CHEMISTRY
CHALLENGES AND SOLUTIONS

Unit 1: *Matter and the Rise of Atomic Theory—The Art of the Meticulous*

Unit Overview

Since the first time early humans lit a fire, cooked food, fermented fruit, or flaked a stone axe, we have been manipulating the matter around us. This unit explores how chemistry evolved from adapting materials for practical purposes to a science that systematically offers solutions to the world's challenges. It is a story that will start with Democritus around 400 BCE, taking us through the early Arab chemist, Jābir ibn Hayyān, to the meticulous work of the Middle Age alchemists, and finally to the birth of chemistry as a science during the Age of Enlightenment in the 18th century. In the accompanying video, we explore the Silicon Age, where the goal of manipulating and purifying matter at the atomic scale is making possible today's technological advances such as cell phones and solar panels.

by Jennifer Weeks

Sections

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Section 1: Introduction

Figure 1-1. Bioluminescent Lobate Ctenophore (comb jellyfish)

Bioluminescent organisms like this jellyfish produce light from chemical reactions within their tissues. Others carry light-producing bacteria within their bodies.

Chemicals are the building blocks of our planet and of the living systems that inhabit it. The science of chemistry analyzes the structure of matter, its properties, and how chemicals combine and change. It enables us to understand countless processes that take place naturally around us—for example, how rocks break down slowly into soil, or why volcanic eruptions can affect weather patterns and air quality across large areas.

Chemistry is also central to numerous functions and characteristics of living organisms. Some chemical processes are common across many species, such as digestion—breaking down food and extracting its nutrients. Others are more specialized and only occur in certain types of organisms. As an example, some bacteria, insects, algae, jellyfish, and other organisms (mainly aquatic and almost all invertebrates) are bioluminescent: They can produce visible light from chemical reactions within their tissues. (Figure 1-1)

Long before humans began to study chemistry, or even formed the concept of science and scientific inquiry, they were using basic chemistry techniques to improve their daily lives. Setting fuel on fire is a chemical process that generates heat. Cooking food over fire causes chemical changes in the food; so do other processes that have been widely used for thousands of years, such as leavening and fermentation (using chemical reactions to make baked goods rise or convert sugars into alcohol). Human civilization progressed from the Stone Age through the Bronze and Iron Ages as humans learned to smelt these metals and cast them into tools and weapons—skills that required an increasingly sophisticated understanding of the properties of metals and how they could be manipulated.

Figure 1-2. Interior of a Laboratory with an Alchemist

Painting of an alchemist from the Chemical Heritage Foundation's "Transmutations" exhibit.

Scholars started thinking analytically about chemistry thousands of years ago. Greek philosophers tried to identify the smallest unit of matter and theorized about which elements were the core ingredients of all other substances. Through the Middle Ages and Renaissance, as chemical scholarship shifted first to the Arab empire and then west to Christian Europe, it blended several ways of thinking. On a practical level, skilled craftspeople developed standard procedures for making paints, medicines, inks, dyes, and many other products used widely in daily life. At the same time, an evolving discipline called "alchemy" pondered broader philosophical challenges that often were framed in religious terms: What were the highest forms of matter? Could one material be transformed into another that was purer? And in doing so, could humans also purify themselves, perhaps even achieving eternal life? (Figure 1-2)

In the 1500s and 1600s, scholars' approach to chemistry started to change and became increasingly rooted in observation, experimentation, and evidence, rather than in religious or philosophical beliefs. Chemistry evolved into an empirical, laboratory-based science in the 18th and 19th centuries, with investigators studying chemical processes systematically, formulating laws about properties of matter, and disproving earlier beliefs. By the late 19th century, chemistry was an established scientific discipline that was contributing practical knowledge to many sectors of modern industrial life. And researchers were pursuing a new goal: penetrating the atom.

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Section 2: Chemistry as a Science

Chemistry has shaped human lives for at least a quarter of a million years, and perhaps much longer, starting when prehistoric people mastered the controlled use of fire to generate heat and cook food.[1] Over many millennia, humans learned to manipulate materials in more sophisticated ways, first to produce necessities like tools and weapons, and later to create materials that enhanced their lives, from soap to medicines. Making many of these products required a deep understanding of the raw materials and skill in techniques such as refining and purifying them.

However, to understand how chemistry developed into a modern science, it is useful to consider the difference between skilled craftsmanship and scientific inquiry. Blacksmiths, potters, and cooks are craftspeople: They combine and use materials to create practical products, often according to formulas that have been refined and passed down by their predecessors. In the process, they may experiment and develop new products or better methods.

Figure 1-3. Alchemy vs. Science

Text of cartoon above: "Of course you can't replicate my experiment. There's a secret incantation that you have to chant, and I'm not telling it to anyone."

