CHAPTER 3

Atomic Clues

Investigators search for human remains on the property of Ray Marsh in Noble, Georgia, in February 2002. (Tammi Chappell/Reuters/Corbis)

CASE STUDY: To Burn or Not to Burn

The sight was worse than a scene in a Stephen King novel or a Hollywood horror movie. The body of an elderly man lay decomposing under the hot glare of the sun, shaded only by the junked remains of a 1976

Buick Century. Another corpse, most likely that of a teenage boy, was half submerged in a stagnant puddle. The skeleton of a young woman protruded from the grass and weeds on a hillside. A middle-aged man's body in an unusually well-preserved state slumped in the corner of a locked work shed. But these horrors were just the tip of the iceberg: Investigators were about to find 334 bodies in all in this grisly landscape.

Not a single one of the deceased had been reported missing by their families. How could so many deaths have occurred without someone raising an alarm? It gradually became clear on investigation that the dead were people whose bodies had been sent to a crematorium after death. Their families believed that the remains of their loved ones rested in the funeral urns returned to them from the crematorium.

This case garnered national attention in 2002 when a family-owned crematorium in Noble, Georgia, was found to have been accepting bodies for cremation for several years, charging families for cremation services, and then dumping the bodies anywhere on the property. What, then, was in the urns that supposedly held the ashes of the deceased?

This case study focuses on the content of one of the urns about which a family asked a simple question: "Does this urn contain Chigger, or is he somewhere in the acre of rotting remains yet to be identified?" But before this question could be answered, the family would have to know if the cremated remains, called cremains, in the urn they had been given were even human, let alone those of their loved one. The family obtained legal advice, and their attorney turned to Dr. Bill Bass, one of the leading experts in the world on death and decomposition.

This case, however, presented Bass with a new problem. Bass specializes in working with skeletal remains and decomposed bodies, not piles of ashes. He needed the advice of a chemist, and he turned to Dr. Al Hazari of the University of Tennessee in Knoxville. The problem for Hazari was to find a method for identifying the contents of the urn as either ashes from a human body or merely filler material of some kind, such as cement or wood ashes. DNA evidence could not be used to answer this question because the fires of a crematorium destroy all traces of DNA. In fact, cremation converts all carbon in the body to carbon dioxide gas, and the ashes consist of substances that do not burn or escape as gases.

Hazari solved the problem by considering known facts about what is left when a human body is cremated. Then, to determine what was present in the remains reported to be those of Chigger, he used methods of analysis that depend on knowledge of atomic structure and the behavior of electrons when energy is added to an atom.

First, let's investigate atoms and their structures . . .

3.1 Origins of the Atomic Theory: Ancient Greek Philosophers

Learning Objective

Distinguish the two early schools of thought on the nature of the atom.

The very presence or absence of certain atoms in an evidence sample can mean the release of an innocent suspect or the conviction of a criminal. The ability to determine the elemental makeup of evidence is based on our knowledge of atomic structure and how atoms behave. The gradual elucidation of the nature and structure of atoms constitutes one of the greatest detective stories in science. It took over 2300 years to solve the case! In fact, the case was closed only about seventy years ago. Moreover, the first mug-shot of an atom was taken only in 1983 when IBM researchers invented an instrument called the scanning tunneling microscope (STM), which was capable of sensing the presence of an individual atom and creating an image. Figure 3.1 shows an STM image of an oval of iron atoms arranged on a copper surface. The STM image is not a traditional picture; it is a computer-generated image depicting the forces between the electrons in an atom and the STM instrument.

The mystery began in the year 440 B.C. in ancient Greece. Two philosophers, Leucippus and his student Democritus, started a revolution of thought by claiming that matter was made of small, hard, indivisible particles they called *atoms*. According to their theory, atoms came in various sizes, shapes, and weights, were in constant motion, and combined to make up all the various forms of matter. The observable properties of matter could be directly related to the types of atoms it contained. Wherever atoms did not exist, there was a void or vacuum.

This theory of Leucippus and Democritus set the stage for a confrontation with the philosopher Aristotle, who believed in a continuous model of matter. Aristotle taught that matter could be infinitely divided, which meant that no indivisible particles (atoms) existed. He convinced the majority of his colleagues that the atomic view of matter was illogical.

Democritus (460 B.C.–370 B.C.) (Nimatallah/Art Resource, NY)

Aristotle (384 B.C.–322 B.C.) (Bettman/Corbis)

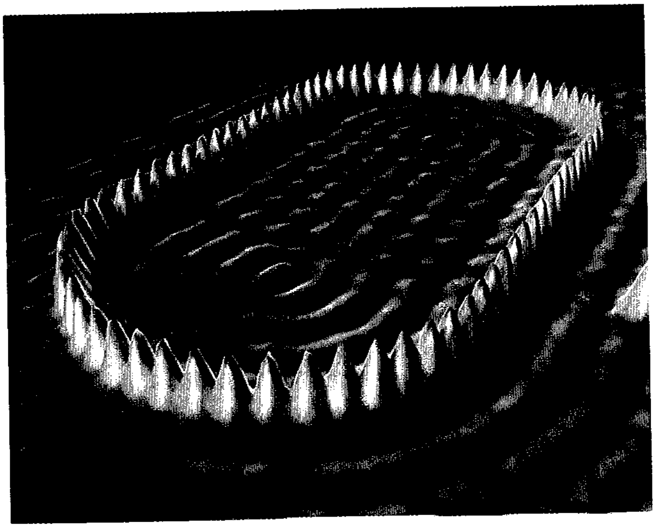


Figure 3.1 A ring of iron atoms on a copper surface imaged by an STM. The colors in the image are computer generated. (Crommie, Lutz & Eigler/IBM Corporation)

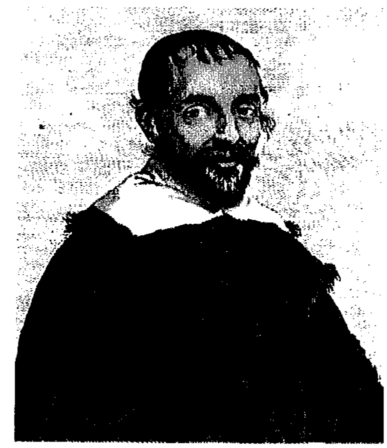
The argument for the existence of atoms went into the cold case file for the next 1900 years. In fact, teachings contrary to Aristotle, including the atomic theory, were against the law in some parts of Europe! To make matters worse, the atomic theory was associated with atheistic beliefs.

3.2 Foundations of a Modern Atomic Theory: Gassendi, Lavoisier, and Proust

Learning Objective

Understand how the political and scientific groundwork for a modern atomic theory was established.

In the 1600s, Pierre Gassendi, a priest, philosopher, and scientist, reopened the atomic debate by publishing a work that defended the atomic theory and argued that the principles of atomic theory were not contradictory to Christian beliefs. He modified the original principles of Leucippus and Democritus to state that all atoms were actually created by God and that their motion was a gift of God. Current atomic theory is neutral on the existence of a supreme being, but Gassendi's work was important because it allowed people to engage in open debate about atomic theory without fear of retribution.



Pierre Gassendi, a seventeenth-century priest, philosopher, and scientist. (Science Photo Library/Photo Researchers, Inc.)

Even though the atomic theory could now be debated and discussed in academic settings, there were no significant developments in the case until the late 1700s. Experiments that laid the groundwork for a better understanding of matter and chemical change were carried out around that time and became necessary precursors to the further development of atomic theory.

Antoine Lavoisier, who is considered the founder of modern chemistry, made a discovery in 1785 that was to become known as the law of conservation of mass. The **law of conservation of mass** states that mass is neither created nor destroyed in a chemical reaction but merely changes form. For many centuries scientists had pondered what happened to matter during chemical reactions. Perhaps even our earliest ancestors who mastered the art of fire wondered what happened to the wood that was burning in their campfires. The fire seemed to consume the wood, since the only tangible evidence left from the fire was a very small amount of ash.

The key to unraveling this mystery was the awareness that matter undergoing a chemical change (such as burning wood) in an open environment only appears to lose mass because one or more of the products of the reaction escapes into the surroundings as a gas. Lavoisier conducted experiments in closed systems in which the substances undergoing a transformation could not exchange matter with the surroundings, as shown in Figure 3.2.

Lavoisier heated mercury(II) oxide in a sealed system to form elemental mercury, which is a silver metallic liquid, and colorless oxygen gas, as shown in Figure 3.3. Taking careful quantitative measurements, he found that the mass of the mercury(II) oxide before heating equaled the combined masses of the liquid mercury and oxygen gas that formed after heating. Thus there was no overall change in mass as long as the reaction was done in a sealed system.

The ashes left by countless campfires could finally be explained as the solid remains of a combustion reaction that also produced carbon dioxide

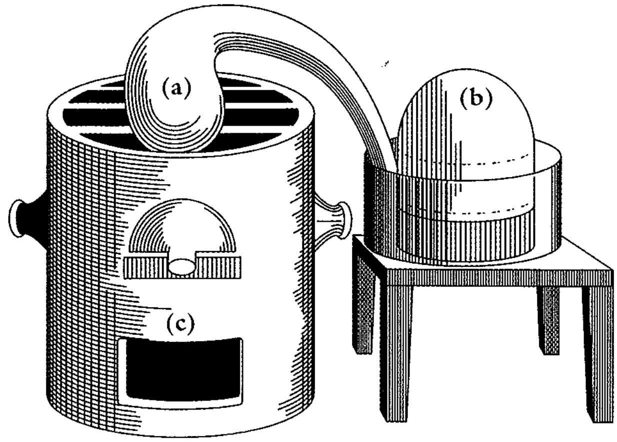


Figure 3.2 Lavoisier's reaction vessel (a) could be heated by the furnace (c) and any gases that formed during the reaction would be collected in the jar (b).

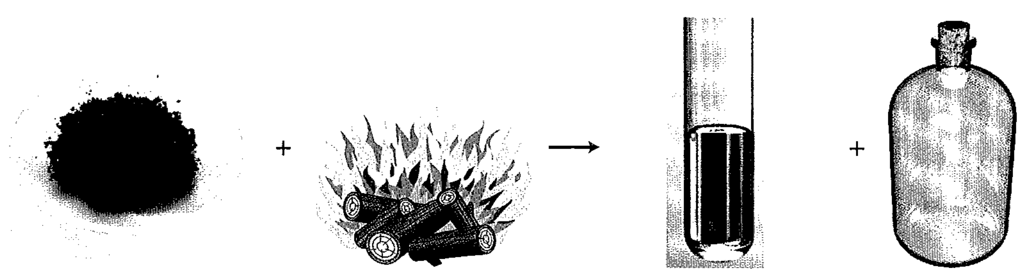
gas and water vapor. The carbon dioxide and water vapor escape into the surrounding air.

Worked Example 1

Lavoisier studied the production of water from hydrogen and oxygen gases. If he produced 36.0 g of water starting with 4.0 g of hydrogen, how many grams of oxygen must have reacted with the hydrogen?

SOLUTION According to the law of conservation of mass, the total mass of reactants must equal the total mass of products:

$$\begin{aligned} \text{grams hydrogen} + \text{grams oxygen} &= \text{grams water} \\ 4.0\text{ g} + \text{g oxygen} &= 36.0\text{ g} \\ \text{g oxygen} = 36.0\text{ g} - 4.0\text{ g} &= 32\text{ g oxygen} \end{aligned}$$



$$2HgO(s) \quad + \quad \text{Heat} \quad \longrightarrow \quad 2Hg(l) \quad + \quad O_2(g)$$

Figure 3.3 In Lavoisier's reaction, the heating of the mercury(II) oxide caused the solid compound to decompose into its constituent elements, mercury and oxygen gas. The reaction was a visually dramatic illustration of the law of conservation of mass: A red solid was converted by heat into a silver liquid and a colorless gas. (Mercury oxide: Charles D. Winters/Photo Researchers, Inc.; liquid mercury: Richard Mengus/Fundamental Photographs)

Practice 3.1

Alcohol in our digestive system reacts with oxygen gas to form carbon dioxide and water. How many grams of carbon dioxide are released if a 10.00-g alcohol sample reacts with 20.85 g of oxygen gas and produces 11.77 g of water?

