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CHAPTER

THE ATOM IN MODERN CHEMISTRY

- 1.1 The Nature of Modern Chemistry
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Connection to Nanotechnology:
Imaging Atoms, Molecules, and Chemical Reactions by Scanning Tunnelling Microscopy

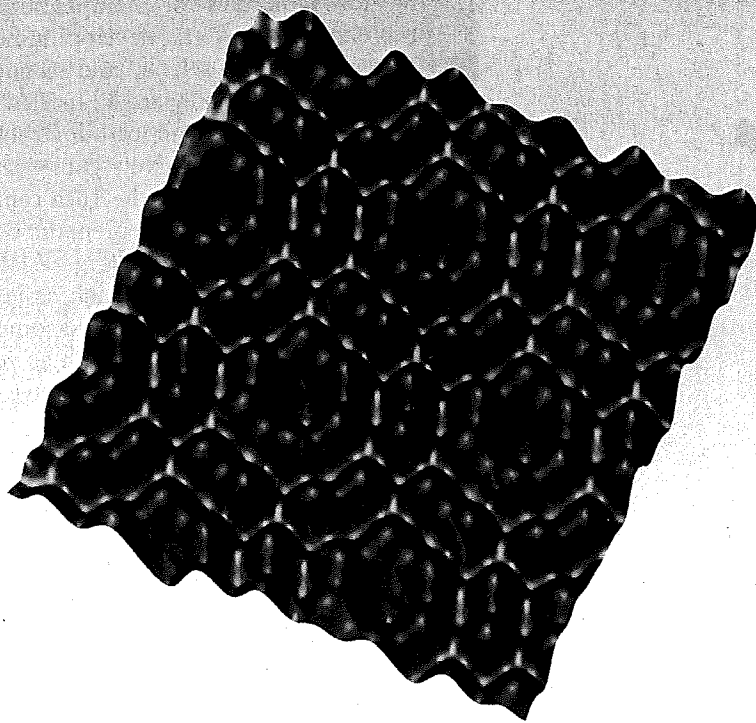


Photo courtesy of Wilson Ho, University of California, Irvine

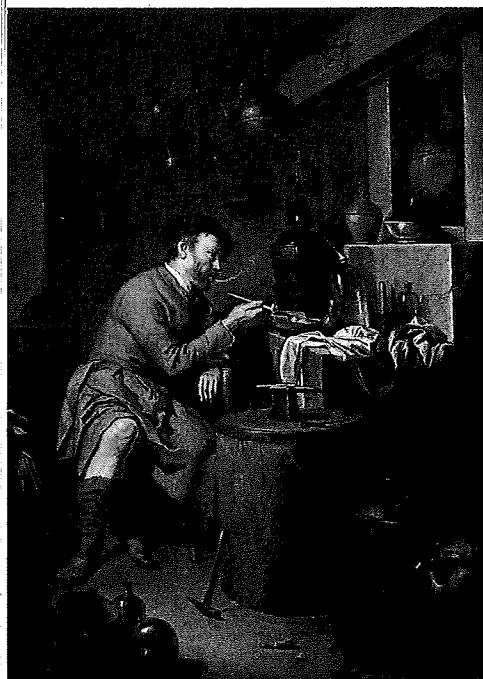
Reversible single atom transfer using the scanning tunneling microscope. This image was taken under the same conditions as the one shown opposite page 1. One of the "center" silicon atoms (imaged in red) has been transferred halfway to another center atom site by the scanning tunneling microscope tip. The atom is stable in this position at low temperatures but returns to its home site as the temperature is raised above -100°C .

1.1 THE NATURE OF MODERN CHEMISTRY

Chemists study the properties of substances and the reactions that transform substances into other substances. Chemists are particularly interested in understanding how and why specific chemical reactions occur, in order to tailor the properties of existing substances to meet particular needs—and to create entirely new substances designed to have specific properties. Chemistry has improved agricultural production, helped prevent and cure many diseases, increased the efficiency of energy production, and reduced environmental pollution, to cite just a few advances. A

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Painting The Alchemist by Hendrick Heershop, 1671. Courtesy of Dr. Alfred Bader

FIGURE 1.1 Alchemists searched in vain for procedures that would turn base metals into gold. Their apparatus foreshadowed equipment in modern chemical laboratories.

particularly exciting challenge for modern chemical research is to understand the dynamics of these chemical transformations, because they govern phenomena as diverse as the evolution of small carbon-containing molecules in interstellar space, changes in terrestrial atmospheric and climatic patterns caused by pollutants, and the unfolding of life processes in living organisms. Chemistry influences almost every area of science and technology; advances in chemistry inform disciplines as different as solid-state physics and molecular biology, and the synthetic methods and analytical techniques developed by chemists support research and manufacturing in important areas like medicine and microelectronics. Perhaps no other science covers as broad a range of topics as does chemistry. Within a single modern chemistry department, you're likely to find chemists creating new materials and developing strategies for sustainable energy, devising synthetic routes that conserve all of the atoms in starting materials, detecting and identifying single molecules, designing new molecules for therapeutic purposes and translating those developments into clinical trials, and developing highly selective integrated sensors for a variety of applications in science and technology. Despite the diversity of these areas of scientific inquiry, they are all unified by a single set of fundamental scientific principles, to which we will introduce you in this textbook.

Chemistry is a relatively young science, and its foundations weren't established until the last quarter of the 18th century. Before that, most chemists were known as *alchemists*—early entrepreneurs who sought to transform the properties of materials for economic gain (Fig. 1.1). For many centuries their obsession was to transform “base” metals, such as lead, into gold. They boldly assumed that the properties of one material could somehow be extracted and transferred to another. If the essential properties—such as yellow color, softness, and ductility—could be assembled from various inexpensive sources, then gold could be created at great profit.

The alchemists persisted in their efforts for more than a thousand years. Although they collected many useful, empirical results that have since been incorporated into modern chemistry, they never transformed base metals into gold. Many scientists had begun to challenge the basic assumptions of the alchemists by the middle of the 17th century. These doubts culminated with the publication of *The Sceptical Chymist* by Robert Boyle in England in the 1660s, one of the pivotal events that marked the beginning of modern chemistry. Another century was required to establish the conceptual foundations of modern chemistry, a field that flourished throughout the 19th and 20th centuries and remains vibrant today.

The error of the alchemists is obvious to modern observers: they did not follow the scientific method. A new idea is accepted only temporarily in the scientific method, in the form of a hypothesis. It is then subjected to rigorous testing, in carefully controlled experiments. A hypothesis is elevated to a scientific law only after it has survived many such tests. A scientific law must be predictive, in addition to being explanatory; failure to accurately predict the results of a new experiment is sufficient to invalidate a scientific law. Concepts or ideas that have earned the status of scientific laws by direct and repeated testing then can be applied with confidence in new environments. Had a proper set of tests been made in separate, independent experiments, the alchemists would have recognized that the properties of a material are, in fact, intrinsic, inherent characteristics of that material and cannot be extracted from it.

The history of the alchemists shows the origin of a certain duality in the nature of modern chemistry, which persists to the present. Because chemistry contributes to the foundations of numerous professions and industries, we see the urge to apply established chemical knowledge for profit. But we also see the urge to create new chemical knowledge, driven by both intellectual curiosity and by the desire to have reliable information for applications. Many scientists and engineers from different disciplines contribute to both basic and applied chemical research and development. Irrespective of the specific context, conducting chemical research requires scrupulous adherence to the scientific method, in which the new knowledge generated is subjected to rigorous scrutiny before it earns the confidence of the scientific community.

Most students who study chemistry will apply what they have learned during the course of their professional careers rather than conduct research in chemistry. Still, a useful strategy for learning to think like an experienced chemist is to assume that you are personally responsible for establishing the scientific foundations of chemistry for the very first time. Upon encountering a new topic, try this: imagine that you are the first person ever to see the laboratory results on which it is based. Imagine that you must construct the new concepts and explanations to interpret these results, and that you will present and defend your conclusions before the scientific community. Be suspicious. Cross-check everything. Demand independent confirmations. Always remain, with Boyle, the “skeptical chemist.” Follow the scientific method in your acquisition of knowledge, even from textbooks. In this way, you will make the science of chemistry your own, and you will experience the intellectual joys of discovery and interpretation. Most important, you will recognize that chemistry is hardly a closed set of facts and formulas. Quite the contrary, it is a living, growing method for investigating all aspects of human experience that depend on the changes in the composition of substances. Finally, learning to examine critically what we call “the nature of the evidence” will help you make better decisions as consumers and citizens in a world where science and technology continue to become increasingly important parts of modern life.

Conservation of Matter and Energy

The science of chemistry rests on two well-established principles: the conservation of matter and the conservation of energy. The total amount of matter involved in chemical reactions is conserved—that is, it remains constant during the course of every chemical reaction. Matter is neither created nor destroyed in chemical reactions; the components of the reactants are simply rearranged to form products.

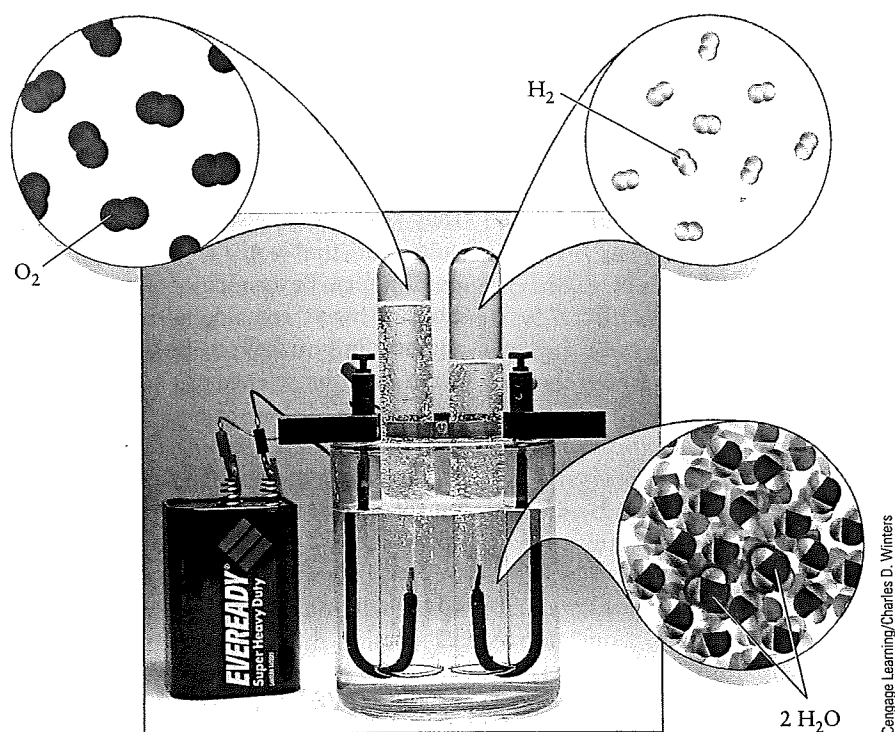
These rearrangements are inevitably accompanied by changes in energy, which brings us to the second principle. The total amount of chemical energy stored in the reactants is almost always different than that stored in the products; this difference manifests itself in the form of thermal, electrical, or mechanical energy required for, or produced by, chemical reactions. But energy is neither created nor destroyed during chemical reactions; it has always been found to be conserved.

These two core principles must be modified slightly for nuclear reactions, which occur at energies so high that matter and energy can be converted into one another through Einstein’s relation, $E = mc^2$. The sum of mass and energy is conserved in nuclear reactions.

Macroscopic Methods and Nanoscopic Models

Chemical reasoning, as used both in applications and in basic research, resembles a detective story in which tangible clues lead to a mental picture of events never directly witnessed by the detective. Chemical experiments are conducted in laboratories equipped with beakers, flasks, analytical balances, pipettes, optical and infrared spectrometers, lasers, vacuum pumps, pressure gauges, mass spectrometers, centrifuges, and other apparatus. Each of these devices exists on the *macroscopic* scale—that is, it is perceptible by ordinary human senses. Macroscopic objects range in size from about 1 meter (m) down to about 1 millimeter (mm), which is 1×10^{-3} m. But the actual chemical transformation events occur in the *nanoscopic* world of atoms and molecules—objects far too small to be detected by the naked eye, even with the aid of a first-class microscope. One nanometer (nm) is 1×10^{-9} m. So our modern laboratory instruments are the bridge between these worlds, giving us the means not only to influence the actions of the atoms and molecules but also to measure their response. Figure 1.2 shows views of both worlds simultaneously. In illustrating the chemical decomposition of water into gaseous hydrogen and oxygen by electrolysis,

FIGURE 1.2 Hydrogen and oxygen gas are produced in the ratio 2:1 when an electric current is passed through water that contains dissolved sulfuric acid. The insert illustrates how chemists view this macroscopic chemical reaction as arising from the rearrangements of atoms on the nanoscale.



Cengage Learning/Charles D. Winters

the figure shows the relationship between events on the macroscale and on the nanoscale. Chemists *think* in the highly visual nanoscopic world of atoms and molecules, but they *work* in the tangible world of macroscopic laboratory apparatus. These two approaches to the chemical sciences cannot be divorced, and we emphasize their interplay throughout this textbook. Students of chemistry must master not only the fascinating concepts of chemistry, which describe the nanoscopic world of atoms and molecules, but also the macroscopic procedures of chemistry on which those concepts are founded.

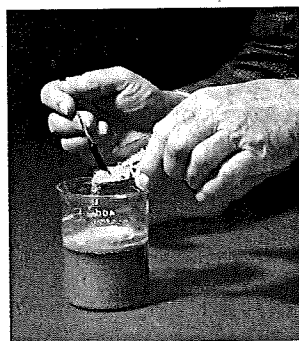
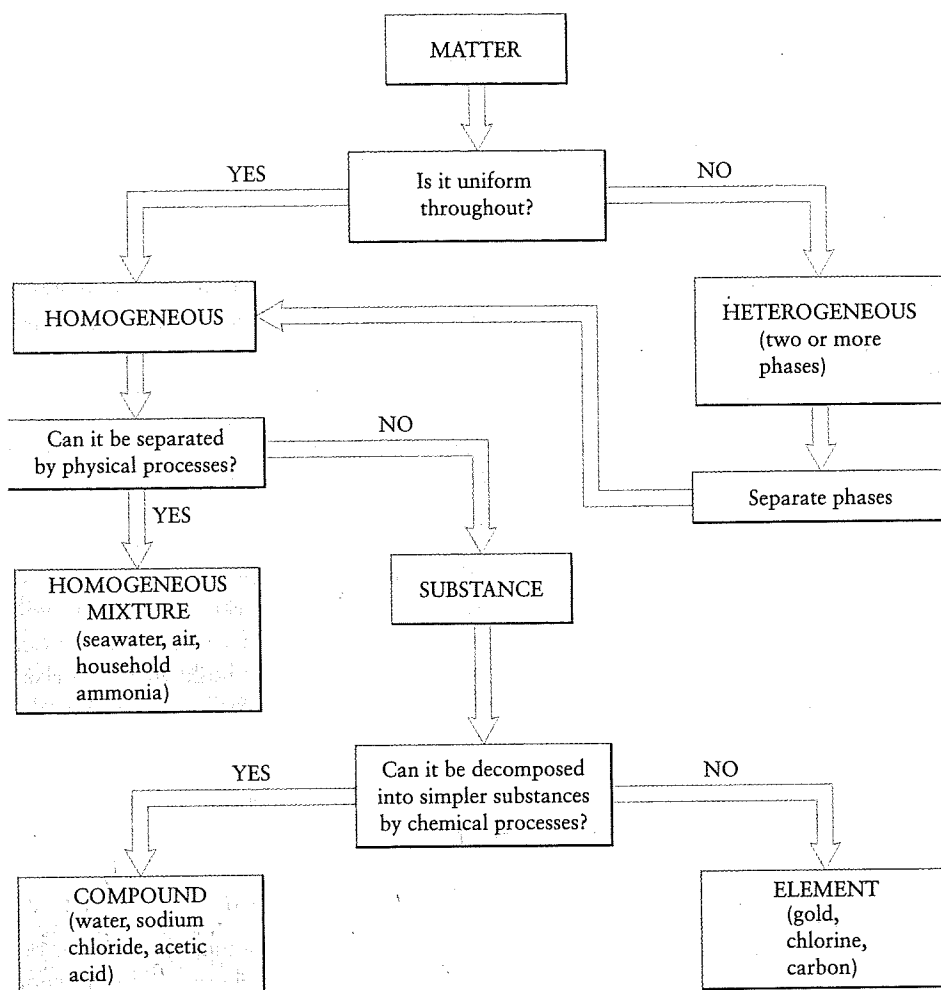
1.2 MACROSCOPIC METHODS FOR CLASSIFYING MATTER

Chemists study how sets of pure substances transform into other sets of pure substances in chemical reactions. These investigations apply two modes of reasoning and physical procedures—analysis (taking things apart) and synthesis (putting things together)—that go back to early Greek philosophers, who sought to analyze the constituents of all matter for four elements: air, earth, fire, and water. Contemporary chemists classify matter using a very different set of fundamental building blocks, but the analysis and synthesis steps are basically unchanged.

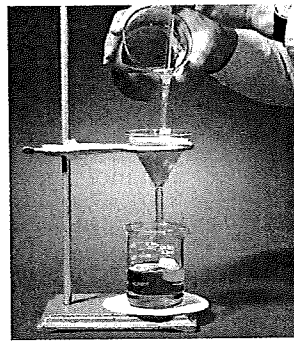
Substances and Mixtures

Investigating chemical reactions can be greatly complicated and often obscured by the presence of extraneous materials. So, the first step, therefore, is to learn how to analyze and classify materials to ensure that you are working with *pure* substances before initiating any reactions (Fig. 1.3). Suppose you take a sample of a material—a gas, liquid, or solid—and examine its various properties or distinguishing characteristics, such as its color, odor, or density. How uniform are those properties throughout the sample? Different regions of a piece of wood, for example, have

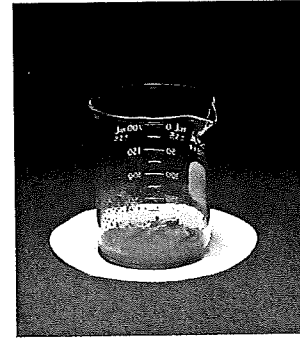
FIGURE 1.3 Process flowchart for analyzing matter.



