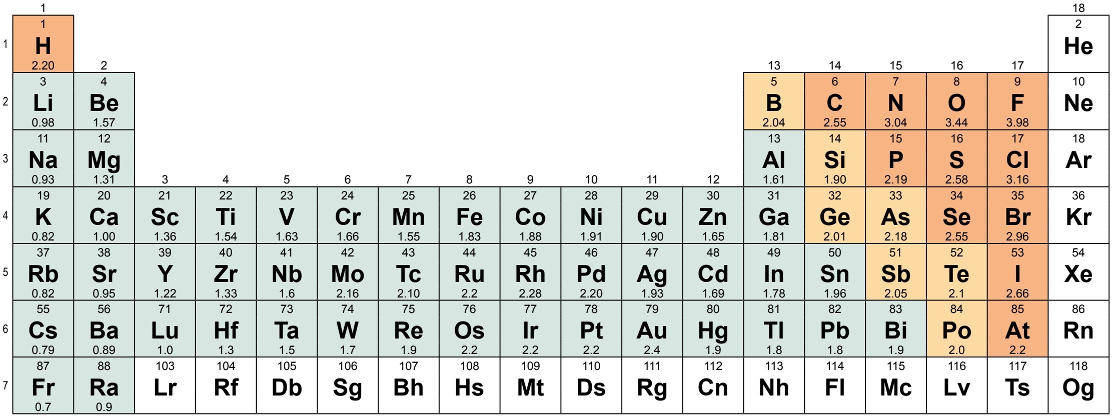


Figure 2.17. The arrows show the trends of increasing electronegativity from the lowest value at francium to the highest value at fluorine.



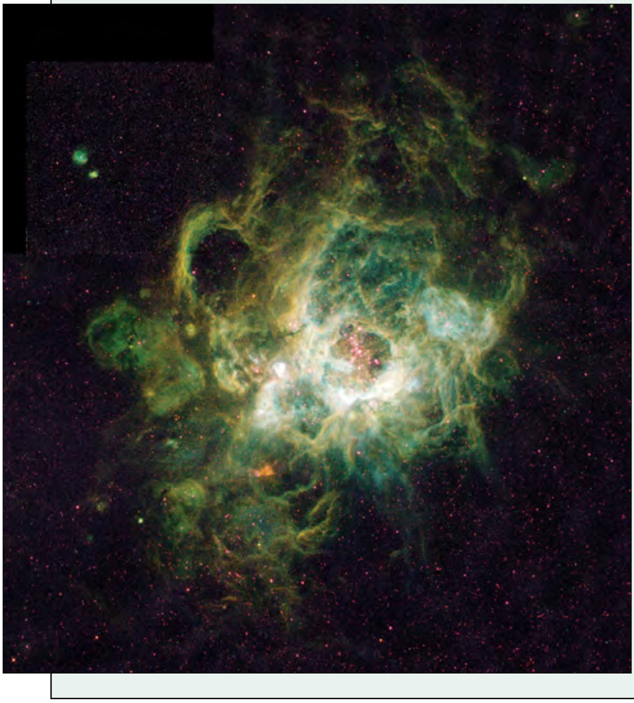
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** 2.20																	2 **He**
2	3 **Li** 0.98	4 **Be** 1.57											5 **B** 2.04	6 **C** 2.55	7 **N** 3.04	8 **O** 3.44	9 **F** 3.98	10 **Ne**
3	11 **Na** 0.93	12 **Mg** 1.31											13 **Al** 1.61	14 **Si** 1.90	15 **P** 2.19	16 **S** 2.58	17 **Cl** 3.16	18 **Ar**
4	19 **K** 0.82	20 **Ca** 1.00	21 **Sc** 1.36	22 **Ti** 1.54	23 **V** 1.63	24 **Cr** 1.66	25 **Mn** 1.55	26 **Fe** 1.83	27 **Co** 1.88	28 **Ni** 1.91	29 **Cu** 1.90	30 **Zn** 1.65	31 **Ga** 1.81	32 **Ge** 2.01	33 **As** 2.18	34 **Se** 2.55	35 **Br** 2.96	36 **Kr**
5	37 **Rb** 0.82	38 **Sr** 0.95	39 **Y** 1.22	40 **Zr** 1.33	41 **Nb** 1.6	42 **Mo** 2.16	43 **Tc** 2.10	44 **Ru** 2.2	45 **Rh** 2.28	46 **Pd** 2.20	47 **Ag** 1.93	48 **Cd** 1.69	49 **In** 1.78	50 **Sn** 1.96	51 **Sb** 2.05	52 **Te** 2.1	53 **I** 2.66	54 **Xe**
6	55 **Cs** 0.79	56 **Ba** 0.89	71 **Lu** 1.0	72 **Hf** 1.3	73 **Ta** 1.5	74 **W** 1.7	75 **Re** 1.9	76 **Os** 2.2	77 **Ir** 2.2	78 **Pt** 2.2	79 **Au** 2.4	80 **Hg** 1.9	81 **Tl** 1.8	82 **Pb** 1.8	83 **Bi** 1.9	84 **Po** 2.0	85 **At** 2.2	86 **Rn**
7	87 **Fr** 0.7	88 **Ra** 0.9	103 **Lr**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112 **Cn**	113 **Nh**	114 **Fl**	115 **Mc**	116 **Lv**	117 **Ts**	118 **Og**

Figure 2.18. Electronegativity values, according to the Pauling electronegativity scale.

2.5 A Few Notes About Hydrogen

Hydrogen is located in Group 1 for a couple of reasons. First, it is an *s*-block element. Its lone electron is in a partially filled *s* subshell, just like the alkali metals. Second, hydrogen usually ionizes by losing an electron to form a cation, like all metals. In fact hydrogen forms the most basic of all cations—a lone proton. Third, in an aqueous solution (a solution with water as the solvent), acids, which are formed with hydrogen, dissociate (come apart) just as ionic compounds do. And just as the metal in a soluble ionic compound is a cation, so is the hydrogen

Hmm... Interesting. *Hydrogen in space*



Hydrogen is the most abundant element in the universe, making up about 75% of the mass of all matter. The image below, taken by the Hubble Space Telescope, is of the NGC 604 nebula, an enormous region of ionized hydrogen gas (a plasma) in the constellation *Triangulum*. The gas cloud is about 1,500 light years across, and has been called a “nursery of new stars” because of all the new stars formed within it. At the center are over 200 hot stars, each 10–15 times the size of our sun. These hot stars excite the hydrogen atoms, causing them to fluoresce, and heat the nebula to 10,000 kelvins—about twice the temperature at the surface of our sun.

from a dissolved acid. Hydrogen's atomic structure and its normal ionization as a cation with a charge of +1 indicate that hydrogen belongs at the top of Group 1.

But though hydrogen's *structure* assures that its place in Group 1 is probably not going to change, hydrogen's chemical *behavior* is more like a halogen than an alkali metal. For one thing, hydrogen shares electrons in covalent bonds with other elements to form molecules, just as nonmetals do. In contrast, when metals bond they form crystals. A second factor is that hydrogen atoms bond to *themselves* to form molecules of H_2, something no metal does. (An exception is the ion Hg_2^{2+}.) Third, hydrogen can ionize by *gaining* an electron to fill the 1*s* subshell and become H^-, an anion known as *hydride*.

With its only subshell half full with one electron, easily emptied by losing one electron and easily filled by gaining one electron or sharing one pair of electrons (details next chapter), hydrogen is unique among the elements in the periodic table.

Chapter 2 Exercises

SECTION 2.1

1. What entire group of elements did not appear in Mendeleev's original periodic table? Why were they left out and how were they put in?
2. Write a paragraph explaining the general structure and arrangement of the periodic table.

SECTION 2.2

3. State the chief chemical property that distinguishes the metals from the nonmetals.
4. Distinguish between cations and anions.
5. What is the "long form" of the periodic table, and why are there two forms?

SECTION 2.3

6. Use the data in the table below to estimate the following bond lengths. In each case, determine the percent difference between the accepted value given and your estimate (see Section A.4.2 in Appendix A).
   a. the N—H bond length in a molecule of ammonia, NH_3 (accepted value: 1.012 Å).
   b. the C—O bond length in carbon monoxide, CO (accepted value: 1.128 Å).
   c. the C—O bond length in carbon dioxide, CO_2 (accepted value: 1.160 Å).
   d. the P—F bond length in phosphorus trifluoride, PF_3 (accepted value: 1.570 Å).
7. Describe the trend in atomic radius going down a group and across a period.
8. Using the concept of effective nuclear charge, Z_{eff}, write a description accounting for the trends in atomic size in the periodic table.
9. From your knowledge of the periodic table, put the elements rubidium (Rb), silver (Ag), xenon (Xe),

Element	*Z*	Atomic Radius (Å)	Bonding Atomic Distance of Diatomic Molecule (Å)
hydrogen	1	0.32	0.741
carbon	6	0.75	1.242
nitrogen	7	0.71	1.098
oxygen	8	0.64	1.208
fluorine	9	0.60	1.413
phosphorus	15	1.09	1.893
sulfur	16	1.04	1.889
chlorine	17	1.00	1.987
selenium	34	1.18	2.166
bromine	35	1.17	2.281
iodine	53	1.36	2.666

and yttrium (Y) in order of increasing atomic radius. Explain your order by referring to trends in the periodic table.

10. From your knowledge of the periodic table, put the elements sodium (Na), barium (Ba), cesium (Cs), and magnesium (Mg) in order of increasing atomic radius. Explain your order by referring to trends in the periodic table.
11. Based on your knowledge of trends in the periodic table, place the following atoms and ions in order of decreasing size: Be^{2+}, Mg, Ca, and Mg^{2+}.
12. Based on your knowledge of trends in the periodic table, arrange the following atoms and ions in order of size from largest to smallest: S^{2-}, Ar, K^+, Cl^-, and Ca^{2+}.

SECTION 2.4

13. Aluminum and scandium both ionize to +3, even though scandium is in Group 3 and aluminum is in Group 13. Explain why this is.
14. Estimate the effective nuclear charge, Z_{eff}, for vanadium (V), magnesium (Mg), chlorine (Cl), and arsenic (As).
15. Define ionization energy and describe the trends for ionization energy in the periodic table across periods and down groups.
16. Referring again to Table 2.1, explain the large increase in ionization energy that occurs in the yellow shaded region of that table.
17. Write a description accounting for the trends in ionization energy in terms of effective nuclear charge, Z_{eff}, and other factors.
18. Write the condensed electron configurations for Cu^{2+}, As^{5+}, Ag^+, and Au^{3+}.
19. Why are ionization energies so much higher when core electrons are involved than they are when only valence electrons are involved?
20. Based on your knowledge of trends in the periodic table, place the following atoms in order of increasing ionization energy: Ar, Sr, P, Mg, and Ba.
21. Distinguish between ionization energy and electron affinity.
22. Based on your knowledge of trends in the periodic table, place the following atoms in order of increasing electron affinity: Br, Rb, and S.
23. Explain what the electronegativity scale is used for and how it arose.
24. Of the following cations, which is least likely to form: Ca^{3+}, Mg^{2+}, K^+? Explain your response.
25. Why do the chalcogens form ions with a charge of –2?
26. Distinguish between electron affinity and electronegativity.
27. Referring to the periodic table, describe the chemical properties of potassium (K), sulfur (S), xenon (Xe), iodine, (I), and manganese (Mn).
28. Which of the following is likely to have the greatest difference between the third and fourth ionization energies: Cl, Sc, Na, C?
29. Using only the periodic table as a reference (without electronegativity data), predict the relative electronegativities of these elements and put them in order from least to greatest: Ni, Ta, Se, F, Cs, Cl.
30. Develop an explanation for why the electron affinity values for the chalcogens are each significantly lower than those of their halogen neighbors.

31. Why don't the noble gases have electronegativity values listed in Figure 2.16?

SECTION 2.5

32. Describe the chemical properties that place hydrogen in Group 1, and the chemical properties hydrogen shares with Group 17 elements.

GENERAL REVIEW EXERCISES

33. Determine the energy released by the largest electron transition in the Lyman series (see Figure 1.8). State your answer in eV.

34. If a beam of laser light consists of photons with energies of 5.09×10^{-19} J, is the light visible? Explain your response.

35. Identify the block, period, and group for the elements represented by each of the following condensed electron configurations:
    a. $[\mathrm{Ne}]3s^2 3p^3$
    b. $[\mathrm{Xe}]6s^2 4f^{14} 5d^{10} 6p^1$
    c. $[\mathrm{Kr}]5s^1 4d^5$
    d. $[\mathrm{Ar}]4s^2 3d^3$

36. How many orbitals are there in the shell associated with $n = 4$? How many electrons can this shell hold?

37. Determine the number of carbon atoms present in 112 g CO_2.

38. Given 35.0 g H_2SO_4 (hydrogen sulfate, which is called sulfuric acid in aqueous solution), determine the percent composition. Then determine numbers of hydrogen, sulfur, and oxygen atoms present.

39. Identify some specific differences between the chemical properties of the alkali metals and those of the transition metals.

40. Naturally occurring bromine consists of the two isotopes bromine-79 and bromine-81. Given bromine's atomic mass of 79.904 u, is the percentage of bromine-79 found in nature likely to be closer to 25%, 52%, 67%, or 80%? Explain your response.

41. How many grams of calcium are there in 3.00 mol $CaBr_2$?

42. Analysis of a certain sample finds that the sample consists of 53.64% chlorine and 46.36% tungsten. Determine the empirical formula for this compound.

43. What is meant by the phrase, "chemistry is all about modeling"?

44. Why is it that scientists, when they are being accurate in their speech, avoid using the term *truth*? What are they likely to say instead?

45. Is there a difference between scientific facts and historical facts? If so, what is it?

46. What is the difference between molar mass and molecular mass?

47. Why must a calculation of molecular mass based on periodic table data necessarily be an average mass and not the mass of a specific molecule?

48. Distinguish between the two definitions for the mole.

Chapter 10

Thermochemistry and Kinetics

In the 19th century, physicists learned how to quantify the amount of heat released or absorbed in chemical reactions, such as in the beautiful exothermic reaction pictured above. For reactions that occur at constant pressure like the one pictured above, this quantity of heat is called the *enthalpy of reaction*. In the 1870s, American scientist Josiah Willard Gibbs combined enthalpy, entropy, and temperature together in an equation that defines a quantity called the *Gibbs free energy*. The Gibbs free energy is a powerful theoretical tool used to predict if reactions will occur at stated conditions.