ANSWER
19.08 g CO_2

Another series of important experiments, carried out by Joseph Louis Proust in 1797, led to a principle that became known as the law of definite proportions (also called the law of constant composition). The **law of definite proportions** states that a compound is always made up of the same relative masses of the elements that compose it. At the time Proust was investigating compounds, some scientists believed that a compound could contain any ratio of its elements and still be the same substance. Their argument was that only the type of elements in the compound mattered, not necessarily the amounts of each element. Proust was the first to show that analysis of a carefully prepared and purified compound always showed the same mass ratio of elements—even if different methods were used to prepare the compound—from one experiment to another.

The key to Proust's work was that he did it very carefully so that he was able to obtain both accurate and precise results. The work by earlier scientists had not been carried out as carefully as Proust's, and therefore earlier scientists based their conclusions on inaccurate data.

3.3 | Dalton's Atomic Theory

Learning Objective

Show how Dalton's atomic theory could explain and predict the behavior of matter.

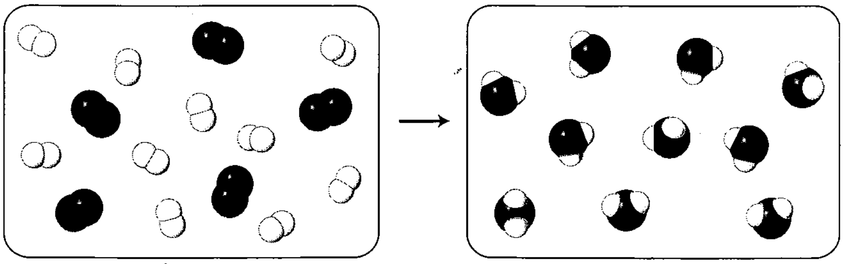
John Dalton is credited with giving the world the first modern atomic theory. The word *theory* in the sciences is the term for the best current explanation of a phenomenon. It is *not* synonymous with an opinion and does *not* change as a result of political or personal agendas. A **theory** is accepted by the scientific community until such time that new data contradict the theory.

Dalton's passion was studying meteorology and weather patterns, and this led him to study how gas mixtures behave. As a result of his studies, he developed an atomic theory that explained the behavior of gases and the previous findings of Lavoisier and Proust. Dalton's atomic theory of matter, published in 1803, had four basic tenets:

Dalton's Atomic Theory

1. All matter is made up of tiny, indivisible particles called atoms.
2. Atoms cannot be created, destroyed, or transformed into other atoms in a chemical reaction.
3. All atoms of a given element are identical.
4. Atoms combine in simple, whole-number ratios to form compounds.

With **Dalton's atomic theory,** the law of conservation of mass could now be explained. When a chemical reaction occurs, the atoms of each



Hydrogen (○) reacts with oxygen (●) to form water (●)

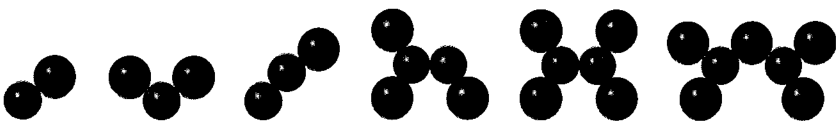
Figure 3.4 The law of conservation of mass explains a chemical reaction as the rearrangement of atoms. The number of atoms before or after the reaction is constant (10 oxygen and 20 hydrogen); the arrangement of chemical bonds changes.

compound are rearranged to form new compounds, as shown in Figure 3.4, but the number of atoms remains the same. Thus no mass is lost or gained in the process.

Dalton's atomic theory could also explain the law of definite proportions. According to the atomic theory, compounds are made up of atoms in simple ratios. Pure water always has two hydrogen atoms to every oxygen atom, regardless of where the water comes from or how it is created. This constant atomic ratio provides the reason the mass ratio of elements in the compound is also constant.

Finally, Dalton's atomic theory predicted the law of multiple proportions formulated by Dalton himself. The **law of multiple proportions** states that any time two or more elements combine in different ratios, different compounds are formed. For example, laughing gas, which has the chemical formula N_2O, is quite different from the gas NO_2, a by-product of explosions and burning diesel fuel. Figure 3.5 shows various compounds of nitrogen and oxygen.

In spite of the success of Dalton's theory in explaining the behavior of matter and the widespread support the theory received, it took almost another hundred years before the atomic theory of matter was completely accepted. In fact, there were still a few major scientists who disbelieved the atomic theory into the early 1900s. It would take more than logical reasoning and circumstantial evidence to get a unanimous decision by a jury of scientists.



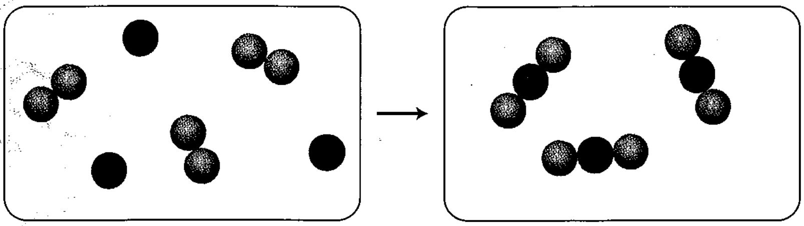
Nitrogen (●)
Oxygen (●)

Figure 3.5 Nitrogen atoms can combine with oxygen atoms in a variety of simple ratios. Each combination represents a unique compound, illustrating the law of multiple proportions.

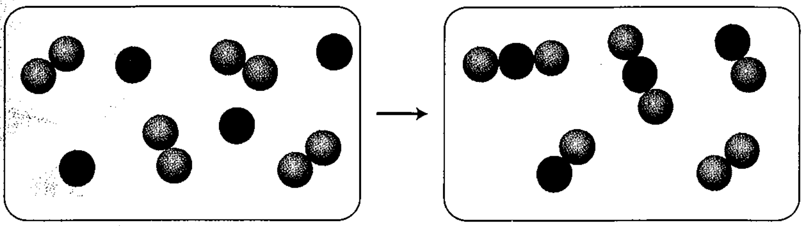
Worked Example 2

Label each of the following drawings as illustrating the law of conservation of mass (LCM), the law of multiple proportions (LMP), the law of definite proportions (LDP), or more than one law, if applicable.

(a)



(b)



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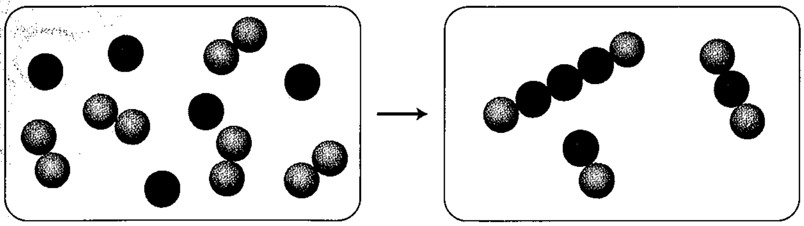


SOLUTION

(a) LCM, LDP. The reaction illustrates the law of conservation of mass because both reactants and products have an identical number of atoms. The law of definite proportions is also illustrated because a single compound has been created with a constant formula.

(b) LCM and LMP. The reaction illustrates the law of conservation of mass because both reactants and products have an identical number of atoms. The law of multiple proportions is also illustrated because several compounds have been created, each with a unique formula.

(c) LMP. The law of multiple proportions is illustrated because several compounds have been created, each with a unique formula.

Practice 3.2

Write the chemical formulas for all the nitrogen-oxygen compounds shown in Figure 3.5. Explain how the figure illustrates the law of multiple proportions.

ANSWER

NO, NO_2, N_2O, N_2O_3, N_2O_4, N_2O_5. The law of multiple proportions states that elements can combine in multiple whole-number ratios of their elements (1:1, 1:2, 2:1, and so forth), but each new ratio of atoms represents a new compound.

3.4 Atomic Structure: Subatomic Particles

Learning Objective

List the main subatomic particles and show how their discovery furthered our insight into of the nature of the atom.

Some of the most convincing evidence for the existence of atoms came from experiments that actually contradicted the first principle of Dalton's atomic theory. Experimental evidence began to show that atoms were not indivisible; in fact, there were three major components to the atom. These subatomic particles were the positively charged **proton,** the negatively charged **electron,** and the **neutron,** which had no electrical charge and was thus electrically neutral.

Experiments that led to the discovery of the electron depended on the invention in the 1850s of the cathode ray tube, the direct ancestor of the conventional television picture tube and computer monitor. A **cathode ray tube** is a sealed glass tube from which nearly all gases inside have been removed to create a vacuum. In the cathode ray tube are two metal electrodes called the *cathode* and the *anode* to which a large voltage is applied. When this process occurs, rays can be seen emanating from the cathode. The rays can be deflected by the poles of a magnet, moving away from the north-seeking (N) pole and toward the south-seeking (S) pole, as shown in Figure 3.6.

In 1897, the British physicist J. J. Thomson was able to measure the deflection of the cathode rays from magnetic and electric fields. Using the data from his deflection experiments, he calculated that the mass-to-charge ratio of the cathode ray particles was less than 1/1000 of the value calculated for any other known element. Thomson thus discovered that whatever made up the cathode rays was smaller than the smallest atom! Thomson correctly concluded that the cathode rays consisted of negatively-charged subatomic particles called *electrons.*

The discovery of the electron presented a problem for scientists. They knew that atoms are electrically neutral, yet now they had evidence that atoms also contain negative particles. A positive charge had to balance the negative charge, but where in the atom is it? One popular theory at the time was that the electron particles were randomly stuck into a ball of positive charge. This model was commonly called the *plum pudding model,* referring to the way the fruit is distributed throughout a plum pudding. A more familiar model today might be a chocolate chip muffin.

In 1909, Ernest Rutherford set out to investigate the plum pudding model, which he thought was correct, by taking an extremely thin layer of gold foil and exposing it to a radioactive element. **Radioactivity** is the spontaneous emission of particles from unstable elements. The alpha particle, which is emitted from some radioactive elements, has a positive electrical charge and a mass four times that of a hydrogen atom. In Ruther-

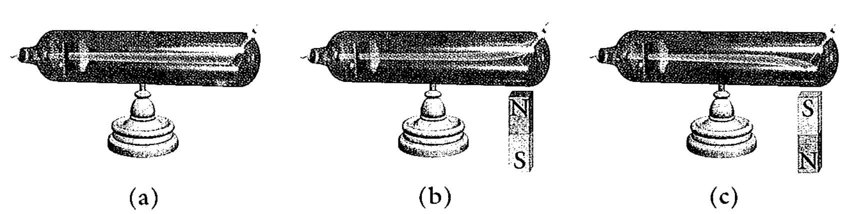
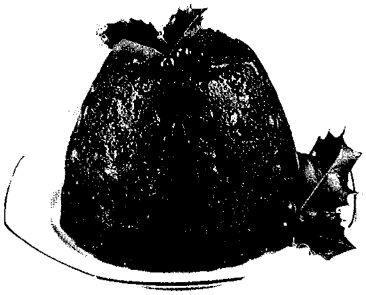
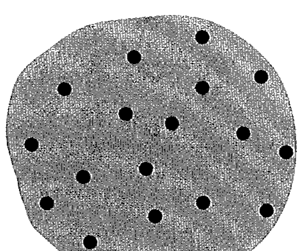


Figure 3.6 A beam of cathode rays is attracted to the south-seeking pole of a magnet and deflected by the north-seeking pole.