(a)



(b)



(c)

FIGURE 1.4 (a) A solid mixture of blue $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and yellow CdS is added to water. (b) Although the $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolves readily and passes through the filter, the CdS remains largely undissolved and is retained by the filter. (c) Evaporation of the solution leaves nearly pure crystals of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

different properties, such as variations in color and texture. Wood, then, is said to be **heterogeneous**. Other materials, such as air or mixtures of salt and water, are classified as **homogeneous** materials because their properties are the same throughout a given sample. We cannot call these homogeneous materials pure substances, however. We still have to call them **mixtures**, because it is possible to separate them into components by ordinary physical means such as melting, freezing, boiling, or dissolving in solvents (Fig. 1.4). These operations provide ways of separating ma-

materials from one another by their properties, freezing points, boiling points, and solubilities. Air, for example, is a mixture of several components—oxygen, nitrogen, argon, and various other gases. If air is liquefied and then warmed slowly, the gases with the lowest boiling points evaporate first, leaving behind in the liquid those with higher boiling points. Such a separation would not be perfect, but the processes of liquefaction and evaporation could be repeated to improve the purity of the component gases to any required degree.

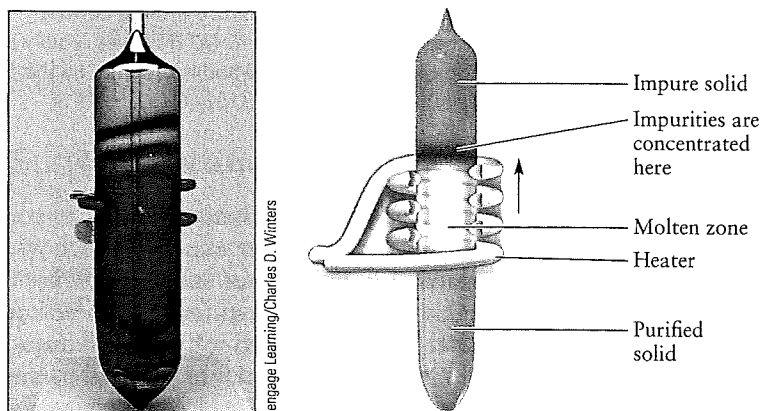
If all these physical procedures (and many others) fail to separate matter into portions that have different properties, the material is said to be a **pure substance**. What about the common material sodium chloride, which we call table salt? Is it a substance? The answer is yes if we use the term *sodium chloride*, but no if we use the term *table salt*. Table salt is a mixture of sodium chloride that contains small amounts of sodium iodide (needed by the thyroid gland) and magnesium carbonate (needed to prevent the salt from caking). Even if these two components were not added, table salt contains other impurities that had not been removed in its preparation, so to that extent, table salt is a mixture. In contrast, when we refer to sodium chloride, we imply that it is a pure substance that contains only sodium and chlorine.

Nothing is absolutely pure in practice, so the word *substance* is an idealization. Among the purest materials ever prepared are silicon (Fig. 1.5) and germanium. These elements are used in electronic devices and solar cells, and their electronic properties require either high purity or else precisely controlled concentrations of deliberately added impurities. Meticulous chemical and physical methods have enabled scientists to prepare germanium and silicon with concentrations of impurities that are less than one part per billion. Any higher concentrations of certain impurities would alter the electrical properties of these materials.

Elements

Literally millions of substances have so far been either discovered or synthesized and formally identified. Are these the fundamental building blocks of matter? Happily not, for their classification alone would pose an insurmountable task. In fact, all of these substances are merely combinations of much smaller numbers of building blocks called **elements**. Elements are substances that cannot be decomposed into two or more simpler substances by ordinary physical or chemical means. The word *ordinary* excludes the processes of radioactive decay, whether natural or artificial, and high-energy nuclear reactions that *do* transform elements into one another. When a substance contains two or more chemical elements, we call it a **compound**. For example, hydrogen and oxygen are elements because no further chemical separation is possible, whereas water is a compound because it can be separated into hydrogen and oxygen by passing an electric current through it (see Fig. 1.2). *Binary* compounds are substances, such as water, that contain two elements, *ternary* compounds contain three elements, *quaternary* compounds contain four elements, and so on.

FIGURE 1.5 Nearly pure elemental silicon is produced by pulling a 10-inch-long solid cylinder (called a boule) out of the melt, leaving most of the impurities behind.



At present, scientists have identified some 118 chemical elements. A few have been known since before recorded history, principally because they occur in nature as elements rather than in combination with one another in compounds. Gold, silver, lead, copper, and sulfur are the most common of these. Gold is found in streams in the form of little granules (placer gold) or nuggets in loosely consolidated rock. Sulfur is associated with volcanoes, and copper often can be found in its native state in shallow mines. Iron occurs (only rarely) in its elemental state (in meteorites); it usually is combined with oxygen or other elements. Ancient metallurgists, in the second millennium B.C., somehow learned to reduce iron oxide to metallic iron using charcoal in forced-draft fires, and the Iron Age was born.

The names of the chemical elements and the symbols that designate them have a fascinating history. The symbols for many elements come from their Latin names, such as gold (aurum, symbol Au), copper (cuprum, Cu), and iron (ferrum, Fe). Some elements have names that describe their characteristic reactions or source; Hydrogen (H), for example, means “water former” and potassium (kalium, K) takes its common name from potash (potassium carbonate), a useful chemical obtained in early times by leaching the ashes of wood fires with water. Many elements take their names from Greek and Roman mythology: cerium (Ce) from Ceres, goddess of plenty; tantalum (Ta) from Tantalus, who was condemned in the afterlife to an eternity of hunger and thirst while close to water and fruit that were always tantalizingly just out of reach; niobium (Nb) from Niobe, daughter of Tantalus; and mercury (hydrargyrum, Hg), which means silver water, named after the quickly moving god. Some elements are named for continents: europium (Eu) and americium (Am). Other elements are named after countries: germanium (Ge), francium (Fr), and polonium (Po). Cities provided the names of other elements: holmium (Stockholm, Ho), ytterbium (Ytterby, Yb), and berkelium (Berkeley, Bk). Some are named for the planets: uranium (U), plutonium (Pu), and neptunium (Np). Other elements take their names from colors: praseodymium (green, Pr), rubidium (red, Rb), and cesium (sky blue, Cs). Still others honor great scientists: curium (Marie Curie, Cm), mendelevium (Dmitri Mendeleev, Md), fermium (Enrico Fermi, Fm), einsteinium (Albert Einstein, Es), and seaborgium (Glenn Seaborg, Sg).

1.3 INDIRECT EVIDENCE FOR THE EXISTENCE OF ATOMS: LAWS OF CHEMICAL COMBINATION

How did we acquire the chemical evidence for the existence of atoms and the scale of relative atomic masses? It is an instructive story, both in its own right and as an illustration of how science progresses.

We may know the elements to be the most fundamental substances, and we may know that they can be combined chemically to form compound substances, but that knowledge provides us no information about the nanoscopic structure of matter or how that nanoscopic structure controls and is revealed by chemical reactions. Ancient philosophers dealt with these fascinating questions by proposing assumptions, or *postulates*, about the structure of matter. The Greek philosopher Democritus (c. 460–370 B.C.) postulated the existence of unchangeable *atoms* of the elements, which he imagined to undergo continuous random motion in the vacuum, a remarkably modern point of view. It follows from this postulate that matter is not divisible without limit; there is a lower limit to which a compound can be divided before it becomes separated into atoms of the elements from which it is made. Lacking both experimental capabilities and the essentially modern scientific view that theories must be tested and refined by experiment, the Greek philosophers were content to leave their views in the form of assertions.

The ratios of the masses of compounds that react to form other compounds is also fixed. These results could be interpreted only by inferring that the smallest indivisible

units of the elements (atoms) combined to form the smallest indivisible units of the compounds (molecules). The definite mass ratios involved in reactions suggested a convenient method for counting the number of atoms of each element participating in the reaction. These results, summarized as the **laws of chemical combination**, provided overwhelming, if indirect, evidence for the existence of atoms and molecules.

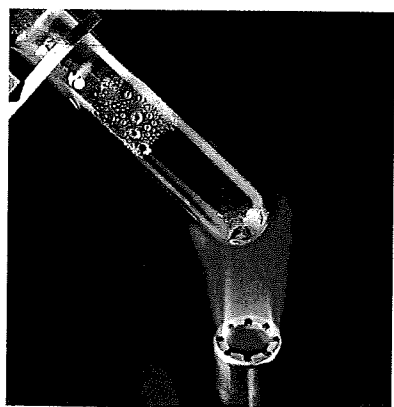
For more than a century, we have become so accustomed to speaking of atoms that we rarely stop to consider the experimental evidence for their existence that was collected in the 18th and 19th centuries. Twentieth-century science developed a number of sophisticated techniques to measure the properties of single atoms and powerful microscopes to observe them (see *Connection to Nanotechnology*). But long before single atoms were detected, chemists could speak with confidence about their existence and the ways in which they combine to form molecules. Moreover, although the absolute masses of single atoms of oxygen and hydrogen were not measured until the early 20th century, chemists could assert (correctly) some 50 years earlier that the *ratio* of their masses was close to 16:1.

Law of Conservation of Mass

The first steps toward formulating the laws of chemical composition were taken during the 18th century in the course of studies of heat and combustion. It had been observed that an organic material, such as wood, left a solid residue of ash when burned; similarly, a metal heated in air was transformed into a “calx,” which we now call an oxide. The popular explanation for these phenomena in the early 18th century was that a property called *phlogiston* was driven out of wood or metal by the heat of a fire. From the modern perspective, this seems absurd, because the ash weighed less than the original wood, whereas the calx weighed more than the metal. The principle of conservation of mass had not yet been established at that time, however, and people saw no reason why the mass of a material should not change when heated.

Further progress could be made only by carefully measuring the changes in mass¹ that occur in chemical reactions. The balance had been known since antiquity, but it had been used principally as an assayer’s tool and for verifying the masses of coins or commodities in commerce. The analytical balance developed in the 18th century, however, was accurate to perhaps 1 part in 10,000, enabling much more accurate measurements of mass changes accompanying chemical reactions than had been possible previously. French chemist Antoine Lavoisier used the analytical balance (see the photo on page 35) to demonstrate that the sum of the masses of the products of a chemical reaction equals the sum of the masses of the reactants to the high degree of accuracy provided by the instrument. Lavoisier heated mercury in a sealed flask that contained air. After several days, a red substance, an oxide of mercury, was produced. The gas remaining in the flask was reduced in mass and could no longer support life or combustion; a candle was extinguished by it, and animals suffocated when forced to breathe it. We now know that this residual gas was nitrogen, and that the oxygen in the air had reacted with the mercury. Lavoisier then took a carefully weighed amount of the red oxide of mercury and heated it to a very high temperature (Fig. 1.6). He weighed both the mercury and the gas that were produced and showed that their combined mass was the same as that of the mercury oxide with which he had started. After further experiments, Lavoisier was able to state the **law of conservation of mass**:

Mass is neither created nor destroyed in chemical reactions; it is conserved.

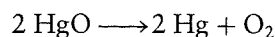


Richard Megna/Fundamental Photographs

FIGURE 1.6 The red solid, mercury oxide, decomposes into liquid mercury and oxygen gas, when heated. Note the drops of liquid mercury condensing on the side of the test tube.

¹Chemists sometimes use the term *weight* in place of *mass*. Strictly speaking, weight and mass are not the same. The mass of a body is an invariant quantity, but its weight is the force exerted on it by gravitational attraction (usually by the Earth). Newton’s second law relates the two ($w = m \times g$, where g is the acceleration due to gravity). As g varies from place to place on the Earth’s surface, so does the weight of a body. In chemistry, we deal mostly with ratios, which are the same for masses and weights. In this textbook we use the term *mass* exclusively, but *weight* is still in colloquial chemical use.

Lavoisier was the first to observe that a chemical reaction is analogous to an algebraic equation. We would write his second reaction as



although during Lavoisier's lifetime, the identity of the gas (oxygen) was not known.

Law of Definite Proportions

Rapid progress ensued as chemists began to make accurate determinations of the masses of reactants and products. A controversy arose between two schools of thought, led by a pair of French chemists, Claude Berthollet and Joseph Proust. Berthollet believed that the proportions (by mass) of the elements in a particular compound were not fixed, but could actually vary over a certain range. Water, for example, might contain more or less than 11.1% hydrogen by mass, the generally accepted value. Proust disagreed, arguing that any apparent variation was due to impurities and experimental errors. He also stressed the difference between homogeneous mixtures and chemical compounds. In 1794, Proust published the fundamental **law of definite proportions**:

In a given chemical compound, the proportions by mass of the elements that compose it are fixed, independent of the origin of the compound or its mode of preparation.

Pure sodium chloride contains 60.66% chlorine by mass, whether we obtain it from salt mines, crystallize it from waters of the oceans or inland salt seas, or synthesize it from its elements, sodium and chlorine.²

The law of definite proportions was a crucial step in the development of modern chemistry, and Proust's conclusions had become widely accepted by the time Dalton published his atomic theory. We now recognize that this law is not strictly true in all cases. Although all gaseous compounds obey Proust's law, certain solids called **nonstoichiometric compounds** have compositions that vary over small ranges. An example is wüstite, which has the nominal chemical formula FeO (with 77.73% iron by mass), but the composition of which, in fact, ranges continuously from Fe_{0.95}O (with 76.8% iron) down to Fe_{0.85}O (74.8% iron), depending on the method of preparation. Such compounds are called **berthollides**, in honor of Berthollet. We now know, on the atomic level, why they are nonstoichiometric (see the discussion in Section 21.4).

The development of the law of definite proportions provides an excellent example of how science progresses. Measurements of the compositions of a large number of compounds supported the law of definite proportions, but later, more precise measurements uncovered exceptions to the general principle that had been established. The following explanation of the exceptions leads to a deeper understanding.

Dalton's Atomic Theory

English scientist John Dalton was by no means the first person to propose the existence of atoms; as we have seen, speculations about them date back to ancient Greek times (the word *atom* is derived from Greek *a-* ["not"] plus *tomos* ["cut"], meaning "not divisible"). Dalton's major contribution to chemistry was to marshal the evidence for the existence of atoms. He showed that the mass relationships found by Lavoisier and Proust could be interpreted most simply by postulating the existence of atoms of the various elements.

²This statement needs some qualification. As explained in the next section, many elements have several *isotopes*, which are species whose atoms have almost identical chemical properties but different masses. Natural variation in isotope abundance leads to small variations in the mass proportions of elements in a compound, and larger variations can be induced by artificial isotopic enrichment.

In 1808, Dalton published *A New System of Chemical Philosophy*, in which the following five postulates comprise the **atomic theory of matter**:

1. Matter consists of indivisible atoms.
2. All the atoms of a given chemical element are identical in mass and in all other properties.
3. Different chemical elements have different kinds of atoms; in particular, their atoms have different masses.
4. Atoms are indestructible and retain their identities in chemical reactions.
5. Atoms of the elements combine with each other in small integer ratios to form compounds.

Dalton's fourth postulate clearly is related to the law of conservation of mass. The fifth aims to explain the law of definite proportions. Perhaps Dalton's reasoning went something like this: Suppose you reject the atomic theory and believe instead that compounds are subdivisible without limit. What, then, ensures the constancy of composition of a substance such as sodium chloride? Nothing! But if each sodium atom in sodium chloride is matched by one chlorine atom, then the constancy of composition can be understood. So in this argument for the law of definite proportions, it does not matter how small the atoms of sodium and chlorine are. It is important merely that there be some lower bound to the subdivisibility of matter, because the moment we put in such a lower bound, arithmetic steps in. Matter becomes countable, and the units of counting are simply atoms. Believing in the law of definite proportions as an established experimental fact, Dalton *postulated* the existence of the atom.

Law of Multiple Proportions

The composition of a compound is shown by its **chemical formula**. The symbol H_2O for water specifies that there are two atoms of hydrogen for each atom of oxygen in one unit of water. We now know that the two hydrogen atoms are strongly bound to the oxygen atom in a discrete unit called a **molecule** and that the atoms in one water molecule are not strongly bound to the atoms of any other water molecule. Many solid substances do not exist as molecules but as infinite arrays of ions or atoms bonded to each other in ways that do not allow us to identify a particular molecule uniquely; they are called ionic and covalent solids. The chemical formula for these pure substances gives the relative ratios of the numbers of their constituent atoms. How do we know that these are the true proportions? The determination of chemical formulas (and the accompanying determination of relative atomic masses), building on the atomic hypothesis of Dalton, was a major accomplishment of 19th-century chemistry.

The simplest compounds made from two different elements are **diatomic molecules** that contain one atom of each element. Eighteenth- and nineteenth-century chemists knew, however, that two elements often combine in different proportions, suggesting the existence of multiple compounds that are more complicated than diatomic molecules.

Carbon (C) and oxygen (O), for example, combine under different conditions to form two different compounds, which we will call A and B. Analysis shows that A contains 1.333 grams (g) of oxygen per 1.000 g of carbon, and B contains 2.667 g of oxygen per 1.000 g of carbon. Although at this point we know nothing about the chemical formulas of the two oxides of carbon, we can say immediately that molecules of compound A contain half as many oxygen atoms per carbon atom as do molecules of compound B. The evidence for this is that the ratio of the masses of oxygen in A and B, for a fixed mass of carbon in each compound, is 1.333:2.667, or 1:2. If the formula of compound A were CO , then the formula of compound B would have to be CO_2 , C_2O_4 , C_3O_6 , or some other multiple of CO_2 . We cannot say from these data which of these (or an infinite number of other possibilities) are the true formulas of the molecules of compounds A and B, but we do know this: The number of oxygen atoms per carbon atom in the two compounds is the *quotient of integers*.

Let's consider another example. Arsenic (As) and sulfur (S) combine to form two sulfides, A and B, in which the masses of sulfur per 1.000 g of arsenic are 0.428 and 0.642 g, respectively. The ratio of these masses is $0.428:0.642 = 2:3$. We conclude that *if* the formula of compound A is a multiple of AsS, then the formula of compound B must be a multiple of As_2S_3 .

These two examples illustrate the **law of multiple proportions**:

When two elements form a series of compounds, the masses of one element that combine with a fixed mass of the other element are in the ratio of small integers to each other.

In the first example, the ratio of the masses of oxygen in the two compounds, for a given mass of carbon, was 1:2. In the second example, the ratio of the masses of sulfur in the two compounds, for a given mass of arsenic, was 2:3. Today, we know that the carbon oxides are CO (carbon monoxide) and CO_2 (carbon dioxide), and the arsenic sulfides are As_4S_4 and As_2S_3 . Dalton could not have known this, however, because he had no information from which to decide how many atoms of carbon and oxygen are in one molecule of the carbon-oxygen compounds or how many atoms of arsenic and sulfur are in the arsenic-sulfur compounds.

EXAMPLE 1.1

Chlorine (Cl) and oxygen form four different binary compounds. Analysis gives the following results:

Compound	Mass of O Combined with 1.0000 g Cl
A	0.22564 g
B	0.90255 g
C	1.3539 g
D	1.5795 g

- (a) Show that the law of multiple proportions holds for these compounds.
(b) If the formula of compound A is a multiple of Cl_2O , then determine the formulas of compounds B, C, and D.