After studying this chapter, you will be able to look at the reaction pictured above and state whether the Gibbs free energy for the reaction is positive or negative.

Objectives for Chapter 10

After studying this chapter and completing the exercises, you should be able to do each of the following tasks, using supporting terms and principles as necessary.

SECTION 10.1

1. Define *enthalpy of reaction* and relate this term to the energy pathways for exothermic and endothermic reactions.
2. Interpret enthalpy diagrams and thermochemical equations.
3. Use the *First Law of Thermodynamics* to distinguish between *enthalpy* and *energy*.
4. Define *enthalpy of combustion* and *enthalpy of formation*.

SECTION 10.2

5. State Hess's law.
6. Use enthalpy of combustion and enthalpy of formation data with the principle of Hess's law to calculate the enthalpy of reaction and enthalpy of formation for given reactions.

SECTION 10.3

7. Describe the relationships between entropy and temperature, entropy and phase, and entropy and the number of moles or particles of a substance.
8. Define the *Gibbs free energy*.
9. Outline the four possibilities for ΔH and ΔS in a chemical reaction, describe the resulting possibilities for ΔG, and describe the conditions under which a reaction occurs spontaneously.
10. Calculate the Gibbs free energy two different ways and use the result to determine if a reaction occurs spontaneously.

SECTION 10.4

11. Describe collision theory and identify the two requirements for a collision between molecules of reactants to be effective in leading to the formation of product species.
12. Describe four factors scientists can control that influence the rate of reactions.
13. Explain the related concepts of *reaction mechanism* and *intermediates*.
14. Explain the related concepts of *activation energy* and the *activated complex*.
15. Using the Haber-Bosch process as an example, explain how metal catalysts work.
16. Distinguish between heterogeneous and homogeneous reactions.
17. Given a reaction mechanism with reaction speeds labeled, identify the rate-determining step and determine the rate law for the reaction.
18. Given a rate law, determine the effect on the reaction rate of altering the concentrations of reactants by specific proportions.
19. Explain how an experimentally determined rate law can provide clues to help chemists determine a reaction's mechanism.
20. Identify the order of a rate law and the order of a reaction with respect to the concentrations in the rate law.

10.1 Energy in Chemical Reactions

10.1.1 Introduction

Energy plays a huge role in chemical reactions. The purpose for many chemical reactions is specifically to deliver energy. Examples of reactions like this are metabolism in animals, electrochemical reactions in batteries to power electronic devices, and burning of fuels to power machines. Figure 10.1 shows the test firing of one of the Space Shuttle main engines. The fuel for this engine is liquid hydrogen and liquid oxygen, which means there is nothing coming out of this engine except water vapor and heat. And yet there is enough energy released by this reaction to power a vehicle weighing over 2,000 tons.

Figure 10.1. The chemical reaction between liquid hydrogen and liquid oxygen is the energy source used by the Space Shuttle main engine. The white formation under the engine at the bottom is water vapor that has condensed to liquid droplets, allowing the water vapor to become visible.

Throughout this text, we have seen that one of the major principles of nature is that processes tend to go in directions that minimize energy. But in Section 8.2.1 we saw that some processes, such as the dissolution of an ionic crystal, entail an energy increase. The melting of an ice cube is another example of a process that spontaneously goes in a direction leading to higher particle energy.

In Section 8.2.3, we saw that the reason such processes can occur is that there is another factor involved in natural processes besides energy—entropy. The entropy of a system is a measure of the disorder present in the system. Just as spontaneous processes tend to go in a direction that minimizes energy, they also tend to go in a direction that maximizes entropy. Several of these examples are discussed in Section 8.2.3. Together, the energy and the entropy pathways open to a substance or combination of substances determine what the substances do. Applying these topics to the study of chemical reactions is the subject of a branch of chemistry known as *thermochemistry*. A tour through the basic principles of thermochemistry will occupy us for the first three sections of this chapter.

We begin with a study of energy in reactions. In Section 10.3.3, we come back to the topic of entropy, and we combine energy and entropy together into a single reaction-governing principle known as the *Gibbs free energy*. Before proceeding further in this chapter, you may wish to reread the paragraphs in Section 8.2.3 on entropy.

10.1.2 Enthalpy

Recall from Section 8.2.2 that the *enthalpy* in a chemical system is related to the heat flow that occurs during chemical processes. The net amount of heat that flows into or out of a chemical system during a reaction at constant pressure is called the *change in enthalpy*, ΔH. By change in enthalpy we mean the difference between the enthalpy of the reaction products and the enthalpy of the reactants, as shown in the following equation:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \tag{10.1}$$

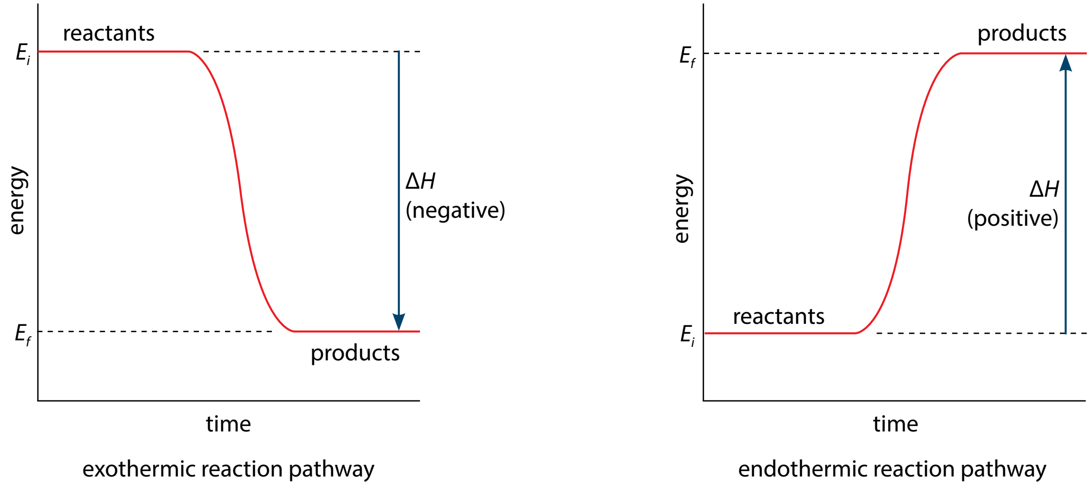


Figure 10.2. Energy pathways for exothermic and endothermic reactions.

The change in enthalpy represents the heat that flows into (is absorbed by) or out of (is released from) a system during a process occurring at a constant pressure. During any process, the change in enthalpy is either positive or negative, as illustrated in Figure 10.2. In this figure, the red curves illustrate the *energy pathway* during the course of a reaction. As the reaction proceeds, the substances involved either release heat or absorb heat.

As shown on the left side of the figure, if ΔH is negative, heat is released during the process, and the process is exothermic. In this case, the energy in the reaction products, E_f, is less than the energy in the reactants, E_i. For processes at constant pressure, this change in energy is equal to the change in enthalpy, ΔH. If ΔH is positive, as shown on the right, heat is absorbed during the process and the process is endothermic. In this case, the chemical potential energy in the reaction products is higher than the energy in the reactants.

The enthalpy, H, of the reactants or products in a reaction cannot be measured directly. Only changes in enthalpy can be measured. As mentioned in Section 8.2.2, we are not going to concern ourselves too much with what enthalpy itself is, although in Section 10.1.3 we briefly explore how enthalpy relates to the internal energy in a system and the ways energy can flow into or out of a system. Our main concern here is with what the change in enthalpy represents.

The general term for the change in enthalpy during a chemical reaction is *enthalpy of reaction*, also called the *heat of reaction*. The enthalpy of reaction is often listed with a chemical equation to form a *thermochemical equation*. For example, we have regularly encountered the reaction between hydrogen gas and oxygen gas to form water vapor:

$$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightarrow 2\mathrm{H_2O}(g)$$

In this reaction, two moles of hydrogen react with one mole of oxygen to produce two moles of water vapor, and in the process 483.6 kJ of heat are released. We write the thermochemical equation this way:

$$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightarrow 2\mathrm{H_2O}(g) \qquad \Delta H = -483.6\ \mathrm{kJ} \tag{10.2}$$

Again, ΔH is negative because the energy in the reaction products is less than the energy in the reactants and heat is released during the reaction. The information in Equation (10.2) can also be represented on an *enthalpy diagram*, as shown in Figure 10.3. The horizontal lines in this diagram indicate the enthalpies of the reactants and the products. The reaction goes in the direction of the red arrow, releasing 483.6 kJ of heat at constant pressure.

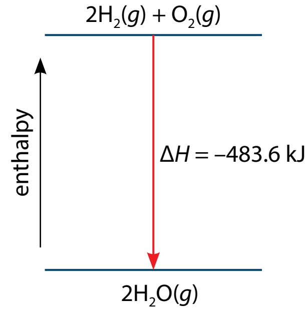


Figure 10.3. Enthalpy diagram showing the enthalpy of reaction for the combustion of hydrogen.

Several comments are in order about thermochemical equations such as Equation (10.2). First, enthalpy is an extensive property. This means that ΔH depends on the amount of the substances present in the reaction. For this reason, when interpreting thermochemical equations we always take the coefficients in the equation to represent numbers of moles rather than numbers of atoms. In fact, sometimes fractional coefficients are used in thermochemical equations. (We see why in Section 10.2.1.) Thus, for the reaction of hydrogen and oxygen involving half as many moles as shown in Equation (10.2), we write the thermochemical equation this way:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \Delta H = -241.8 \text{ kJ}$$

When half as many moles are involved in the reaction, the enthalpy of reaction is half as much.

Second, it is conventional to state enthalpy values in thermochemical equations at 25°C (and, again, constant pressure). This means that the reactants begin at 25°C and after the reaction are returned to 25°C. Equation (10.2) is written according to this convention, even though the H_2O is shown as a vapor in the equation. As written, the equation states that when the reaction occurs and the H_2O vapor is returned to 25°C, the total energy released is 483.6 kJ.

Third, as you can see from the previous comment, it is important always to indicate the states for each reactant and product in thermochemical equations. In the hydrogen reaction shown in Equation (10.2), the enthalpy of reaction is different if H_2O is in the liquid state instead of the vapor state shown in the equation. This is because energy must be removed from H_2O vapor in order to condense it to liquid. At 25°C, the molar heat of vaporization for water is 44.0 kJ/mol, so to condense two moles of H_2O, 88.0 kJ of heat must be removed. The thermochemistry of this condensation can be represented as

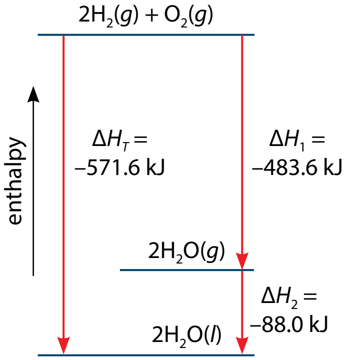


Figure 10.4. Enthalpy diagram showing the enthalpy of reaction for the combustion of hydrogen to produce water vapor, and the additional enthalpy change required to condense the water.

$$2H_2O(g) \rightarrow 2H_2O(l) \qquad \Delta H = -88.0 \text{ kJ}$$

So then, to write Equation (10.2) showing water in the liquid state, we must include the enthalpy change associated with condensing two moles of H_2O, an additional decrease of 88.0 kJ. Including this quantity of heat in ΔH gives:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H = -571.6 \text{ kJ} \qquad (10.3)$$

The combined process of combustion and condensation is represented in the enthalpy diagram of Figure 10.4. In this diagram, the enthalpy change in the combustion step is labeled ΔH_1 and the enthalpy change for the condensation step is labeled ΔH_2. The total enthalpy change is denoted by ΔH_T.

Finally, thermochemical equations are often written in reverse, as we see in Section 10.2.1. When we do this, the enthalpy change for the reverse reaction has the opposite sign. For example, the thermochemical equation for the combustion of methane is:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.8\ \text{kJ} \qquad (10.4)$$

This is an exothermic reaction that releases 890.8 kJ of heat for each mole of methane burned. If we imagine the reverse reaction of combining water and carbon dioxide to form methane, we have

$$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g) \qquad \Delta H = 890.8\ \text{kJ}$$

This reverse reaction is endothermic, and the same amount of energy has to be supplied as is released in the forward reaction. Accordingly, the sign on ΔH is reversed to show that energy is absorbed by the reactants. ΔH is now a positive quantity, as it always is for an endothermic reaction.

▼ Example 10.1

Hydrogen peroxide, H_2O_2, is a compound that decomposes to water and oxygen according to the following reaction:

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g) \qquad \Delta H = -196\ \text{kJ}$$

Answer the following questions about this process:

1. Is this process exothermic or endothermic?
2. What is the change in enthalpy for each mole of hydrogen peroxide that decomposes?
3. If 25.0 g of H_2O_2 decomposes at 25°C, determine the net amount of heat released or absorbed.

First, since ΔH is a negative quantity, the products of the reaction have less energy than the reactants, so heat is released during the reaction. The reaction is exothermic.

Second, the heat of reaction shown is for two moles of H_2O_2, as the coefficient in the thermochemical equation indicates. The change in enthalpy for one mole—half this amount—is half as much, or –98.0 kJ.

Third, we begin by determining how many moles of H_2O_2 we have. The molecular mass is 34.01 g/mol. Calculating the number of moles from this, we have

$$25.0\ \text{g} \cdot \frac{1\ \text{mol}}{34.01\ \text{g}} = 0.7351\ \text{mol}$$

Finally, the given equation tells us that 196 kJ are released for every two moles of H_2O_2 involved. We use this ratio as a conversion factor and apply it to the number of moles we have.

$$0.7351\ \text{mol} \cdot \frac{196\ \text{kJ}}{2\ \text{mol}} = 72.0\ \text{kJ}$$

We find that 72.0 kJ of heat is released by the decomposition of 25.0 g H_2O_2.

▲

10.1.3 Understanding Enthalpy and Energy

Before we move on, you may be wondering why we need to use the term *enthalpy change* to describe the heat being absorbed or released by a chemical reaction. The term *enthalpy* is probably unfamiliar to you and may sound strange or conceptually difficult. So why can't we just use a term such as *energy change* or *internal energy change*, since we are talking about heat energy entering or leaving the thermochemical system? The answer has to do with the fact that there is more than one way for energy to enter or leave a thermochemical system. Thus, in general, the change in enthalpy may or may not be equal to the change in the internal energy of the substances in the reaction or the heat absorbed or released. Let's consider these energy possibilities.