Typically, however, craftspeople do not strive to explain *why* something works in a certain way, or to generate new knowledge that is relevant beyond their own specialized work. In contrast, scientific inquiry is a broader process. Scientists observe phenomena, such as the fact that combining two substances produces a third product different from the other two, and form hypotheses that seek to explain the results. Then they develop experiments to test their theories and analyze their findings to see whether they confirm or disprove the original hypothesis. The goal is to produce accurate data and results that other researchers can reproduce consistently. (Figure 1-3)

Chemistry draws from both of these traditions, and many of the innovators who are described in the first two units of this course were both researchers and practitioners. Most important, chemistry became a formal scientific discipline when chemical researchers started to analyze and understand chemical processes, rather than just carry them out.

One key aspect of chemistry as a science is the importance of meticulous attention to detail, especially as researchers focused on smaller and smaller units of matter. Measurement is an essential part of chemistry research, and is central to concepts such as conservation of matter—the principle that matter is not created or destroyed in chemical reactions. As we see chemists in the 18th century begin to use notation and summarize reactions using symbolic equations, they follow the guiding principle that equations should balance, so that the initial reactants contain the same amount of matter as the final products. While chemists developed increasingly sophisticated equipment and procedures, they improved their ability to measure mass, volume, pressure, temperature, and other variables that affect states of matter, and gained greater insight into chemical changes.

In thinking about reliable measurement, it is important to distinguish two concepts that are often confused: precision and accuracy. In a scientific context, accuracy describes how closely a measurement agrees with a true or accepted value; precision, in contrast, describes how closely measurements agree with each other. As seen in Figure 1-4 below, archer A is neither accurate nor precise. Archer B is more accurate because her arrows are closer to the bull's-eye. Archer C is precise, since his arrows all hit the same spot, but is not accurate. Only archer D is both precise and accurate. The larger point for chemistry is that results may agree with one other yet still be incorrect. Accurate equipment and techniques are central to the practice of modern chemistry.

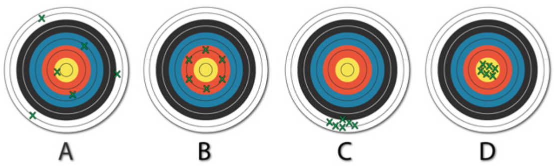

Figure 1-4. Precision vs. Accuracy

Archer A is neither accurate nor precise. Archer B is more accurate because her arrows are closer to the bull's-eye. Archer C is precise, since his arrows all hit the same spot, but is not accurate. Only archer D is both precise and accurate.

[1] Paul Rincon, "Bones hint at first use of fire," *BBC News Online*, March 22, 2004.

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Section 3: Chemistry in the Ancient World

Metallurgy is chemistry's oldest ancestor, dating back to the Bronze Age, the period when humans learned to smelt copper and tin from natural ores (rocks containing these metals, along with many other materials). Smelting is a reduction process. Heating an ore in the presence of carbon, usually charcoal, produces a reaction in which the carbon from the charcoal combines with oxygen in the ore, leaving pure metal behind. (For more on redox chemistry, see Unit 11.) Blending copper and tin produces bronze, an alloy that is harder than either copper or tin alone, resists corrosion, and has a fairly low melting point, which makes it easy to cast into many forms. Civilizations entered the Bronze Age at different points, starting in roughly 3000 BCE (Before Common Era).

Next they progressed into the Iron Age, starting as early as 1800 BCE in the Middle East but later in Europe. Iron requires much higher temperatures for smelting than copper or tin, so producing it requires specially designed furnaces. But iron is also much harder than bronze, and more common than tin. Once in use, it replaced bronze for many purposes. (Figure 1-5)

Figure 1-5. Iron Age Swords and Spearheads from Kirkburn, England

Shown here are a sword, scabbard (the sheath for holding the sword), and several spearheads, which date from around 300-200 BCE, during England's Iron Age. The sword and spearheads are made of iron and the scabbard has a decorated copper alloy front and an iron back. The detail on the sword indicates that it was made by a skilled metalworker.

Metallurgical techniques were widespread in many areas by the 6th century BCE, including ancient Greece and the Middle East. But Greek philosophers were some of the first thinkers who sought to develop theories about *why* materials formed and interacted as they did. In about 400 BCE, Democritus sought to identify the smallest unit of matter that could not be subdivided further and still retain its characteristic properties. He proposed that all matter was made up of tiny, indestructible units called "atoms," which moved about in an infinite void and combined to create visible objects. Differences among the properties of atoms created different types of objects. This concept was pure theory, not based on experimental evidence, and would remain so for several thousand years, until English chemist John Dalton (discussed in Section 8 of this unit) gave it a scientific foundation in the early 19th century.