Solution

- (a) Form ratios by dividing each mass of oxygen by the smallest, which is 0.22564 g:

$$0.22564 \text{ g} : 0.22564 \text{ g} = 1.0000 \text{ for compound A}$$

$$0.90255 \text{ g} : 0.22564 \text{ g} = 4.0000 \text{ for compound B}$$

$$1.3539 \text{ g} : 0.22564 \text{ g} = 6.0003 \text{ for compound C}$$

$$1.5795 \text{ g} : 0.22564 \text{ g} = 7.0001 \text{ for compound D}$$

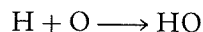
The ratios are whole numbers to a high degree of precision, and the law of multiple proportions is satisfied.

- (b) If compound A has a formula that is some multiple of Cl_2O , then compound B is Cl_2O_4 (or ClO_2 , or Cl_3O_6 , and so forth) because it is four times richer in oxygen than is compound A. Similarly, compound C, which is six times richer in oxygen than compound A, is Cl_2O_6 (or ClO_3 , or Cl_3O_9 , and so forth), and compound D, which is seven times richer in oxygen than compound A, is Cl_2O_7 (or a multiple thereof).

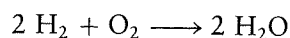
Related Problems: 7, 8, 9, 10

Dalton made a sixth assumption, which was incorrect, to resolve the dilemma of the absolute number of atoms present in a molecule; he called it the "rule of

greatest simplicity." If two elements A and B form only one compound then the chemical formula for that compound will be the simplest possible: AB. Thus, he assumed that when hydrogen and oxygen combine to form water, the reaction is



Dalton was wrong, however, as we now know, and the correct reaction is



Law of Combining Volumes

French chemist Joseph Gay-Lussac conducted some important experiments, at about the same time as Dalton, on the relative volumes of gases that react completely with one another to form new gases. He discovered the **law of combining volumes**:

The ratio of the volumes of any pair of gases in a gas phase chemical reaction (at the same temperature and pressure) is the ratio of simple integers.

Here are three examples:

2 volumes of hydrogen + 1 volume of oxygen \longrightarrow 2 volumes of water vapor

1 volume of nitrogen + 1 volume of oxygen \longrightarrow 2 volumes of nitrogen oxide

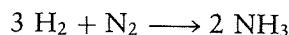
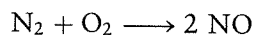
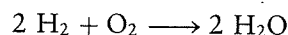
3 volumes of hydrogen + 1 volume of nitrogen \longrightarrow 2 volumes of ammonia

Avogadro's Hypothesis

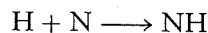
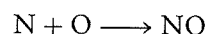
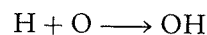
Gay-Lussac did not interpret his experimental findings theoretically but, shortly after their publication in 1811, the Italian chemist Amedeo Avogadro used them to formulate an important postulate that became known as Avogadro's hypothesis:

Equal volumes of different gases at the same temperature and pressure contain equal numbers of particles.

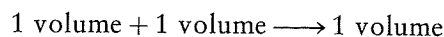
The question immediately arose: Are "particles" of the elements the same as Dalton's atoms? Avogadro believed that they were not; rather, he proposed that elements could exist as diatomic molecules. Avogadro's hypothesis could explain Gay-Lussac's law of combining volumes (Fig. 1.7). Thus, the reactions we wrote out in words become



The coefficients in the above reactions are proportional to the volumes of the reactant and product gases in Gay-Lussac's experiments, and the chemical formulas of the reactions agree with modern results. Dalton, on the other hand, would have written those reactions as



The combining volumes predicted by Avogadro's hypothesis for all three of these reactions as written would be



which did not agree with the results of Gay-Lussac's experiments.

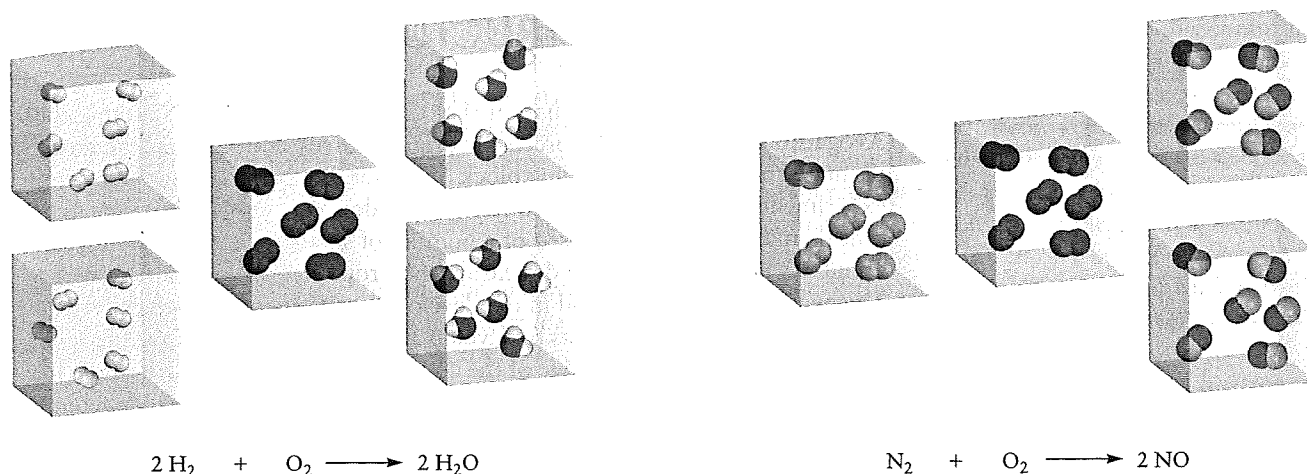


FIGURE 1.7 The cubes shown contain equal volumes of different gases at the same temperature and pressure. The combining volumes that Gay-Lussac observed for the two reactions can be understood if each cube contains the same number of molecules (Avogadro's hypothesis), and if hydrogen, oxygen, and nitrogen exist as diatomic molecules, as shown.

Avogadro's hypothesis not only predicted the correct molecular formulas but also the correct relative atomic masses of the elements. Chemical analysis during the 18th century had demonstrated that 1 g of hydrogen gas reacts completely with 8 g of oxygen gas to produce 9 g of water. If Dalton's formula for water, HO, were correct, then an atom of oxygen would weigh 8 times as much as an atom of hydrogen; that is, Dalton's assumption requires the **relative atomic mass** of oxygen to be 8 on a scale where the relative atomic mass of hydrogen had been chosen to be 1. Avogadro's hypothesis predicted, however, that each water molecule has twice as many atoms of hydrogen as oxygen; therefore, to explain the observed experimental mass relation, the relative mass for oxygen must be 16, a result consistent with modern measurements.

We might expect that Dalton would have welcomed Avogadro's brilliant hypothesis, but he did not. Dalton and others insisted that elements could not exist as diatomic molecules. One reason for their belief was the then-popular idea that a force called *affinity* held molecules together. Affinity expressed the attraction of opposites, just as we think of the attraction between positive and negative electric charges. Why should two atoms of the same type be held together in a molecule if the affinity theory were true? Moreover, if atoms of the same element did bond together somehow in pairs, why shouldn't they aggregate further to form molecules with three, four, or six atoms, and so forth? Avogadro's reasoning did not attract the attention it deserved because so many chemists continued to believe in the affinity theory, resulting in great confusion due to the adoption of different chemical formulas for the same molecule. A textbook published in 1861 by the German chemist August Kekulé titled *Lehrbuch der Organischen Chemie* gave 19 different chemical formulas for acetic acid!

In 1860, 50 years after Avogadro's work, Italian chemist Stanislao Cannizzaro presented a paper at the First International Chemical Congress in Karlsruhe, Germany, that convinced others to accept Avogadro's approach. Cannizzaro had analyzed many gaseous compounds and was able to show that their chemical formulas could be established with a consistent scheme that used Avogadro's hypothesis and avoided any extra assumptions about molecular formulas. Gaseous hydrogen, oxygen, and nitrogen (as well as fluorine, chlorine, bromine, and iodine), did indeed turn out to be diatomic molecules under ordinary conditions, thus vindicating Avogadro and his hypothesis.

1.4 THE PHYSICAL STRUCTURE OF ATOMS

The laws of chemical combination that culminated in Dalton's atomic theory and Avogadro's hypothesis reinforced the original Greek concept that the atom was the ultimate and indivisible building block of matter. By the end of the 19th century, new experimental results forced scientists to abandon this view and to conclude that atoms themselves were composed of a number of smaller, *elementary* particles. It took about 40 years to identify and measure the properties of these sub-atomic particles. This was a fascinating period in the development of modern science. Physicists built upon the advances of chemists to develop a deeper understanding of the fundamental structure of matter. Knowledge of the components of the atom and of the forces that hold them together stimulated entirely new fields of basic science and technology that continue to the present. Three themes characterize the research in this period: (1) how electric and magnetic fields (at that time only recently understood and described by the empirical laws of electricity and magnetism) became the dominant probes of the structure of matter, (2) the importance of clearly formulated hypotheses that could be tested experimentally, and (3) how the results we describe for several key experiments led to the general conclusions and insights that were drawn.

We suggest that you review the relevant sections of Appendix B before continuing on because interpreting the results of experiments described in the following paragraphs requires an elementary understanding of electricity and magnetism.

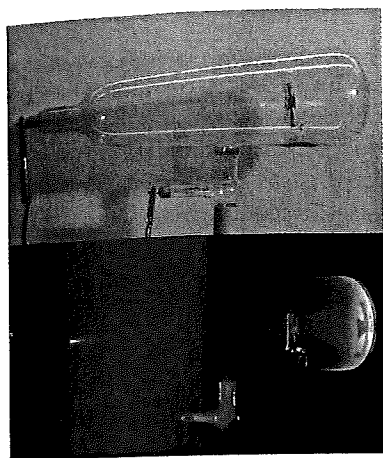
Electrolysis and the Existence of Ions

The story begins around the last quarter of the 19th century, by which time Faraday's laws of electrolysis had been generally accepted. Faraday had studied electrochemical reactions extensively; reactions in which the passage of an electrical charge produces chemical changes (see Section 17.1). The electrolysis of water, shown in Figure 1.2, is an example of an electrochemical reaction—the electrical current passing through the water decomposes it into the elements hydrogen and oxygen. Faraday discovered that the amount of water decomposed, and the amount of hydrogen and oxygen produced at the electrodes, were directly proportional to the quantity of charge passed. He observed the same result for many different electrochemical reactions, which led him to suggest that there must exist a fixed unit of electricity that is transferred in all these reactions. This conclusion was perhaps the first suggestion that all matter is composed of some electrical component that can be stripped away and transferred from reactants to products. Faraday named the electrically charged entities **ions**, the Greek word for “wanderer.” He measured the amount of charge necessary to produce 1 g of hydrogen from the electrolysis of water and thus calculated the **charge-to-mass ratio** for the hydrogen ion, which was about 10^8 C kg^{-1} in modern units.

Faraday's measurement was important, for nothing was known about the detailed structure or even the mass of the hydrogen ion at the time. Knowing the charge-to-mass ratio made it possible to investigate the properties of ions through their response to electric and magnetic fields. These studies would have to be carried out in gases at reduced pressure, where the charged particles could travel long distances without collisions, and their deflections by electric and magnetic fields could be measured. Also, Faraday's measurement established the order of magnitude for this quantity against which the charge-to-mass ratios of other particles would later be compared.

Glow Discharges and the Crookes Tube

The electrical components of gaseous substances were discovered in studies of the *glow discharge*, a process in which soft and beautiful light is emitted when electricity is forced to pass through a gas at low pressure. This phenomenon created great excitement among physicists and stimulated intense research projects to explain the



D-Kuru/Wikimedia Commons

FIGURE 1.8 A Crookes tube. (a) The Crookes tube is a glass cylinder that is evacuated and then filled with different gases to study the properties of glow discharges. A discharge is established when voltages are applied between the cathode (the electrode on the left) and the anode (the electrode in the arm below the main tube). The glass face on the right side of the tube is coated with a phosphor that glows when irradiated. (b) A weak blue glow discharge that disappears at low pressure is shown. The phosphorescence from the end of the tube persists even when no gas is present, providing evidence for the existence of cathode rays.

nature of the discharge and the origin of the light. Let's begin our discussion by introducing the *Crookes tube*, an apparatus that was invented by William Crookes to study the principles of electric discharges but which also became popular for lecture demonstrations and entertainment. Modern neon signs are examples of glow discharge tubes. The color of the glow depends upon the gas; neon produces a red emission, argon is purple, and mercury is blue, as shown in Figure 1.8. Glow discharge tubes in the late 19th century were extremely simple devices, but their importance to the development of modern science can hardly be overstated—they led to the discovery and measurement of the charge-to-mass ratio of the electron, to the determination of the properties of atomic nuclei, to the discovery of X-rays and isotopes, and to the invention of the mass spectrometer.

A particular version of a Crookes tube is shown in Figure 1.8a. It is a horizontal glass cylinder connected to a gas handling system by the small vertical glass tube at the bottom. The tube is fitted with two electrodes, the disk-shaped **cathode** on the left side of the large cylinder and the wire **anode** in the small glass arm at the bottom. The wire clips connect the cathode to the negative terminal of a battery and the anode to the positive terminal. A small metal Maltese cross is suspended near the right side of the tube, and the glass on that end of the tube has been coated with a phosphor that glows when illuminated by radiation. Figure 1.8b shows a faint blue glow discharge that becomes weak as the gas pressure is reduced and eventually disappears at very low pressures. The phosphor at the end of the tube continues to glow, however, even when all of the gas has been evacuated. The image of the cross observed in the phosphor-coated end of the tube suggests that it is being illuminated by some mysterious rays being emitted from the cathode and that these rays are very different from ordinary light because they travel in straight lines, as suggested by the sharpness of the image. To understand this conclusion, imagine the different images produced if you were to illuminate the cross using an ordinary light bulb or a flashlight that throws a well-defined beam. Because these mysterious rays persist even when there is no gas in the tube, they must be emitted from the cathode and so were named **cathode rays**. Subsequent refinements of the Crookes tube led to the discovery of a second kind of radiation a few years later, with rays that traveled in the opposite direction of the cathode rays. We discuss these two different kinds of rays in the sections that follow.

Negative Charge in the Atom: Electrons

Crookes and others had established qualitatively that cathode rays were negatively charged particles that could be deflected by electric and magnetic fields, that they traveled in straight lines, like light emitted from a point source, and that they carried energy that could be transferred in the form of heat to a metal target. But the failure to make a quantitative connection between the cathode rays observed and the current that flowed in an external circuit left skeptics unconvinced about their nature until the definitive experiments conducted by the British physicist J. J. Thomson resolved any doubt.

Thomson conducted a set of experiments that established that the cathode rays and the charged particles deflected by magnetic fields were one and the same. Thomson demonstrated this fact using a Crookes tube apparatus that allowed him to control the position of the rays with a magnet, to observe their trajectories, and to measure the current detected as the beam of rays entered a current meter fitted to the end of the tube. He followed the movement of the cathode rays by observing the phosphorescence of the glass, and he monitored the current as a function of position of the rays. The current rose as the rays entered the current meter and then fell as they left the meter, establishing for the first time that the rays were indeed charged particles. The second experiment in the series demonstrated that these negatively charged particles were deflected by an electric field and that the direction of the displacement was consistent with their negative charge. Others had

tried this experiment before, with inconclusive results, because residual gas molecules scattered the rays. Thomson succeeded where his predecessors had failed by achieving better vacuum conditions to minimize collisions with residual gas molecules. Thomson varied the gases used in the third experiment; the deflections observed were completely independent of the different gases used, suggesting that these particles were a common constituent of all gases. Recalling that Faraday had come to a similar conclusion in his electrochemistry experiments, Thomson next set out to determine the charge-to-mass ratio of these particles, which have been identified as electrons since at least 1897.

Charge-to-Mass Ratio of the Electron

The cathode ray tube used to measure the charge-to-mass ratio of the electron is shown schematically in Figure 1.9. The glass tube is evacuated to very low pressures so that electrons can travel the length of the tube without being scattered by residual gases. The glass face on the right side of the tube is coated with a phosphor that emits light when irradiated. Electrons emitted from the cathode are accelerated toward the anode, and those that pass through the hole in the anode form a collimated beam that lights up the phosphor where it hits. The electric deflection plates bend the beam down, and the displacement is measured directly from the positions of the phosphorescent spots on the screen. The magnetic field is then turned on, and the field strength required to restore the beam to its original position is recorded. The charge-to-mass ratio of the electron can be calculated by measuring the displacement and knowing the strengths of the electric and magnetic fields applied.