First, energy can enter or leave the system through the absorption or release of heat. This can occur by means of an exothermic chemical reaction releasing heat into the system or an endothermic reaction absorbing heat from the system. Heat exchange can also occur by means of heating or cooling the system.

Next, energy can enter or leave by means of work being done by or on the system. For example, imagine a chemical reaction—such as an explosive combustion of fuel—that occurs inside a cylinder, as depicted in Figure 10.5. This is, in fact, exactly what happens when a mixture of gasoline and air is ignited in one of the cylinders of a car engine. The explosion products are gas molecules at high pressure. This high pressure pushes the piston, which is mechanically connected to the machinery that makes the wheels of the car turn. Pushing the piston is an example of *mechanical work*: force is applied to an object and moves it a certain distance. Work is energy, and when the expanding gases push the piston, the energy involved—the work—leaves the thermochemical system (the gases in the cylinder) and is converted into the kinetic energy of the moving car. This is called *expansion work*, and is energy that leaves the thermochemical system by a mechanism other than heat.

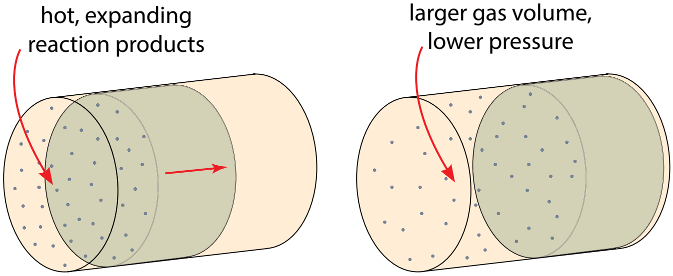


Figure 10.5. Energy leaves a system when a gas does mechanical work by expanding inside a cylinder and pushing a piston.

Third, there are other forms of work by which energy can enter or leave the system, such as electromagnetic interactions, or mechanical parts driven from the outside that stir (accelerate) the gases in the system and thus increase their internal energy. For the rest of this discussion, we assume these play no role in our system and that only expansion work is involved.

In general, the change in enthalpy in a system is a function of pressure and entropy. But *if the pressure is held constant*, then the mathematics allows us to describe the change in enthalpy more simply as follows:

$$\Delta H = \Delta U + P\Delta V \qquad (10.5)$$

In this equation, ΔU is the change in internal energy in the system (see Section 6.1.1), P is the system pressure, and ΔV is the change in the system volume. Again, Equation (10.5) can only be written because we are holding the pressure constant.[1]

Now to see how this change in enthalpy can be equal to the heat absorbed or released, we start with the so-called *first law of thermodynamics*, which is:

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[1] An example of a reaction at constant pressure is a chemical reaction that occurs in the open atmosphere. The pressure is atmospheric pressure throughout the reaction.

$$Q = \Delta U + W \tag{10.6}$$

In this equation, Q is the heat entering or leaving the system, ΔU is the change in the internal energy of the molecules as before, and W is the work done by (or on) the system. Now, since we are considering only the expansion work, you may recall from an earlier physics class that the work associated with pushing an object is defined as

$$W = F \cdot d \tag{10.7}$$

In this equation, F represents a force (in newtons) and d represents a distance (in meters). We can easily relate this expression for work to the pressure and volume of a gas. Recall from Section 6.1.4 that pressure is defined as force per unit area, or

$$P = \frac{F}{A} \tag{10.8}$$

Solving this equation for the force, we have

$$F = P \cdot A \tag{10.9}$$

Substituting this expression into Equation (10.7) gives us

$$W = P \cdot A \cdot d \tag{10.10}$$

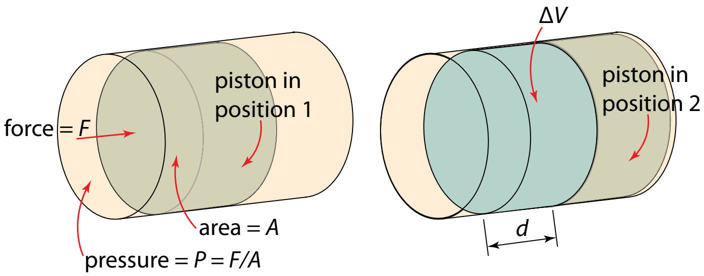

Figure 10.6. Given $W = F \cdot d$, $F = P \cdot A$, and $A \cdot d = \Delta V$, we get $W = P\,\Delta V$.

Figure 10.6 relates these quantities to a piston in a cylinder. The force applied to the end of the piston is equal to the pressure in the cylinder times the surface area of the end of the piston. The force causes the piston to move a distance d. (Again, we assume this happens in a way that allows the pressure to remain constant.) When this happens, the volume change, ΔV, in the cylinder, shown in blue, is equal to the surface area of the end of the piston, A, times the distance it moves, d, or

$$\Delta V = A \cdot d \tag{10.11}$$

Substituting this expression into Equation (10.10) gives us

$$W = P\Delta V \tag{10.12}$$

Finally, substituting this expression for the expansion work into Equation (10.6) gives:

$$Q = \Delta U + P\Delta V \tag{10.13}$$

Comparing this equation to Equation (10.5), you see that $\Delta H = Q$, and thus the change in enthalpy equals the heat entering or leaving the system. This result depends on the pressure being constant and on the expansion work being the only form of work affecting the system. As a quick application, the chemical reaction of an outdoor explosion releases heat and produces expansion work as the hot gases formed by the explosion push back the atmosphere. In this case, the change in enthalpy of the chemical system is equal to the heat released by the reaction.

10.1.4 Enthalpy of Combustion

The heat released by the complete combustion of one mole of a substance at a constant pressure is called the *molar enthalpy of combustion* (or *heat of combustion*). The enthalpy of combustion is a special case of the enthalpy of reaction we have been discussing. Conventionally, enthalpy of combustion values are listed for controlled conditions in which reactants and products are in their so-called *standard states* at standard conditions ($T = 25°\text{C}$ and $P = 1$ bar). The standard state is the state compounds are normally in at standard conditions. Table 10.1 lists enthalpy of combustion values for a number of representative substances. Notice in the table that the value for hydrogen is listed as –285.8 kJ/mol. For two moles, this is –517.6 kJ, which agrees with Equation (10.3).

We use a special notation to designate enthalpy of combustion. Using hydrogen as an example, the enthalpy of combustion is

$$\Delta H_c^\circ = -285.8\ \frac{\text{kJ}}{\text{mol}}$$

The subscript *c* designates *combustion*, and the superscript ° indicates that the value pertains to the reactants and products in their standard states. As another example, the thermochemical equation for the combustion of butane is

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \qquad \Delta H_c^\circ = -2877.6\ \frac{\text{kJ}}{\text{mol}}$$

Enthalpy of combustion values have been measured for many common substances. As we see in Section 10.2, these values may be used along with other data to perform thermochemical

Substance	Formula	ΔH_c° (kJ/mol)	Substance	Formula	ΔH_c° (kJ/mol)
acetic acid (*l*)	CH_3COOH	−874.2	methane (*g*)	CH_4	−890.8
acetone (*l*)	C_3H_5OH	−1789.9	ethyne (acetylene) (*g*)	C_2H_2	−1301.1
ammonia (*g*)	NH_3	−382.8	ethene (ethylene) (*g*)	C_2H_4	−1411.2
carbon (graphite) (*s*)	C	−393.5	ethane (*g*)	C_2H_6	−1560.7
carbon monoxide (*g*)	CO	−283.0	propane (*g*)	C_3H_8	−2219.2
ethanol (*l*)	C_2H_5OH	−1366.8	butane (*g*)	C_4H_{10}	−2877.6
ethylene glycol (*l*)	$C_2H_6O_2$	−1189.2	pentane (*l*)	C_5H_{12}	−3509.0
formic acid (*l*)	CH_2O_2	−254.6	benzene (*l*)	C_6H_6	−3267.6
glucose (*s*)	$C_6H_{12}O_6$	−2805	hexane (*l*)	C_6H_{14}	−4163.2
hydrogen (*g*)	H_2	−285.8	toluene (*l*)	C_7H_8	−3910.3
methanol (*l*)	CH_3OH	−726.1	heptane (*l*)	C_7H_{16}	−4817.0
sucrose (*s*)	$C_{12}H_{22}O_{11}$	−5640.9	naphthalene (*s*)	$C_{10}H_8$	−5156.3

Table 10.1. Standard molar enthalpy of combustion values for representative substances at $T = 25°\text{C}$ and $P = 1$ bar. Common hydrocarbons are shown in the right column.

calculations that can be used to predict how chemical reactions would proceed without the need for additional experimentation. Being able to predict the results of a reaction without actual experimental data is a powerful analytical tool.

Figure 10.7. A bomb calorimeter.

Scientists measure the enthalpy of combustion using a device called—believe it or not—a *bomb calorimeter*. In general, a *calorimeter* is an insulated container with accommodations for measuring the temperature of the contents. Substances at different temperatures are placed inside the calorimeter, and allowed to reach thermal equilibrium without any heat flowing into or out of the calorimeter from the outside. Combined with the known masses of the substances inside the calorimeter, the temperature at thermal equilibrium may be used to determine thermal properties (such as the molar heat capacity) of one of the substances inside. Calculations like this are based on the heat calculations we encountered in Chapter 6 and are not difficult. For simple experiments, a calorimeter can be as rudimentary as an insulated coffee cup with a lid and a thermometer.

The bomb calorimeter used for measuring enthalpy of combustion values is significantly more sophisticated, as the photo in Figure 10.7 shows. The sample to be burned is placed in the steel canister, called a *bomb*. Inside the canister is an electronic ignition source. After being sealed, the air in the canister is replaced with oxygen and the canister is lowered into the larger chamber shown in the figure. The larger chamber contains a precisely measured amount of water at a precisely measured temperature and is insulated to prevent heat flowing in from or out to the outside. The ignition source is used to ignite the sample under test, which burns completely in the presence of pure oxygen. The energy released by the reaction is calculated from the temperature rise of the water in the outer chamber.

10.1.5 Enthalpy of Formation

The reaction shown in Equation (10.2) describes the formation of water from its elements, hydrogen and oxygen. In a manner similar to the enthalpy of combustion, the *molar enthalpy of formation* is defined as *the amount of heat released or absorbed when one mole of a substance is formed from its elements*. As with enthalpy of combustion, enthalpy of formation values are stated assuming that the reactants and products are at standard conditions (25°C, 1 bar) and in their standard states. The notation used for designating enthalpy of formation is

$$\Delta H_f^\circ$$

In this notation, the subscript *f* denotes *formation*.

For most substances, the formation of the substance from its elements is an exothermic reaction, resulting in a negative heat of formation. The enthalpy of formation for water is the same as the enthalpy of combustion of hydrogen (since hydrogen and oxygen are the elements composing water), and so for water

$$\Delta H_f^\circ = -285.8 \ \frac{\text{kJ}}{\text{mol}}$$

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
acetylene (*g*)	C_2H_2	227.4	hydrogen chloride (*g*)	HCl	–92.3
ammonia (*g*)	NH_3	–45.9	hydrogen fluoride (*g*)	HF	–273.3
benzene (*l*)	C_6H_6	49.1	hydrogen iodide (*g*)	HI	26.5
calcium chloride (*s*)	$CaCl_2$	–795.4	methane (*g*)	CH_4	–74.6
carbon monoxide (*g*)	CO	–110.5	methanol (*l*)	CH_3OH	–239.2
carbon dioxide (*g*)	CO_2	–393.5	propane (*g*)	C_3H_8	–103.8
ethane (*g*)	C_2H_6	–84.0	sodium chloride (*s*)	NaCl	–411.2
ethanol (*l*)	C_2H_5OH	–277.6	sucrose (*s*)	$C_{12}H_{22}O_{11}$	–2226.1
ethylene (*g*)	C_2H_4	52.4	sulfur dioxide (*g*)	SO_2	–296.8
glucose (*s*)	$C_6H_{12}O_6$	–1273.3	water (*l*)	H_2O	–285.8
hydrogen bromide (*g*)	HBr	–36.3	water (*g*)	H_2O	–241.8

Table 10.2. Standard molar enthalpy of formation values for representative substances at $T = 25°C$ and $P = 1$ bar. See Appendix B, Table B.7 for a more extensive list.

Considering all we have discussed so far in this text about energy, it should make sense to you that substances with a large negative value for the enthalpy of formation are very stable because a lot of energy is required to undo the formation of the substance. Substances with a small negative value for the enthalpy of formation are relatively unstable, since only a small amount of energy can disrupt the structure of the atoms in such a substance.

Table 10.2 contains enthalpy of formation values for a number of representative substances. As you see, some substances have a positive value for ΔH_f°. The formation of such compounds is endothermic, and the compounds are quite unstable. These compounds can spontaneously decompose or react violently. As examples, hydrogen iodide spontaneously decomposes when stored at room temperature. Acetylene is the gas used with oxygen in the cutting torches welders use to cut through steel. A lot of energy has to be supplied to form acetylene, so the molecules are unstable and combust very violently, releasing a lot of energy as heat in the process. Although it is not listed in the table, mercury(II) fulminate, $Hg(CNO)_2$, has a high positive enthalpy of formation, $\Delta H_f^\circ = 270$ kJ/mol. This substance is very sensitive to shock, which makes it a great detonator to set off larger charges of more environmentally safe explosives (safer, that is, because they don't contain mercury). Interestingly, although mercury(II) fulminate was first prepared in 1800, its crystal structure was not known until 2007. A space-filling model of a portion of the crystal lattice for this compound is shown in Figure 10.8. This compound has made an appearance in a number of popular movies and TV series.

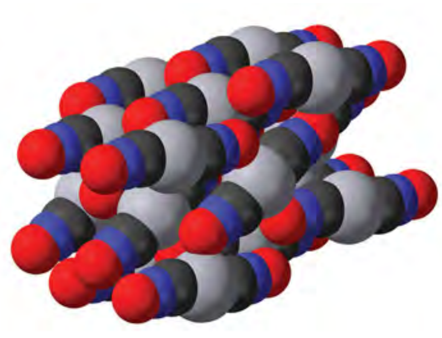

Figure 10.8. Crystal structure of mercury(II) fulminate. Mercury atoms are shown in gray.