A competing view, proposed by another philosopher named Empedocles and elaborated on by the famed scientist and philosopher Aristotle around 350 BCE, held that all matter was made up of four elements: fire, air, earth, and water. Aristotle called these substances "prime matter," and theorized that they had various levels of four properties—hot, cold, wet, and dry. Each element in its pure form combined two of these properties: Water was cold and wet, earth was cold and dry, fire was hot and dry, and air was hot and wet. An element could not be both hot and cold, or wet and dry. (Figure 1-6)

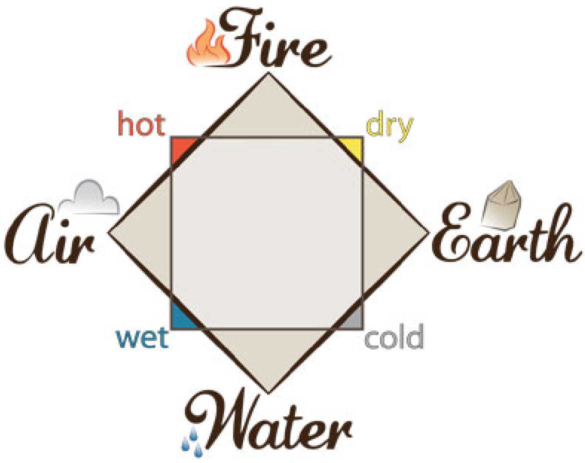

Figure 1-6. Aristotle's Four Elements and Four Properties

Aristotle's conception of four elements was not grounded in science, but was widely accepted for centuries after his death.

These ideas owed as much to philosophy and spirituality as they did to any kind of scientific thinking. Empedocles associated each of the elements with one of the Greek gods: Air represented Zeus (king of the gods), earth was Hera (his wife), fire stood for Hades (the god of the underworld), and water was associated with Nestis (Persephone, the queen of the underworld, who triggered the flowering of plants when she visited Earth in spring and the end of growth when she went back underground in the fall). Aristotle believed that metals grew in the earth, and that by changing their qualities, they could be transmuted from one form of matter into another. Aristotelian ideas about matter and the elements helped to inspire the next major stage in the evolution of chemistry thinking: alchemy.

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Section 4: Chemistry in the Arab World

After the fall of the Greek and Roman Empires, the expanding Arab Muslim Empire emerged as the next important center of learning in the 7th and 8th centuries. Islamic scholars translated texts from earlier civilizations, including ancient Egypt and Greece, into Arabic for their own use. From roughly 750 through 1258 CE (Common Era), Arabic scientists made important discoveries in many fields, including astronomy, mathematics, geography, and chemistry. At the center of Arabic chemistry innovation stood one of the first practitioners of chemistry as a science, a chemist and alchemist named Jābir ibn Hayyān, now widely referred to as Jābir.

Figure 1-7. Arab Chemists

Detail from a miniature from Ibn Butlan's Risalat da`wat al-atibba.

© Chemical Heritage Magazine, L.A. Mayer Museum for Islamic Art, Jerusalem.

Jābir was born in the city of Tus, in what is now Iran, and lived until about 803. He served as the court alchemist of a political and spiritual leader named Hārūn al-Rashīd, who ruled in the late 700s. His training combined practical work making medications and other everyday products with studies of mathematics, science, and Greek philosophy. Jābir and other Arab alchemists were influenced by Aristotle's theory of elements and properties, which they incorporated into the evolving practice of alchemy. They accepted the idea that minerals grew underground in mines, and believed that all metals were made up of various blends of two primary metals: mercury and sulfur. Gold was a blend of mercury and sulfur in ideal proportions.[2] (Figure 1-7)

Figure 1-8. Alembic from 13th-Century Tabriz

A 13th-century alembic made in Tabriz (now part of modern-day Iran), shown upside-down. An Arab chemist would distill a substance by heating it with the tube inverted over the liquid. Vapor would rise through the tube, cool under the large glass dome, and condense into the flask underneath it.

In their laboratories, Arab alchemists sought to re-create the processes that they believed produced gold in nature. Since these alchemists believed that gold was the highest form of metal, they thought that working to generate it by changing the compositions of other substances was a process that mimicked God's creative power. Later, European alchemists would associate the purification process with spiritual cleansing and a search for divinity or eternal life. (See Section 5 of this unit.)

Jābir and his followers also carried out extensive basic research into classifying substances and reactions. Arabic alchemists refined many laboratory processes, including **crystallization**, **sublimation**, and **calcination**. By systematizing and repeating these techniques, they were able to identify and describe important chemicals such as muriatic (hydrochloric) acid, sulfuric acid, nitric acid, soda (an old term for sodium salts), and potassium salts. Jābir is credited with inventing the alembic (Figure 1-8) an apparatus used to refine the process of **distillation**. The *Corpus Jabirianum*, a collection of more than 300 books on chemistry and alchemy attributed to Jābir, is widely believed to include many works written by followers who wanted to associate themselves with Jābir and his work.