The voltage applied to the deflection plates establishes a uniform electric field between them that exerts a constant downward force on electrons in the region that is given by

$$F_E = eE = ma \quad [1.1]$$

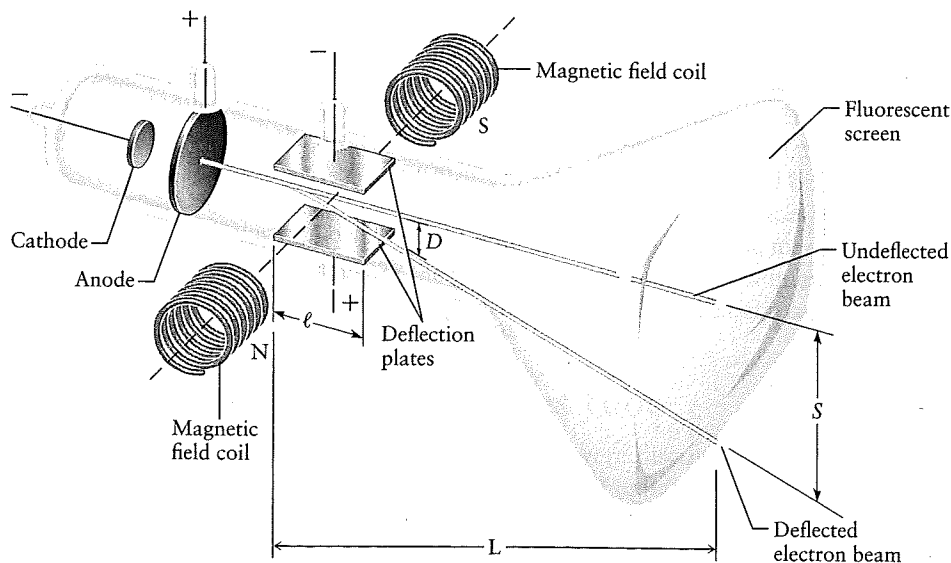
where e is the charge on the electron and E is the strength of the electric field. The constant acceleration that results from this force is calculated using Newton's second law

$$a = (em_e)E \quad [1.2]$$

which results in a displacement given by

$$D = \frac{1}{2} at^2 \quad [1.3]$$

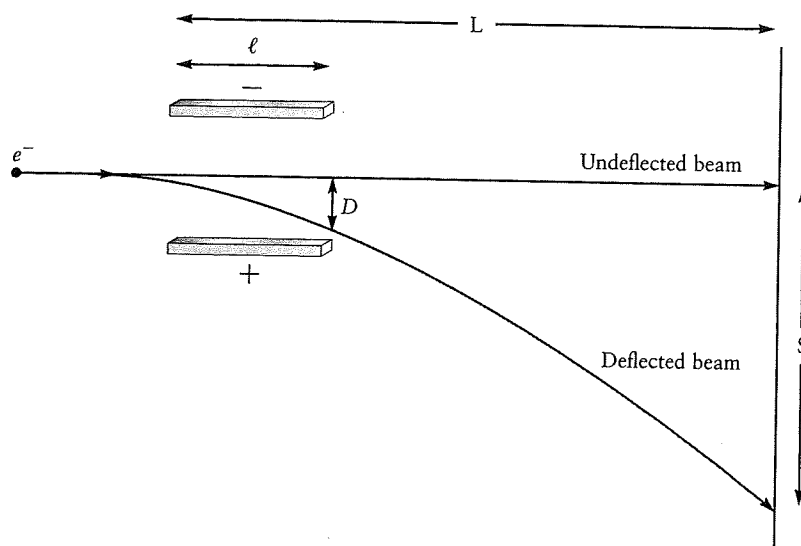
FIGURE 1.9 Thomson's apparatus, used to measure the charge-to-mass ratio, e/m_e , of the electron. Electrons emitted from the cathode (cathode rays) travel across the tube from left to right. An electric field deflects the beam down and a magnetic field deflects the beam up. The deflection S , due to the electric field alone, was measured. The beam was then restored to its original position by applying the magnetic field. The charge-to-mass ratio for the electron was determined from these two measurements, as discussed in the text. (ℓ is the length of the electric deflection plates.)



where t is the time required to travel the distance ℓ , the length of the plates. Substituting $t = \ell/v$, for electrons traveling through the plates at constant velocity, and a from Equation 1.2 into Equation 1.3 gives

$$D = \frac{1}{2} at^2 = \frac{1}{2} \left(\frac{e}{m_e} \right) \left(\frac{\ell}{v} \right)^2 E \quad [1.4]$$

for the displacement. The deflected electrons travel in straight lines after they leave the plates, because there are no additional forces acting on them, and they strike the fluorescent screen at a distance S below the position of the undeflected beam. This extra path length “magnifies” the displacement by the factor L/ℓ , where L is the distance from the left edge of the plates to the screen, as shown in the adjacent construction.



Electrons arriving at the screen have been displaced by

$$S = \left(\frac{L}{\ell} \right) D = \frac{1}{2} \left(\frac{e}{m_e} \right) \left(\frac{\ell}{v} \right)^2 \left(\frac{L}{\ell} \right) E \quad [1.5]$$

Equation 1.5 could be solved for the charge-to-mass ratio, if the velocity of the electrons could be determined, because all of the other quantities could be measured directly in this experiment.

Thomson made an ingenious modification to his experiment to measure the velocity of the electrons directly and thereby determine e/m_e . He established a magnetic field in the same region as the electric field by passing an electric current through a pair of coils, as shown in Figure 1.9. The magnetic field was oriented perpendicular to both the electric field and to the flight path of the electrons, and it exerted an upward force on them. Thomson could return the deflected beam to its original position by varying the strengths of the two fields so that the net force on the electrons was zero. The force due to the electric field E was

$$F_E = eE = \quad [1.6]$$

and the force due to the magnetic field B was

$$F_B = evB \quad [1.7]$$

so the velocity can be calculated by setting these equations equal to one another to get

$$v = \frac{E}{B} \quad [1.8]$$

Substituting this result for the velocity into Equation 1.5 gives the deflection observed under the influence of the electric field alone as

$$S = \frac{1}{2} \left(\frac{e}{m_e} \right) \left(\frac{\ell B}{E} \right)^2 \left(\frac{L}{\ell} \right) E \quad [1.9]$$

which can be solved to find the charge-to-mass ratio of the electron.

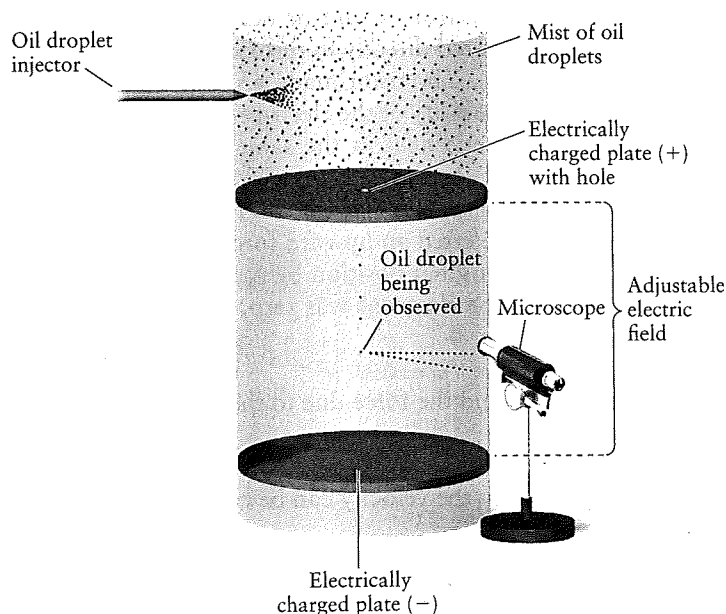
$$\frac{e}{m_e} = \frac{2SE}{\ell LB^2} \quad [1.10]$$

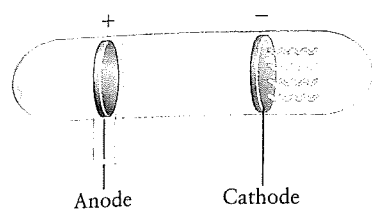
Each of the quantities on the right-hand side of Equation 1.10 was measured directly in Thomson's experiment, allowing him to determine the charge-to-mass ratio for the electron for the first time. The currently accepted value is $e/m_e = 1.7588202 \times 10^{11} \text{ C kg}^{-1}$, with the charge and mass measured in the SI units coulombs and kilograms, respectively. (See Appendix B for a full discussion of units of measure.)

Charge of the Electron

Thomson was able to measure only the charge-to-mass *ratio* of the electron in his experiment, and so an independent measurement of either the charge or the mass was required to determine the values of both of these fundamental physical quantities. The American physicist Robert Millikan and his student H. A. Fletcher measured the charge of the electron in 1906, in an elegant experiment that is illustrated schematically in Figure 1.10. An atomizer, like one used to spray perfume, injects very small (about $1 \mu\text{m}$) droplets of oil into a chamber above a pair of electrically charged plates that are separated by an insulator. From time to time a drop falls through a hole in the upper plate and enters the region between the plates; the droplets pick up a charge during the spraying process or by collisions with ions in the chamber air. The voltage applied to the plates establishes a constant electric field in this region that pushes negatively charged particles up, countering the downward pull of gravity. Millikan and his student observed hundreds to thousands of single droplets for extended periods of time (as long as many hours), and they were able to control the motions of individual droplets by controlling the applied voltage. Individual droplets could be suspended for long periods of time by balancing the gravitational force by an opposing electrical force. Once suspended,

FIGURE 1.10 Millikan's apparatus, used to measure the charge of the electron, e . Individual drops are suspended by adjusting the electric field to provide an electrostatic force that opposes the gravitational force; the charge on the electron was determined by equating these two forces as discussed in the text.





Modified Crookes tube.

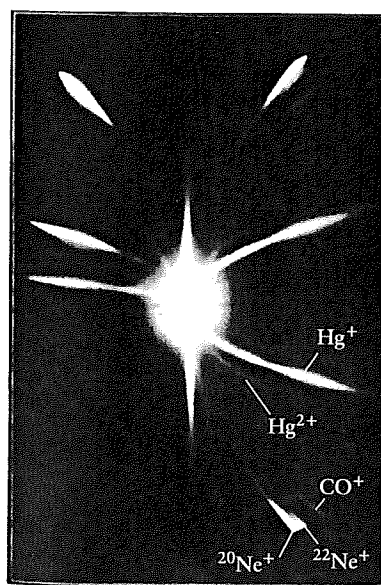
individual droplets were sometimes observed to suddenly jump either upward or downward as they acquired negative or positive charges from ions in the air; they could be returned to their stable positions by adjusting the voltages on the plates.

The net force on stationary droplets is zero; balancing the electrical and gravitational forces gives $Mg = QE$, where M is the mass of the droplet, g is the acceleration due to gravity, Q is the charge on the droplet, and E is the electric field strength. The masses of individual droplets were calculated by multiplying their densities by their volumes (determined by measuring their diameters using the microscope). The gravitational acceleration g is a known constant, and the electric field strength was controlled and measured in each experiment, allowing Millikan to calculate the charge Q for each individual drop. The charges observed varied significantly from droplet to droplet but they were always an integral multiple of the one smallest unit of charge. Millikan pointed out for the first time that the magnitude of the fundamental unit of positive charge was exactly the same as the magnitude of the fundamental unit of negative charge. The value that Millikan reported for the charge of the electron was 1.59×10^{-19} C. The currently accepted value is $e = 1.60217646 \times 10^{-19}$ C which, along with the currently accepted value for the e/m_e ratio gives $m_e = 9.1093819 \times 10^{-31}$ kg for the electron mass.

Positive Charge in the Atom: The Nucleus

Careful observation of the discharges in Crookes tubes showed that there was a glow that extended behind the cathode; a special version of the Crookes tube, shown in the adjacent schematic (based upon an original sketch by Thomson), was used to study the origin of this glow. The holes in the cathode (called canals) allowed part of the discharge to pass through and create pencils of light that were called **canal rays**. The German physicist Wilhelm Wien proceeded to study their properties by measuring their deflections in both electric and magnetic fields. He drew the following conclusions from these measurements:

1. The canal rays passing through the cathode were deflected by magnetic fields in a direction that established them as positively charged particles.
2. The electric and magnetic fields required to deflect these particles were much larger than those used in Thomson's experiments, proving that the particles were much more massive than the electron, at least as massive as the hydrogen atom.
3. The electric and magnetic fields required to deflect particles from different gases by the same amount were different, proving that the positively charged particles associated with different gases had different masses.



Thomson, J.J. Elements of the mathematical theory of electricity and magnetism. Cambridge University Press, 1921

FIGURE 1.11 Traces of parabolic paths produced by positive ions in Thomson's experiments on the "positive rays". The ions giving rise to particular trajectories in the lower right quadrant of the figure are identified.

Thomson took up the further study of these "rays of positive electricity," as he called them, using a variation of his cathode ray tube apparatus. Imagine a version of the apparatus shown in Figure 1.9 with three modifications: (1) The voltages on the anode (the plate with the hole) and cathode are reversed so that positively charged particles pass through the hole and strike the front of the tube; (2) the magnetic field coils are rotated by 90° so that the electric and magnetic fields are now parallel to one another and (3) the front of the tube is fitted with a photographic plate. The magnetic field deflects the particles horizontally while the electric field deflects them vertically, as before, and the film shows parabolic traces that depend upon the charge-to-mass ratio of the ions and on their velocities. Figure 1.11 shows one such set of traces, the identity of the particles being established by calculating the trajectories expected from their charge-to-mass ratios and the known field strengths. The particles are recognized as positively charged *ions* formed by removal of one or more electrons from an atom or molecule, usually by collisions with high-energy electrons. Mercury ions (from the vacuum pump) are clearly identified, a set with one unit of positive charge and a second set with two

units of positive charge. CO^+ and neon ions with two different masses were identified (see later). Other experiments (not shown) established the utility of the method for identifying the individual components of complex mixtures of gases. Thomson did not fail to point out the importance of this new method for chemical analysis, which forms the basis for mass spectrometry, one of our most important methods for determining molecular weights and structures.

Thomson and Wien had discovered two new, and quite different, types of electrically charged particles that comprise matter: a light particle with a negative charge that appeared to be a common constituent of all atoms, and a number of much heavier, positively charged particles whose relative masses depended on the elements from which they were produced. Although it was generally then agreed that these particles were the building blocks of atoms, it was not at all clear how they were assembled. That piece of the puzzle remained unsolved until a stunning discovery was made in the laboratory of Ernest Rutherford in 1911, which relied upon results in earlier studies of radioactivity.

Discovery of the Atomic Nucleus

Radioactivity from natural sources was discovered in 1889 by the French physicists Henri Becquerel and Marie and Pierre Curie. Becquerel showed that rays emitted from uranium salts and uranium metal darkened nearby photographic plates that had been shielded from light by black paper. The Curies discovered the radioactive elements thorium, polonium, and radium. They demonstrated that while emitting radiation these elements were transformed into other elements by *radioactive decay*. This apparent violation of one of the key postulates of Dalton's atomic theory stimulated intense interest in discovering the mechanism of radioactive decay. Chapter 19 describes this very important process from a modern point of view, and reassures us that elements are not transmuted one into another by ordinary chemical reactions. Radioactive decay is not a revival of medieval alchemy! Our interest here is to use the emitted radiation as another probe of atomic structure.

By 1911, New Zealander Ernest Rutherford and his students at the University of Manchester had been investigating radioactive decay for a number of years. They had determined that the emitted radiation has at least two components, which they labeled α and β on the basis of their relative ability to penetrate solid materials. They had shown that α particles are doubly charged He atoms, by measuring their charge-to-mass ratios and by physically trapping and identifying the He gas produced. Now they wanted to study their interactions with matter to see if they could serve as probes of atomic structure. Rutherford chose to work with very thin gold foils (600 nm or about 2000 gold atoms thick) so the α particles could pass through the sample and their properties be measured after they exited the foil. Deflections of a collimated beam of alpha particles by a gold foil were measured by observing the scintillations they produced on a fluorescent ZnS screen (Fig. 1.12). Almost all of the alpha particles passed straight through the foil, but a few were deflected through large angles. Some particles even scattered backwards, in a few rare events! Rutherford was astounded, because the alpha particles were relatively massive and fast moving. In his words, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." He and his students studied the frequency with which such large deflections occurred. They concluded that most of the mass in the gold foil was concentrated in dense, extremely small, positively charged particles that they called nuclei. By analyzing the trajectories of the particles scattered by the foil, they estimated the radius of the gold nucleus to be less than 10^{-14} m and the positive charge on each nucleus to be approximately $+100e$ (the actual value is $+79e$).

Rutherford's Planetary Model of the Atom

Based on these experimental results, Rutherford proposed a model of the atom in which the charge on the nucleus is $+Ze$, with Z electrons surrounding the nucleus out to a distance of about 10^{-10} m (0.1 nm). This integer Z is called the atomic

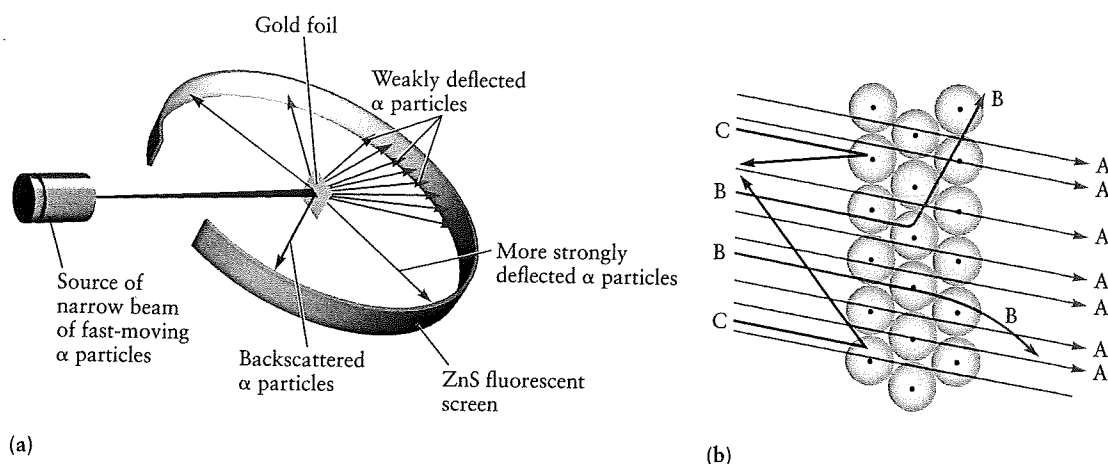


FIGURE 1.12 Schematic of Rutherford's experiment on the scattering of particles by thin (600 nm) gold foils. (a) Flashes of light mark the arrival of alpha particles at the fluorescent screen. More than 100,000 alpha particles per minute were weakly deflected, and only about 20 alpha particles per minute were deflected backwards, under typical conditions. (b) Interpretation of the Rutherford experiment: Most of the alpha particles pass through the space between nuclei and are deflected only slightly (A). A few pass close to a nucleus and are more strongly deflected (B). Some are even scattered backward (C). The size of the nucleus, relative to the size of a gold atom, is much smaller than the diagram suggests.

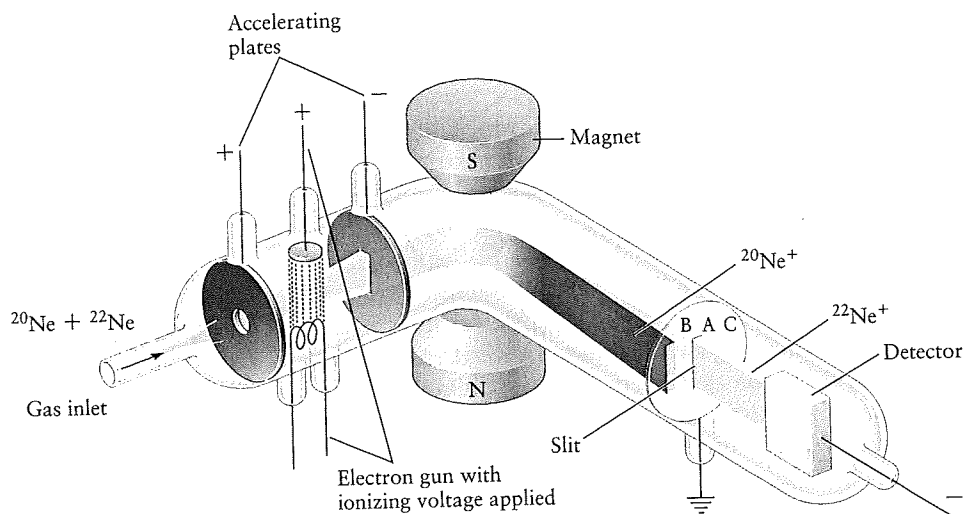
number of the element. Atomic numbers are given on the inside front cover of this book. The Rutherford model for a gold atom has 79 electrons (each with charge $-1e$) arranged about a nucleus of charge $+79e$. The electrons occupy nearly the entire volume of the atom, whereas nearly all its mass is concentrated in the nucleus.