Plum pudding

Chocolate chip muffin



Plum pudding model

The plum pudding model consisted of a positively charged matrix in which the negative electrons are imbedded into the positive region. (Top: Foodfolio/Alamy; center: Index Stock) ford's experiment, the alpha particle emitter was aimed at the target placed inside a detector that would show a flash of light when an alpha particle struck it (Figure 3.7).

The three major experimental observations made during the gold foil scattering experiment, with the conclusions Rutherford made from each observation, are as follows.

Observation 1: The vast majority of alpha particles passed directly through the solid gold foil.

Conclusion 1: The atom must consist mostly of empty space for the alpha particles to go directly through.

Observation 2: Occasionally an alpha particle would veer from a straight-line path and hit the detector on the side.

Conclusion 2: (a) The positively charged alpha particle was pushed off course when it came close to a positive region of the atom because like charges repel. (b) The positive region had to be small because only a few alpha particles ever came close enough to be repelled.

Observation 3: Rarely, an alpha particle would bounce directly back toward the alpha particle source after striking the gold foil.

Conclusion 3: (a) In these instances the alpha particle made a direct hit on a very dense object that caused it to bounce back. (b) Since the direct hits were a rare event, the dense object must be very small and must be positively charged to repel the alpha particle.

The final result stunned Rutherford. He would later compare it with firing an artillery shell at a piece of paper and having it bounce back at you! The dense positive region Rutherford discovered in the atom is called the **nucleus.** Rutherford continued to explore the structure of the atom and would later discover that the positively charged hydrogen ion has the simplest nucleus consisting of only one positively charged subatomic particle called the *proton.* The model Rutherford put forward is illustrated in Figure 3.8.

The task of determining the structure and components of an atom was complete except for an explanation for the fact that protons made up

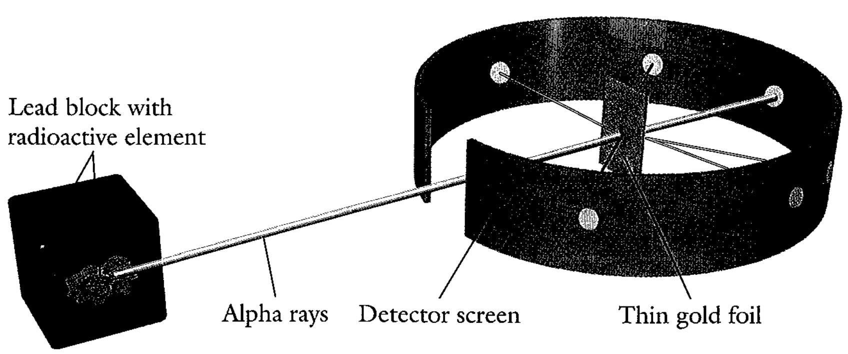


Figure 3.7 In Rutherford's gold foil scattering experiment, alpha rays from a radioactive element are directed out of a lead container toward a gold foil target surrounded by a detector screen that flashes at any location struck by an alpha particle.

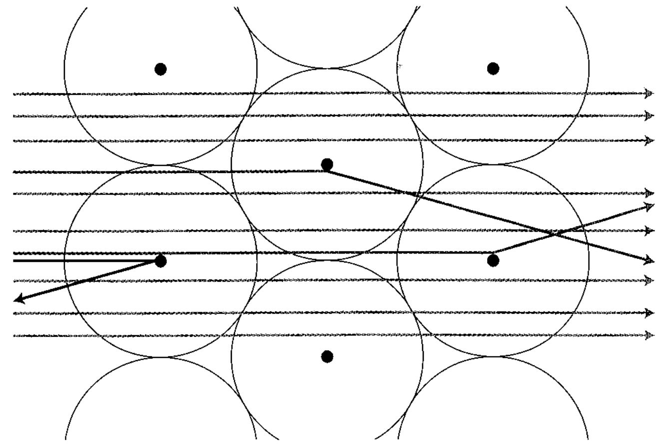


Figure 3.8 Rutherford's model of the atom consisted almost entirely of empty space in which the protons were located in a very small, dense nucleus. This model could account for the three experimental observations: (1) Most rays pass through (gray). (2) Some rays are deflected (orange). (3) Rarely, an alpha ray is returned (purple).

only a portion of the mass of most atoms. The difference in mass could not be explained by the presence of electrons because they were so much lower in mass that they contributed very little to the overall mass of the atom. The search for the missing mass continued until 1932, when James Chadwick correctly interpreted several nuclear experiments that were producing heavy neutral particles called *neutrons*. A neutron has a mass equal to that of a proton but no electronic charge.

Neutrons were later linked to the violation of another principle of Dalton's original atomic theory. Dalton had postulated that all atoms of an element are identical, but, in fact, some atoms of the same element have different numbers of neutrons than others. These atoms are called **isotopes.** Isotopes of an element behave and react chemically like all other atoms of that element, but they differ in their atomic masses.

Because the masses of single atoms and subatomic particles are so small, using units of grams to express mass does not make sense. Instead, mass is expressed in a unit called the **atomic mass unit (amu).** The amu is defined as 1/12 the mass of a carbon atom that contains 6 protons and 6 neutrons. The properties of the subatomic particles are summarized in Table 3.1. Note how small the mass of the electron is compared with the masses of the proton and the neutron. The electron's mass is only 1/1838 (or 0.0005486) the mass of a proton or neutron. For most applications, the mass of the proton and neutron can be rounded to 1 amu, and the mass of the electron to 0 amu.

Table 3.1 Subatomic Particles

Particle	Charge	Mass (amu)	Symbol
Electron	−1	0.0005486	e^-
Proton	+1	1.0073	p or p^+
Neutron	0	1.0087	n

3.5 | Nature's Detectives: Isotopes

Learning Objective

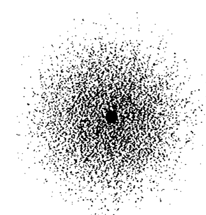
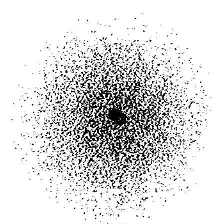
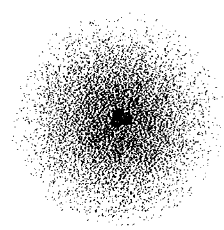
Distinguish isotopes and describe how they can be used in scientific research.

Isotopes are used quite often for solving chemical and medical mysteries. For example, radioactive isotopes are used routinely at most hospitals to investigate whether a patient has properly functioning organs or to locate traces of cancer. Isotopes are also commonly used in the laboratory to investigate how each step of a chemical reaction occurs. A closer look at the periodic table and the nature of isotopes is warranted because of the important role isotopes play in science and medicine.

Isotopes differ only in the masses of their atoms and therefore have the same chemical symbol. How then do we represent the different isotopes of an element symbolically to distinguish one from another? The goal of any symbolic form used in chemistry is to clearly relay the relevant information in an abbreviated form.

For example, the element hydrogen has three isotopes, as shown in Table 3.2. The **mass number (A)** is the mass of the isotope measured in atomic mass units (amu). The mass of the isotope is the mass of the protons plus the mass of the neutrons; each particle has a mass of 1 amu. The mass of an electron is so small that it does not affect the mass of the atom to any important extent. It would take the mass of almost 2000 electrons to equal the mass of just one proton or neutron.

Table 3.2 Isotopes of Hydrogen

Isotope Name	Number of Neutrons	Number of Protons	Number of Electrons	Mass Number	Model Protons • Neutrons •
Protium	0	1	1	1	
Deuterium	1	1	1	2	
Tritium	2	1	1	3	

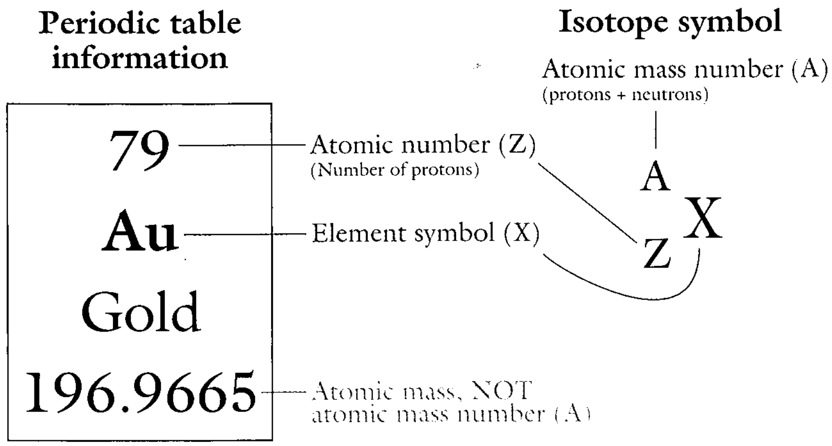


Figure 3.9 Relationship between the information in the periodic table and the information in the isotope symbol.

The number of protons in each isotope of an element is the same. In this example, each isotope of hydrogen has one proton. All atoms of an element, regardless of the number of neutrons, have the same number of protons. The periodic table is organized by ascending number of protons, shown in the upper center or upper right corner of the block for each element. The number of protons in an element is called the **atomic number (Z).** Figure 3.9 shows the pattern that is used to represent specific isotopes.

The isotopes of hydrogen can then be written ${}^{1}_{1}H$ for protium, ${}^{2}_{1}H$ for deuterium and ${}^{3}_{1}H$ for tritium. This system makes clear the distinction between isotopes without the need for memorization of names or formulas. One common modification of this method is the omission of the atomic number. The three isotopes of hydrogen could just as easily be written ${}^{1}H$, ${}^{2}H$, and ${}^{3}H$. This shortcut is valid because all isotopes of hydrogen have the same atomic number, which can be determined from the periodic table.

Giving each isotope a distinct name would be impractical. Therefore, an isotope is simply given the name of the element and the atomic mass number (Z). For example, ${}^{3}H$ is written *hydrogen-3* and is properly pronounced "hydrogen three." This terminology may be familiar to you: The technique of carbon-14 dating of artifacts is commonly mentioned in the popular media in discussions of archeological discoveries.

Worked Example 3

Write the isotope symbol for each of the following isotopes:

(a) Carbon atom containing 6 neutrons

(b) Nitrogen atom containing 8 neutrons

(c) Uranium atom containing 143 neutrons

SOLUTION

(a) Carbon's atomic number is 6 (also the number of protons). The mass number is equal to protons + neutrons: 6 + 6 = 12. The isotope symbol is ${}^{12}_{6}C$.

(b) Nitrogen's atomic number is 7 (also the number of protons). The mass number is equal to protons + neutrons: 7 + 8 = 15. The isotope symbol is $^{15}_{7}N$.

(c) Uranium's atomic number is 92 (also the number of protons). The mass number is equal to protons + neutrons: 92 + 143 = 235. The isotope symbol is $^{235}_{92}U$.

Practice 3.3

Write the isotope symbols for the following:

(a) Atom containing 26 protons and 28 neutrons

(b) Atom containing 14 protons and 15 neutrons

(c) Atom containing 16 protons and 18 neutrons

ANSWER

(a) $^{54}_{26}Fe$ (b) $^{29}_{14}Si$ (c) $^{34}_{16}S$

Given the isotope symbol, it is possible to determine the number of protons, neutrons, and electrons of any given atom using simple mathematics. The mass number of an atom is the sum of protons and neutrons. Subtracting the number of protons (the atomic number) from the mass number yields the number of neutrons. The number of electrons present in an atom is always equal to the number of protons as long as the atom does not have a positive or negative charge.