Jābir and other Arab scientists connected the theoretical world of alchemy with the practical world of laboratory chemistry for the first time. Fittingly, many core terms in chemistry have Arabic roots, including "alcohol" (*al-kohl*), "elixir" (*al-iksīr*), "alembic" (*al-anbīq*), and "chemistry" itself (*al-kimya*).

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[2] Gabriele Farrerrio, "Al-Kimya: Notes on Arabic Chemistry," *Chemical Heritage Magazine*, Fall 2007, http://www.chemheritage.org/discover/media/magazine/articles/25-3-al-kimya-notes-on-arabic-alchemy.aspx.

Glossary

Calcination
The process of heating an ore in the presence of air to decompose it.

Crystallization
The process in which a material forms a solid whose atoms, molecules, or ions form a regularly repeating pattern.

Distillation
The process of purifying a liquid by evaporating it, then collecting and condensing the vapors.

Sublimation
A process in which a substance changes directly from a solid phase to a gas phase without first becoming a liquid.

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Section 5: Pre-Chemistry in Medieval Europe—Alchemists and Apothecaries

During the High Middle Ages, from about 1050 through 1300, civilization was consolidated and agricultural production expanded across western Europe. Scholars translated classic Greek and Arabic texts into Latin, importing ideas from many fields, including mathematics, astronomy, and chemistry. However, daily life in medieval Europe was influenced more strongly by religious teachings than by science. Many Europeans also believed in magic, witches, potions, and charms. As a result, alchemy was widely embraced, but adherents interpreted its ideas in many ways. Some studied it as a refined spiritual quest, others as a practical science, and still others as a window into the world of magic.

Skeptics who doubted claims that alchemists could transmute baser minerals into gold saw the practice as a refuge for frauds and swindlers. In Chaucer's *Canterbury Tales*, written in the late 1300s, the yeoman who narrates "The Canon's Yeoman's Tale" confesses that his master's showy experiments are failures, although Chaucer shows some familiarity with chemistry:

> Our arsenic sulphides, sublimated mercury,
> Our lead oxides ground down fine on porphyry;
> Of each of these some ounces went for certain—
> Nothing helped; we laboured all in vain!
> Neither the vapours in their ascension,
> Nor the solids left settling all adown
> Did in our workings anything avail,
> For lost was all our labour and travail.
> And all the cost, all gone the devil's way,
> Was lost also, whatever we had to pay.[3]

But others took alchemy more seriously. Nicolas Flamel, a French scholar (c. 1330–1418), spent his life decoding a mysterious book filled with alchemical symbols. Flamel believed that the text would help him create the Philosopher's Stone—a talisman that would turn lead into gold. Flamel's scientific contributions are debatable, but his house in Paris—the oldest private residence still standing in the city today—is a tourist destination. In the first book of the fictional Harry Potter series, *Harry Potter and the Sorcerer's Stone* (published in Britain as *Harry Potter and the Philosopher's Stone*), Flamel is mentioned as a "noted alchemist and opera lover" who owns the only known Philosopher's Stone.[4] Other scientists, including figures as legendary as Sir Isaac Newton (1642–1727), also were captivated by alchemical ideas such as **transmutation** and the existence of a Philosopher's Stone. (Figure 1-9)

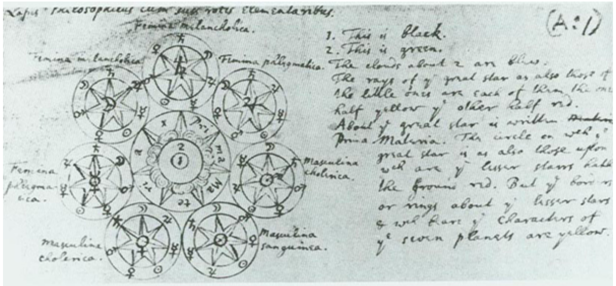

Figure 1-9. Philosopher's Stone

Sir Isaac Newton, one of the towering figures of modern science, also was fascinated by alchemy and the concept of a Philosopher's Stone. He may have believed that it would help him decipher scientific problems.

A more important and better-documented figure than Flamel, the Swiss chemist known as Paracelsus (1493–1541) was trained in both alchemy and practical medicine, and sought to unite these two disciplines. Paracelsus supported central alchemical ideas, such as the belief that all elements were blends of a few primary substances: Along with mercury and sulfur, he believed that this set included salt. But he rejected the prevalent idea that illness was caused by an imbalance of four humors (black bile, yellow bile, blood, and phlegm) within the body, arguing instead that each ailment had its own specific cause and required a specific medicine to cure it. Notably, he diagnosed silicosis, a disease common among miners, as being caused by inhaling metallic vapors (actually, mineral fragments).