The enthalpy of formation for pure elements in their standard states is defined as $\Delta H_f^\circ = 0$. This value applies to molecules for elements that are naturally molecular at standard conditions. Thus, for H_2, O_2, and the other diatomic elements, $\Delta H_f^\circ = 0$. However, the enthalpy of formation for atomic hydrogen, H, is $\Delta H_f^\circ = 218.0$ kJ/mol. To separate an H_2 molecule, energy must be supplied to break the covalent bond in

H_2. If you refer back to Table 3.9, you see that the bond energy for one mole of H_2 is −436.0 kJ. Since two atoms of H are in each H_2 molecule, the heat of formation for a mole of individual H atoms is half this amount (and positive).

The implication of defining the enthalpy of formation for pure elements to be zero is that substances with a negative value for ΔH_f° are more stable than the elements from which they are formed. Compounds with a positive value for the molar enthalpy of formation are less stable than the elements from which they are formed.

10.2 Calculating Enthalpy of Reaction and Enthalpy of Formation

10.2.1 Hess's Law

Hess's law[2] states that *the enthalpy change in a chemical reaction is independent of the pathway the reaction takes*. Another way of stating this principle is that the enthalpy change in a reaction is the same whether the reaction takes place in one step or in many steps. So if we can imagine a sequence of reaction steps that leads, in principle, from the same reactants to the same products as for a single-step reaction, the sum of the enthalpy changes for the individual steps must equal the enthalpy change for the single-step reaction. This important principle can be used to determine the enthalpy of reaction in cases where measuring ΔH is difficult or even impossible. We can use Hess's law to solve for any unknown enthalpy of reaction so long as we know either the enthalpy of combustion values for all the reactants and products, or the enthalpy of formation values for all the reactants and products.

To illustrate the use of Hess's law for such calculations, we calculate the enthalpy of formation for methane gas, CH_4. The elements composing methane are solid carbon (graphite) and hydrogen gas. This means the equation showing the formation of methane from its elements is

$$C(s) + 2H_2(g) \rightarrow CH_4(g) \qquad \Delta H_f^\circ = \ ? \qquad (10.12)$$

For this illustration, *we derive the enthalpy of formation for methane using only enthalpy of combustion values* for the three reactants and products (C, H_2, and CH_4) in Equation (10.12). These three thermochemical equations, with enthalpy values from Table 10.1, are as follows:

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_c^\circ = -393.5 \text{ kJ/mol}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_c^\circ = -285.8 \text{ kJ/mol}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c^\circ = -890.8 \text{ kJ/mol}$$

Notice that the equation for the combustion of hydrogen is written to represent the combustion of one mole of H_2 because the enthalpy of combustion value from Table 10.1 is for a single mole. Writing the equation this way requires the use of a fractional coefficient on O_2.

Our plan now is essentially to *add these equations together* to generate the formation equation for methane, Equation (10.12). To do this, we must arrange the equations so that the desired compounds are on the correct side of the equation in each case. Unwanted terms in the addi-

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[2] American orthography would normally have us write Hess' law. However, the British orthography with the final *s* added is used universally when referring to Hess's law.

tion cancel out if we have the same term (with the same coefficient) appearing on both sides. To assure proper cancellation, it may be necessary to multiply one or more of the equations by a constant. So we are about to make these two preparatory maneuvers before adding the equations: (1) reverse equations and signs on the enthalpy as necessary to get compounds on the correct side according to Equation (10.12), and (2) multiply equations by constants as necessary so that when the equations are added together Equation (10.12) results without any extra terms.

In Equation (10.12), carbon and hydrogen are on the left side. In the first two combustion equations, carbon and hydrogen are on the left, so these equations are fine in this respect. However, methane is on the right in Equation (10.12), so we need to reverse the methane combustion equation to show methane on the right. Recall from earlier in the chapter that when we reverse a thermochemical equation, the sign on the enthalpy of reaction changes.

$$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g) \qquad \Delta H^\circ = 890.8 \text{ kJ/mol}$$

(Note that the enthalpy is now written ΔH°, without the subscript, because written in reverse this is no longer a combustion reaction.)

Now let's list our equations in preparation for adding them together.

$$\begin{array}{ll}
C(s) + O_2(g) \rightarrow CO_2(g) & \Delta H_c^\circ = -393.5 \text{ kJ/mol} \\
H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H_c^\circ = -285.8 \text{ kJ/mol} \\
CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g) & \Delta H^\circ = 890.8 \text{ kJ/mol} \\
\hline
\end{array}$$

When we add these together, we need all the CO_2, H_2O, and O_2 terms to cancel out because none of these compounds appears in Equation (10.12). Let's look at what it takes for this to happen in the case of O_2. We see that if we multiply the entire second equation by 2, the $\frac{1}{2}O_2$ term becomes just O_2, and the O_2 terms on the left add to be equal the $2O_2$ shown on the right, enabling them to cancel out. It turns out that doubling the coefficients on the second equation enables everything to cancel out that needs to cancel out. Accordingly, we multiply this entire equation by 2, *including the enthalpy*. Doing so and canceling out terms that appear on both sides gives us the following set of equations. These we now add together to give the equation at the bottom, which is identical to Equation (10.12).

$$\begin{array}{ll}
C(s) + \cancel{O_2(g)} \rightarrow \cancel{CO_2(g)} & \Delta H_c^\circ = -393.5 \text{ kJ/mol} \\
2H_2(g) + \cancel{O_2(g)} \rightarrow \cancel{2H_2O(l)} & 2\Delta H_c^\circ = 2(-285.8 \text{ kJ/mol}) \\
\cancel{CO_2(g)} + \cancel{2H_2O(l)} \rightarrow CH_4(g) + \cancel{2O_2(g)} & \Delta H^\circ = 890.8 \text{ kJ/mol} \\
\hline
C(s) + 2H_2(g) \rightarrow CH_4(g) & \Delta H_f^\circ = -74.3 \text{ kJ/mol}
\end{array}$$

Adding together the enthalpy values gives us the desired result, the enthalpy of formation of methane, –74.3 kJ/mol. Comparing this value to the one given in Table 10.2, we see a slight difference. This is probably due to rounding in the values stated in Tables 10.1 and 10.2.

Figure 10.9 is an enthalpy diagram that compares the artificially constructed multistep reaction pathway we used in our calculation (Path 1) to the single-step reaction pathway we sought to compute (Path 2). The two pathways are indicated in the figure by yellow circles. Hess's law says that the net enthalpy change is the same for all such paths. This is why we can use the ΔH values for the sequence of three reactions in Path 1 to determine the ΔH for the desired single-step reaction in Path 2. The diagram looks complicated—but ignore the dashed arrows for the moment as we walk through it.

Both pathways begin with solid carbon, C(*s*), at a reference enthalpy of 0 kJ/mol. If you follow the red arrows and yellow circles for each path, you see they both end up at $CH_4(g)$ at $H = -74.3$ kJ/mol.

The simplest path is Path 2. The enthalpy change for the path is what we sought to compute (the unknown). We computed it using Hess's law applied to the sequence of known reactions with known enthalpy of combustion values in Path 1. To follow any path, keep this in mind: the reactants in the reaction we sought to compute are C(*s*) and $2H_2(g)$. We can make use of these reactants in the path whenever we need to. But whenever a path requires other reactants that have not been produced yet, we "borrow" them from the environment for the purpose of our calculation, knowing that we can pay them back later in the reaction sequence. (Since this computation is a mathematical model, we should not be bothered if we need to "borrow" some oxygen for a moment.)

Path 1 begins with a reaction between C(*s*) and $O_2(g)$ because this is the first reaction listed in our computation. (We could take these reactions in any sequence, but I am just taking them in the same order as they are listed in the computation.) So, we borrow one mole of O_2 to begin. This reaction produces $CO_2(g)$, and the change in enthalpy is −393.5 kJ/mol. The second reaction is between $2H_2(g)$ and $O_2(g)$. Thus, we now borrow another mole of O_2 in order to proceed. We don't yet need our CO_2 from the previous reaction, so we will simply bring it with us for later use. This is indicated by the dashed blue arrow. The product of the second reaction is $2H_2O(l)$, with an additional enthalpy change of −571.6 kJ/mol, bringing the total enthalpy change so

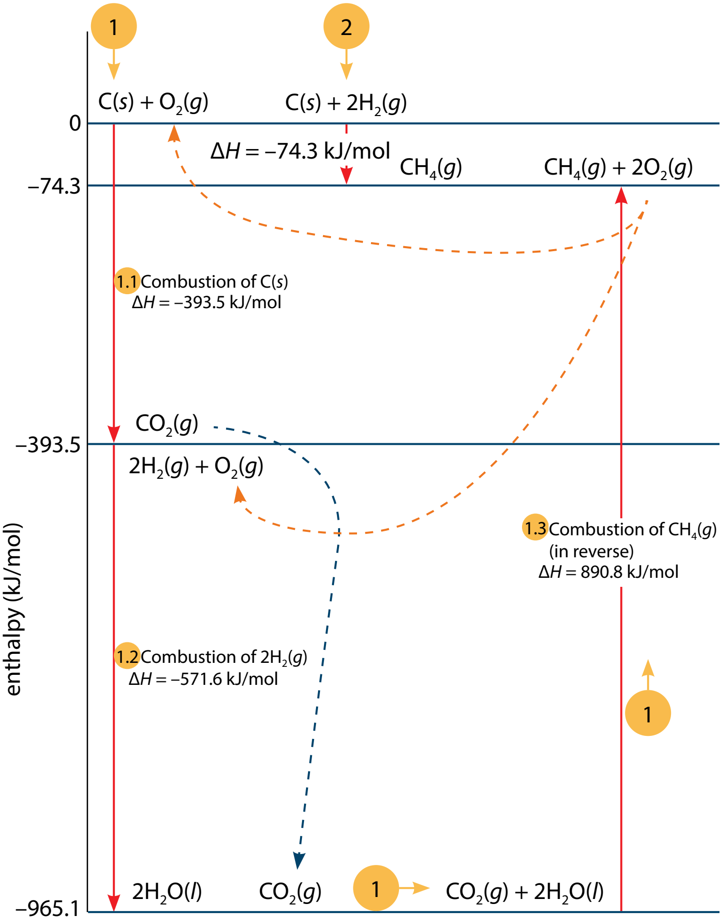


Figure 10.9. Enthalpy diagram comparing the net enthalpy of reaction for two separate pathways leading from C(*s*) + $2H_2(g)$ to $CH_4(g)$. According to Hess's law, the net enthalpy change is the same for all such paths.

far to –965.1 kJ/mol. For the third reaction in Path 1, we take the $CO_2(g)$ and $2H_2O(l)$ produced by the first two reactions, and together they undergo an endothermic reaction to produce $CH_4(g)$ and $2O_2(g)$. This reaction entails an increase in enthalpy of 890.8 kJ/mol, bringing us up to an enthalpy level of –74.3 kJ/mol. Here we are at the end of Path 1. We arrived at $CH_4(g)$, and created two moles of $O_2(g)$ along the way. As shown by the orange dashed arrows, we use these to pay back what we borrowed, leaving us with $CH_4(g)$ and a net enthalpy change of

$$\Delta H_f^\circ = -74.3 \text{ kJ/mol}$$

Now notice what we just did. We calculated the *enthalpy of formation* for CH_4 using only *enthalpy of combustion* data. In the next example, we calculate an *enthalpy of combustion* using only *enthalpy of formation data.*

▼ Example 10.2

Use Hess's law to determine the enthalpy of combustion for propane, given the enthalpy of formation for each of the reactants and products in the thermochemical equation for the combustion of propane:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H_c^\circ = ? \qquad (10.13)$$

The thermochemical equations for the formation of the other three reactants and products are as follows. There is no formation equation for O_2 because the enthalpy of formation for pure elements is zero. Enthalpy of formation values are from Table B.7 in Appendix B.

$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g) \qquad \Delta H_f^\circ = -103.8 \text{ kJ/mol}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_f^\circ = -393.5 \text{ kJ/mol}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f^\circ = -285.8 \text{ kJ/mol}$$

To prepare for adding these together, we must get each compound on the correct side and adjust coefficients so the addition cancels out all unwanted terms. In Equation (10.13), propane is on the left, so we reverse the first equation and change the sign on the enthalpy. Carbon dioxide and water are both on the right in Equation (10.13) and they are also on the right in the formation equations. Reversing the first equation gives us

$$C_3H_8(g) \rightarrow 3C(s) + 4H_2(g) \qquad \Delta H^\circ = 103.8 \text{ kJ/mol}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_f^\circ = -393.5 \text{ kJ/mol}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f^\circ = -285.8 \text{ kJ/mol}$$

Looking now at the coefficients, Equation (10.13) has no $C(s)$ or $H_2(g)$ in it. Multiplying the second equation by three enables the carbons to cancel, and multiplying the third equation by four enables the hydrogens to cancel. Remember, when multiplying an equation by a constant, the enthalpy must be multiplied as well. The following equations show the new coefficients and enthalpies after the multiplications, the cancellations of terms, and the summed equation at the bottom.

$$C_3H_8(g) \rightarrow \cancel{3C(s)} + \cancel{4H_2(g)} \qquad \Delta H^\circ = 103.8 \text{ kJ/mol}$$

$$\cancel{3C(s)} + 3O_2(g) \rightarrow 3CO_2(g) \qquad 3\Delta H_f^\circ = 3(-393.5) \text{ kJ/mol}$$

$$\cancel{4H_2(g)} + 2O_2(g) \rightarrow 4H_2O(l) \qquad 4\Delta H_f^\circ = 4(-285.8) \text{ kJ/mol}$$

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H_c^\circ = -2219.9 \text{ kJ/mol}$$

The bottom equation is identical to Equation (10.13), as required. We calculate the enthalpy of combustion for propane to be –2219.9 kJ/mol. Comparing this to the value listed in Table 10.1, we again see a small difference in the last digit due to rounding.

▲

Notice this important tip from this example: CO_2 and H_2O are compounds that appear in the final equation and each appears only once in the formation equations. When this happens, simply multiply their equations by the coefficients you need in the final equation. Everything else works out. (This tip will come in handy in the exercises.)