Worked Example 4

Determine the number of protons, neutrons, and electrons found in each of the following isotopes:

(a) $^{22}_{10}Ne$ (b) $^{136}_{56}Ba$ (c) $^{106}_{46}Pd$

SOLUTION

(a) $^{22}_{10}Ne \Rightarrow {}^{p+n=22}_{p=10}Ne$
$p = 10$
$n = 22 - 10 = 12$
$e^- = p = 10$

(b) $^{136}_{56}Ba \Rightarrow {}^{p+n=136}_{p=56}Ba$
$p = 56$
$n = 136 - 56 = 80$
$e^- = p = 56$

(c) $^{106}_{46}Pd \Rightarrow {}^{p+n=106}_{p=46}Pd$
$p = 46$
$n = 106 - 46 = 60$
$e^- = p = 46$

Practice 3.4

Determine the number of protons, neutrons, and electrons in each of the following isotopes:

(a) Krypton-84 (b) Tin-117 (c) Zinc-66

ANSWER

(a) 36 p, 48 n, 36 e^- (b) 50 p, 67 n, 50 e^- (c) 30 p, 36 n, 30 e^-

Some elements, such as beryllium and fluorine, do not have any naturally occurring isotopes. Other elements, such as mercury and osmium, have seven naturally occurring, stable (nonradioactive) isotopes. When an element has isotopes, the proportion of each isotope is generally constant in natural samples. For example, 92.23% of silicon atoms are silicon-28, 4.67% of silicon atoms are silicon-29, and the remaining 3.10% are silicon-30. Distribution of isotopes and percentages is unique to each element.

The fact that the abundance of each isotope is constant in natural samples can be a useful tool in the fight against terrorism. For example, 98.90% of carbon atoms are ^{12}C, whereas 1.10% of carbon atoms exist as ^{13}C. An explosives manufacturer could replace the standard ^{12}C atoms with ^{13}C atoms at specific positions in the compound and make a code that could identify the company and the production batch from which it came. If the explosive were then used by a criminal or terrorist, a forensic scientist could determine where the explosive came from and investigators could try to link the explosive to a suspect.

This idea is not currently being used in the United States because of concerns about added costs for production and record keeping. Switzerland, however, has mandated since 1980 that all explosives produced or sold in their country be physically or chemically tagged. There is also a concern that the manufacturers may open themselves to potential lawsuits by those who might be harmed through misuse of their product, just as some gun manufacturers have had to face lawsuits from victims of shootings.

3.6 Atomic Mass: Isotopic Abundance and the Periodic Table

Learning Objective

Determine the atomic mass of an element with isotopes.

What is the mass of a single atom? If you're thinking not very much, you're right. A single atom of hydrogen has a mass of 1.67×10^{-24} g. For most purposes scientists do not use grams to communicate atomic masses. They use the atomic mass unit (amu), introduced earlier in this chapter. One amu is defined as 1/12 of the mass of a carbon-12 atom. The masses of the rest of the elements are calculated by the ratio of the mass of an element to that of carbon-12. For example, if the mass of an atom were twice that of carbon-12, the mass would be near 24 amu.

The existence of isotopes complicates the matter of reporting the atomic weights of the elements in the periodic table. How do we determine the atomic mass of an element with isotopes? To explore this problem, consider the isotopes of silver, ^{107}Ag and ^{109}Ag. The natural abundance of ^{107}Ag is 51.8% and that of ^{109}Ag is 48.2%. The atomic mass reported on the periodic table should reflect that a little more than 50% of all silver atoms have a mass of 107 amu, and a little less than 50% of all silver atoms have a mass of 109 amu. It should be no surprise that the atomic mass of silver is reported as 107.865 amu, just under 108 amu. No single atom of silver will ever have a mass of exactly 107.865 amu, but on average it is the correct value. This method of determining atomic mass by natural abundance is called a **weighted average.**

Worked Example 5

Oxygen has three isotopes: oxygen-16, oxygen-17, and oxygen-18. Which of these isotopes has the highest natural abundance?

SOLUTION The atomic mass of oxygen in the periodic table is very close to 16 amu (its actual value is 15.999 amu), which indicates that the vast majority of oxygen atoms exist as the oxygen-16 isotope.

Practice 3.5

Bromine has two isotopes: bromine-79 and bromine-81. Which of these isotopes has the highest natural abundance?

ANSWER
Bromine-79 has a slightly higher abundance.

3.7 Atomic Structure: Electrons and Emission Spectra

Learning Objective

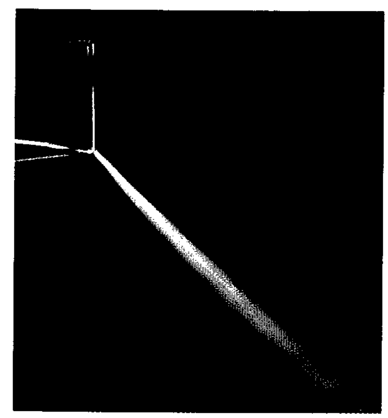
Assess data from clues that the emission spectra of elements provide about the location of electrons within an atom.

To complete the understanding of atomic structure, scientists had to investigate where electrons are located in an atom. Do electrons orbit the nucleus the way planets orbit the sun, or do the electrons move around the nucleus in random paths? The clues needed to solve this atomic mystery came from experiments involving light and its relationship to the behavior of electrons in atoms.

When white light passes through a prism, all the colors of the rainbow appear in a **continuous spectrum,** as shown in Figure 3.10. It is extremely difficult to look at a continuous spectrum and be able to pick an exact point where one color starts and another stops. Instead, the colors gradually transition from one to another. A musical analogy of a continuous spectrum is the unbroken progression of sound made by a trombone as the trombone player pushes the slide all the way out and back in one smooth motion.

The opposite of a continuous spectrum is a **line spectrum,** the single lines of various colors that are clearly separated when certain types of light pass through a prism. A musical analogy to a line spectrum is a scale of individual notes played on an instrument.

Experimentally it had been shown that atoms produce light when placed in a flame or when electricity is passed through a gas vapor of the element. The colors of fireworks are an example of light produced by atoms in a flame, whereas neon light is an example of light that results from electricity flowing through a gas vapor. If the light emitted from excited atoms (such as those in a flame) passes through a prism, it appears as the thin bands of a line spectrum. What is especially interesting



White light is being separated into its continuous spectrum by a prism. (Paul Silverman/Fundamental Photographs)

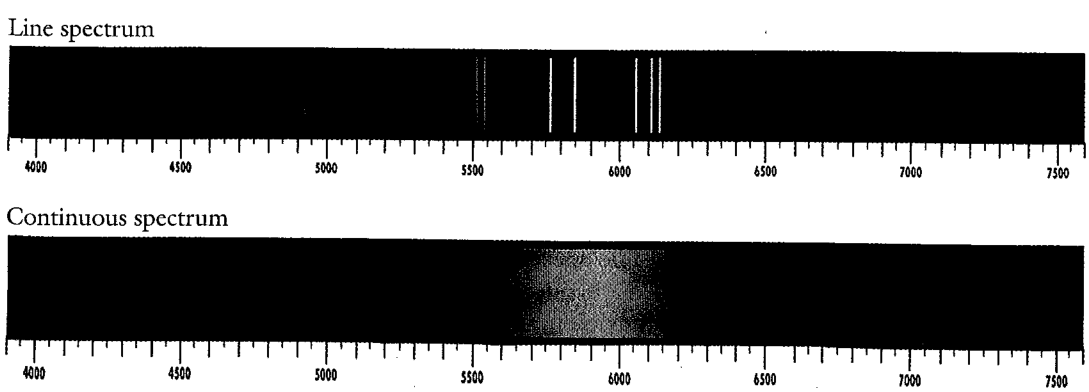


Figure 3.10 A continuous spectrum has no clear distinction between colors, whereas a line spectrum has clear separation between colors. (Wabash Instrument Corp./Fundamental Photographs)

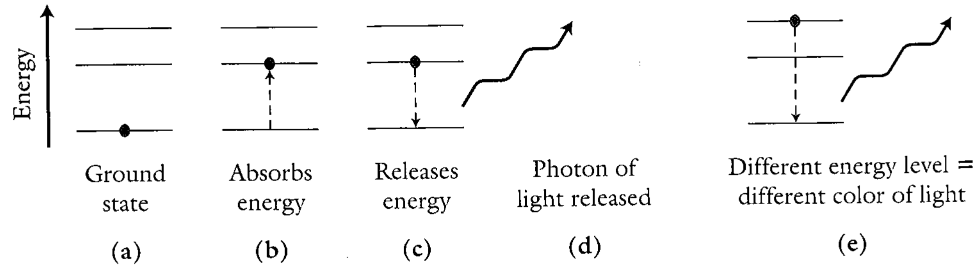


Figure 3.11 (a) The ground-state electron (b) absorbs energy and then (c) spontaneously releases excess gained energy as (d) a photon of light. If the electron were to absorb a different amount of energy corresponding to a higher excited state, the photon of light produced as the electron releases the excess energy would be of a different color (e).

is that every element produces a different line spectrum. The unique spectrum of each element helps forensic scientists detect the presence of trace elements in samples such as arsenic in hair, barium and antimony in gunshot residue, and trace elements in glass fragments.

The discovery of line spectra posed a scientific mystery: Why do they occur? The answer turned out to provide a strong clue to how electrons are arranged in the atom. When atoms are at room temperature, the electrons are located in the lowest possible energy level, called the **ground state** (Figure 3.11a). When an atom absorbs energy, the electrons are pushed into higher energy levels, called **excited states** (Figure 3.11b). The excited state of an atom is unstable, and electrons have a tendency to go back to the lower energy ground state. For the electron to go back to the ground state, the excess energy it absorbed must be released (Figure 3.11c–e).

The electron emits the excess energy in the form of a **photon**—a single "particle" or bundle of light. Multiple colors of light, corresponding to photons of different energies, are produced when electrons make the transition from higher energy levels back to the ground state. The energy of the photon, which equals the difference in energy between an excited state and the ground state of an electron, dictates the color.

The production of line spectra with a limited number of lines of color suggests that electrons in atoms are found in a few fixed energy levels. In the terminology of science, we say that the electrons are found in **quantized energy levels.** An analogy for quantized energy levels would be stair steps: The allowed states are a fixed distance apart, and it is impossible to pause partway between stair steps. If the energy levels of electrons were not quantized, electrons in excited atoms could emit photons of all energies and colors and would produce continuous spectra.

Each line in a spectrum is the result of an electron releasing energy from a higher quantized excited state to the ground state. Figure 3.12 shows the visible line spectra for several of the Group 1 elements. Many lines are produced outside the visible spectrum, such as in the infrared region and the ultraviolet region, which are not shown in the figure. Note how the complexity of the line spectra increases for elements with more electrons. The complex spectra result because a greater number of electrons are available for excitation, and there are more possible excited energy levels for the electrons to occupy.

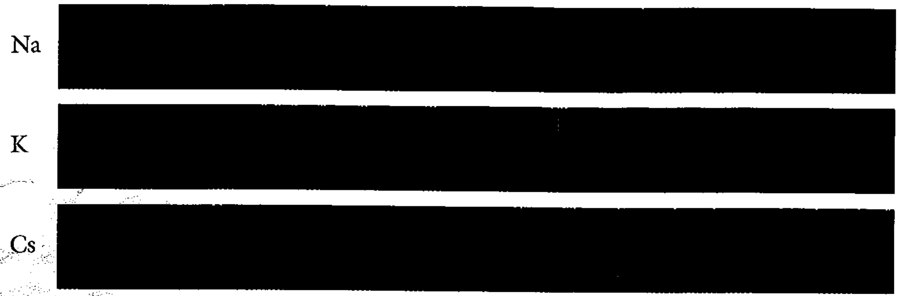


Figure 3.12 Line spectra of the elements in the first column of the periodic table. Each spectrum increases in complexity as the number of electrons increases. (Wabash Instrument Corp./Fundamental Photographs)

3.8 | Mathematics of Light

> **Learning Objective**
> Examine and use the relevant mathematical equations to describe the behavior of light.