Paracelsus launched the field of medical chemistry, using techniques from his alchemy laboratory to develop salves and medicines. Many of his writings were published after his death and spurred doctors to search for single-ingredient medications for individual diseases—a trend that made medicine more effective than popular medieval techniques like bloodletting.

Other professionals were also making medicines in the Middle Ages, although their work focused on practical chemistry, not on spiritual or magical concepts. Starting in the 1200s, these apothecaries split off from the grocery profession and began establishing their own guilds, formulas, and guidelines. Apothecaries used standard chemical processes like distillation and fermentation to prepare medicines from plants, minerals, and other common sources. Trainees worked as apprentices and had to pass an examination to join the profession.[5] Apothecaries published pharmacopoeias—compendiums of information about the preparation and properties of various drugs—into the 19th century, and were the forerunners of modern pharmacists.

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[3]Geoffrey Chaucer, *The Canterbury Tales*, XVIII, "The Canon's Yeoman's Tale," http://www.poetryintranslation.com/PITBR/English/CanterburyTalesXVIII.htm#_Toc166150057.

[4] U.S. National Library of Medicine, "Do Mandrakes Really Scream? Magic and Medicine in Harry Potter," http://www.nlm.nih.gov/exhibition/mandrakes/flamel.html.

[5]Science Museum, London, History of Medicine, "Apothecaries," http://www.sciencemuseum.org.uk/broughttolife/people/apothecaries.aspx

Judith S. Woolf, “Women’s Business: 17th-Century Female Pharmacists,” *Chemical Heritage Magazine*, Fall 2009, http://www.chemheritage.org/discover/media/magazine/articles/27-3-womens-business.aspx.

Glossary

Transmutation

The conversion of an element into another element. Atoms of one element can be changed into atoms of another element. When the number of protons in an atom is changed, the atom is transmuted into an atom of another element.

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Section 6: Modernizing Chemistry—Antoine Lavoisier

Alchemy and practical chemistry continued on parallel and often overlapping paths throughout the 17th century. Some eminent early modern scientists, including Robert Boyle (discussed in Unit 2, Section 5) and Sir Isaac Newton, actively studied both practices. But with the appearance of French scientist Antoine-Laurent Lavoisier (1743–1794), chemistry underwent a revolution. Lavoisier explained major chemical processes in scientific terms, disproving previous theories, and developed research methods that are readily recognizable to chemists working today.

Lavoisier was born in Paris in 1743 and studied science (mainly physics and mathematics) as a university student, followed by a stint as assistant to a prominent French geologist. At age 25, he joined the *Ferme Generale*, France's private tax collection agency. From that point forward, he divided his career between tax enforcement and scientific research into issues ranging from gunpowder production to the composition of water.

One of Lavoisier's most important contributions was disproving phlogiston theory, a widely supported explanation for the process of combustion. Chemists prior to Lavoisier believed that combustible substances contained an odorless, colorless substance called "phlogiston," from the Greek word *phlogistos* (inflammable). The idea was rooted in the theory of four elements; some scientists referred to this material as "sulfurous earth" or "phlogistic earth," and metals were believed to contain varying levels of phlogiston. According to the theory, when substances burned, rusted, or decomposed, they released phlogiston into the air.

Joseph Priestley, a prominent British gas chemist and contemporary of Lavoisier (discussed further in Unit 2, Section 5), believed that this process polluted "atmospherical air" and made it unbreathable:

> ... for that the phlogiston with which it [ambient air] becomes loaded from bodies burning in it, and animals breathing it, and various other chemical processes, so far alters and depraves it, as to render it altogether unfit for inflammation, respiration, and other purposes ...[6]

An Official Language for Chemistry

Antoine Lavoisier's contributions to chemistry extended well beyond the laboratory. He paid great attention to language, and in 1787 published a book called *Methode de Nomenclature* (*Essay on Chemical Nomenclature*), which proposed a system for naming and classifying chemicals based on their properties.

Up to this point, there was no authoritative system for identifying different chemicals. Some were named for ancient gods: for example, lead was "Saturn" and lead nitrate was "nitre of Saturn." Others were described based on their real or assumed properties, such as Priestley's dephlogisticated air. Many substances had multiple names: carbonic acid might be known to one person as "Spiritus Sylvestris" and to another as "mephitic acid," "cretaceous acid," or "acid of charcoal."

Lavoisier's approach held that a substance should have one fixed name, based on its composition and usually stemming from a Greek or Latin root. The *Methode* was laid out like a dictionary, with new names in both French and Latin for seven hundred chemicals. Groupings followed simple rules. For example, nitrates were defined as "salts formed by the union of the nitric acid with different bases," so that the chemical once known as "nitrous alum" or "argillaceous earth" was now "aluminum nitrate" ("nitrat of alumine" in Lavoisier's phrasing, which reversed the parts of the name), and nitre of Saturn became "lead nitrate."[8]

Many of Lavoisier's contemporaries criticized the nomenclature when it was published. Some argued that it dismissed ancient knowledge (including ideas like phlogiston). Others argued that it was unacceptable for any one thinker, or school, to impose such a comprehensive framework on an entire science. Nonetheless, Lavoisier's approach quickly won support across Europe and in the newly independent United States, and his nomenclature created a modern language for chemistry.