An enthalpy diagram for the reaction sequence in Example 10.2 is shown in Figure 10.10. Path 2 represents the combustion of propane, the enthalpy of combustion we sought to compute. Path 1 is the sequence of three reactions we put together using Hess's law. Reactants we can use whenever we need them are the $C_3H_8(g)$ and $5O_2(g)$. As before, the blue dotted arrows indicate reac-

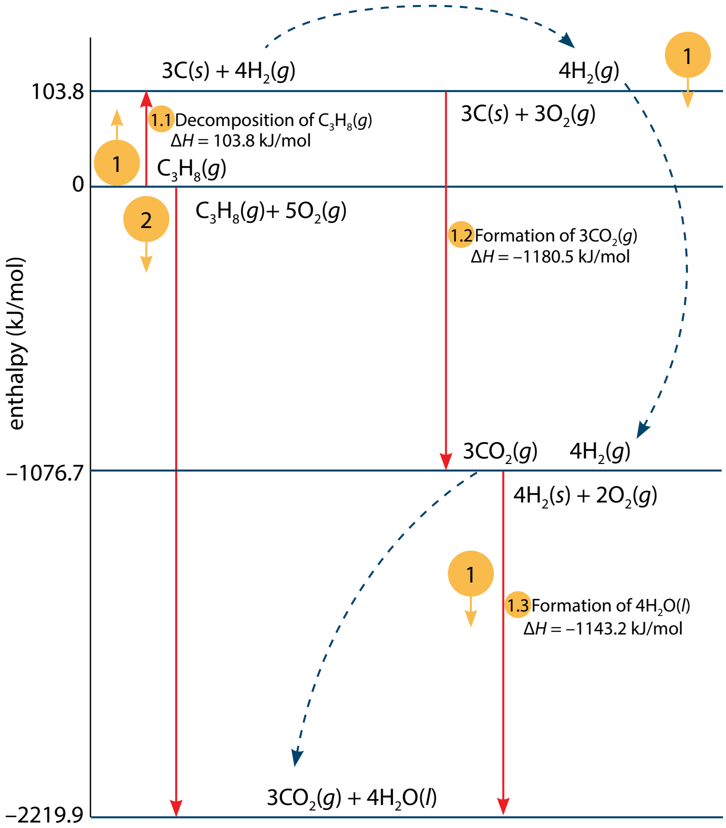


Figure 10.10. Enthalpy diagram comparing the net enthalpy of reaction for two separate pathways leading from $C_3H_8(g) + 5O_2(g)$ to $3CO_2(g) + 4H_2O(l)$.

tion products that we carry along from one step to another until they are needed. No "borrowing" is needed this time.

10.2.2 Hess's Law and the General Enthalpy Change Equation

Recall that Equation (10.1) defines the change of enthalpy for a reaction as the difference between the enthalpy of the products and the enthalpy of the reactants. This relationship may be expressed using the enthalpy of formation values, ΔH_f°, for products and reactants as follows:

$$\Delta H^\circ = \Sigma\Delta H^\circ_{f,\text{products}} - \Sigma\Delta H^\circ_{f,\text{reactants}} \tag{10.14}$$

In this expression, the upper case Greek letter sigma, Σ, means "sum." So this expression tells us that *we can calculate any enthalpy of reaction by summing the enthalpy of formation values for the products, summing the enthalpy of formation values for the reactants, and then taking the difference between these two sums*. This is a powerful computational tool. The entire process of manipulating reactions we just described boils down to the difference between two sums of enthalpy of formation values.

To illustrate, we will revisit Example 10.2, noting that Table B.7 in Appendix B contains an extended list of enthalpy of formation values. The goal is to calculate the enthalpy of reaction for the following reaction:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

We tabulate the ΔH_f° values for the reactants and for the products, recalling that the enthalpy of formation for a pure element in its standard state (such as O_2) is zero. We need to take into account the number of moles for each reactant and product in the equation. Pulling the ΔH_f° values from Appendix B, Table B.7, we have:

	Reactants		Products	
		ΔH_f° (kJ/mol)		ΔH_f° (kJ/mol)
	$C_3H_8(g)$	–103.8	$3CO_2(g)$	3(–393.5) = –1180.5
	$5O_2(g)$	0	$4H_2O\ (l)$	4(–285.8) = –1143.2
Sum (Σ)		–103.8		–2323.7

Now we use Equation (10.14) to compute this enthalpy of reaction:

$$\Delta H^\circ = \Sigma\Delta H^\circ_{f,\text{products}} - \Sigma\Delta H^\circ_{f,\text{reactants}} = \left(-2323.7\ \frac{\text{kJ}}{\text{mol}}\right) - \left(-103.8\ \frac{\text{kJ}}{\text{mol}}\right) = -2219.9\ \frac{\text{kJ}}{\text{mol}}$$

This is the same value we calculated before in Example 10.2.

▼ Example 10.3

Use Equation (10.14) to calculate the enthalpy of reaction for the following reaction:

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$$

Tabulating the enthalpy of formation values from Appendix B, we have:

	Reactants		Products	
		ΔH_f° (kJ/mol)		ΔH_f° (kJ/mol)
	$SiCl_4(l)$	–687.0	$SiO_2(s)$	–910.7
	$2H_2O(l)$	2(–285.8) = –571.6	$4HCl(g)$	4(–92.3) = –369.2
Sum (Σ)		–1258.6		–1279.9

Inserting these two sums into Equation (10.14), we have the following:

$$\Delta H^\circ = \Sigma\Delta H^\circ_{f,\,\text{products}} - \Sigma\Delta H^\circ_{f,\,\text{reactants}} = \left(-1279.9\ \frac{\text{kJ}}{\text{mol}}\right) - \left(-1258.6\ \frac{\text{kJ}}{\text{mol}}\right) = -21.3\ \frac{\text{kJ}}{\text{mol}}$$

10.3 Free Energy

10.3.1 Brief Review of Enthalpy and Entropy

We are now ready to put enthalpy and entropy together into a single law that can predict whether a process spontaneously occurs. As we saw in Chapter 8, the tendency in nature is for processes to go in a direction that decreases potential energy and increases entropy. But these tendencies may or may not point in the same direction, so we need a way to weigh them against each other so we can determine if a reaction occurs or not. The goal of this section is to present the equation that does this. Let's first summarize what we have seen so far about enthalpy and entropy. For enthalpy, we know the following:

Enthalpy Summary

1. For processes at constant pressure, the change in enthalpy, ΔH, is equal to the heat absorbed or released during the process.
2. For exothermic reactions, ΔH is negative; for endothermic reactions, ΔH is positive.
3. Most reactions that occur in nature are exothermic.
4. When an exothermic reaction occurs, heat is released. This means that the potential energy in the molecules of the products is lower than in those of the reactants, so the product molecules are more stable.
5. Nature favors processes in which the enthalpy decreases, but processes in which the enthalpy of a system increases also occur.
6. The First Law of Thermodynamics for constant-pressure processes may be written as $\Delta H = \Delta U + P\Delta V$.

And now, a summary of what we have seen about entropy, along with two new pieces of information added for completeness:

Entropy Summary

1. The entropy of a system is a measure of the disorder or randomness in the system.
2. For every process, the entropy of the universe increases. If the entropy decreases in a certain system, this can only happen by a larger increase in entropy somewhere else. (This is one way of stating the Second Law of Thermodynamics.)

3. Nature favors processes in which the entropy increases, but processes in which the entropy of a system decreases also occur.
4. (New) Entropy is denoted by S, and a change in entropy by ΔS.
5. (New) The entropy of a pure crystalline substance at absolute zero (0 K) is equal to zero. As temperature increases, entropy does as well.

10.3.2 More on Entropy

The last point above about entropy deserves comment. I have described entropy as a measure of the disorder in a system. The mathematical way physicists characterize entropy is by assessing the number of different possible states that are available for a system to be in. In this statement, the term "states" refers to every possible combination of position and velocity available to all the atoms in the system. Since we are talking about the states of atoms, the term scientists use for all these states is *microstates*.[3]

At absolute zero, molecular motion ceases. A perfectly ordered crystal in which there is no movement at all can only be in one state, so there is no randomness at all—no uncertainty at all about where an atom might be or how fast it might be moving. Thus, the entropy of a pure crystal at 0 K is zero.

Now, if the temperature of the crystal is a bit above 0 K, the atoms in the crystal are vibrating. There is not much randomness in this crystal because the atoms are not free to translate, but since there is now a bit of uncertainty associated with the position and velocity of each of the vibrating atoms, there is entropy in the system. In general, the higher the temperature of a system gets, the more entropy there is because there is more randomness—more microstates available to the particles in the system. A large increase in entropy occurs when the substance melts to become a liquid because then the particles are free to move around a bit. And when vaporization occurs, an even larger increase in entropy takes place. In the gaseous state, the velocities of particles are high and the particles are spread out, so the number of microstates available to all the particles in the system is huge. These generalizations about the entropy of a system with respect to temperature are depicted graphically in Figure 10.11.

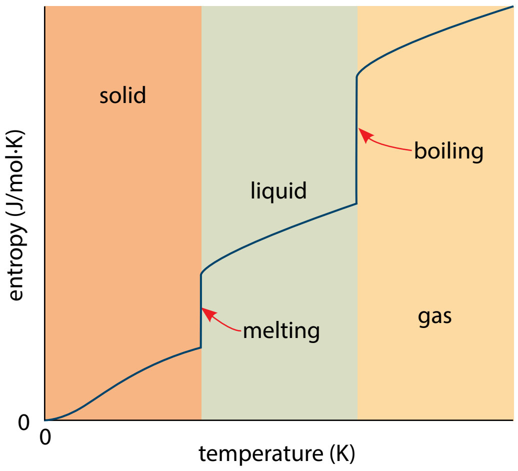


Figure 10.11. Variation of entropy with temperature and phase transitions in a substance.

One more observation we can make about entropy pertains to the numbers of moles indicated by chemical equations. The Haber-Bosch process for the manufacture of ammonia goes according to this equation:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad (10.15)$$

---

[3] It was Ludwig Boltzmann's work in statistical mechanics in the 1870s that led to the equation that quantifies the entropy of a system: $S = k \log W$, where W is the number of microstates available to the particles in a system, and k is the Boltzmann constant, 1.3806×10^{-23} J/K. At Ludwig Boltzmann's grave in Vienna, Austria, this equation is engraved in the marble above a bust of Boltzmann. Nowadays, the equation is typically written $S = k_B \log \Omega$.

We have seen this reaction a few times before. Note that for every four moles of reactants, only two moles of products are produced. This reaction entails a reduction in entropy since there are fewer moles of gas in the products than in the reactants. The next equation represents a process called *steam reforming*, which is used to produce a gas mixture called *syngas*.

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \qquad (10.16)$$

Syngas is a mixture of carbon monoxide and hydrogen used as a fuel and as a precursor for the manufacture of methanol and a number of other industrial substances. The steam reforming reaction is strongly endothermic, but there is also an increase in entropy, since every two moles of reactants produce four moles of gas products. An increase in the number of moles of gas means more microstates are available to the particles in the gas, and thus indicates an increase in entropy.

10.3.3 Gibbs Free Energy

There are three names associated with the foundations of statistical mechanics that you should know. We have already encountered James Clerk Maxwell and Ludwig Boltzmann (Section 6.1.2), who gave us the Maxwell-Boltzmann speed distributions for gas particles. The third is the great American scientist Josiah Willard Gibbs (Figure 10.12). In the 1870s, Gibbs introduced a concept he called "available energy," a quantity based on both the enthalpy and entropy in a system. Today, this quantity is called the *Gibbs free energy* or simply *free energy*. The Gibbs free energy, *G* (J/mol), in a system is defined as

$$G = H - TS \qquad (10.17)$$

In this equation, *H*, *T*, and *S* are the molar enthalpy (J/mol), temperature (K), and molar entropy [J/(mol·K)] of the system. As with enthalpy, the Gibbs free energy cannot be measured directly, but changes in the free energy can be measured. Thus, we work with the change to the Gibbs free energy, ΔG. For processes at constant temperature involving the standard states of reactants and products, Equation (10.17) may be re-expressed as follows:

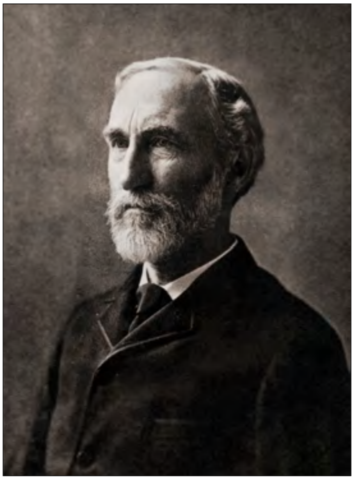


Figure 10.12. American scientist Josiah Willard Gibbs (1839–1903).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (10.18)$$

Spontaneous processes in nature favor energy decreases and entropy increases. The Gibbs free energy equation relates them together, and *spontaneous processes in nature always go in the direction that reduces the Gibbs free energy of the system*. In other words, if ΔG° for a process is negative, the process happens spontaneously. Also, any process in which ΔG° increases at the stated conditions does not occur spontaneously.

Since the absolute temperature is always positive, the terms in Equation 10.17 that determine if ΔG° is negative are ΔH° and ΔS°. Either of these can be positive or negative, and this gives us four possibilities to consider when seeking to determine if a reaction will occur. These are summarized in Table 10.3. First, any exothermic process in which the entropy increases occurs spontaneously. In this case, nature's preferences for minimizing energy and increasing entropy are both being satisfied, and such a process always occurs.

The use of the term "spontaneous" here is the traditional language used to describe a process with a negative value for ΔG°, but the term can be misleading and requires some explanation.

ΔH°	ΔS°	ΔG°	Example
negative (exothermic)	positive (increases disorder)	always negative (spontaneous)	$2O_3(g) \rightarrow 3O_2(g)$
negative (exothermic)	negative (decreases disorder)	negative at lower temperatures (spontaneous at lower temperatures)	$H_2O(l) \rightarrow H_2O(s)$
positive (endothermic)	positive (increases disorder)	negative at higher temperatures (spontaneous at higher temperatures)	$H_2O(s) \rightarrow H_2O(l)$
positive (endothermic)	negative (decreases disorder)	never negative (never spontaneous)	$3O_2(g) \rightarrow 2O_3(g)$

Table 10.3. Four possible combinations of Δ*H* and Δ*S* lead to the different possibilities for the sign of Δ*G*.

The fact that the Gibbs free energy is negative means that a chemical reaction will occur *so long as the activation energy is present to initiate the reaction*. (We address activation energy in just a few pages.) Reactions such as fuel combustion always have a negative value for ΔG°, but fuels generally don't ignite "spontaneously" (for which we are thankful). A spark or flame is required to initiate the reaction; after that it goes by itself.