Light travels through space in the form of waves, much as waves travel across the oceans. Waves can be described mathematically by their **wavelength,** symbolized by the Greek letter lambda (λ). The wavelength is the distance from one wave peak to another, as illustrated in Figure 3.13. The unit used to measure wavelength for light in the visible spectrum is typically the nanometer (nm). The prefix *nano* represents the multiplier 1×10^{-9}, or one billionth of a meter.

Waves are also mathematically described by their frequency, symbolized by the Greek letter nu (ν). **Frequency** is the number of times the wave peak passes a point in space within a specific time period. It is measured in units called *hertz* (Hz), and 1 Hz represents a wave that passes a point once per second ($1\ \text{Hz} = 1\ \text{s}^{-1}$). Mathematically, s^{-1} and $1/\text{s}$ are equivalent.

Wavelength and frequency are related to the **speed of light** (c), as shown in equation 1. The speed of light in a vacuum is a constant value equal to 3.00×10^8 m/s. Equation 1 is commonly rearranged to solve for the wavelength, as shown in equation 2, or for the frequency, as shown in equation 3. One of the most common mistakes made in using equations 1–3 is failing to make sure that the units of distance are the same. The speed of light is measured in meters per second (m/s), whereas light from the visible spectrum is measured in nanometers. Just remember to use the appropriate conversion factors for units!

$$c = \lambda \times \nu \tag{1}$$

$$\frac{c}{\nu} = \frac{\lambda \times \cancel{\nu}}{\cancel{\nu}} \Rightarrow \lambda = \frac{c}{\nu} \tag{2}$$

$$\frac{c}{\lambda} = \frac{\cancel{\lambda} \times \nu}{\cancel{\lambda}} \Rightarrow \nu = \frac{c}{\lambda} \tag{3}$$

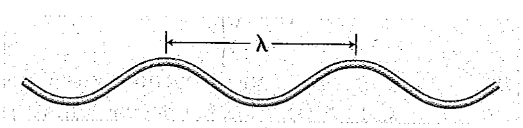


Figure 3.13 Light travels as a wave described by the wavelength (the distance between peaks) and the frequency of wave oscillations that occur in a given time period.

Worked Example 6

Napoleon Bonaparte was exiled to the island of St. Helena after his defeat at Waterloo. Soon after his exile, his health started to deteriorate. Historical documents show that his symptoms matched those of arsenic poisoning, although his illness had been diagnosed at the time as stomach cancer. Arsenic, when in an excited state, will emit light at wavelength 193.7 nm. In 2001, Napoleon's hair was analyzed and tested positive for arsenic. Calculate the frequency (Hz) of light that corresponds to the wavelength of arsenic.

SOLUTION Using equation 3,

$$\nu = \frac{c}{\lambda}$$

but first we must convert 193.7 nm to meters:

$$193.7\ \cancel{\text{nm}} \times \frac{1 \times 10^{-9}\ \text{m}}{1\ \cancel{\text{nm}}} = 1.937 \times 10^{-7}\ \text{m}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{1.937 \times 10^{-7}\ \text{m}} = 1.549 \times 10^{15}\ 1/\text{s} = 1.55 \times 10^{15}\ \text{Hz}$$

Practice 3.6

The detection of lead from gunshot residue is accomplished by measuring emitted light that corresponds to a wavelength of 220.4 nm. What is the frequency (Hz) of this wavelength of light?

ANSWER
1.36×10^{15} Hz

Worked Example 7

Glass fragments recovered from a crime scene can be analyzed for trace elements to determine whether or not the fragments are consistent with the fragments recovered from a suspect. Determine the wavelength (nm) of light used for measuring cobalt given that the frequency of the light is 1.2976×10^{15} Hz.

SOLUTION Using equation 2,

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8}\ \text{m/s}}{1.298 \times 10^{15}\ 1/\text{s}} = 2.3112 \times 10^{-7}\ \text{m}$$

$$2.3112 \times 10^{-7}\ \cancel{\text{m}} \times \frac{1\ \text{nm}}{1 \times 10^{-9}\ \cancel{\text{m}}} = 231.12\ \text{nm} \Rightarrow 231\ \text{nm}$$

Practice 3.7

Crystal is a distinctive form of glass that contains a high level of lead. The lead content can be used to determine whether two fragments are likely to have a common origin. Calculate the wavelength of light that lead atoms in an excited state will emit given that the frequency of light is 1.361×10^{15} Hz.

ANSWER
2.20×10^2 nm

Recall that the color of each line present in a spectrum represents the transition from an excited-state energy level to a lower ground-state energy level. The difference in energy between these two levels can be calculated by the frequency of light according to equation 4, where E is energy with units of joules (J) and h is *Planck's constant*, which has a value of 6.626×10^{-34} J · s.

$$E = h \times \nu \tag{4}$$

$$\overbrace{E = h \times \nu \text{ and } \nu \times \frac{c}{\lambda}}^{\text{Combine (4) and (3)}} \Rightarrow E = \frac{h \times c}{\lambda} \tag{5}$$

Worked Example 8

Determine the energy emitted from an arsenic atom as it releases a photon of light with a wavelength of 193.7 nm.

SOLUTION

$$E = \frac{h \times c}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J} \cdot \cancel{\text{s}}) \times (3.00 \times 10^{8}\ \cancel{\text{m}}/\cancel{\text{s}})}{193.7\ \cancel{\text{nm}} \times \dfrac{1 \times 10^{-9}\ \cancel{\text{m}}}{1\ \cancel{\text{nm}}}}$$

$$= \frac{1.9908 \times 10^{-25}\ \text{J}}{1.937 \times 10^{-7}} = 1.03 \times 10^{-18}\ \text{J}$$

Practice 3.8

Determine the energy emitted from a lead atom as it releases a photon of light with a wavelength of 220.4 nm.

ANSWER
9.02×10^{-19} J

Worked Example 9

Determine the energy emitted from a cobalt atom as it releases a photon of light with a frequency of 1.2976×10^{15} Hz.

SOLUTION

$$E = h \times \nu = (6.626 \times 10^{-34}\ \text{J} \cdot \cancel{\text{s}})(1.2976 \times 10^{15}\ 1/\cancel{\text{s}}) = 8.598 \times 10^{-19}\ \text{J}$$

Practice 3.9

Determine the energy emitted from a lead atom as it releases a photon of light with a frequency of 1.361×10^{15} Hz.

ANSWER
9.018×10^{-19} J

3.9 Atomic Structure: Electron Orbitals

Learning Objective

Describe the modern model of the atom and contrast it to earlier, obsolete models.

The quantized energy levels in which electrons exist led to speculation about where these levels were located around the nucleus. Early models showed electrons orbiting the nucleus as planets orbit the sun. In fact, we still draw a similar model when discussing the emission of photons from an excited energy level. However, you should recognize that what is fixed are the energy levels of electrons, *not* the locations of the electrons. Scientists often use models that are known to be oversimplified, but these tools help us understand a topic, and we also recognize that the model is not perfect. An analogy to police work would be the use of profiles to catch a serial murderer. The police know that even though the profiles are not 100% accurate, they provide helpful information for understanding the criminal.

One challenge that arises when we attempt to locate the exact position of an electron is that we cannot do so without disturbing the energy of that electron. If we attempt to measure the energy of an electron, the corresponding location is altered. Therefore, finding the exact location of electrons that have a specific, fixed energy level is impossible. This physical limitation to the measurement of electrons is summarized in the **Heisenberg uncertainty principle:**

> The more precisely the position is determined, the less precisely the momentum is known in this instant, and vice versa.
>
> —Werner Heisenberg, 1927

The energy of a particle is related to the momentum to which Heisenberg refers in his statement.

The best scientists can do is to predict the highest probability of the location of an electron of a given energy around the nucleus of an atom. The details of how these predictions are made are in an area of study known as quantum mechanics, which requires an extensive background in calculus, chemistry, and physics to grasp. However, a full understanding of quantum mechanics is not necessary to comprehend and use the results. Just as we do not need an extensive knowledge of computer chip technology to use a computer, we do not have to dwell on the details of quantum mechanics to gain some understanding of electrons in atoms.

Examine the crime map shown in Figure 3.14. Although police officers do not know the exact location of future crimes, they can examine a map that shows where crimes have been committed in the past and predict where the greatest probability of the occurrence of crimes will be. In Figure 3.14 the circled area shows the greatest density of purse snatchings, so it makes sense to expect this crime to have the highest probability in the future of occurring in the circled region.

Through the mathematics of quantum mechanics, density maps for electrons of a fixed energy level have been determined. The **orbital** of an electron is a three-dimensional region of space in which an electron has the highest probability of being located. In a similar fashion to the crime map example, an area of highest probability is defined and shown in Figure 3.15. Figure 3.15a shows the cross-sectional (two-dimensional) electron density map for locating the single electron of the hydrogen atom. It is apparent from the figure that the greatest probability of locating the

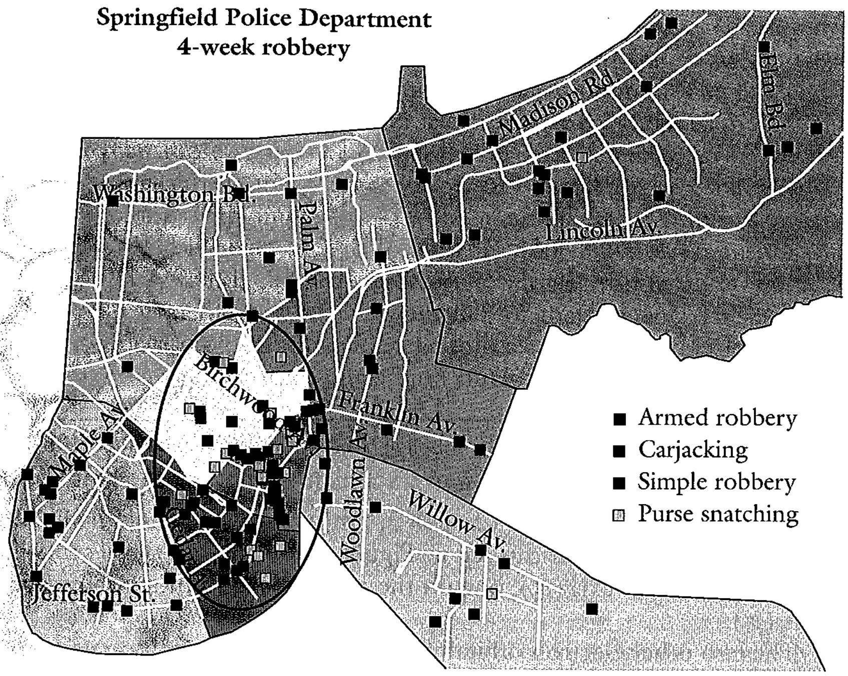


Figure 3.14 This crime map of Springfield shows a high density of purse snatchings occurring over four weeks in a roughly oval-shaped area. The probability of purse snatching occurring in the future is greatest in this region.

electron is in a region surrounding the center of the atom. The probability of finding the electron decreases at distances farther away from the nucleus. Figure 3.15b is the three-dimensional representation of the orbital, which has a spherical shape. A sphere-shaped orbital is known as an ***s* orbital.** (The *s* actually stands for "sharp," not "spherical," as one might predict. The term *sharp* was used because it describes the emission lines observed when the electrons in the atom are excited.)