The model of the atom Rutherford proposed is often called the “planetary model” of the atom because he envisioned the electrons occupying most of the atomic volume (like the planets in a solar system), centered on the small, dense nucleus (like the sun). The Rutherford model has become the universally accepted picture of the structure of the atom. The properties of a given chemical element arise from the charge $+Ze$ on its nucleus and the presence of Z electrons around the nucleus. Although the planetary model has been extremely successful in explaining many of the properties of atoms, it has an inherent flaw that was recognized later: it couldn't possibly exist according to the laws of classical physics! We discuss this and other failures of classical physics to explain the properties of atoms in Chapter 4.

Mass Spectrometry, Isotopes, and the Measurement of Relative Masses

Mass spectrometry developed rather quickly after Thomson had shown how relative atomic and molecular masses could be measured directly by observing the deflections of ions in electric and magnetic fields. The most startling new result of his studies was the appearance of a new ion with a relative mass of 22 (see Fig. 1.11) that did not correspond to any known element; the doubly charged ion appeared at mass 11, leaving little doubt that this was a new species. This result was obtained with every sample of neon gas studied, including those of exceptional purity, and led Thomson to propose that neon was in fact not a simple gas but a mixture of two gases, the more abundant component having a relative mass of 20 and the less abundant component a relative mass of 22. It appeared, therefore, that the atomic mass of neon, determined by chemical means to be 20.2, was

FIGURE 1.13 A simplified representation of a modern mass spectrometer. A gas mixture containing the isotopes ^{20}Ne and ^{22}Ne is introduced through the gas inlet. Atoms are ionized by electron impact and then accelerated by the electric field established between the accelerating plates. The ion beam passes into a magnetic field, where it is separated into components on the basis of the ions' charge-to-mass ratios. The conditions chosen for this illustration allow the heavier $^{22}\text{Ne}^+$ ions to pass through the slit in the plate (A) and reach the detector while the lighter $^{20}\text{Ne}^+$ ions strike the plate at position B and are not detected. Different conditions would move the $^{22}\text{Ne}^+$ beam to position C and allow the $^{20}\text{Ne}^+$ ions to pass through the slit and reach the detector.



somehow an average of the masses of the two kinds of neon atoms. This was an astonishing result that seemed inconsistent with what was known about the elements at the time. The sample was chemically pure, and there was no room in the periodic table for a new element of mass 22 whose chemical properties were identical to those of neon. This interpretation was later confirmed using more advanced mass spectrometric methods, and this experiment provided one of the earliest clues for the existence of what became known as **isotopes** (from the Greek *isos*- ["equal"] plus *topos* ["place"]).

Refinements of Thomson's technique made it possible to measure relative masses extremely accurately and led to the discovery of the isotopes of many elements. A simple mass spectrometer, like the one shown schematically in Figure 1.13, consists of three elements: a region in which atoms or molecules are ionized and accelerated, one in which their flight paths are bent by magnetic forces, and a detector that measures the ion current. Positive ions are created by electron impact, the electrons being emitted from a heated filament and accelerated by an applied voltage as shown. The ions are then accelerated by an electric field created by a voltage applied to the plates shown, and enter the magnetic field region where they experience a magnetic force given by

$$F_B = qvB$$

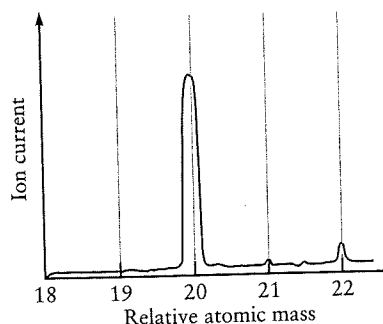


FIGURE 1.14 A sketch of the mass spectrum of Ne, showing only the two isotopes ^{20}Ne and ^{22}Ne .

The deflection due to this force can be calculated using the same approach we described for Thomson's experiments, but for the present purpose it is sufficient to note that the lighter ions are deflected more than the heavier ions for a given magnetic field strength. The figure shows, for example, that ^{20}Ne has been deflected more than ^{22}Ne , which is passing through the slit and being detected under this set of conditions. A mass spectrum is acquired by scanning the magnetic field and measuring the ion current as a function of the magnetic field strength. The mass spectrum of neon, for example, consists of two peaks, as shown schematically in Figure 1.14; the more intense peak is ^{20}Ne and the less intense peak is ^{22}Ne , the relative intensities reflecting their relative natural abundances.

Mass spectrometry confirmed the existence of isotopes for many elements and established a physical method for determining relative atomic masses. One consequence of this development was the realization that the relative atomic masses of the elements determined from the laws of chemical combination are actually averages of the relative atomic masses of its isotopes weighted by their relative natural

abundances, averages that could now be calculated from its mass spectrum as follows. Suppose, for example, that there existed only the two neon isotopes identified so far and that 91% of the neon atoms were ^{20}Ne and 9% were ^{22}Ne . The average relative atomic mass would then be $(0.91)(20) + (0.09)(22) = 20.18$, which is close to the value reported in the table of relative atomic masses of the elements on the inside front cover of the book. Similarly, chlorine has two isotopes, about 75% being ^{35}Cl and 25% being ^{37}Cl , from which we calculate an average mass of 35.5, which is also close to the value reported in the table just cited. The average relative atomic mass of an element comprised of n isotopes with relative atomic masses A_i and relative fractional abundances p_i is given by

$$A = p_1A_1 + p_2A_2 + \cdots + p_nA_n = \sum_{i=1}^n p_iA_i$$

The discovery of isotopes created a major problem for chemists and physicists trying to establish a relative mass scale that was acceptable to both communities. Prior to the discovery of isotopes, and especially the isotopes of oxygen, the masses of the elements were determined from the laws of chemical composition using oxygen as the reference, whose relative atomic mass was defined to be exactly 16. Oxygen was a logical choice for the reference mass because it forms many compounds with the elements through combustion reactions. Having discovered a way to measure the relative atomic masses of the isotopes of all of the elements, the physicists argued that it made more sense, on physical grounds, to set the relative atomic mass of the ^{16}O isotope to 16, exactly. The problem with this choice, from the point of view of the chemists, was that reference data that had been generated for many decades would have to be revised because the error introduced by making this choice would be unacceptably high. A compromise was reached in 1961 in which the mass of the ^{12}C isotope was defined to have a relative atomic mass of 12, exactly. This choice was appealing to the physicists because it was based upon a physical measurement of a particular isotope and it was acceptable to the chemists because a fortuitous distribution of the isotopes of both carbon and oxygen in natural abundance averaged out the errors and reduced them to an acceptable level.

Relative atomic masses have no units because they are ratios of two masses measured in whatever units we choose (grams, kilograms, pounds, and so forth). The *relative molecular mass* of a compound is the sum of the relative atomic masses of the elements that constitute it, each one multiplied by the number of atoms of that element in a molecule. For example, the formula of water is H_2O , so its relative molecular mass is

$$2 (\text{relative atomic mass of H}) + 1 (\text{relative atomic mass of O}) = \\ 2(1.0079) + 1(15.9994) = 18.0152$$

EXAMPLE 1.2

Calculate the relative atomic mass of carbon, taking the relative atomic mass of ^{13}C to be 13.003354 on the ^{12}C scale.

Solution

Set up the following table:

Isotope	Isotopic Mass \times Abundance
^{12}C	$12.000000 \times 0.98892 = 11.867$
^{13}C	$13.003354 \times 0.01108 = 0.144$
Chemical relative atomic mass = 12.011	

Related Problems: 15, 16, 17, 18

CONNECTION TO NANOTECHNOLOGY

Imaging Atoms, Molecules, and Chemical Reactions by Scanning Tunneling Microscopy

The laws of chemical combination provided indirect evidence for the existence of atoms. The experiments of Thomson, Wien, and Rutherford provided direct physical evidence for the existence of the elementary particles that make up the atom. We conclude this chapter by describing an experimental method that allows us not only to image individual atoms and molecules but also to observe and control a chemical reaction at the single molecule level—a feat only dreamed of as recently as the mid-1980s. The ability to manipulate single atoms, molecules, and nanoparticles has developed into a set of technologies that allows scientists and engineers to create two-dimensional arrays of these entities with applications in materials science, biology, and medicine.

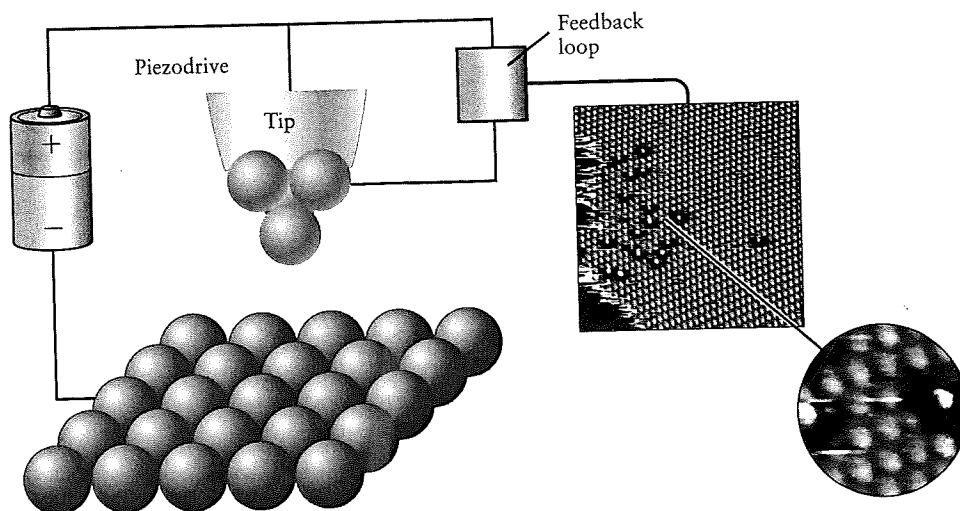
Microscopy began with the fabrication of simple magnifying glasses; the development of the compound microscope in the late 17th century made it possible to observe single biological cells, enabling the study of biology on the cellular level for the first time. The invention of the electron microscope in the 1930s opened the way to observe objects with dimensions much smaller than the wavelength of light, the resolution limit of optical microscopes. Unfortunately, however, sample damage caused by the high energy of the electron beam required is still a limitation of the technique for certain applications. Gerd Binnig and Heinrich Rohrer developed the scanning tunneling microscope (STM), which images atoms using low-energy electrons, for which they received the 1986 Nobel Prize in Physics. The STM measures small currents produced by electrons that tunnel between

a very sharp conducting tip and the sample at very small tip-surface separations, as shown in the schematic. The tunneling current is an exponential function of the tip-surface separation. A feedback loop monitors the tunneling current, which is fed to the piezoelectric element to keep the tip-surface separation constant as the tip is scanned across the sample. The three-dimensional STM images shown are plots of the tip height as a function of the tip position in the plane of the sample. Individual atoms of the single crystal metal surface are clearly resolved, as are some missing atoms (defects) shown in the inset.

Scanning tunneling microscope images have visually confirmed many properties of solids, surfaces, and adsorbed species, such as the sizes of atoms and the distances between them, which are already known from other techniques. But, much new information has been obtained as well. The STM images have shown the positions and shapes of molecules undergoing chemical reactions on surfaces, which helps guide the search for new ways of carrying out such reactions. They have also revealed the shape of the surface of the molecules of the nucleic acid DNA, which plays a central role in genetics.

Images of Single Molecules in Chemical Reactions

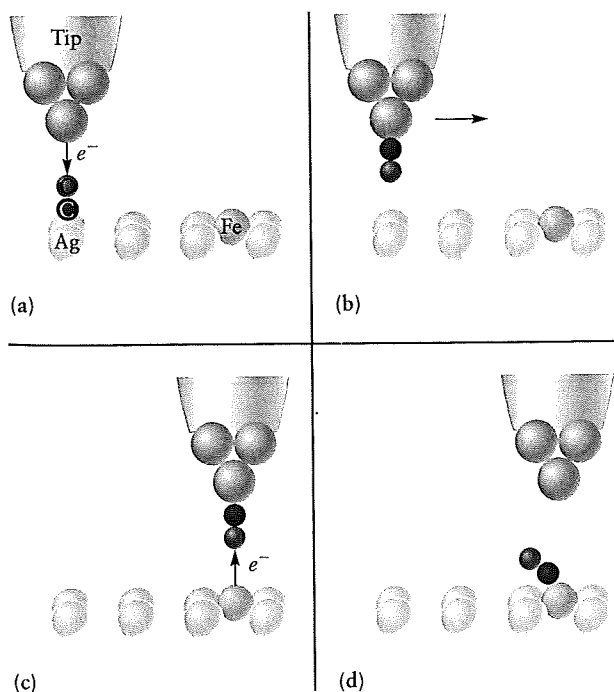
The STM has been used to image the surfaces of materials since the mid-1980s, but only recently has it been used to image single molecules and to initiate chemical reactions at the single molecule level, as we illustrate with the following example. Although the STM can be used to image objects in air, the experiments described here were conducted in ultrahigh vacuum (extremely low pressure) to ensure that only the reactants of inter-



est were present on the surface. The schematic shows an STM tip hovering over a silver (Ag) surface on which an iron (Fe) atom and a carbon monoxide (CO) molecule have been chemically bonded (adsorbed), and a series of steps that leads to the formation of a product molecule Fe(CO).

Part (a) of the figure shows the tip positioned over a single carbon monoxide (CO) molecule, ready to pluck it from the silver (Ag) surface; in part (b) CO is adsorbed onto the tip, bonded via the carbon (C) atom, and the tip is then translated across the surface to a region near an iron (Fe) atom; part (c) shows CO being transferred to the Fe atom and forming an Fe-CO bond; finally, in part (d) the tip is withdrawn with the product molecule, FeCO, remaining bound to the Ag surface. Bonding between the carbon monoxide and the tip is controlled by the tip voltage and current. CO is plucked from the surface when electrons flow from the tip to the surface and it is released to the surface when electrons flow in the opposite direction.

The schematic serves as a guide to the eye for interpreting the real STM images shown in the next figure. Each image represents an area of the surface that measures 6.3×6.3 nm. The false color scale reflects the height of the objects above the plane of the silver surface atoms; the red end of the scale represents protrusions, whereas the purple end represents depressions. The identity of each chemical species was established by the nature of the image and also by the way in which the current varied with the applied voltage. That variation provides a chemical signature.



In part A of the figure, five Fe atoms and five CO molecules are clearly seen; the red arrow identifies one Fe atom that is a bit difficult to see otherwise. The curved white arrow shows a CO molecule in close proximity to an Fe atom. Part B shows the FeCO molecule formed as a result of the transfer of that CO molecule to the Fe atom by the tip, as well as another potentially reactive pair identified by the white curved arrow. From the shape of the resulting image in part C, we can see that another FeCO molecule has been formed. The white curved arrow suggests the possibility of adding an additional CO molecule to the first FeCO synthesized to form $\text{Fe}(\text{CO})_2$, which, indeed, occurs as shown in part D. This remarkable sequence of images shows clearly the synthesis of a pair of distinct Fe(CO) molecules, as well as an $\text{Fe}(\text{CO})_2$ molecule, from the reactants Fe and CO adsorbed onto a silver surface. These syntheses were accomplished by manipulating single CO molecules to place them sufficiently close to Fe atoms to initiate a chemical reaction, demonstrating our ability to observe and control chemical reactions at the single molecule level.

The ability to manipulate single molecules and nanoparticles has led to the recent development of **dip-pen lithography**, a promising approach for synthesizing two-dimensional arrays of a wide variety of materials of interest. The method relies upon the forces between molecules and surfaces (the basis of **atomic force microscopy**) instead of tunneling to assemble arrays of inorganic materials for catalysis, sensing or microelectronics applications as well as arrays of biomolecules for rapid throughput screening.

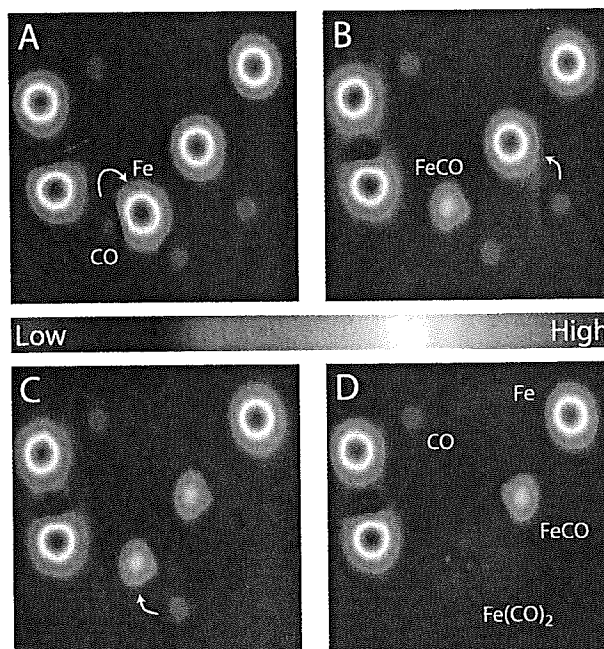


Photo courtesy of Wilson Ho, University of California, Irvine. Reprinted by permission of AAAS SCIENCE 286, 1719-1722 (1999)

The number of significant figures in a table of chemical or natural relative atomic masses (see the inside front cover of this book) is limited not only by the accuracy of the mass spectrometric data but also by any variability in the natural abundances of the isotopes. If lead from one mine has a relative atomic mass of 207.18 and lead from another has a mass of 207.23, there is no way a result more precise than 207.2 can be obtained. In fact, geochemists now use small variations in the $^{16}\text{O}:^{18}\text{O}$ ratio as a “thermometer” to deduce the temperatures at which different oxygen-containing rocks were formed in the Earth’s crust over geological time scales. They also find anomalies in the oxygen isotopic compositions of certain meteorites, implying that their origins may lie outside our solar system. Temperature variations over the past million years of the earth’s history have been established by measuring the $^{16}\text{O}:^{18}\text{O}$ and $^2\text{H}:^1\text{H}$ ratios as a function of depth in the Greenland and Antarctic ice cores and correlated with atmospheric CO_2 concentration, providing important clues as to the origins of climate change (see Section 20.6).

Structure of the Nucleus: Protons, Neutrons, and Isotopes

The experiments described earlier led to the discovery of electrons and nuclei and to the planetary model of the atom, but they did not provide sufficient evidence to establish a model for the structure of the nucleus. Subsequent experiments, of the same general type we have discussed, identified the two other elementary particles, the proton and the neutron, whose properties we describe here. A full discussion of the nature of those experiments is beyond the scope of this textbook. The smallest and simplest nucleus is that of the hydrogen atom—the proton (from the Greek *protos* [“first”])—so named because it is a fundamental component of all nuclei. The proton has a positive charge of $+e$, where e is the elementary charge but its mass is 1.67262×10^{-27} kg, which is 1836 times greater than the electron mass. Nuclei of the other elements contain an integral number of protons, which is given by their **atomic number** Z , which is also the charge on the nucleus. The existence of isotopes, elements with the same atomic number but different masses, implied that there was another nuclear particle whose mass was the same as the proton mass but with no charge—that particle is the neutron. The **mass number** A of a particular isotope is the sum of the numbers of protons and neutrons for the isotope. $A = Z + N$. We write chemical symbols for the isotopes (nuclides) as follows: ${}_Z^AX$, where X is the chemical symbol for the element. The isotopes of hydrogen, for example, are written as: ${}_1^1\text{H}$, ${}_1^2\text{H}$ and ${}_1^3\text{H}$ for hydrogen, deuterium and tritium, respectively. It is customary, though redundant, to include the atomic number in addition to the symbol for the element, primarily because it is helpful when balancing nuclear chemical reactions (see Chapter 19).