The last row in the table is for the opposite case—enthalpy increases and entropy decreases. Such a process never occurs spontaneously because it goes against the natural tendencies of both the enthalpy and entropy. (Such process can be made to occur only by supplying enough energy to drive the process, which increases entropy even more somewhere else.) The two middle rows deal with the cases in which the enthalpy and entropy pull in opposite directions. The deciding factor in each of these scenarios is the temperature because it multiplies the change in entropy and thus determines how significant the entropy contribution is to the Gibbs free energy. Note that in cases such as the phase transition examples shown in the table, the process does occur literally spontaneously. No activation energy is needed to make an ice cube melt; it just happens.

▼ Example 10.4

For the steam reforming reaction to make syngas, shown in Equation (10.16), ΔH° = 206.1 kJ/mol and ΔS° = 0.215 kJ/(mol·K). Determine if this reaction will occur at standard temperature, 298 K.

We use Equation (10.18) to compute the change in the Gibbs free energy for this process, ΔG°. If it is negative, then the reaction occurs.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 206.1\ \frac{\text{kJ}}{\text{mol}} - 298\ \text{K} \cdot 0.215\ \frac{\text{kJ}}{\text{mol} \cdot \text{K}} = 142.0\ \frac{\text{kJ}}{\text{mol}}$$

At standard temperature, the Gibbs free energy increases for this process. Thus, the reaction does not occur spontaneously.

▲

▼ Example 10.5

The equation for the decomposition of ammonium chloride to ammonia and hydrogen chloride is as follows:

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

Given ΔH° = 176 kJ/mol and ΔS° = 285 J/(mol·K), address the following questions about this process:

1. Will the reaction occur spontaneously at standard conditions?
2. What is the effect of increasing the temperature?
3. Is the given value for ΔS° consistent with the reaction equation shown above?

To answer the first question, we need to calculate the change in the Gibbs free energy. The temperature for standard conditions is 25°C, or 298 K. Note that the value for ΔS° is given in J/(mol·K). This must be changed to 0.285 kJ/(mol·K) to make the energy units consistent.

Using Equation (10.18) and the given information, we calculate the change in the Gibbs free energy for this process as follows.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 176\ \frac{\text{kJ}}{\text{mol}} - 298\ \text{K} \cdot 0.285\ \frac{\text{kJ}}{\text{mol} \cdot \text{K}} = 91\ \frac{\text{kJ}}{\text{mol}}$$

The change in the Gibbs free energy is positive, indicating that this reaction does not occur spontaneously at 25°C.

A note about the significant digits in the calculation may be in order here. The product of 298 K and 0.285 kJ/(mol·K) is 84.93 kJ/mol. When this value is subtracted from 176 kJ/mol, the decimal places are all lost because of the addition rule for significant digits. Thus, the result is 91 kJ/mol.

Regarding the second question, we note that although this reaction is endothermic, the entropy change is positive. Thus, at a high enough temperature, the product $T\Delta S$ will be larger than ΔH, making ΔG° negative and enabling the reaction to occur.

Regarding the third question, the reaction equation indicates that one mole of a solid reactant forms two moles of gaseous products, indicating an increase in entropy. Since ΔS° is positive, it is consistent with the equation.

▲

Three more important points remain to be made in this section. First, the mere fact that the Gibbs free energy is negative says nothing about the rate at which a reaction occurs. For the reaction below, $\Delta G^\circ = -3.3\ \text{J}/(\text{mol} \cdot \text{K})$, and thus the reaction is favorable:

$$C(s, \text{diamond}) \rightarrow C(s, \text{graphite})$$

However, the reaction takes place so slowly it is never observed.

Second, make note of this: *the general principle embedded in Equation (10.14) may be used to calculate ΔS° for any reaction*. Data for S° are tabulated in standard reference sources for thousands of standard compounds, including Table B.8 in Appendix B. Thus, ΔS° for any reaction may be calculated as

$$\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$$

The method for calculating ΔS° is the same as that illustrated in Example 10.3. You simply tabulate standard molar entropy values for products and reactants, multiply each by the number of moles in the equation, determine the two sums, and take the difference of the two sums. Thus, one can easily determine whether the reaction entails an increase or decrease in entropy. Make note, though, that *standard entropy values are usually given in J/(mol·K) rather than kJ/(mol·K)*, so you have to watch out for the need to convert the units.

Third, the same idea applies to calculating the change in the Gibbs free energy. Data for the standard *free energy of formation*, ΔG°_f, are tabulated in reference sources for common compounds, including Table B.9 in Appendix B. Just as with the change in enthalpy in Equation (10.14), the change in the Gibbs free energy, ΔG°, for any reaction may be calculated as

$$\Delta G^\circ = \Sigma \Delta G^\circ_{f,\text{products}} - \Sigma \Delta G^\circ_{f,\text{reactants}}$$

Of course, ΔG° may also be calculated according to Equation (10.18), where ΔH° and ΔS° are calculated from standard enthalpy of formation and entropy data as described above.

10.4 Reaction Kinetics

One of the goals of research in chemistry is to understand more precisely what actually happens during a chemical reaction. Such research seeks answers to questions like these: How exactly does chemical species *A* get transformed into chemical species *B*? Does the transformation happen all at once or in a sequence of steps? What factors govern how fast a reaction occurs? What are the physical mechanisms of such factors? The subject of the physical mechanisms of reactions and factors that govern the rates of chemical reactions is known as *reaction kinetics*. In this section, we take a brief tour of these topics.

10.4.1 Collision Theory

Collision theory is a general term that refers to our present understanding of chemical reactions at the molecular level. The essential idea behind collision theory is that chemical reactions occur when molecules of different chemical species collide. However, just because molecules jostle around together does not mean a chemical reaction occurs. You can pour gasoline on the ground but it does not begin reacting with the oxygen in the air (combustion) without a source of ignition.

When molecules collide, the clouds of electrons in the orbitals surrounding the atoms repel each other with a great deal of force. In order for a chemical reaction to occur, a molecular collision must involve enough energy to force the molecules close enough together that existing bonds between atoms can be broken and new bonds formed. Not only does this require enough energy; it also requires that the molecules have the right orientation in space at the moment they collide. For example, the steam reforming reaction shown in Equation (10.16) is depicted in Figure 10.13. On the left side of the figure, the CH_4 and H_2O molecules collide and bounce apart because the orientation of the H_2O molecule is not favorable relative to that of the CH_4 molecule. On the right side of the figure, the H_2O molecule is oriented so that the oxygen atom can disrupt the bonds in both molecules and bond with the carbon atom in CH_4 to produce one molecule of CO.

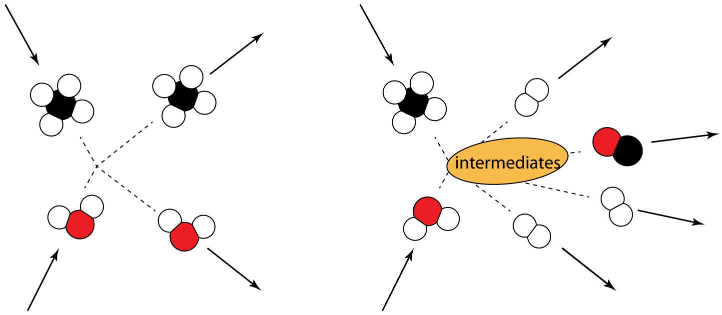


Figure 10.13. If molecular orientation is not favorable, a molecular collision may not result in a reaction (left). A different orientation of molecules may enable a reaction to occur (right). During the reaction, intermediate species form as part of the steps in the reaction mechanism.

The right side of Figure 10.13 also indicates that during the reaction, intermediate species form that are not part of the product species. We return to considering *intermediates* shortly.

10.4.2 Factors Influencing Reaction Rate

The *reaction rate* of a chemical reaction is the rate at which the concentrations of reactants and products are changing. Based on collision theory, there are four important factors we can control that can influence the rate of chemical reactions. These are as follows:

1. *Temperature*

   As you know, the higher the temperature of the reactants, the higher the kinetic energy of the moving particles. At higher speeds, molecules collide more frequently, providing more opportunities for the favorable orientations that lead to the breaking of bonds and formation of new bonds. Note that increasing the temperature only increases the reaction rate if the temperature is high enough for the reaction to commence. We discuss this issue more in Section 10.4.4.

   On rare occasions, higher temperatures can decrease a reaction rate. This can occur, for example, if the higher temperature increases the reverse reaction rate at the expense of the forward reaction rate. We see an example of this in the next chapter, Section 11.1.4.

2. *Surface Area*

   As a factor in chemical reactions, the surface area of solid reactant applies to *heterogeneous reactions*—reactions in which there is more than one state of matter represented among the reactants. A solid reactant that is to react with a liquid or gas has a certain surface area exposed to the liquid or gas reactant. According to collision theory, reactions happen through collisions, so the larger the surface area of the solid reactant, the more the atoms in the solid are exposed to collisions from the fluid reactant molecules.

   A 1-cm cube of solid material has a surface area of 6 cm^2. If the same amount of material is ground to small particles with grains that are also cubes but with side lengths of 0.1 mm, the total surface area of the solid is 600 cm^2. The finer the grains in the powder, the larger the total surface area of the solid.

   Sawdust, coal dust, and powderized aluminum are all examples of substances that may not sound all that dangerous but which can explode violently in a so-called *dust explosion*. In all these cases, the explosion happens because of the enormous surface area provided by a reactant consisting of small particles. If the dust forms a suspension in air, explosive conditions result. Sawdust is essentially powdered carbon, as is coal dust. A spark in a dusty woodworking shop or coal mine has often led to a tragic explosion. Dust from dry grain, flour, powdered milk, and other sources of carbon can produce the same explosive suspension in air. Both aluminum and titanium metals will also form explosive suspensions in air when in powdered form.

3. *Concentration*

Since chemical reactions occur by means of molecular collisions, the more particles of reactant species there are available, the faster a reaction occurs. When one or more of the reactants are in a solution of liquid or gas, the higher the concentrations of those reactants are, the more molecules there are in the solution to react.

As an example, oxygen accounts for about 21% of the gas molecules in the air. At the same pressure, the concentration of oxygen molecules in pure oxygen gas is nearly five times the concentration in air. As a result, a combustion reaction fueled by pure oxygen occurs much faster than the same reaction in air, releasing heat energy at the same increased rate. We have seen that acetylene is an unstable molecule with a large positive enthalpy of formation (Table 10.2). When this gas is combined with pure, high-pressure oxygen and ignited, we have a combustion reaction that gives off so much heat so rapidly that the flame can be used for cutting steel, as illustrated in Figure 10.14. The oxyacetylene torch shown has two separate gas tubes arriving at the nozzle, one for the C_2H_2 and one for the O_2. The two gases are stored in separate steel storage tanks.

Figure 10.14. The flame from an oxyacetylene torch cuts right through steel plate.

The reaction between oxygen and acetylene is an example of a *homogeneous reaction*—one in which all the reactants are in the same state (gas in this case).

4. *Catalysis*

A *catalyst* is a substance that expedites or facilitates a chemical reaction without itself being consumed by the reaction. The process by which a catalyst influences the rate of a chemical reaction is known as *catalysis*. Metals often act as catalysts because of a phenomenon known as *adsorption*. Adsorption is the collection of molecules on a surface, attracted there by electrostatic attraction or Van der Waals forces. When reactant molecules adsorb onto the surface of a catalyst, the surface forces cause reactant molecules to separate into individual atoms, at which time they are free to bond to other atoms to form new molecules.

The presence of iron as a catalyst is the key that allows the formation of NH_3 in the Haber-Bosch process. After the N_2 and H_2 molecules adsorb onto the surface of the iron, the diatomic molecules of nitrogen and hydrogen come apart and individual atoms of nitrogen and hydrogen form on the metal surface. After that, hydrogen atoms begin bonding with nitrogen atoms, building up NH_3 molecules by adding one hydrogen atom at a time. The catalyst works by providing a completely different energy pathway, significantly reducing the energy required to make the reaction occur. We will look at this energy pathway more closely shortly.

A catalyst that is in the same state as the reactants in a chemical system is referred to as a *homogeneous catalyst*. A catalyst in a different state, such as the metal catalyst used with the gases in the Haber-Bosch process reaction, is called a *heterogeneous catalyst*. Note that in reversible reactions such as equilibrium systems, a catalyst increases the reaction rate equally in both directions.

10.4.3 Reaction Mechanisms

Experimental evidence now strongly supports the theory that chemical reactions almost never take place in one simple step. Instead, reactions typically require several separate steps in which the bonds of reactant molecules are rearranged into the bonds of the product molecules. The sequence of steps in which a reaction takes place is called the *reaction mechanism*. A reaction mechanism is a *model* depicting a sequence of steps and *intermediates* involved in a chemical reaction. As mentioned above, intermediates are chemical species that form temporarily during the reaction, but which are not part of the net reaction equation.

As an example, when hydrogen gas, H_2, and iodine gas, I_2, are combined in a sealed container, the gases form the following equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Hydrogen and hydrogen iodide are both colorless gases; iodine gas is purple. At equilibrium, all three gases are present in the container. By means of some ingenious experimental techniques—which include hitting the molecules with certain wavelengths of light—scientists discovered that the H_2 and I_2 molecules do not simply come apart and recombine to form HI gas. Instead, various intermediates are involved.

Figure 10.15 shows three different reaction mechanisms that have been proposed as models for this reaction. All three begin with the formation of individual atoms of iodine, an intermediate. In the first mechanism, the dissociated iodine atoms interact with H_2 to form HI. In the second mechanism, the intermediate I atoms form H_2I, another intermediate, before finally forming HI. In the third mechanism, the dissociated I atoms attach to either side of the H_2 molecule to form yet another intermediate, IH_2I. The attached iodine atoms then cause the breaking of the H_2 bond, leaving separate molecules of HI.

As another example, consider again the Haber-Bosch process. The reaction mechanism for this process, as presently understood, is shown in Figure 10.16 on the next page. This diagram is a combination enthalpy diagram, such as we saw in Figures 10.9 and 10.10, and energy pathway diagram, such as those shown in Figure 10.2. The figure ties together many of the concepts we have already studied in this chapter, as well as a couple of ideas we haven't even gotten to yet, so let's take the time to look it over carefully.

The diagram begins on the left with N_2 and H_2 gas and ends on the right with NH_3. Two different energy pathways are shown. Notice that as Hess's law predicts, the total enthalpy change for the reaction (ΔH = –46 kJ/mol) is the same regardless of the energy pathway. It just happens that one pathway is feasible for an industrial process and the other is not.