The shape of the electron orbital changes as the energy level of an electron increases. Beyond the *s* orbital, there are three other orbitals, starting with the ***p* orbital,** shown as a probability density map in Figure 3.16a. The *p* orbital has a dumbbell shape: Electrons are located on either side of the nucleus in a teardrop-shaped lobe. One major difference between *p* and *s* orbitals is that there are three of the *p* orbitals, all having

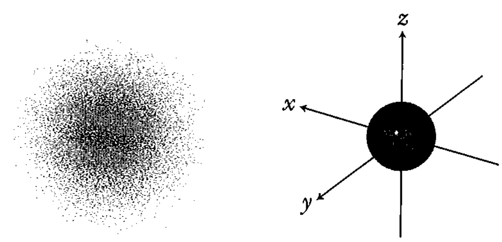


Figure 3.15 (a) Cross-sectional model and (b) spherical three-dimensional model of the *s* orbital.

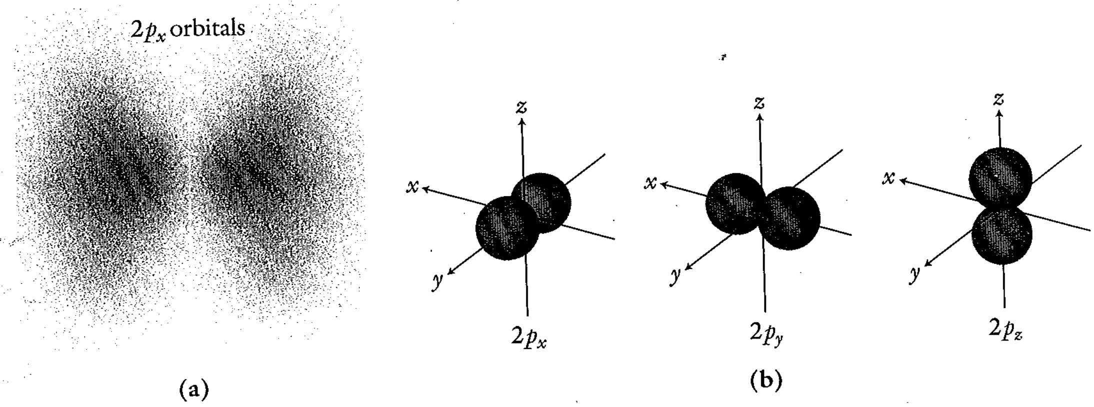


Figure 3.16 (a) Cross-sectional model and (b) the three dumbbell-shaped three-dimensional models of the *p* orbitals.

identical energies. As you can see in Figure 3.16b, one of the *p* orbitals is lined up on the *x* axis (p_x), one on the *y* axis (p_y), and the third on the *z* axis (p_z).

The two other electron orbital types, the ***d*** and ***f*** **orbitals,** are shown in Figure 3.17. The number and complexity of the orbitals increase dramatically, as shown in the figure, and are provided only for completeness; this book does not delve further into the orbital discussion.

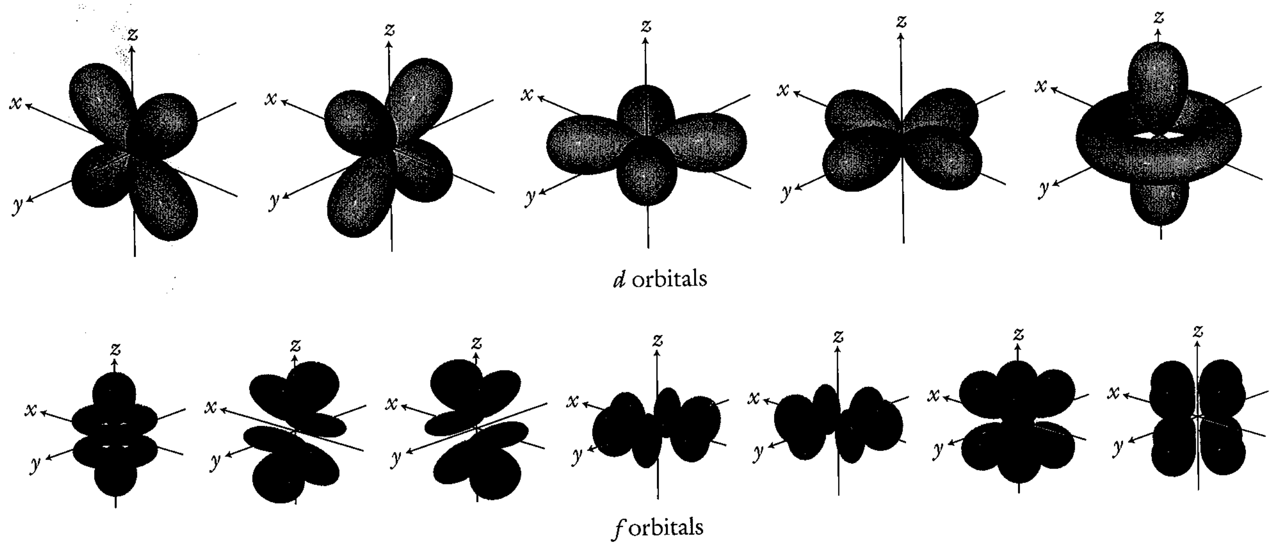


Figure 3.17 There are five separate *d* orbitals and seven separate *f* orbitals. The shapes of the orbitals in a set vary dramatically, but the energy of the orbitals in a set is equivalent.

3.10 | Electron Configurations

Learning Objective

Write the electron configuration for an atom of an element.

Let's take a moment for a brief summary of what has been presented thus far about the behavior of electrons in atoms. The atomic clues that are used to solve crimes come from the transitions of electrons between a ground-state orbital and a vacant, excited-state orbital. When energy is absorbed by an electron, it moves from a lower energy level (usually the ground state) to a higher energy orbital (an excited state). As the electron then returns to the ground state, it emits a photon. The line emission spectra for atoms with fewer electrons (the lighter elements) are simpler than those of heavier elements. Heavier elements have a greater number of electrons and a larger variety of possible excited states.

For atoms with multiple electrons a question then arises: Exactly which electron is being excited to a higher excited state? To answer this question, a system is needed to identify each electron in an atom. This system is called the ***electron configuration*** of the element. The periodic table is a necessary tool for understanding electron configurations.

Two rules govern the distribution of electrons in orbitals:

Rules for Electron Orbitals

1. A single orbital can contain a maximum of two electrons.
2. When filling electrons in the *p*, *d*, and *f* subsets, each orbital of the subset gets a single electron before any orbital of the subset receives a second electron.

Electron configurations can be thought of in much the same way as house numbers in your street address. Each set of orbitals is like a city block. Figure 3.18 is a color-coded map of the orbital blocks. Remember that the periodic table is arranged by increasing number of protons. For each proton that is gained, so is one electron. The electrons go into the orbital designated by the color-coded blocks in the periodic table.

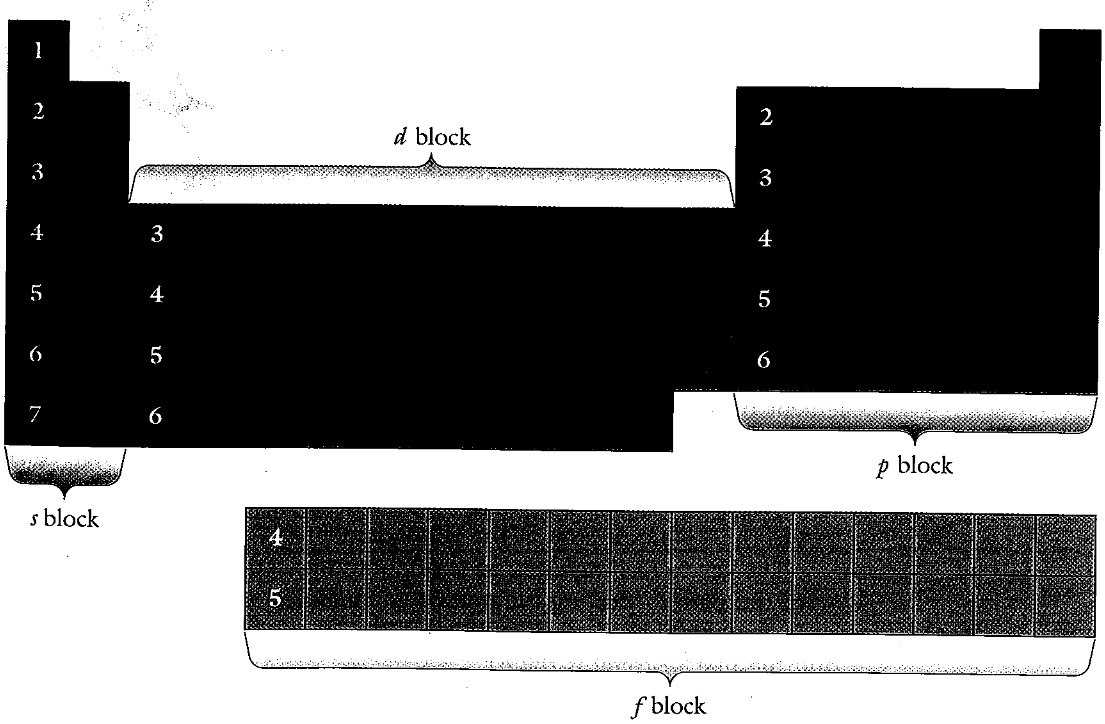


Figure 3.18 In examining the elements by increasing atomic number, it is apparent that electrons first occupy the 1*s* orbital. The second orbital to fill is the 2*s* followed by the 2*p*, and so on.

Let's examine which orbitals the electrons occupy as we increase the atomic number.

Element	Number of e^-	Orbital
H	1	First *s* orbital
He	2	Both e^- located in first *s* orbital
Li	3	2 e^- located in first *s* orbital, 1 e^- in second *s* orbital
Be	4	2 e^- located in first *s* orbital, 2 e^- in second *s* orbital

Writing the electron location in this fashion is cumbersome and time-consuming. Therefore, a shorthand method has been developed:

Number of electrons in orbital

$$\text{Be: } 1\text{s}^2\ 2\text{s}^2$$

Orbital type

Orbital number

Rewriting and expanding on our list of electron configurations:

Element	Number of e^-	Orbital
H	1	$1s^1$
He	2	$1s^2$
Li	3	$1s^2 2s^1$
Be	4	$1s^2 2s^2$
B	5	$1s^2 2s^2 2p^1$*
C	6	$1s^2 2s^2 2p^2$
N	7	$1s^2 2s^2 2p^3$

*Note that the first *p* orbital is in the second energy level.

Let's take a closer look at reading the electron configuration for nitrogen directly from the periodic table. First, starting at the beginning of the periodic table in Figure 3.18, read each row until you get to the element of interest. This is much the same as giving someone driving directions such as "Pass the 100 and 200 block of Elm Street, turn left on Cambridge Street, and go three houses down to 606 Cambridge Street." For nitrogen, we would say, "Pass the $1s^2$ and $2s^2$ block, and when you get to the $2p$ block, stop at the third element."

The key to reading electron configurations is to practice writing them until the pattern becomes ingrained. You should note on a copy of the periodic table that the first *p* orbital is the $2p$, the first *d* orbital is the $3d$, and the first *f* orbital is the $4f$.

Worked Example 10

Write the electron configurations for nitrogen through argon.

SOLUTION

N:	$1s^22s^22p^3$	Al:	$1s^22s^22p^63s^23p^1$
O:	$1s^22s^22p^4$	Si:	$1s^22s^22p^63s^23p^2$
F:	$1s^22s^22p^5$	P:	$1s^22s^22p^63s^23p^3$
Ne:	$1s^22s^22p^6$	S:	$1s^22s^22p^63s^23p^4$
Na:	$1s^22s^22p^63s^1$	Cl:	$1s^22s^22p^63s^23p^5$
Mg:	$1s^22s^22p^63s^2$	Ar:	$1s^22s^22p^63s^23p^6$

Practice 3.10

Write the full electron configurations for xenon, arsenic, and ruthenium.