EXAMPLE 1.3

Radon-222 (^{222}Rn) has recently received publicity because its presence in basements may increase the number of cancer cases in the general population, especially among smokers. State the number of electrons, protons, and neutrons that make up an atom of ^{222}Rn .

Solution

From the table on the inside front cover of the book, the atomic number of radon is 86; thus, the nucleus contains 86 protons and $222 - 86 = 136$ neutrons. The atom has 86 electrons to balance the positive charge on the nucleus.

Related Problems: 19, 20, 21, 22

CHAPTER SUMMARY

We have come a long way since the attempts of the alchemists to turn base metals into gold, to transmute one element into another. Through the early chemical experiments of Dalton, Gay-Lussac, and Avogadro, we have learned that matter is ultimately indivisible, at least as far as its physical and chemical properties are concerned. The experiments of Thomson, Wien, and Rutherford confirmed, from the results of physical measurements, the existence of the atom. These experiments also identified and characterized the elementary particles from which the atom is made, and this led to the modern model of the atom as an object with a small, dense nucleus surrounded by a much larger volume occupied by electrons. Physicists in the 21st century have developed tools of unprecedented power with which to analyze and synthesize single molecules, an achievement that has already led to exciting new applications in almost every area of modern science and engineering.

CONCEPTS AND SKILLS



Interactive versions of these problems are assignable in OWL.

Section 1.1 – The Nature of Modern Chemistry

State and interpret the laws of conservation of energy and conservation of mass and distinguish between macroscopic and nanoscopic length scales.

- Energy and mass are separately conserved in ordinary (not nuclear) chemical reactions. The total mass of the products equals the total mass of the reactants. The total amount of energy contained in the products is equal to the total amount of energy contained in the reactants. Chemical reactions occur on the scale of nanometers with masses of the order 10^{-26} kg, but we observe them in the laboratory on a scale of grams and centimeters.

Section 1.2 – Macroscopic Methods for Classifying Matter

Describe in operational terms how to distinguish among mixtures, compounds, and elements (Problems 1–4).

- Mixtures may be separated into simpler substances by *physical* processes like filtration or distillation. Substances that can be separated into simpler substances by chemical reactions are called compounds; those that cannot are called elements.

13. Pure nitrogen dioxide (NO_2) forms when dinitrogen oxide (N_2O) and oxygen (O_2) are mixed in the presence of a certain catalyst. What volumes of N_2O and oxygen are needed to produce 4.0 L NO_2 if all gases are held at the same conditions of temperature and pressure?
14. Gaseous methanol (CH_3OH) reacts with oxygen (O_2) to produce water vapor and carbon dioxide. What volumes of water vapor and carbon dioxide will be produced from 2.0 L methanol if all gases are held at the same temperature and pressure conditions?

The Physical Structure of Atoms

15. The natural abundances and isotopic masses of the element silicon (Si) relative to $^{12}\text{C} = 12.00000$ are

Isotope	% Abundance	Isotopic Mass
^{28}Si	92.21	27.97693
^{29}Si	4.70	28.97649
^{30}Si	3.09	29.97376

Calculate the atomic mass of naturally occurring silicon.

16. The natural abundances and isotopic masses of the element neon (Ne) are

Isotope	% Abundance	Isotopic Mass
^{20}Ne	90.00	19.99212
^{21}Ne	0.27	20.99316
^{22}Ne	9.73	21.99132

Calculate the atomic mass of naturally occurring neon.

17. Only two isotopes of boron (B) occur in nature; their atomic masses and abundances are given in the following table. Complete the table by computing the relative atomic mass of ^{11}B to four significant figures, taking the tabulated relative atomic mass of natural boron as 10.811.

Isotope	% Abundance	Atomic Mass
^{10}B	19.61	10.013
^{11}B	80.39	?

18. More than half of all the atoms in naturally occurring zirconium are ^{90}Zr . The other four stable isotopes of zirconium have the following relative atomic masses and abundances:

Isotope	% Abundance	Atomic Mass
^{91}Zr	11.27	90.9056
^{92}Zr	17.17	91.9050
^{94}Zr	17.33	93.9063
^{96}Zr	2.78	95.9083

Compute the relative atomic mass of ^{90}Zr to four significant digits, using the tabulated relative atomic mass 91.224 for natural zirconium.

19. The isotope of plutonium used for nuclear fission is ^{239}Pu . Determine (a) the ratio of the number of neutrons in a ^{239}Pu nucleus to the number of protons, and (b) the number of electrons in a single plutonium atom.
20. The last "missing" element from the first six periods was promethium, which was finally discovered in 1947 among the fission products of uranium. Determine (a) the ratio of the number of neutrons in a ^{145}Pm nucleus to the number of protons, and (b) the number of electrons in a single promethium atom.
21. The americium isotope ^{241}Am is used in smoke detectors. Describe the composition of a neutral atom of this isotope for protons, neutrons, and electrons.
22. In 1982, the production of a single atom of $^{266}_{109}\text{Mt}$ (meitnerium-266) was reported. Describe the composition of a neutral atom of this isotope for protons, neutrons, and electrons.

ADDITIONAL PROBLEMS

23. Soft wood chips weighing 17.2 kg are placed in an iron vessel and mixed with 150.1 kg water and 22.43 kg sodium hydroxide. A steel lid seals the vessel, which is then placed in an oven at 250°C for 6 hours. Much of the wood fiber decomposes under these conditions; the vessel and lid do not react.
- (a) Classify each of the materials mentioned as a substance or mixture. Subclassify the substances as elements or compounds.
- (b) Determine the mass of the contents of the iron vessel after the reaction.
24. In a reproduction of the Millikan oil-drop experiment, a student obtains the following values for the charges on nine different oil droplets.

$6.563 \times 10^{-19} \text{ C}$	$13.13 \times 10^{-19} \text{ C}$	$19.71 \times 10^{-19} \text{ C}$
$8.204 \times 10^{-19} \text{ C}$	$16.48 \times 10^{-19} \text{ C}$	$22.89 \times 10^{-19} \text{ C}$
$11.50 \times 10^{-19} \text{ C}$	$18.08 \times 10^{-19} \text{ C}$	$26.18 \times 10^{-19} \text{ C}$

- (a) Based on these data alone, what is your best estimate of the number of electrons on each of the above droplets? (*Hint:* Begin by considering differences in charges between adjacent data points, and see into what groups these are categorized.)
- (b) Based on these data alone, what is your best estimate of the charge on the electron?
- (c) Is it conceivable that the actual charge is half the charge you calculated in (b)? What evidence would help you decide one way or the other?
25. A rough estimate of the radius of a nucleus is provided by the formula $r = kA^{1/3}$, where k is approximately $1.3 \times 10^{-13} \text{ cm}$ and A is the mass number of the nucleus. Estimate the density of the nucleus of ^{127}I (which has a nuclear mass of $2.1 \times 10^{-22} \text{ g}$) in grams per cubic centimeter. Compare with the density of solid iodine, 4.93 g cm^{-3} .

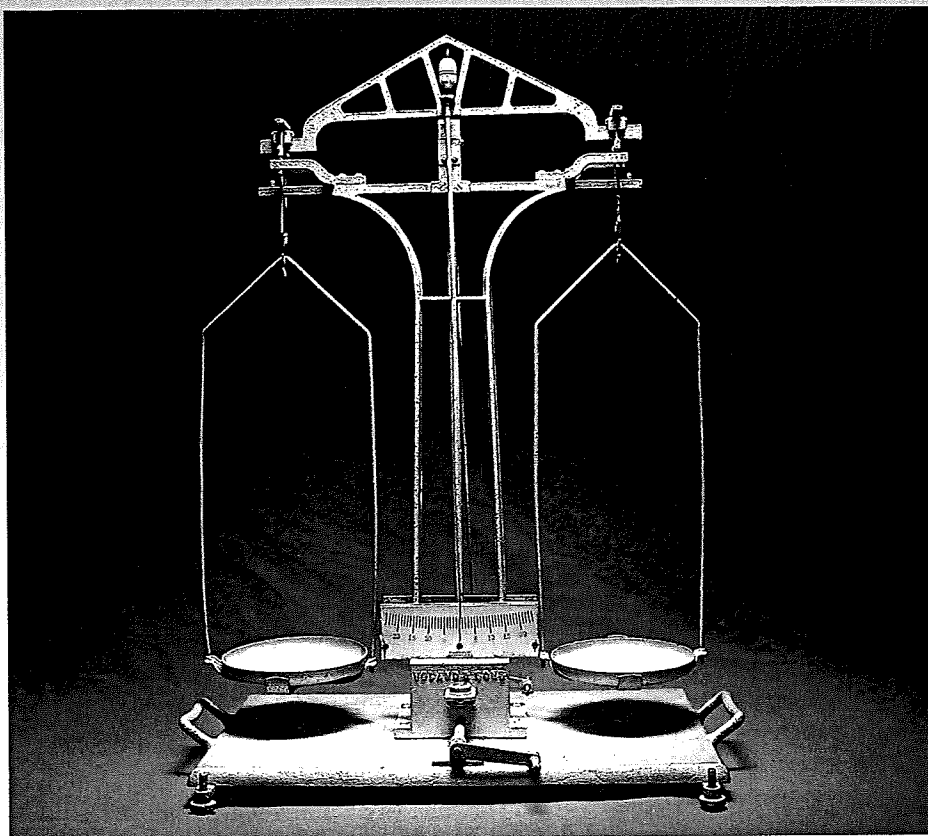
26. In a neutron star, gravity causes the electrons to combine with protons to form neutrons. A typical neutron star has a mass half that of the sun, compressed into a sphere of radius 20 km. If such a neutron star contains 6.0×10^{56} neutrons, calculate its density in grams per cubic centimeter. Compare this with the density inside a ^{232}Th nucleus, in which 142 neutrons and 90 protons occupy a sphere of radius 9.1×10^{-13} cm. Take the mass of a neutron to be 1.675×10^{-24} g and that of a proton to be 1.673×10^{-24} g.
27. Dalton's 1808 version of the atomic theory of matter included five general statements (see Section 1.3). According to modern understanding, four of those statements require amendment or extension. List the modifications that have been made to four of the five original postulates.
28. Naturally occurring rubidium (Rb) consists of two isotopes: ^{85}Rb (atomic mass 84.9117) and ^{87}Rb (atomic mass 86.9092). The atomic mass of the isotope mixture found in nature is 85.4678. Calculate the percentage abundances of the two isotopes in rubidium.

CHEMICAL FORMULAS, EQUATIONS, AND REACTION YIELDS

2

CHAPTER

- 2.1** The Mole: Weighing and Counting Molecules
- 2.2** Empirical and Molecular Formulas
- 2.3** Chemical Formula and Percentage Composition
- 2.4** Writing Balanced Chemical Equations
Connection to Chemical Engineering:
Sulfuric Acid Manufacturing
- 2.5** Mass Relationships in Chemical Reactions
- 2.6** Limiting Reactant and Percentage Yield
Cumulative Exercise:
Titanium in Industry



Charles D. Winters. Balance courtesy of Chandler Museum at Columbia University

An "assay balance of careful construction" of the type used by Lavoisier before 1788. This balance became the production model that served as a general, all-purpose balance for approximately 40 years. Users of this type of balance included Sir Humphrey Davy and his young assistant Michael Faraday.

Chapter 1 explained how chemical and physical methods are used to establish chemical formulas and relative atomic and molecular masses. This chapter begins our study of chemical reactions. We start by developing the concept of the mole, which allows us to count molecules by weighing macroscopic quantities of matter. We examine the balanced chemical equations that summarize these reactions and show how to relate the masses of substances consumed to the masses of substances produced. This is an immensely practical and important subject. The questions how much of a substance will react with a given amount of another substance and how much product will be generated are central to all chemical processes, whether industrial, geological, or biological.



Sign in to OWL at www.cengage.com/owl to view tutorials and simulations, develop problem-solving skills, and complete online homework assigned by your professor.

2.1 THE MOLE: WEIGHING AND COUNTING MOLECULES

The laws of chemical combination assert that chemical reactions occur in such a way that the number of atoms of a given type is conserved in every chemical reaction, except nuclear reactions. It is impractical to count the numbers of atoms or molecules in laboratory or industrial scale reactions, however, so we must find a way to relate the masses of the reactants and products in those reactions to the numbers of atoms or molecules involved. Chemists established a scale of relative atomic masses in the 19th century, while developing the laws of chemical combination; the accuracy of that scale was greatly improved upon in the 20th century using mass spectrometry. That relative atomic mass scale must be converted to a macroscopic scale that allows us to count atoms and molecules by weighing. The concept and methods that allow us to do this are developed in this section.

Relation between Atomic and Macroscopic Masses: Avogadro's Number

Laboratory or industrial chemical reactions are carried out with quantities that range from milligrams to tons, so we must be able to relate the relative atomic mass scale to the macroscopic scales used in practice. The link between the two scales is provided by **Avogadro's number** (N_A), defined as the number of atoms in exactly 12 g of ^{12}C , the currently accepted value of which is

$$N_A = 6.0221420 \times 10^{23}$$

The mass of a single ^{12}C atom is then found by dividing exactly 12 g carbon (C) by N_A :

$$\text{Mass of a } ^{12}\text{C} \text{ atom} = \frac{12.00000 \text{ g}}{6.0221420 \times 10^{23}} = 1.9926465 \times 10^{-23} \text{ g}$$

The masses of individual atoms are truly small and any macroscopic quantity of mass contains an amazingly large number of atoms.

Avogadro's number is defined relative to the ^{12}C atom because that isotope has been chosen by international agreement to form the basis for the modern scale of relative atomic masses. We can find the masses of Avogadro's number of the other elements by simply taking ratios, as follows. Consider sodium, which has a relative atomic mass of 22.98977. A sodium atom is 22.98977/12 times as heavy as a ^{12}C atom. If the mass of N_A atoms of ^{12}C is 12 g, then the mass of N_A atoms of sodium must be

$$\frac{22.98977}{12} (12 \text{ g}) = 22.98977 \text{ g}$$

The mass (in grams) of N_A atoms of *any* element is numerically equal to the relative atomic mass of that element. The same conclusion applies to molecules. From the relative molecular mass of water determined in Chapter 1, the mass of N_A molecules of water is 18.0152 g.

EXAMPLE 2.1

One of the heaviest atoms found in nature is ^{238}U . Its relative atomic mass is 238.0508 on a scale in which 12 is the atomic mass of ^{12}C . Calculate the mass (in grams) of one ^{238}U atom.

Solution

Because the mass of N_A atoms of ^{238}U is 238.0508 g and N_A is 6.0221420×10^{23} , the mass of one ^{238}U atom must be

$$\frac{238.0508 \text{ g}}{6.0221420 \times 10^{23}} = 3.952926 \times 10^{-22} \text{ g}$$

Related Problems: 1, 2

The Mole

Because the masses of atoms and molecules are so small, laboratory scale chemical reactions must involve large numbers of atoms and molecules. It is convenient to group atoms or molecules in counting units of $N_A = 6.0221420 \times 10^{23}$ to measure the **number of moles** of a substance. One of these counting units is called a **mole** (abbreviated mol, whether singular or plural, derived from Latin *moles*, meaning “heap” or “pile”). One mole of a substance is the amount that contains Avogadro’s number of atoms, molecules, or other entities. That is, 1 mol of ^{12}C contains N_A ^{12}C atoms, 1 mol of water contains N_A water molecules, and so forth. We must be careful in some cases, because a phrase such as “1 mol of oxygen” is ambiguous. We should refer instead to “1 mol of O_2 ” if there are N_A oxygen *molecules*, and “1 mol of O” if there are N_A oxygen *atoms*. Henceforth, for *any* species we use “number of moles of a particular species” to describe the number of moles in a sample of that species.

We define the **molar mass** of an element (often called the atomic mass or the atomic weight) as the mass of one mole of that element in grams; it is determined by taking the ratio of the relative atomic mass of the element to that of ^{12}C and multiplying the result by 12 g. The same procedure is used to calculate the molar masses (often called the molecular weights) for molecules. Thus, the relative molecular mass of water is 18.0152, and its molar mass is $18.0152 \text{ g mol}^{-1}$.

To determine the number of moles of a given substance, we use the chemist’s most powerful tool, the laboratory balance. If a sample of iron weighs 8.232 g, then

$$\begin{aligned} \text{moles of iron} &= \frac{\text{number of grams of iron}}{\text{molar mass of iron}} \\ &= \frac{8.232 \text{ g Fe}}{55.847 \text{ g mol}^{-1}} \\ &= 0.1474 \text{ mol Fe} \end{aligned}$$

where the molar mass of iron was obtained from the periodic table of the elements or a table of relative atomic masses (see the inside front and back covers of this book). The calculation can be turned around as well. Suppose a certain amount, for example, 0.2000 mol, of water is needed in a chemical reaction. We have

$$\begin{aligned} (\text{moles of water}) \times (\text{molar mass of water}) &= \text{mass of water} \\ (0.2000 \text{ mol H}_2\text{O}) \times (18.015 \text{ g mol}^{-1}) &= 3.603 \text{ g H}_2\text{O} \end{aligned}$$

We simply weigh 3.603 g water to get the 0.2000 mol needed for the reaction. In both cases, the molar mass is the conversion factor between the mass of the substance and the number of moles of the substance.

Although the number of moles in a sample is generally determined by weighing, it is still preferable to think of a mole as a fixed number of atoms or molecules (Avogadro's number) rather than as a fixed mass. The term *mole* is thus analogous to a term such as *dozen*: the mass of one dozen pennies is 26 g, which is substantially less than the mass of one dozen nickels, 60 g; each group contains 12 coins. Figure 2.1 shows mole quantities of several substances. A mole of most common household substances (water, sugar, salt) is about a tablespoon.

EXAMPLE 2.2

Nitrogen dioxide (NO_2) is a major component of urban air pollution. For a sample containing 4.000 g NO_2 , calculate (a) the number of moles of NO_2 and (b) the number of molecules of NO_2 .