In a 1774 experiment, Priestley heated mercuric oxide (HgO) until it burned, producing mercury and a gas that was notably light and easy to breathe. Priestley had discovered oxygen, but because he interpreted his results according to phlogiston theory, he called the mystery gas "dephlogisticated air"—air that had somehow been purified through the combustion process.

Lavoisier interpreted these findings differently. Replicating Priestley's experiment in 1776, he heated mercury to produce mercuric oxide, then heated the oxide further until it converted back into mercury and a highly reactive, breathable gas. Lavoisier also calculated how much material was gained and lost in each step. Heating the mercury produced 45 grains of mercuric oxide and consumed eight to nine cubic inches of air; when Lavoisier reduced the mercuric oxide, he retrieved eight cubic inches of air and 41.5 grains of pure mercury. His measurements showed that matter had been conserved: The gas produced in the second step was roughly equal to the amount that had been absorbed in the first step. It had a mass of about 3.5 grains. And, as in Priestley's experiment, the gas produced in the second step was much more capable of supporting combustion and respiration than normal atmospheric air.[7]

Lavoisier concluded that ambient air was not a unified element, but was made up of multiple components, some of which could support life. He recognized that Priestley's dephlogisticated air was a distinct gas, which he later named "oxygen." His experiment disproved phlogiston theory by showing that heating mercury to produce mercuric oxide added weight when mercury combined with oxygen in the air. According to phlogiston theory, heating mercury should have made it lighter by releasing phlogiston.

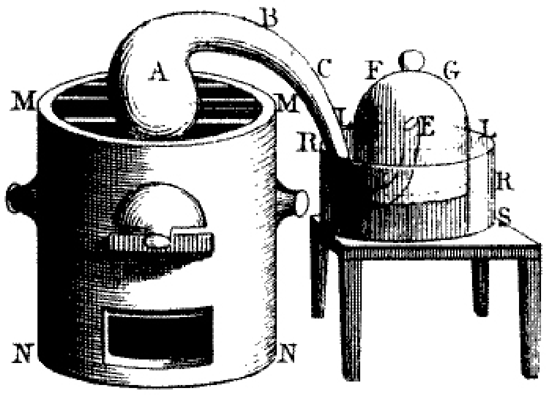

Figure 1-10. Phlogiston Experiment Engraving by Marie Lavoisier

This sketch by Marie Lavoisier shows a retort for heating mercury over a charcoal furnace, which is attached to a vessel for collecting gases produced by the reaction.

His wife, Marie Lavoisier, was an important partner in his work. She recorded the steps in all of Lavoisier's experiments, transcribed his laboratory notes, organized chemistry salons, and corresponded with scientists across Europe. In addition, she produced schematic drawings of Lavoisier's experiments (Figure 1-10) and illustrated his 1789 text, *Traite Elementaire de Chimie* (*Treatise on the Elements of Chemistry*). *Oxygen* (2001), a play by scientists Carl Djerassi (inventor of the birth control pill) and Roald Hoffmann (a Nobel Laureate in chemistry), pays humorous tribute to Marie Lavoisier's role in her husband's groundbreaking chemistry achievements.

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[6] Joseph Priestley, *Experiments and Observations on Different Kinds of Air*, vol. II (1775), quoted at http://web.lemoyne.edu/~giunta/ea/PRIESTLEYann.HTML.

[7] Joe Jackson, *A World on Fire: A Heretic, an Aristocrat, and the Race to Discover Oxygen* (Viking, 2005), pp. 184–86.

[8] For a translation of the largest tables, see "A Dictionary of the New Chymical Nomenclature," http://web.lemoyne.edu/~giunta/nomenclature.html.

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Section 7: The Properties of Chemical Compounds—Claude Louis Berthollet and Joseph Proust

Antoine Lavoisier's research inspired more work to identify chemicals and determine how and why they reacted with each other. Throughout the 18th century, chemists tended to use terms such as **element**, **compound**, and **mixture** loosely, but Lavoisier called for making these terms more precise. He also predicted that some substances that were thought to be indivisible might turn out to be compounds once scientists developed better methods of decomposing them.