ANSWER

Xe: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$
As: $1s^22s^22p^63s^23p^64s^23d^{10}4p^3$
Ru: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^6$

Writing the entire electron configuration for the heavier elements can become time-consuming and repetitive. Additionally, the electrons that are of interest to chemists are the outermost *s* and *p* orbital electrons. These electrons are collectively called the **valence shell electrons** and are of interest because chemical reactions involve the gaining, losing, and sharing of valence shell electrons.

The inner electrons that make up the beginning of the electron configuration are called the **core electrons.** Core electrons are not involved in chemical reactions except in rare cases. The separation of electrons into those that participate in reactions and those that do not leads to a method of abbreviating and shortening the electron configurations. When you provide directions to someone, you usually don't list every single house they will pass. Instead, you provide a reference point to start the direction such as, "Go down to the Y mart, turn left, go two blocks, and stop at the sixth house."

The reference point for electron configurations is the noble gas elements. Always start at the noble gas element that directly precedes the element of interest. For example, if we were to write the electron configuration of sodium, we would start at neon, the noble gas directly before sodium. The newly abbreviated electron configuration of sodium is $[Ne]3s^1$.

Worked Example 11

Write out the abbreviated electron configurations for iron, iodine, phosphorus, zinc, cadmium, and potassium.

SOLUTION

Fe: $[Ar]4s^23d^6$
I: $[Kr]5s^24d^{10}5p^5$
P: $[Ne]3s^23p^3$
Zn: $[Ar]4s^23d^{10}$
Cd: $[Kr]5s^24d^{10}$
K: $[Ar]4s^1$

Practice 3.11

Which elements have the following electron configurations?

$[Ar]4s^23d^2$ $[Kr]5s^24d^{10}5p^1$ $[Ne]3s^23p^2$ $[Ar]4s^23d^{10}4p^5$

ANSWER

Titanium Indium Silicon Bromine

Table 3.3 lists the full and abbreviated electron configurations of the first 54 elements for your reference. An excellent use for this table is in practicing writing both the full and abbreviated electron configurations of all the elements: Check your work against the table. Several elements do not follow the rules for writing electron configurations; these elements are highlighted in red.

Table 3.3 Electron Configuration of the Elements Hydrogen through Xenon

	Full	Abbreviation		Full	Abbreviation
H	$1s^1$	—	Ni	$1s^22s^22p^63s^23p^64s^23d^8$	$[Ar]4s^23d^8$
He	$1s^2$	—	Cu	$1s^22s^22p^63s^23p^64s^1d^{10}$	$[Ar]4s^13d^{10}$
Li	$1s^22s^1$	$[He]2s^1$	Zn	$1s^22s^22p^63s^23p^64s^23d^{10}$	$[Ar]4s^23d^{10}$
Be	$1s^22s^2$	$[He]2s^2$	Ga	$1s^22s^22p^63s^23p^64s^23d^{10}4p^1$	$[Ar]4s^23d^{10}4p^1$
B	$1s^22s^22p^1$	$[He]2s^22p^1$	Ge	$1s^22s^22p^63s^23p^64s^23d^{10}4p^2$	$[Ar]4s^23d^{10}4p^2$
C	$1s^22s^22p^2$	$[He]2s^22p^2$	As	$1s^22s^22p^63s^23p^64s^23d^{10}4p^3$	$[Ar]4s^23d^{10}4p^3$
N	$1s^22s^22p^3$	$[He]2s^22p^3$	Se	$1s^22s^22p^63s^23p^64s^23d^{10}4p^4$	$[Ar]4s^23d^{10}4p^4$
O	$1s^22s^22p^4$	$[He]2s^22p^4$	Br	$1s^22s^22p^63s^23p^64s^23d^{10}4p^5$	$[Ar]4s^23d^{10}4p^5$
F	$1s^22s^22p^5$	$[He]2s^22p^5$	Kr	$1s^22s^22p^63s^23p^64s^23d^{10}4p^6$	$[Ar]4s^23d^{10}4p^6$
Ne	$1s^22s^22p^6$	$[He]2s^22p^6$	Rb	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^1$	$[Kr]5s^1$
Na	$1s^22s^22p^63s^1$	$[Ne]3s^1$	Sr	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$	$[Kr]5s^2$
Mg	$1s^22s^22p^63s^2$	$[Ne]3s^2$	Y	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^1$	$[Kr]5s^24d^1$
Al	$1s^22s^22p^63s^23p^1$	$[Ne]3s^23p^1$	Zr	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^2$	$[Kr]5s^24d^2$
Si	$1s^22s^22p^63s^23p^2$	$[Ne]3s^23p^2$	Nb	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^3$	$[Kr]5s^24d^3$
P	$1s^22s^22p^63s^23p^3$	$[Ne]3s^23p^3$	Mo	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^4$	$[Kr]5s^24d^4$
S	$1s^22s^22p^63s^23p^4$	$[Ne]3s^23p^4$	Tc	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^5$	$[Kr]5s^24d^5$
Cl	$1s^22s^22p^63s^23p^5$	$[Ne]3s^23p^5$	Ru	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^1d^7$	$[Kr]5s^1d^7$
Ar	$1s^22s^22p^63s^23p^6$	$[Ne]3s^23p^6$	Rh	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^1d^8$	$[Kr]5s^14d^8$
K	$1s^22s^22p^63s^23p^64s^1$	$[Ar]4s^1$	Pd	$1s^22s^22p^63s^23p^64s^23d^{10}4p^64d^{10}$	$[Kr]4d^{10}$
Ca	$1s^22s^22p^63s^23p^64s^2$	$[Ar]4s^2$	Ag	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^1d^{10}$	$[Kr]5s^14d^{10}$
Sc	$1s^22s^22p^63s^23p^64s^23d^1$	$[Ar]4s^23d^1$	Cd	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}$	$[Kr]5s^24d^{10}$
Ti	$1s^22s^22p^63s^23p^64s^23d^2$	$[Ar]4s^23d^2$	In	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^1$	$[Kr]5s^24d^{10}5p^1$
V	$1s^22s^22p^63s^23p^64s^23d^3$	$[Ar]4s^23d^3$	Sn	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^2$	$[Kr]5s^24d^{10}5p^2$
Cr	$1s^22s^22p^63s^23p^64s^13d^5$	$[Ar]4s^13d^5$	Sb	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^3$	$[Kr]5s^24d^{10}5p^3$
Mn	$1s^22s^22p^63s^23p^64s^23d^5$	$[Ar]4s^23d^5$	Te	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^4$	$[Kr]5s^24d^{10}5p^4$
Fe	$1s^22s^22p^63s^23p^64s^23d^6$	$[Ar]4s^23d^6$	I	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^5$	$[Kr]5s^24d^{10}5p^5$
Co	$1s^22s^22p^63s^23p^64s^23d^7$	$[Ar]4s^23d^7$	Xe	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$	$[Kr]5s^24d^{10}5p^6$

Evidence Analysis | Scanning Electron Microscopy

Figure 3.19 The smoke cloud created during the discharge of a firearm leaves a residue on any object in the close vicinity of the firearm. (BrandX Pictures)

Figure 3.20 Scanning electron microscope image of gunshot residue. (International Association for Microanalysis)

Figure 3.19 shows the smoke cloud that surrounds the end of the barrel and the chamber of a pistol after firing. The cloud consists of gases formed during the explosive discharge of the gunpowder and small amounts of unburned gunpowder. The gunshot residue is deposited onto the hands and arms of the shooter. Gunshot residue is also deposited on the target if the target is close enough to the end of the barrel. Investigators use the amount and pattern of gunshot residue on a victim to determine an approximate distance to the shooter.

To determine whether or not a person has gunshot residue on his or her hands, detectives take several small metal cylinders that contain an adhesive coating and pat down the suspected shooter's hands. Gunshot residue, if present, sticks to the adhesive on the metal cylinder, which is then placed into a scanning electron microscope (SEM). A scanning electron microscope functions like a traditional microscope except that the SEM uses electrons bouncing off a surface to form an image. The traditional microscope depends on photons of light bouncing off a surface. There are several advantages to using electrons over photons; the main advantage is that electrons make it possible to obtain an image of much smaller particles.

Particles of gunpowder come in very distinctive shapes—cylinders, tubes, discs, spheres, and slabs—a portion of which remain unburned in gunshot residue. The SEM image in Figure 3.20 shows how gunshot residue recovered from a suspect's hand would appear.

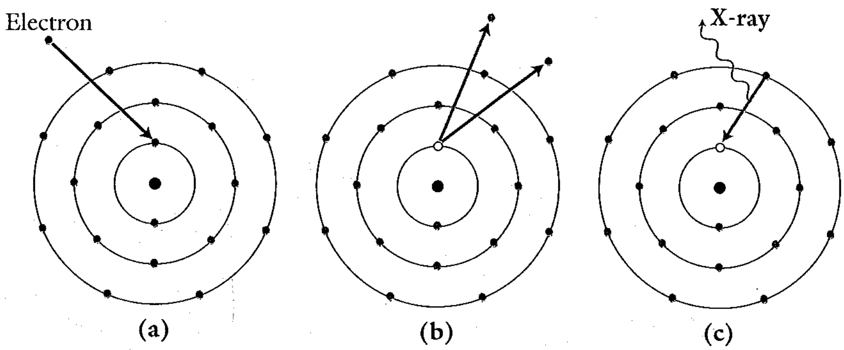


Figure 3.21 Basic principle of an energy-dispersive X-ray spectrometer (EDS).

(*continued*)

Evidence Analysis | Scanning Electron Microscopy (*continued*)

Typical SEM-EDS system. (Lawrence Migdale/Photo Researchers, Inc.)

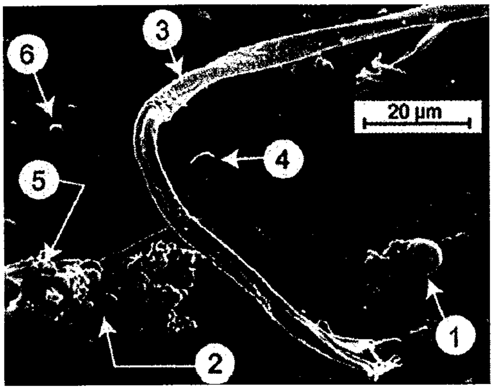


Figure 3.22 Six distinct particles collected from skin near the burn wound of the victim. (Kosanke, K. L.; Dujay, R. C.; Kosanke, B. *J. Forensic Sci,* May 2003, vol. 48, no. 3)

The shape of a particle is not sufficient evidence for the forensic scientist to conclude whether the particle is, in fact, gunshot residue. The scientist must also evaluate the chemical makeup of the particle, which may be only 1.0×10^{-5} m (10 μM) in size! The elemental analysis of the particles can be done simultaneously with the SEM imaging of the particle by an instrument called an energy dispersive X-ray spectrometer (EDS), which is attached to the SEM. The combined analytical system is abbreviated SEM-EDS.

To understand how the EDS system detects the presence of elements, Figure 3.21, showing a simplified orbital model of an atom, can be of help. (Although we know that electrons are not actually in orbits that resemble those of the planets, this simplified model is a convenient device for demonstrating how the EDS system works.) In part (a), an electron from the SEM strikes an atom. Because the electron is so small, it can penetrate the atom and collide with enough energy to force an inner core electron to leave the atom. Part (b) shows the atom with a vacancy in the inner core electrons. This condition is not stable; electrons always go to the lowest possible energy level. Part (c) shows an electron from one of the outer shells, which has a higher energy, dropping down to fill the vacancy in the lower energy orbital and releasing excess energy as a photon.