Solution

- (a) From the tabulated molar masses of nitrogen ($14.007 \text{ g mol}^{-1}$) and oxygen ($15.999 \text{ g mol}^{-1}$), the molar mass of NO_2 is

$$14.007 \text{ g mol}^{-1} + (2 \times 15.999 \text{ g mol}^{-1}) = 46.005 \text{ g mol}^{-1}$$

The number of moles of NO_2 is then

$$\text{mol of NO}_2 = \frac{4.000 \text{ g NO}_2}{46.005 \text{ g mol}^{-1}} = 0.08695 \text{ mol NO}_2$$

- (b) To convert from moles to number of molecules, multiply by Avogadro's number:

$$\begin{aligned} \text{molecules of NO}_2 &= (0.08695 \text{ mol NO}_2) \times 6.0221 \times 10^{23} \text{ mol}^{-1} \\ &= 5.236 \times 10^{22} \text{ molecules NO}_2 \end{aligned}$$

Related Problems: 7, 8

That N_A is the ratio of the molar volume to the atomic volume of any element provides a route to measuring its value, and several methods have been used to determine this ratio. A new method to refine the value is currently under development. Nearly perfectly smooth spheres of highly crystalline silicon (Si) have been prepared and characterized. The surface roughness of these spheres (which affects the determination of their volume) is ± 1 silicon atom. The molar volume is determined by carefully measuring the mass and volume of the sphere, and the atomic volume is determined by measuring the interatomic distances directly using X-ray diffraction. (X-ray diffraction from solids is described in Chapter 21.) Avogadro's number is the ratio of these two quantities.

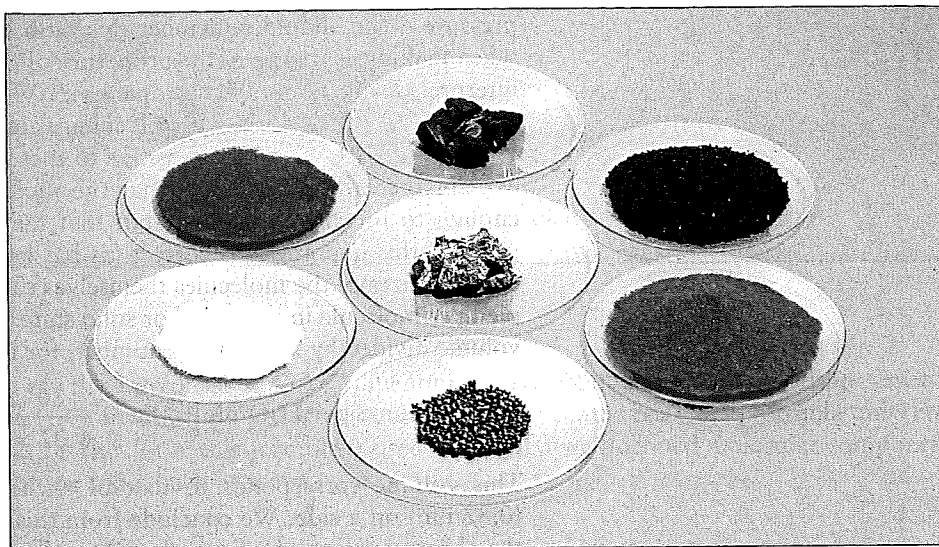
Density and Molecular Size

The **density** of a sample is the ratio of its mass to its volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \quad [2.1]$$

The base unit of mass in the International System of Units (SI; see discussion in Appendix B) is the kilogram (kg), but it is inconveniently large for most practical purposes in chemistry. The gram often is used instead; moreover, it is the stan-

FIGURE 2.1 One mole of a number of different substances. (Clockwise from top) Graphite (C), potassium permanganate (KMnO_4), copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$), copper (Cu), sodium chloride (NaCl), and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). Antimony (Sb) is at the center.



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dard unit for molar masses. Several units for volume are in frequent use. The base SI unit of the cubic meter (m^3) is also unwieldy for laboratory purposes (1 m^3 water weighs 1000 kg, or 1 metric ton). We use the gram (g) for mass and the liter ($1 \text{ L} = 10^{-3} \text{ m}^3$) or the cubic centimeter (cm^3 or milliliter, mL) for volume. ($1 \text{ cm}^3 = 1 \text{ mL} = 10^{-3} \text{ L} = 10^{-6} \text{ m}^3$). Table 2.1 lists the densities of some substances in units of grams per cubic centimeter.

The density of a substance is not a fixed, invariant property of the substance; its value depends on the pressure and temperature at the time of measurement. For some substances (especially gases and liquids), the volume may be more convenient to measure than the mass, and the density provides the conversion factor between volume and mass. For example, the density of liquid benzene (C_6H_6) is 0.8765 g cm^{-3} near room temperature. Suppose that we wanted to find the mass of benzene contained in a volume that measured 0.2124 L. We simply multiply the volume by the density as follows:

$$m = \rho V$$

where m is the mass, ρ is the density, and V is the volume. Therefore, the value of the mass of benzene is

$$m = 0.2124 \text{ L} \times (1 \times 10^3 \text{ cm}^3 \text{ L}^{-1}) \times (0.8765 \text{ g cm}^{-3}) = 186.2 \text{ g}$$

If we wanted to know the number of moles of benzene in that sample we would simply divide the mass by the molar mass of benzene ($78.114 \text{ g mol}^{-1}$) to get 2.384 mol.

Knowing the density and molar mass of a substance, we can readily compute its **molar volume**, that is, the volume occupied by one mole of a substance:

$$V_m = \frac{\text{molar mass } (\text{g mol}^{-1})}{\text{density } (\text{g cm}^{-3})} = \text{molar volume } (\text{cm}^3 \text{ mol}^{-1})$$

For example, near 0°C , ice has a density of 0.92 g cm^{-3} ; thus, the molar volume of solid water under these conditions is

$$V_m = \frac{18.0 \text{ g mol}^{-1}}{0.92 \text{ g cm}^{-3}} = 20 \text{ cm}^3 \text{ mol}^{-1}$$

The molar volume of a gas is much larger than that of either a liquid or a solid. For O_2 under room conditions, the data in Table 2.1 give a molar volume of $24,600 \text{ cm}^3 \text{ mol}^{-1} = 24.6 \text{ L mol}^{-1}$, which is more than 1000 times larger than the molar volume just computed for ice under the same conditions of temperature and

TABLE 2.1
Densities of Some Substances

Substance	Density (g cm^{-3})
Hydrogen	0.000082
Oxygen	0.00130
Water	1.00
Magnesium	1.74
Sodium chloride	2.16
Quartz	2.65
Aluminum	2.70
Iron	7.86
Copper	8.96
Silver	10.5
Lead	11.4
Mercury	13.5
Gold	19.3
Platinum	21.4

These densities were measured at room temperature and at average atmospheric pressure near sea level.

pressure. (You should remember this ratio because you will use it often later on, when making estimates of the properties of gases, liquids, and solids.) How can we interpret this fact on a microscopic level? We also note that the volumes of liquids and solids do not shift much with changes in temperature or pressure, but that the volumes of gases are quite sensitive to these changes. One hypothesis that would explain these observations is that the molecules in liquids and solids are close enough to touch one another, but that they are separated by large distances in gases. If this hypothesis is correct (as has been well established by further study), then the sizes of the molecules themselves can be estimated from the volume occupied per molecule in the liquid or solid state. The volume per molecule is the molar volume divided by Avogadro's number; for ice, this gives

$$\text{Volume per H}_2\text{O molecule} = \frac{20 \text{ cm}^3 \text{ mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 3.3 \times 10^{-23} \text{ cm}^3$$

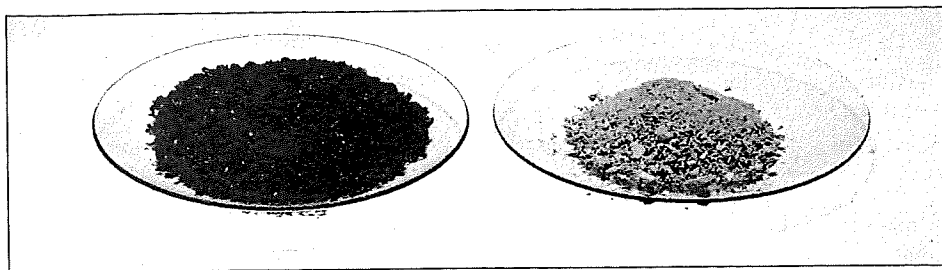
This volume corresponds to that of a cube with edges about $3.2 \times 10^{-8} \text{ cm}$ (0.32 nm) on a side. We conclude from this and other density measurements that the characteristic size of atoms and small molecules is about 10^{-8} cm , or about 0.1 nm. This length, 0.1 nm or $1 \times 10^{-10} \text{ m}$, occurs so frequently in chemistry that it has been given a special name, the ångström (Å), in honor of the Swedish physicist Anders Ångström. Avogadro's number provides the link between the length and mass scales of laboratory measurements and the masses and volumes of single atoms and molecules.

2.2 EMPIRICAL AND MOLECULAR FORMULAS

According to the laws of chemical combination, each substance may be described by a chemical formula that specifies the relative numbers of atoms of the elements in that substance. We now distinguish between two types of formulas: the molecular formula and the empirical formula. The **molecular formula** of a substance specifies the number of atoms of each element in one molecule of that substance. Thus, the molecular formula of carbon dioxide is CO_2 ; each molecule of carbon dioxide contains 1 atom of carbon and 2 atoms of oxygen. The molecular formula of glucose is $\text{C}_6\text{H}_{12}\text{O}_6$; each glucose molecule contains 6 atoms of carbon, 6 atoms of oxygen, and 12 atoms of hydrogen. Molecular formulas can be defined for all gaseous substances and for those liquids or solids that, like glucose, possess well-defined molecular structures.

In contrast, the **empirical formula** of a compound is the simplest formula that gives the correct relative numbers of atoms of each kind in a compound. For example, the empirical formula for glucose is CH_2O , indicating that the numbers of atoms of carbon, hydrogen, and oxygen are in a ratio of 1:2:1. Molecular formulas, when known, are clearly preferable to empirical formulas because they provide more detailed information. In some solids and liquids, however, distinct small molecules do not exist, and the only meaningful chemical formula is an empirical one. Solid cobalt(II) chloride, which has the empirical formula CoCl_2 , is an example. There are strong attractive forces between a cobalt atom and two adjoining chlorine (Cl) atoms in solid cobalt(II) chloride, but it is impossible to distinguish the forces *within* such a "molecule" of CoCl_2 from those operating *between* it and a neighbor; the latter are equally strong. Consequently, cobalt(II) chloride is represented with an empirical formula and referred to by a **formula unit** of CoCl_2 , rather than by "a molecule of CoCl_2 ." Many solids can be represented only by their formula units because it is not possible to identify a molecular unit in a unique way; other examples include sodium chloride (NaCl), the major component in table salt; and silicon dioxide (SiO_2), the major component of sand (see Figure 3.3). In some cases, small molecules are incorporated into a solid structure, and the chemical formula is written to show this fact explicitly. Thus, cobalt and chlorine form not

FIGURE 2.2 When cobalt(II) chloride crystallizes from solution, it brings with it six water molecules per formula unit, producing a red solid with the empirical formula $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$. This solid melts at 86°C ; it loses some of the water when heated above 110°C to form a lavender solid with the empirical formula $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$.



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only the anhydrous salt CoCl_2 mentioned earlier but also the hexahydrate $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, in which six water molecules are incorporated per CoCl_2 formula unit (Fig. 2.2). The dot in this formula is used to set off a well-defined molecular component of the solid, such as water.

2.3 CHEMICAL FORMULA AND PERCENTAGE COMPOSITION

The empirical formula H_2O specifies that for every atom of oxygen in water, there are two atoms of hydrogen. Equivalently, one mole of H_2O contains two moles of hydrogen atoms and one mole of oxygen atoms. The number of atoms and the number of moles of each element are present in the same ratio, namely, 2:1. The empirical formula for a substance is clearly related to the percentage composition by mass of that substance. This connection can be used in various ways.

Empirical Formula and Percentage Composition

The empirical formula of a compound can be simply related to the mass percentage of its constituent elements using the mole concept. For example, the empirical formula for ethylene (molecular formula C_2H_4) is CH_2 . Its composition by mass is calculated from the masses of carbon and hydrogen in 1 mol of CH_2 formula units:

$$\text{mass of C} = 1 \text{ mol C} \times (12.011 \text{ g mol}^{-1}) = 12.011 \text{ g}$$

$$\text{mass of H} = 2 \text{ mol H} \times (1.00794 \text{ g mol}^{-1}) = 2.0159 \text{ g}$$

Adding these masses together gives a total mass of 14.027 g. The mass percentages of carbon and hydrogen in the compound are then found by dividing each of their masses by this total mass and multiplying by 100%, giving 85.628% C and 14.372% H by weight, respectively.

Determination of Empirical Formula from Mass Composition

We can reverse the procedure just described and determine the empirical formula from the elemental analysis of a compound, as illustrated by Example 2.3.

EXAMPLE 2.3

A 60.00-g sample of a dry-cleaning fluid was analyzed and found to contain 10.80 g carbon, 1.36 g hydrogen, and 47.84 g chlorine. Determine the empirical formula of the compound using a table of atomic masses.

Solution

The amounts of each element in the sample are

$$\text{carbon: } \frac{10.80 \text{ g C}}{12.011 \text{ g mol}^{-1}} = 0.8992 \text{ mol C}$$

$$\text{hydrogen: } \frac{1.36 \text{ g H}}{1.008 \text{ g mol}^{-1}} = 1.35 \text{ mol H}$$

$$\text{chlorine: } \frac{47.84 \text{ g Cl}}{35.453 \text{ g mol}^{-1}} = 1.349 \text{ mol Cl}$$

The ratio of the amount of carbon to that of chlorine (or hydrogen) is $0.8992:1.349 = 0.6666$, which is close to $2:3$. The numbers of moles form the ratio $2:3:3$; therefore, the empirical formula is $\text{C}_2\text{H}_3\text{Cl}_3$. Additional measurements would be necessary to find the actual molecular mass and the correct *molecular* formula from among $\text{C}_2\text{H}_3\text{Cl}_3$, $\text{C}_4\text{H}_6\text{Cl}_6$, or any higher multiples $(\text{C}_2\text{H}_3\text{Cl}_3)_n$.

Related Problems: 19, 20, 21, 22, 23, 24

Empirical Formula Determined from Elemental Analysis by Combustion

A **hydrocarbon** is a compound that contains only carbon and hydrogen. Its empirical formula can be determined by using the combustion train shown in Figure 2.3. In this device, a known mass of the hydrocarbon is burned completely in oxygen, producing carbon dioxide and water whose masses are measured. The empirical formula for the compound is then calculated from these data by the procedure illustrated in Example 2.4.

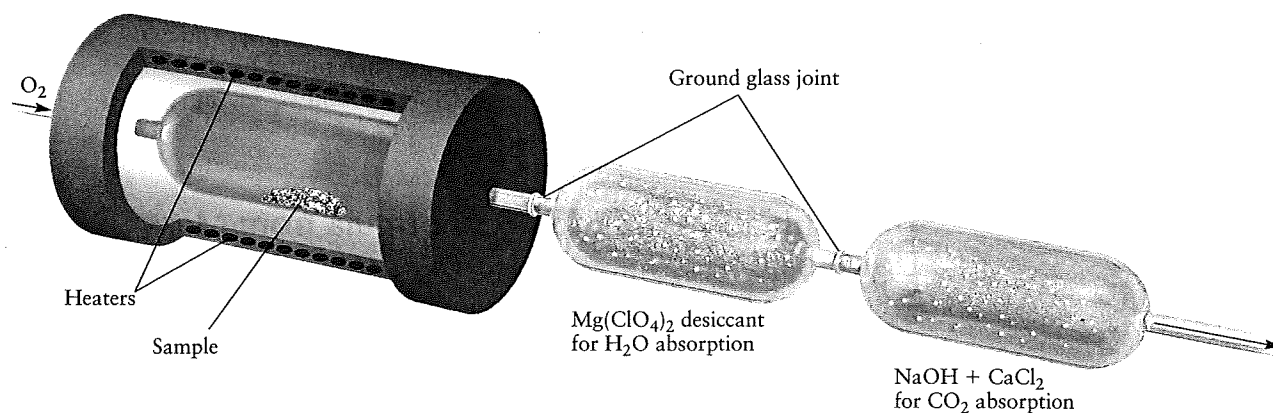


FIGURE 2.3 A combustion train used to determine the relative amounts of carbon and hydrogen in hydrocarbons. A sample of known weight is burned in a flow of oxygen to produce water and carbon dioxide. These combustion products pass over a drying agent, such as magnesium perchlorate, $\text{Mg}(\text{ClO}_4)_2$, which absorbs the water. The carbon dioxide then passes through to the second stage where it is absorbed on finely divided particles of sodium hydroxide, NaOH , mixed with calcium chloride, CaCl_2 . The masses of the water and carbon dioxide produced in the reaction are determined by weighing the absorption tubes before and after the reaction.

EXAMPLE 2.4

A certain compound, used as a welding fuel, contains only carbon and hydrogen. Burning a small sample of this fuel completely in oxygen produces 3.38 g CO₂, 0.692 g water, and no other products. What is the empirical formula of the compound?

Solution

We first compute the amounts of CO₂ and H₂O. Because all the carbon has been converted to CO₂ and all the hydrogen to water, the amounts of C and H in the unburned gas can be determined:

$$\begin{aligned}\text{mol of C} &= \text{mol of CO}_2 = \frac{3.38 \text{ g}}{44.01 \text{ g mol}^{-1}} = 0.0768 \text{ mol} \\ \text{mol of H} &= 2(\text{mol of H}_2\text{O}) = \left(\frac{0.692 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) = 0.0768 \text{ mol}\end{aligned}$$

Because each water molecule contains two hydrogen atoms, it is necessary to multiply the number of moles of water by 2 to find the number of moles of hydrogen atoms. Having found that the compound contains equal numbers of moles of carbon and hydrogen, we have determined that its empirical formula is CH. Its molecular formula may be CH, C₂H₂, C₃H₃, and so on.

Related Problems: 25, 26

Connection between Empirical and Molecular Formulas

The molecular formula is some whole-number multiple of the empirical formula. To determine the molecular formula, you must know the approximate molar mass of the compound under study. From Avogadro's hypothesis, the ratio of molar masses of two gaseous compounds is the same as the ratio of their densities, provided that those densities are measured at the same temperature and pressure. (This is true because a given volume contains the same number of molecules of the two gases.) The density of the welding gas from Example 2.4 is 1.06 g L⁻¹ at 25°C and atmospheric pressure. Under the same conditions, the density of gaseous oxygen (which exists as diatomic O₂ molecules with molar mass of 32.0 g mol⁻¹) is 1.31 g L⁻¹. The approximate molar mass of the welding gas is, therefore,

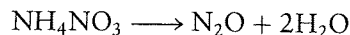
$$\text{molar mass of welding gas} = \frac{1.06 \text{ g L}^{-1}}{1.31 \text{ g L}^{-1}} (32.0 \text{ g mol}^{-1}) = 25.9 \text{ g mol}^{-1}$$

The molar mass corresponding to the *empirical* formula CH is 13.0 g mol⁻¹. Because 25.9 g mol⁻¹ is approximately twice this value, there must be two CH units per molecule; therefore, the molecular formula is C₂H₂. The gas is acetylene.