Two French chemists, Claude Louis Berthollet and Joseph Proust, both of whom had worked with Antoine Lavoisier, debated extensively in the early 19th century over whether chemicals in compounds always combined in fixed proportions. Proust (1754–1826), a professor and research chemist, proposed his Law of Definite Proportions in 1797. In a series of experiments, he heated varying quantities of copper carbonate ($CuCO_3$) (Figure 1-11) to decompose it into copper, carbon, and oxygen and then compared the ratios of the masses of these components. Based on the results, Proust contended that the composition of chemical compounds was fixed, with each component accounting for a specific fraction by weight.

Figure 1-11. Copper Carbonate Forming on a Copper Roof; Pure Copper Carbonate in a Vial

The roof of the Château Frontenac in Quebec City, Canada, shows the blue-green color associated with copper carbonate forming on the surface of copper roofing plates. This is a natural process whereby the elements of nature, including acid rain, heat, and sunlight, cause the copper roof to react. The reaction that took place on the copper roof is the reverse of the reaction that Proust had done when he was converting the copper carbonate back to copper metal. The second image shows a close-up of purified copper carbonate powder.

Berthollet (1749–1822) was equally experienced. He had helped develop Lavoisier's chemical nomenclature and researched many chemistry applications, including bleaches, dyes, metalworking, and munitions. Some of his notable discoveries included the bleaching properties of chlorine and the chemical composition of ammonia. While traveling on a French military expedition to Egypt in 1798, Berthollet observed an unusual phenomenon at the Natron Lakes, a group of saltwater lakes in limestone beds northwest of Cairo. (Figure 1-12) There, he saw that *natron*, a Greek term for "soda ash" (sodium carbonate, Na_2CO_3, a chemical used for glassmaking and many other industrial applications), had formed along the shoreline, produced by reactions between saltwater and limestone (calcium carbonate):

$$CaCO_3 + 2\,NaCl \rightarrow Na_2CO_3 + CaCl_2$$

Berthollet realized that this was the reverse of a reaction that he had seen in the laboratory, in which calcium chloride reacted with soda ash to produce calcium carbonate and salt:

$$Na_2CO_3 + CaCl_2 \rightarrow 2\,NaCl + CaCO_3$$

Figure 1-12. Owens Lake: A Mostly Dry Lake with Salt Deposits

Similar to the Natron lakes in Egypt, Owens Lake in California was a site for soda processing due to the salts that surrounded it as well. The reddish color around the lake now comes from bright pink halophilic (salt-loving) bacteria that grow on these deposits.

Berthollet had discovered a reversible reaction, which chemists would later notate using a double arrow ($\rightleftarrows$) to indicate that the reaction could move in both directions. This indicated to Berthollet that conditions such as heat, pressure, and the amount of reagents present influenced the course and products of chemical reactions. After further study, he concluded that the composition of some compounds could vary within certain limits.

Proust and Berthollet debated this issue for nearly a decade, until John Dalton's atomic theory (discussed in Section 8) confirmed Proust's position. Dalton's work clarified the difference between mixtures, whose compositions can vary, and chemical compounds, which have constant compositions. Berthollet's reaction mixtures contained impurities, so in fact they were mixtures, not pure compounds. The debate between Berthollet and Proust shows the importance of accurate measurement: To determine the exact composition of a compound, chemists had to measure the relative masses of the elements of which it was composed.

Glossary

Compound

A substance composed of two or more elements that are chemically combined in definite proportions. A compound's makeup never changes: For example, a molecule of carbon dioxide always contains one atom of carbon and two atoms of oxygen.

Element

A substance that cannot be broken down into simpler substances through chemical processes.

Mixture

A combination of two or more substances in which each ingredient retains its own chemical identity. Unlike chemical compounds, the makeup of mixtures can vary: For example, air samples from a polluted city and a forest will have different compositions.

CHEMISTRY
CHALLENGES AND SOLUTIONS

Unit 1: *Matter and the Rise of Atomic Theory—The Art of the Meticulous*

Section 8: Early Atomic Theory—John Dalton

John Dalton (1766–1844), a self-taught English scientist, formulated the first chemical atomic theory. Priestley and Lavoisier had shown that air was a mixture of gases, not an indivisible element; Dalton was interested in meteorology, which led him to study the composition of the atmosphere, and to wonder why gases mingled uniformly instead of forming layers with the heaviest gases near the ground. In 1801, Dalton proposed his Law of Partial Pressures, which stated that: (a) in any mixture of gases, each gas exerted the same pressure that it would alone; and (b) the total pressure exerted by the atmosphere or any other mixture of gases was equivalent to the sum of all the partial pressures of its component gases.