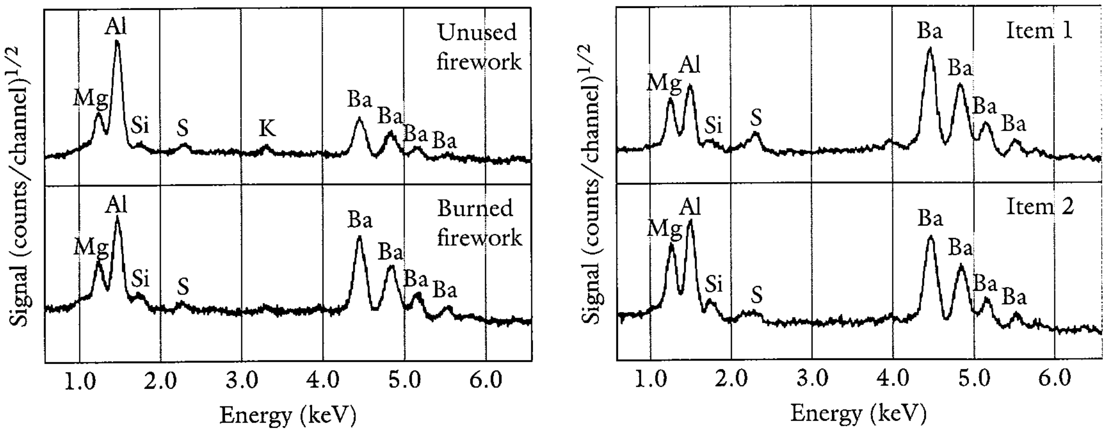


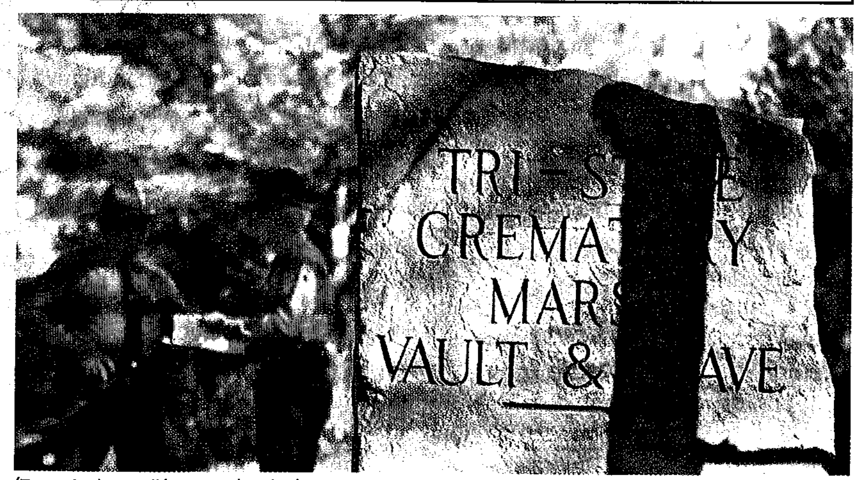
Figure 3.23 EDS spectra. Elemental analysis of the explosive particles in an unused firework and a carefully burned firework are compared with particles found on the victim and suspected to be from the firework.

The photons emitted from atoms in this process are X-rays. The process involves the same basic concepts studied earlier for the creation of line spectra from energetically excited electrons relaxing to a lower energy level. Just as the line spectra of excited electrons in atoms can fingerprint an element, each element detected in an EDS emits X-rays that have a unique energy for that element.

An SEM-EDS system can be used to investigate any material in which the combination of high magnification and elemental analysis would be useful to investigators. Consider an investigation into an accidental explosion of consumer fireworks. A person claimed to have been severely burned by the negligent use of fireworks by neighbors. The neighbors admitted to having launched fireworks but disputed the claim that they were responsible for causing the burns. If the victim's claim were true, residue from the explosives in the fireworks should be found in the vicinity of the burn. Figure 3.22 is an SEM image of the trace evidence residue obtained from skin near the burn.

The next step of the investigation was to determine if any of the particles were in fact from the firework itself. The forensic scientists obtained unused fireworks of the same type used on the evening in question and compared the elemental makeup of the particles shown in Figure 3.22 to the unused fireworks. Two recovered particles were determined to be residue from an explosive material and had the same elemental composition, as shown in Figure 3.23.

3.11 Case Study Finale: To Burn or Not to Burn



(Tammi Chappell/Reuters/Corbis)

Dr. Al Hazari contemplated the fate of Chigger's remains and the puzzle of how to determine if the ashes were human or if a filler material had been used to dupe the family. The investigation into the crematorium had led investigators to believe that a variety of materials, from regular wood ash to cement mix, were being used to fill family urns. Dr. Hazari came up with a simple method for solving the problem. He considered the known facts about the elemental content of a typical human body, shown in Figure 3.24. He noted that the human body contains only about 1 gram of silicon, and he knew that this element would have survived the heat of a crematorium oven. He calculated that if the contents of the urn were, in fact, human ashes, only a small fraction—less than 1%—would be silicon. If the cremains were in actuality cement or mortar mix, the sample would contain a much higher proportion of silicon.

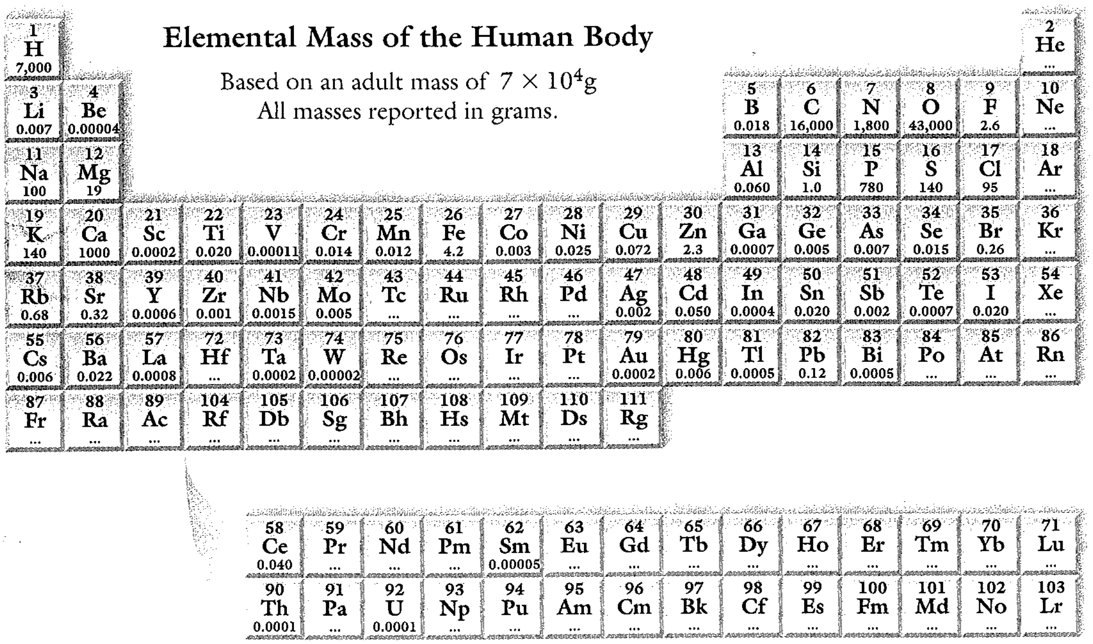
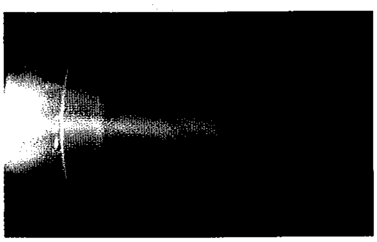


Figure 3.24 Periodic table of the human body.



The temperature of the plasma in an ICP-OES can reach 10,000°C. (Courtesy of Dave Aeschliman)

The cremains were sent to a professional laboratory for analysis of silicon content. The instrument used to analyze the sample was an inductively coupled plasma-optical emission spectrometer, or ICP-OES. This instrument is commonly used to detect elemental concentrations as low as one part per billion.

When silicon atoms are heated to extremely high temperatures, the electrons reach a higher-energy excited state and emit light at a wavelength of 516 nm. An ICP-OES is capable of exciting the silicon atoms in the plasma and detecting the wavelength of light emitted by the excited atoms. The **plasma** of the ICP-OES is a gaseous region that is electrically conductive and can reach a temperature of 10,000°C. The temperature of a plasma is about three times hotter than the temperature of a flame. It causes more atoms to be excited and permits lower detection limits.

The results of the analysis came back as the family had feared: 19% silicon. The cremains were certainly not those of Chigger or any other human. The skeletal remains of Chigger were later identified among the 334 bodies by the use of DNA analysis. This time the family had Dr. Bill Bass provide an independent identification and also personally supervise the cremation of the remains.

CHAPTER SUMMARY

- Leucippus and Democritus first proposed an atomic theory of matter in ancient Greece. In the 1700s, work by Antoine Lavoisier and Joseph Proust provided sufficient experimental data for John Dalton to develop his atomic theory of matter.
- Experiments to prove the atomic theory produced results that seemed to contradict the indivisible nature of the atom. The experiments would lead to the discovery of the subatomic particles: electrons, protons, and neutrons.

- In Rutherford's model of the atom, most of the atom was empty space. The protons were in an extremely small region called the nucleus. Later experiments showed that the nucleus also contained neutrons.
- Isotopes are atoms of the same element that have a different number of neutrons. The isotopes undergo identical chemical reactions, which allow them to be used as medical and investigative indicators. The atomic weight of an element listed in the periodic table is actually a weighted average of all the isotopes, taking into consideration the natural abundance of each isotope.
- When energy is absorbed by an atom, the electrons can be promoted to higher quantized energy levels. The excited atoms then release photons of light as the electrons relax back to the ground state, forming a unique line spectrum that can be used to identify the element.
- Determining the exact location and the energy of an electron is impossible, according to the Heisenberg uncertainty principle, because measuring one variable inevitably alters the other. Modern atomic theory uses quantum mechanics to determine the region in space with the highest probability of containing an electron. There are four distinct orbital types, the *s*, *p*, *d*, and *f* orbitals. The *s* orbital is spherical in shape and the *p* orbital is shaped like a dumbbell. The *d* and *f* orbitals are more complex.
- Electron configurations provide a method for identifying each electron within an atom. The configuration lists each orbital in the atom and the number of electrons located in the orbitals.
- The SEM-EDS is a powerful investigative tool. It uses electrons scattered from the surface of an object to provide magnification beyond that available using a traditional light microscope, easily viewing objects that are only 10 μm in size. As the electrons strike the surface, core electrons are ejected. As a higher energy valence electron assumes the place of the missing core electron, it releases a photon of light corresponding to the X-ray region of the spectrum. The energy of the X-ray is unique to the element producing it and provides the chemical makeup of the particles being viewed.

KEY TERMS

law of conservation of mass, p. 59
law of definite proportions (law of constant composition), p. 61
theory, p. 61
Dalton's atomic theory, p. 61
law of multiple proportions, p. 62
proton, p. 64
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CONTINUING THE INVESTIGATION Additional Readings, Resources, and References

Bass, B., and Jefferson, J. *Death's Acre,* Putnam, New York, 2003.

Beard, B. L., and Johnson, C. M. Strontium isotope composition of skeletal material can determine the birthplace and geographic mobility of humans and animals. *Journal of Forensic Science* 45(5), September 2003.

Emsley, J. *Nature's Building Blocks: An A–Z Guide to the Elements,* Oxford University Press, New York, 2001.

Kosanke, K. L., Dujay, R. C., and Kosanke, B. Characterization of pyrotechnic reaction residue particles by SEM/EDS. *Journal of Forensic Science* 48(3), May 2003.

Investigating Chemistry

A Forensic Science Perspective

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