The upper path models the way the reaction might proceed without the metal catalyst. The first step is a huge en-

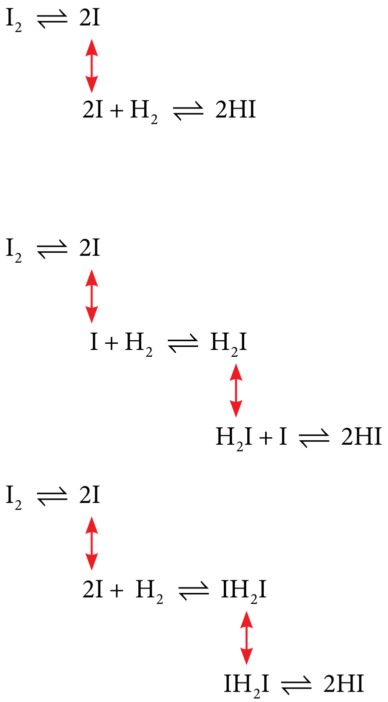


Figure 10.15. Three proposed reaction mechanisms for the formation of HI gas from H_2 and I_2.

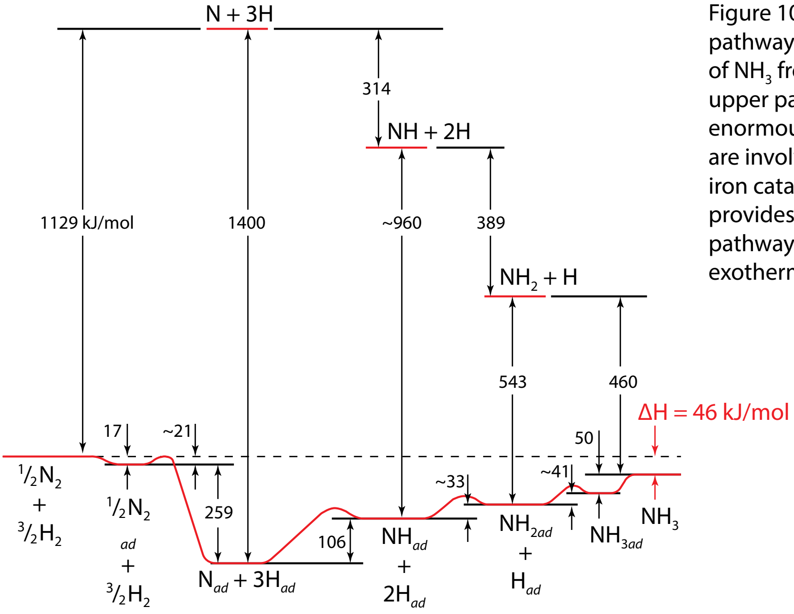


Figure 10.16. Energy pathways for the formation of NH_3 from N_2 and H_2. The upper pathway indicates the enormous enthalpies that are involved without the iron catalyst. The catalyst provides a different energy pathway which is initially exothermic.

dothermic reaction, in which 1,129 kJ/mol of heat must be supplied to break the N_2 triple bond and the H_2 bonds. This produces separate atoms of N and H, which are intermediates. Afterwards, a sequence of exothermic steps leads to the net enthalpy change of $\Delta H = -46$ kJ/mol. In these exothermic steps, hydrogen atoms are added one at a time to the nitrogen to form the intermediates NH and NH_2, and then finally NH_3.

Look now at the fascinating energy pathway at the bottom of the figure, which shows the mechanism for the catalyzed process. The first step is the adsorption (*ad*) of the N_2 and H_2 molecules on the surface of the metal catalyst. Next, while adsorbed on the metal surface, the diatomic molecules separate and this separation is actually *exothermic* under these conditions (!). So instead of having to supply the reactants with 1,129 kJ/mol of heat to break apart the N_2 and H_2 molecules, only about 21 kJ/mol have to be supplied to get over the little energy hump there (more on that soon) and then the molecules release 259 kJ/mol as they dissociate while adsorbed on the catalyst surface. This forms the adsorbed N and H intermediates. From here, several small endothermic steps lead to the intermediates NH and NH_2, and then finally to NH_3. Notice that all these steps occur while the molecules are still adsorbed on the catalyst. Only after the NH_3 molecules are formed is a final boost of heat supplied (50 kJ/mol) to remove the NH_3 molecules from the catalyst and form them into NH_3 gas. The net enthalpy change for this pathway is the same as for the other energy pathway, and the same intermediate species are formed. But with the intermediates adsorbed onto the catalyst, the energies involved are quite different.

10.4.4 Activation Energy and the Activated Complex

Look again at the lower energy pathway in Figure 10.16. Before each energy transition, the reactants need a small energy boost in order for the next step in the reaction to commence. This small energy boost is seen for both exothermic transitions and endothermic transitions.

Figure 10.17 shows an enlarged view of generic energy pathways for both exothermic and endothermic reactions. To commence the reaction, an amount of energy labeled E_a or E_a' must be supplied. This energy is the *activation energy*, E_a (or E_a'), roughly defined as *the amount of energy required to initiate the chemical reaction*. Depending on the specifics of the reaction, the activation energy may be supplied by heating, a spark, a flame, an electrical current, or even by mechanical means such as physical shock or compression (which supplies energy to a gas by

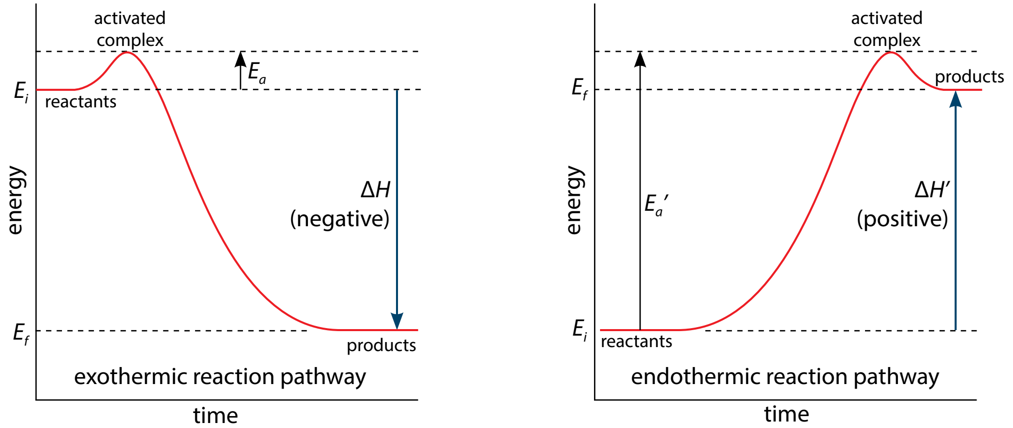


Figure 10.17. To initiate the exothermic or endothermic reaction, the activation energy E_a or E_a' must first be supplied. E_a is the energy required to form the activated complex. Once the activated complex is formed, the reaction commences.

doing work on the gas). However the activation energy is supplied, its effect is to increase the temperature, giving the molecules the kinetic energy they need so that effective molecular collisions occur with enough force to break molecular bonds. Current theory holds that when these effective, energetic collisions occur, a so-called *activated complex* results. An activated complex is a range of transitional molecular structures of partially formed bonds that results from an effective molecular collision with adequate energy. The activated complex lasts only while bonds are in the process of breaking and reforming. The formation of the activated complex is shown in Figure 10.17 at the peak of the energy curve; once this peak is reached and the activated complex forms, the reaction commences. The formation of the activated complex gives us a more nuanced definition for the activation energy: *the activation energy is the minimum energy necessary to transform the reactant molecules into the activated complex for a given reaction.*

Figure 10.17 displays separate diagrams for exothermic and endothermic reactions. However, these diagrams can also be interpreted as representing the energy pathways for the forward and reverse directions in a single reversible reaction. In the exothermic reaction, the total energy change from the energy of the activated complex to the energy of the reaction products is

$$E_a - \Delta H = E_a + |\Delta H|$$

This amount of energy becomes the activation energy, E_a', for the reverse reaction.

$$E_a' = E_a + |\Delta H|$$

The energy required to form the activated complex is the same in either direction. But the energy that must be supplied to the reactants, E_a or E_a', depends on the energy the reactants are starting with.

In some cases, the reactants already have enough energy at room temperature to form an activated complex. Just pour a bit of vinegar into some baking soda and watch what happens—no additional heating is necessary. But in a great many cases, an extra amount of energy must be supplied. As an example, when there is a natural gas leak, why doesn't the gas spontaneously combust when coming in contact with the air? The reason is that although the reactants (methane and oxygen) are together, the activation energy has not been supplied. An open flame might be enough to do the job. Another example is illustrated in Figure 10.18. I hope you have seen

Figure 10.18. Burning magnesium, which lights with a butane lighter, but not with a match.

the bright light of burning magnesium before because the picture doesn't do it justice. One thing I always point out to my students when performing this demonstration is that the magnesium does not ignite with a match, but it does light with a butane gas-grill lighter. The flame of the burning match is not as hot as the butane flame, so it does not produce enough heat to supply the activation energy. I also like to note that the flame always goes out when it is about 1/4 inch from the pliers I use to hold the strip of magnesium metal. The pliers are metal and conduct heat pretty well, cooling the magnesium metal strip. When the flame gets close enough to the pliers, the pliers conduct heat away from the flame so fast that the energy supplied by the flame falls below the activation energy needed to keep the reaction going. Without the requisite amount of energy, the activated complex cannot form and the reaction does not happen.

Now that we have introduced the concepts of reaction mechanism and activation energy, let's return for a moment to the general topic of how catalysts work. Figure 10.19 compares the energy pathway for a single-step exothermic reaction to the alternative, three-step energy pathway provided by the presence of a catalyst. Instead of the large activation energy, E_a, required to initiate the single-step process, the catalyst lowers the activation energy by providing an alternative reaction mechanism. In the generic case shown in the figure, the alternative mechanism consists of three separate reaction steps, each with its own activation energy. But since none of these activation energies is as great as the activation energy in the pathway without the catalyst, the catalyst allows the desired reaction to occur more expeditiously. We saw in the case of the iron catalyst used in the Haber-Bosch process that surface attractions between metal atoms and adsorbed particles reduce the energy required to break apart molecular bonds in the reactants, so much so that the reactant dissociation actually becomes exothermic. Endothermic steps occur after that as the product molecules begin to form, but again energy requirements are substantially lower than the energy required to break apart reactant molecules without the catalyst.

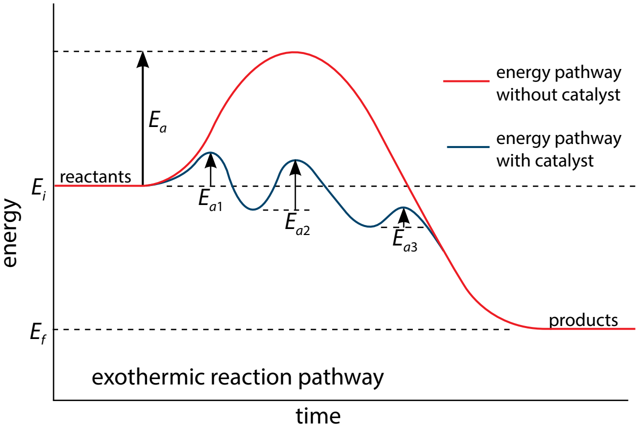


Figure 10.19. The catalyst provides an alternative energy pathway for the reaction with lower activation energy. The alternative path shown entails a three-step reaction.

10.4.5 Reaction Rate Laws

A few pages back, we saw that the concentration of reactants in solution affects the rate of the reaction. In referring to reaction rate, we are referring to the rate at which the molarity of the reactants and products are changing per unit time. This means that the reaction rate, *R*, of a chemical reaction has units of *M*/s, molarity per second.

Consider the reaction between ammonium and nitrite ions to form nitrogen and water:

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l) \tag{10.19}$$

This reaction has two reactants. One of the ways to investigate the effect of concentration on the reaction rate is to vary the concentration of one reactant while holding the concentration of the other reactant constant. For the reaction above, experiments have shown that the reaction rate, *R*, is directly proportional to the NH_4^+ concentration, $[NH_4^+]$. This means that if $[NH_4^+]$ is doubled or tripled, the rate of the reaction doubles or triples, respectively. We model this relationship algebraically as:

$$R = k\left[NH_4^+\right]$$

As we have seen before, *k* is a constant of proportionality. Thus, this expression says that the reaction rate, *R*, is directly proportional to the ammonium ion concentration.

It has also been found experimentally that for the reaction in Equation (10.19), the following holds:

$$R = k\left[NO_2^-\right]$$

Or, in words, the reaction rate is directly proportional to the nitrate ion concentration. Combining these two expressions gives

$$R = k\left[NH_4^+\right]\left[NO_2^-\right] \tag{10.20}$$

Equation (10.20) is an example of a *rate law*—a mathematical expression that characterizes reaction rates in terms of the concentrations of the reactants. The constant *k* is known as the *rate constant*. The units for the rate constant are such as to allow the reaction rate to have units of *M*/s. (The units for *k* are illustrated in the next example.)

In general, we can consider a generic chemical equation such as the following:

$$aA + bB \rightarrow cC + dD \tag{10.21}$$

The reaction rate law for such a reaction is of the following form:

$$R = k[A]^m[B]^n \tag{10.22}$$

In Equation (10.22), the terms in square brackets are the concentrations of the reactants. The exponents *m* and *n*, as well as the rate constant *k*, must be determined experimentally. The values of the exponents *m* and *n* are typically 0, 1, or 2. In Equation (10.20), the exponent on both concentrations is 1, so we say that "the reaction rate is first-order in $[NH_4^+]$" and "the reaction rate is first-order in $[NO_2^-]$." When two first-order terms are multiplied in a rate law, the overall rate law is second order—the orders on the individual terms add together to make the overall rate law order.

Note that the rate constant, *k*, is a *constant* at a given temperature, but the concentrations and reaction rate are clearly not. From the initial concentrations, these vary exponentially (at least, for first-order reactions), decreasing from their initial concentrations and finally stabilizing at their equilibrium concentrations. But once we know the rate law, we can calculate the rate for any given set of concentrations.

Example 10.6

Use the rate data in Table 10.4 to derive the rate law and rate constant for the reaction of ammonium and nitrate ions in water.

Trial	$[NH_4^+]$, initial (M)	$[NO_2^-]$, initial (M)	R, Initial (M/s)
1	0.0050	0.100	1.35×10^{-7}
2	0.0100	0.100	2.70×10^{-7}
3	0.0200	0.100	5.40×10^{-7}
4	0.100	0.0100	2.70×10^{-7}
5	0.100	0.0200	5.40×10^{-7}
6	0.100	0.0300	8.10×10^{-7}

Table 10.4. Rate data for the reaction of ammonium and nitrite ions in aqueous solution (25°C).