Dalton's Law was based on an important insight: Gases that were mixed together in the atmosphere did not interact. Rather, they continued to behave within the mixture as they would if they were the only substance present. Next, Dalton tried to determine why some gases were more soluble in water than others. Since he assumed that individual gas particles remained intact when they were combined in such a mixture, it followed that some properties of the particles affected their behavior when they were mixed. Dalton theorized that the key property was mass, and he proposed a theory of the atom based on these assumptions:

- All matter consists of tiny particles (atoms).
- Atoms cannot be created, destroyed, divided into smaller parts, or transmuted into other substances.
- All atoms of a chemical element have the same mass.
- When elements combine, their atoms combine in simple, whole-number ratios, such as 1:1, 1:2, or 1:3. This assumption supported Proust's Law of Definite Proportions: The ratios by mass of chemicals in a compound were the ratios of the atomic mass of their atoms.

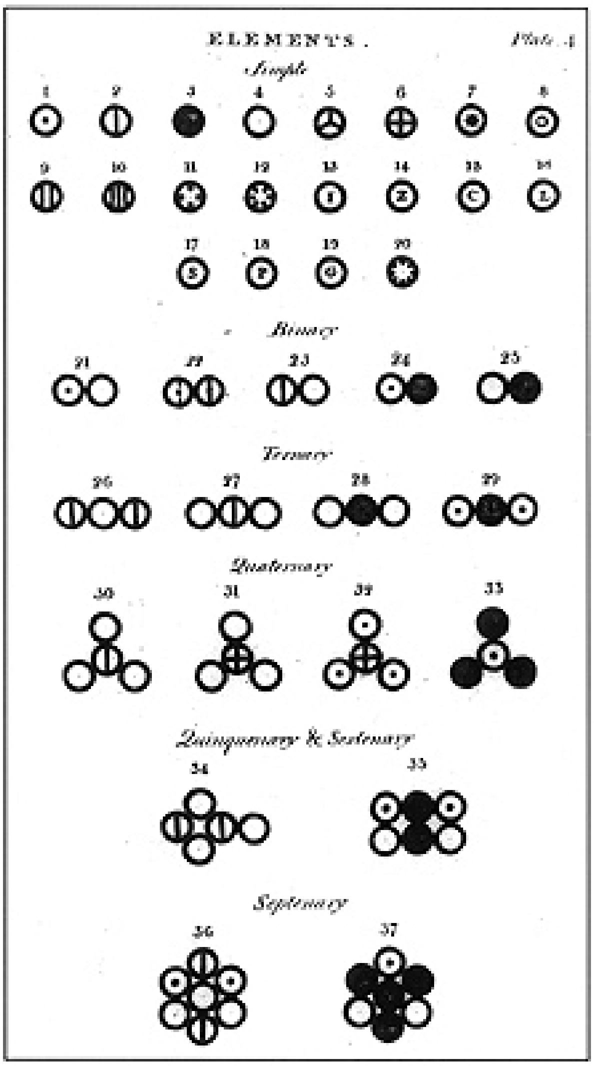

Figure 1-13. Elements and Their Combinations

A plate showing the elements from Dalton's *New System of Chemical Philosophy*. English chemist John Dalton proposed an early version of modern atomic theory that classified substances according to the mass of their particles.

Dalton calculated the atomic masses of a number of elements and compounds, making assumptions about the structure of the various compounds (Figure 1-13). These estimates were a precursor to the periodic table (discussed in Unit 4), which is organized according to atomic masses.

Dalton also recognized that elements could combine with each other in more than one simple whole-number ratio. For example, carbon and oxygen can form carbon monoxide (CO) or carbon dioxide (CO_2). His Law of Multiple Proportions states that when two elements combine to make a series of compounds, the masses of element X that can combine with a constant mass of element Y will be in the ratio of small whole numbers. For example, the ratio of oxygen in carbon monoxide to that in carbon dioxide is 1:2. These ratios also can be seen in chemical series, such as oxides of nitrogen (NO, N_2O, N_2O_4).

Dalton developed his theories to explain laboratory observations without being able to see into units as small as atoms. Nonetheless, his assumptions made it possible to predict how chemicals combined, draw formulas that depicted those reactions, and look for similarities among groups of chemicals. Ironically, by reviving classical atomic theory—an idea first proposed in ancient Greece—and giving it a quantitative foundation, Dalton helped chemistry to become a modern science.

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Section 9: Further Reading

Djerassi, Carl, and Hoffmann, Roald. *Oxygen.* New York: Wiley, February 2001.

Jackson, Joe. *A World on Fire: A Heretic, an Aristocrat, and the Race to Discover Oxygen.* New York: Viking, 2005.

Levore, Trevor H. *Transforming Matter: A History of Chemistry from Alchemy to the Buckyball.* Baltimore: Johns Hopkins University Press, 2011.

Salzberg, Hugh. *From Caveman to Chemist: Circumstances and Achievements.* American Chemical Society, 1991.

U.S. National Institute of Health, National Library of Medicine. *Paracelsus and the Medical Revolution of the Renaissance: A 500th Anniversary Celebration.* http://www.nlm.nih.gov/exhibition/paracelsus/index.html.