Looking at trials 1 and 2, we see that when the initial value of $[NH_4^+]$ is doubled while holding $[NO_2^-]$ constant, the initial reaction rate doubles. Trials 1 and 3 show us that when $[NH_4^+]$ is increased by a factor of four ($[NO_2^-]$ constant), the initial rate increases by the same factor. From these data, we see that the reaction rate is first order in $[NH_4^+]$, or

$$R = k\left[NH_4^+\right]$$

Looking at trials 4 and 5, we see that when $[NO_2^-]$ is doubled ($[NH_4^+]$ constant), the initial rate doubles. Trials 4 and 6 show that when $[NO_2^-]$ is tripled ($[NH_4^+]$ constant), the initial rate increases by the same factor. From these data, we see that the reaction rate is first order in $[NO_2^-]$, or

$$R = k\left[NO_2^-\right]$$

We now know that the rate law is of the form

$$R = k\left[NH_4^+\right]\left[NO_2^-\right]$$

To determine the rate constant, we solve the rate law for k and insert experimental data from one of the trials. Data from any trial gives the same value for k. We will use data from trial 2 so that all values have three significant digits.

$$k = \frac{R}{\left[NH_4^+\right]\left[NO_2^-\right]} = \frac{2.70\times10^{-7}\ \frac{M}{\text{s}}}{(0.0100\ M)(0.100\ M)} = 2.70\times10^{-4}\ M^{-1}\text{s}^{-1}$$

The complete rate law is found to be

$$R = 2.70\times10^{-4}\ M^{-1}\text{s}^{-1}\left[NH_4^+\right]\left[NO_2^-\right]$$

10.4.6 Rate Laws and Reaction Mechanisms

The form and order of a reaction rate law is determined by the reaction mechanism. For a single-step reaction, the powers m and n on the reactant concentrations are equal to the coefficients on the reactants. Thus, if Equation (10.21) represents a single-step reaction, the rate law is

$$R = k[\mathrm{A}]^a[\mathrm{B}]^b$$

However, if a reaction takes place by means of a multistep mechanism, the steps occur at different rates and one of the steps occurs more slowly than the others. This step is referred to as the *rate-determining step*. The rate-determining step determines the rate law, and the coefficients on the reactants in the rate-determining step form the powers on the terms in the rate law. This is a powerful clue that helps chemists figure out the actual reaction mechanism.

For example, consider the following reaction:

$$\mathrm{CO}(g) + \mathrm{NO_2}(g) \rightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g) \qquad (10.23)$$

It has been found experimentally that the rate law for this reaction is

$$R = k[\mathrm{NO_2}]^2$$

This rate law is second order in $[\mathrm{NO_2}]$ and doesn't depend on [CO] at all. The fact that the rate law in this case is second order in $[\mathrm{NO_2}]$ implies that the reaction in Equation (10.23) is a multistep reaction, and that its rate-determining step begins as follows:

$$2\mathrm{NO_2} \rightarrow$$

We conclude this because, as mentioned above, the rate law for a single-step reaction is formed by multiplying the reactant concentrations together and raising each one to a power that is the same as the coefficient on that reactant. In fact, the mechanism proposed for the reaction in Equation (10.23) is the following:

step 1: $2\mathrm{NO_2} \rightarrow \mathrm{NO_3} + \mathrm{NO}$ (slow)
step 2: $\mathrm{NO_3} + \mathrm{CO} \rightarrow \mathrm{NO_2} + \mathrm{CO_2}$ (fast)

▼ Example 10.7

Nitrogen dioxide reacts with fluorine as follows:

$$2\mathrm{NO_2}(g) + \mathrm{F_2}(g) \rightarrow 2\mathrm{NO_2F}(g)$$

A proposed mechanism for the reaction is the following two-step sequence:

step 1: $\mathrm{NO_2} + \mathrm{F_2} \rightarrow \mathrm{NO_2F} + \mathrm{F}$ (slow)
step 2: $\mathrm{F} + \mathrm{NO_2} \rightarrow \mathrm{NO_2F}$ (fast)

Identify the rate-determining step and propose a rate law for the reaction of nitrogen dioxide and fluorine.

The rate-determining step in a multistep reaction is the slowest step. Thus, the first step in the proposed mechanism is the rate-determining step. From this reaction step, the rate law is

$$R = k[\mathrm{NO_2}][\mathrm{F_2}]$$

▲

Example 10.8

Consider the reaction between nitric oxide and hydrogen:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

From experiments, the rate law for this reaction has been found to be

$$R = k[NO]^2[H_2]$$

Address these questions:

1. What is the reaction order for this rate law?
2. If the concentration of H_2 is doubled, what is the effect on the reaction rate?
3. If [NO] is tripled, what is the effect on the reaction rate?

The rate law is second order in [NO] and first order in $[H_2]$. We add these together to get the overall order of the rate law. This rate law is third order.

The rate law is first order in $[H_2]$. Thus, doubling $[H_2]$ doubles the reaction rate.

The rate law is second order in [NO]. Tripling [NO] increases the reaction rate by a factor of $(3)^2 = 9$.

Chapter 10 Exercises

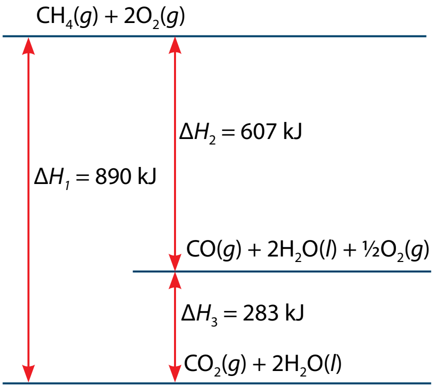
SECTION 10.1

1. Describe how a thermochemical system might do mechanical work. Consider (a) a gas in a cylinder, and (b) reaction products in the open air.
2. Why is ΔH negative for an exothermic reaction?
3. Use the first law of thermodynamics to distinguish between the change in enthalpy and the change in internal energy of a thermochemical system during a reaction.
4. Use the enthalpy diagram shown on the next page to address the following questions.
    a. Is the reaction $CO_2(g) + 2H_2O(l) \rightarrow CO(g) + 2H_2O(l) + \frac{1}{2}O_2(g)$ exothermic or endothermic?
    b. What is the enthalpy change for $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$?
    c. Write the thermochemical equations, including the enthalpy change, for the three endothermic processes represented in the diagram.
5. Distinguish between enthalpy of combustion and enthalpy of formation.
6. Why is it important to specify the states of the compounds in a thermochemical equation?

SECTION 10.2

7. Use the enthalpy diagram shown below as an example to explain Hess's law.
8. What practical advantages are there to being able to use Hess's law to compute the enthalpy of reaction for a given process?

9. For each of the following compounds, write the reaction illustrating the formation of the compound from its elements. Show the enthalpy of formation with each equation (see Appendix B, Table B.7 for enthalpy of formation data).
   a. $C_2H_2(g)$
   b. $Li_2SO_4(s)$
   c. $SO_3(g)$
   d. $NH_3(g)$



10. Use the method illustrated in Example 10.2 to determine the enthalpy of reaction for each of the following reactions. In each case, solve by using enthalpy of formation data from Appendix B.
    a. $NO(g)+\frac{1}{2}O_2(g) \rightarrow NO_2(g)$
    b. $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
    c. $Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$
    d. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
    e. $Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(l)$
11. Use Equation (10.14) and the method illustrated in Example 10.3 to verify your results for the five reactions in the previous item.
12. Determine the enthalpy of formation for the following compounds. Solve by using enthalpy of combustion data from Table 10.1. (No combustion equation is required for O_2.)
    a. ethylene, $C_2H_4(g)$
    b. formic acid, $CH_2O_2(l)$
    c. benzene, $C_6H_6(l)$
13. In a combustion reaction at standard conditions, each of the following compounds produces $CO_2(g)$ and $H_2O(l)$. Determine the enthalpy of combustion for one mole of each by using enthalpy of formation data.
    a. methanol, CH_3OH
    b. ethanol, C_2H_5OH

SECTION 10.3

14. For the reactions listed below, inspect the equation and predict whether ΔS° is positive or negative.
    a. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
    b. $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$
    c. $Ba(OH)_2(s) \rightarrow BaO(s) + H_2O(g)$
15. Describe how the entropy of a substance relates to the state (solid, liquid, or gas) and temperature of the substance.
16. Why is the entropy of a pure crystalline substance at absolute zero equal to zero?

17. Consider a reaction for which $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$. Explain why this reaction does not happen spontaneously in nature.

18. The boiling point for benzene, C_6H_6, is 80°C. At 60°C, which do you expect to be greater for the vaporization of benzene, ΔH or $T\Delta S$? Explain your response.

19. Determine the change in the standard Gibbs free energy for each of the following reactions at 25°C. For each, state whether the reaction is spontaneous at the given conditions.

    a. $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta H^\circ = 182.6$ kJ and $\Delta S^\circ = 24.8$ J/K

    b. $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H^\circ = -393.5$ kJ and $\Delta S^\circ = 2.70$ J/K

20. For the following reactions, ΔH and ΔS are given for the temperature indicated. Calculate ΔG for each and indicate whether the reaction is spontaneous at the given conditions.

    a. $\Delta H = 108$ kJ/mol, $\Delta S = 0.0375$ kJ/(mol·K), $T = 292$ K

    b. $\Delta H = -93.1$ kJ/mol, $\Delta S = 0.105$ kJ/(mol·K), $T = 135$°C

    c. $\Delta H = -278$ kJ/mol, $\Delta S = 0.375$ kJ/(mol·K), $T = 775$ K

21. Using enthalpy and entropy data in Appendix B (Tables B.7 and B.8), determine the change in the standard Gibbs free energy for the Haber-Bosch process, in which ammonia is formed from nitrogen and hydrogen gases. First calculate ΔG° at 25°C, then calculate ΔG at 500°C, assuming that the values for ΔH_f and S do not change. (In fact, they do change a little, but this calculation is a good approximation.) Comment on what these two values tell you about the prospect of running the Haber-Bosch process at a pressure of 1 bar (standard pressure).

22. Using data from Appendix B, calculate ΔG°, ΔH°, and ΔS° for each of the following reactions. Then compare your ΔG° values to the values obtained from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ for each reaction. (You will find the values are virtually the same.)

    a. $6Cl_2(g) + 2Fe_2O_3(s) \rightarrow 4FeCl_3(s) + 3O_2(g)$

    b. $H_2(g) + F_2(g) \rightarrow 2HF(g)$

    c. $NO_2(g) + N_2O(g) \rightarrow 3NO(g)$

    d. $SO_2(g) + 2H_2(g) \rightarrow S(s) + 2H_2O(g)$

    e. $MgCl_2(s) + H_2O(l) \rightarrow MgO(s) + 2HCl(g)$

SECTION 10.4

23. Explain the two factors that determine whether a molecular collision will result in the breaking and reforming of chemical bonds.

24. What is a reaction mechanism?

25. In a certain demonstration, a teacher fills a metal can with non-dairy coffee creamer and makes it explode. The demonstration works by placing a small amount of explosive black powder in the bottom of the metal can, covering the black powder with a paper towel, and filling up the can with coffee creamer. The black powder is ignited with a fuse and this blows the coffee creamer out of the can. The instant the coffee creamer is out of the can it explodes. Explain why coffee creamer, which is basically carbon, explodes as described. (Do not try this demonstration without expert supervision and full attention to safety procedures.)

26. The change in Gibbs free energy for the combustion of gasoline is a large negative number. Explain why gasoline doesn't immediately burst into flames when it is spilled on the ground.

27. A certain reaction is found to occur in a single step, with the following mechanism:

$A + 2B \rightarrow AB_2$

Determine the rate law for this reaction and use it to predict the effect on the reaction rate of tripling [B].

28. Given the following reaction mechanism:

step 1: $A_2 + A_2 \rightarrow C + D_3$ slow
step 2: $B + D_3 \rightarrow A_2 + E_2$ fast

Determine the overall balanced equation for the reaction, identify the rate determining step, identify the intermediates, and propose an appropriate rate law for the reaction.

29. Draw energy diagrams similar to those shown in Figure 10.18 to fit the following reactions:
    a. $\Delta H = -20$ kJ/mol, $E_a = 15$ kJ/mol
    b. $\Delta H = 30$ kJ/mol, $E_a = 50$ kJ/mol
    c. $\Delta H = -5$ kJ/mol, $E_a = 45$ kJ/mol

30. Consider a reversible reaction. Compare the activation energy and enthalpy change in the forward direction to those of the reverse direction.

31. A certain chemical reaction is described by the single-step mechanism $2A + B \rightarrow C$. Rate data are collected for this reaction, indicating the reaction rates for different concentrations of reactants. These data are shown in the chart.
    a. Determine the rate law for the reaction.
    b. Determine the value of the rate constant.
    c. Determine the initial value of the reaction rate if the initial concentrations of A and B are both 0.25 *M*.

Trial	Initial [A]	Initial [B]	Initial Rate of Forming C
1	0.10 *M*	0.20 *M*	1.15×10^{-4} *M*/s
2	0.10 *M*	0.40 *M*	2.30×10^{-4} *M*/s
3	0.20 *M*	0.40 *M*	9.20×10^{-4} *M*/s

GENERAL REVIEW EXERCISES

32. Determine the volume in liters of 3.55 g of SO_3 gas at STP.

33. Aluminum oxidizes to form Al_2O_3. Assume 0.046 mol Al is combined with 0.028 mol O_2. Determine the limiting reactant and the mass of Al_2O_3 formed.

34. Fluorine gas reacts violently with water to produce HF and O_3. What volumes of HF and O_3 are produced if 5.500 L of F_2 reacts with water? Gas volumes are all at STP.

35. Determine the molarity of a solution of citric acid, $C_6H_8O_7$, if 132.7 g of citric acid are diluted in water and the resulting solution is diluted to a volume of 2500.0 mL.

36. Determine the pOH, $[H_3O^+]$, and $[OH^-]$ for a solution with a pH of 9.81.

37. Determine the expected boiling and freezing points of brine solution formed by dissolving 175.00 g KBr in 450.0 g H_2O.

38. A volume of 17.00 mL of 0.650 *M* NaOH is required to reach the equivalence point in a titration of vinegar. Determine the molarity of acetic acid in the vinegar if the vinegar volume is 18.50 mL.