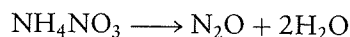
2.4 WRITING BALANCED CHEMICAL EQUATIONS

Chemical reactions combine elements into compounds, decompose compounds back into elements, and transform existing compounds into new compounds. Because atoms are indestructible in chemical reactions, the same number of atoms (or moles of atoms) of each element must be present before and after any ordinary (as opposed to nuclear) chemical reaction. The conservation of matter in a chemical change is represented in a balanced chemical equation for that process. The study of the relationships between the numbers of reactant and product molecules is called **stoichiometry** (derived from the Greek *stoicheion*, meaning "element," and *metron*, meaning "measure"). Stoichiometry is fundamental to all aspects of chemistry.

An equation can be balanced using stepwise reasoning. Consider the decomposition of ammonium nitrate (NH_4NO_3) when heated gently to produce dinitrogen oxide (N_2O) and water. An *unbalanced* equation for this reaction is



Substances on the left side of the arrow are called reactants, and those on the right side are called products. We read chemical equations just like we read sentences; reactions progress from left to right. This equation is unbalanced because there are 3 mol of oxygen atoms on the left side of the equation (and 4 mol of hydrogen atoms), but only 2 mol of oxygen atoms and 2 mol of hydrogen atoms on the right side. To balance the equation, begin by assigning 1 as the coefficient of one species, usually the species that contains the most elements—in this case, NH_4NO_3 . Next, look for elements in that substance that appear only once elsewhere in the equation and assign coefficients to balance the number of moles of that element on both sides. The only other species in this reaction that contains nitrogen is N_2O , and assigning a coefficient of 1 for the N_2O ensures that there are 2 mol of nitrogen atoms on each side of the equation. Hydrogen appears in H_2O ; thus, its coefficient is 2 to balance the 4 mol of hydrogen atoms on the left side. This gives

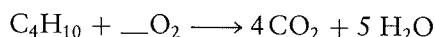


Finally, verify that the last element, oxygen, is also balanced by noting that there are 3 mol of oxygen atoms on each side. The coefficients of 1 in front of the NH_4NO_3 and N_2O are omitted by convention.

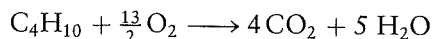
As a second example, consider the reaction in which butane (C_4H_{10}) is burned in oxygen to form carbon dioxide and water:



Spaces have been left for the coefficients that specify the number of moles of each reactant and product. Begin with 1 mol of butane, C_4H_{10} . It contains 4 mol of carbon atoms and must produce 4 mol of carbon dioxide molecules to conserve the number of carbon atoms in the reaction. Therefore, the coefficient for CO_2 is 4. In the same way, the 10 mol of hydrogen *atoms* must form 5 mol of water *molecules*, because each water molecule contains 2 hydrogen atoms; thus, the coefficient for the H_2O is 5:



Four moles of CO_2 contain 8 mol of oxygen atoms, and 5 mol of H_2O contain 5 mol of oxygen atoms, resulting in a total of 13 mol of oxygen atoms. Thirteen moles of oxygen atoms are equivalent to $\frac{13}{2}$ moles of oxygen molecules; therefore, the coefficient for O_2 is $\frac{13}{2}$. The balanced equation is



There is nothing wrong with fractions such as $\frac{13}{2}$ in a balanced equation, because fractions of moles are perfectly meaningful. It is often customary, however, to eliminate such fractions because the equation can be interpreted on the molecular level as well as on the macroscopic level. Your instructor will very likely have a preference on this matter, so make sure that you know what it is and balance equations accordingly. In this case, multiplying all coefficients in the equation by 2 gives



The procedure may be summarized as follows:

1. Assign 1 as the coefficient of one species. The best choice is the most complicated species; that is, the species with the largest number of elements.

- Identify, in sequence, elements that appear in only one chemical species, the coefficient of which has not yet been determined. Choose that coefficient to balance the number of moles of atoms of that element. Continue until all coefficients have been identified.
- If desired, multiply the whole equation by the smallest integer that will eliminate any fractions.

This method of balancing equations “by inspection” works in many, but not all, cases. Section 11.4 presents techniques for balancing certain more complex chemical equations.

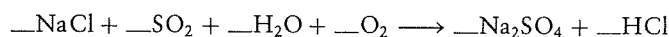
Once the reactants and products are known, balancing chemical equations is a routine, mechanical process of accounting. We often tell students something like “if you have three dimes, two nickels, and a penny before the reaction, make sure that you have three dimes, two nickels, and a penny after the reaction” to give them a visual image. The difficult part (and the part where chemistry comes in) is to know which substances will react with each other and to determine which products are formed. We return to this question many times throughout this book.

EXAMPLE 2.5

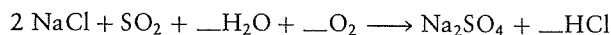
Hargreaves process is an industrial procedure for making sodium sulfate (Na_2SO_4) for use in papermaking. The starting materials are sodium chloride (NaCl), sulfur dioxide (SO_2), water, and oxygen. Hydrogen chloride (HCl) is generated as a by-product. Write a balanced chemical equation for this process.

Solution

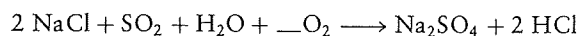
The unbalanced equation is



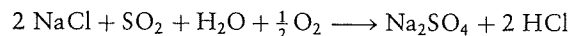
Begin by assigning a coefficient of 1 to Na_2SO_4 because it is the most complex species, composed of 3 different elements. There are 2 mol of sodium atoms on the right; therefore, the coefficient for NaCl must be 2. Following the same argument, the coefficient for SO_2 must be 1 to balance the 1 mol of sulfur on the right. This gives



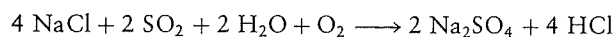
Next, we note that there are 2 mol of Cl atoms on the left (reactant) side; therefore, the coefficient for HCl must be 2. Hydrogen is the next element to balance, with 2 mol on the right side, and therefore a coefficient of 1 for the H_2O :



Finally, the oxygen atoms must be balanced. There are 4 mol of oxygen atoms on the right side, but there are 2 mol from SO_2 and 1 mol from H_2O on the left side; therefore, 1 mol of oxygen atoms must come from O_2 . Therefore, the coefficient for O_2 is $\frac{1}{2}$:



Multiplying all coefficients in the equation by 2 gives



In balancing this equation, oxygen was considered last because it appears in several places on the left side of the equation.

Related Problems: 31, 32

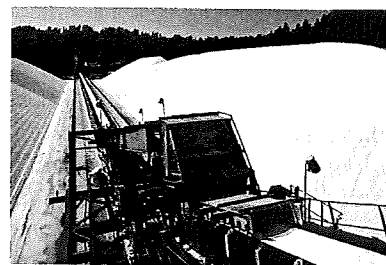
CONNECTION TO CHEMICAL ENGINEERING

Sulfuric Acid Manufacturing

Chemistry is big business. The chemical industry in the United States alone generates nearly a trillion dollars per year in annual sales—a significant component of the U.S. gross domestic product. It is impossible to overstate the importance of the chemical industry to our modern way of life; we depend on chemicals for energy, materials, agriculture, and health. The chemical and petrochemical industries transform raw ingredients, such as minerals and petroleum, into a variety of products on truly large scales. The process by which sulfuric acid is manufactured illustrates the practical importance of the topics developed in this chapter.

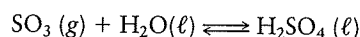
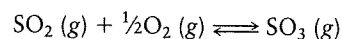
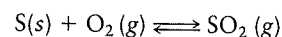
Sulfuric acid is produced in greater quantity than any other chemical; about 200 million metric tonnes (10^3 kg) were manufactured worldwide in 2010. Most sulfuric acid plants are located near their product's point of use—phosphate fertilizer manufacturing plants, nickel ore leaching plants, and petroleum refineries—because it is less expensive to transport elemental sulfur (the starting material) than it is to transport sulfuric acid (the product). Sulfuric acid is also used in a variety of industrial chemical processes that include the manufacture of commodity and specialty chemicals, polymers, pharmaceuticals, soaps, and detergents and in the pulp and paper industry. The lead acid storage battery in your car is one of the few consumer products that actually contains sulfuric acid as such.

Elemental sulfur mined from historically important locations like Sicily, and later Indonesia, Chile, and Japan, used to be the dominant source of the raw material. Most sulfur occurs as fine powders or in polycrystalline form, but brightly colored yellow single crystals of sulfur are occasionally found, like the one shown in the figure. Virtually all of the sulfur used to manufacture sulfuric acid today was removed from petroleum fuels or feedstocks by a process called hydrosulfurization, because sulfur poisons the catalysts used in petroleum refining and other processes. Canada has become the world's largest exporter of elemental sulfur; the figure shows a stockpile of bright yellow sulfur awaiting shipment.

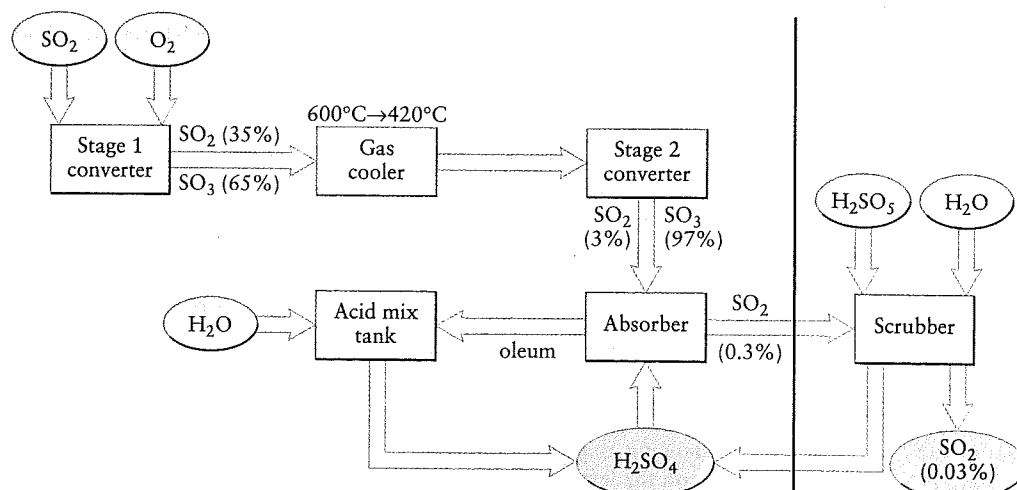


Gunter Marx/Corbis

Most sulfuric acid produced today is made by the contact process, which got its name because the second step in the reaction is carried out in contact with a catalyst, typically vanadium pentoxide (V_2O_5) mixed with proprietary (secret) additives. The main steps of the overall reaction sequence are:



The first step is the combustion of elemental sulfur in air to produce sulfur dioxide, which is further oxidized catalytically in the second reaction to produce sulfur trioxide. The second step is the key reaction of the process, and considerable effort has been devoted to optimizing the conditions under which this reaction takes place. Sulfuric acid is produced by the reaction between sulfur trioxide and water in the final step of the sequence. As you will see later in this textbook, optimizing the yields and rates of industrial chemical processes requires careful consideration of both the thermodynamics (Chapter 13) and the kinetics (Chapter 18) of the reactions. As is often the case in industrial chemical processes, thermodynamic considerations favor low temperatures, whereas kinetic considerations favor high temperatures, so the operating temperatures of sulfuric acid plants represent a compromise between those competing factors. The catalyst (something that speeds up a chemical reaction) is required for



the conversion of SO_2 to SO_3 , because the reaction rate would be unacceptably slow without it.

The schematic shows two stages of a typical modern multi-stage sulfuric acid plant that is designed to achieve maximum conversion yields at acceptable rates; these plants typically convert 99.7% of the elemental sulfur into sulfuric acid. The high yields are due to several important design features. First, and most important, the temperature of the SO_2 produced by the initial combustion reaction is lowered prior to subsequent reaction with molecular oxygen. This step is taken to enhance the conversion of SO_2 to SO_3 , and it would be repeated several times in a multistage plant. Second, unreacted SO_3 is absorbed by sulfuric acid in one or more absorbing towers, which allows any unreacted SO_2 to make one or more passes over the catalytic reactor to increase the amount converted. Finally, most modern plants have scrubbers that remove trace amounts of SO_2 from the exhaust gases, primarily for environmental reasons (see Section 20.6), but also to recover a marketable product.

Understanding reaction stoichiometries is clearly essential in order to design and operate chemical plants efficiently.

The masses of raw materials necessary to produce the desired quantity of products is calculated using basic stoichiometry relationships, taking into account the limiting reactant(s) involved. Many practical reactions are run with an excess of one or more of the reactants to ensure complete conversion. Designing the air handling system to provide sufficient oxygen for the combustion and subsequent oxidation of sulfur requires quantitative understanding of the reaction stoichiometry.

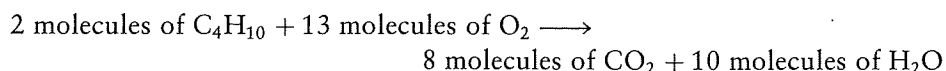
To give you a feel for the amount of material converted in a modern sulfuric acid plant, let's calculate the amount of sulfur needed as raw material for a new plant under construction in Saudi Arabia in 2010. This plant, when complete, will produce 13,500 tons of sulfuric acid *per day* with the entire output devoted to phosphate fertilizer manufacture. H_2SO_4 is 32.7% S by weight, so we need $(.327) \times (13,500 \text{ tons}) = 4400 \text{ tons}$ of sulfur *per day*. A typical rail car holds 100 tons, so the owners of this plant need to provide 44 rail cars of sulfur *per day*, or a full trainload of sulfur every three days—truly a staggering amount!

2.5 MASS RELATIONSHIPS IN CHEMICAL REACTIONS

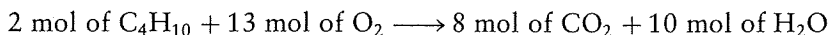
A balanced chemical equation makes a quantitative statement about the relative masses of the reacting substances. The chemical equation for the combustion of butane,



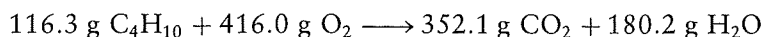
can be interpreted as either



or



Multiplying the molar mass of each substance in the reaction by the number of moles represented in the balanced equation gives



The coefficients in a balanced chemical equation relate the amounts of substances consumed in or produced by a chemical reaction. If 6.16 mol butane react according to the preceding equation, the amounts of O_2 consumed and CO_2 generated are

$$\text{mol O}_2 = 6.16 \text{ mol C}_4\text{H}_{10} \times \left(\frac{13 \text{ mol O}_2}{2 \text{ mol C}_4\text{H}_{10}} \right) = 40.0 \text{ mol O}_2$$

$$\text{mol CO}_2 = 6.16 \text{ mol C}_4\text{H}_{10} \times \left(\frac{8 \text{ mol CO}_2}{2 \text{ mol C}_4\text{H}_{10}} \right) = 24.6 \text{ CO}_2$$

For most practical purposes we are interested in the *masses* of reactants and products, because those are the quantities that are directly measured. In this case, the molar masses (calculated from a table of atomic masses) are used to convert the number of moles of a substance (in moles) to its mass (in grams), as illustrated by Example 2.6. Sometimes, however, we are also interested in knowing the number of molecules in a sample. The mole concept allows us to convert easily from mass to numbers of molecules as follows:

$$\text{mass} \xleftrightarrow{\text{molar mass}} \text{moles} \xleftrightarrow{N_A} \text{number of molecules}$$

Mass and moles are related by the molar mass; Avogadro's number N_A relates number and moles. You should practice using these relationships to calculate any desired quantity from any given quantity. You can use dimensional analysis to help you figure out whether to divide or multiply in any given problem.

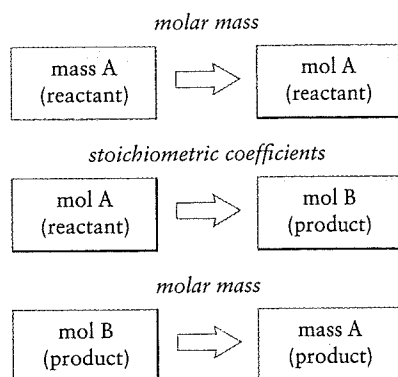
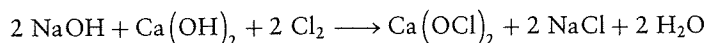


FIGURE 2.4 The steps in a stoichiometric calculation. In a typical calculation, the mass of one reactant or product is known and the masses of one or more other reactants or products are to be calculated using the balanced chemical equation and a table of relative atomic masses.

EXAMPLE 2.6

Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, is used as a bleaching agent. It is produced from sodium hydroxide, calcium hydroxide, and chlorine according to the following overall equation:



How many grams of chlorine and sodium hydroxide react with 1067 g $\text{Ca}(\text{OH})_2$, and how many grams of calcium hypochlorite are produced?

Solution

The amount of $\text{Ca}(\text{OH})_2$ consumed is

$$\frac{1067 \text{ g Ca}(\text{OH})_2}{74.09 \text{ g mol}^{-1}} = 14.40 \text{ mol Ca}(\text{OH})_2$$

where the molar mass of $\text{Ca}(\text{OH})_2$ has been obtained from the molar masses of calcium, oxygen, and hydrogen as

$$40.08 + 2(15.999) + 2(1.0079) = 74.09 \text{ g mol}^{-1}$$

According to the balanced equation, 1 mol $\text{Ca}(\text{OH})_2$ reacts with 2 mol NaOH and 2 mol Cl_2 to produce 1 mol $\text{Ca}(\text{OCl})_2$. If 14.40 mol of $\text{Ca}(\text{OH})_2$ reacts completely, then

$$\begin{aligned} \text{mol NaOH} &= 14.40 \text{ mol Ca}(\text{OH})_2 \left(\frac{2 \text{ mol NaOH}}{1 \text{ mol Ca}(\text{OH})_2} \right) \\ &= 28.80 \text{ mol NaOH} \end{aligned}$$

$$\begin{aligned} \text{mol Cl}_2 &= 14.40 \text{ mol Ca}(\text{OH})_2 \left(\frac{2 \text{ mol Cl}_2}{1 \text{ mol Ca}(\text{OH})_2} \right) \\ &= 28.80 \text{ mol Cl}_2 \end{aligned}$$

$$\begin{aligned} \text{mol Ca}(\text{OCl})_2 &= 14.40 \text{ mol Ca}(\text{OH})_2 \left(\frac{1 \text{ mol Ca}(\text{OCl})_2}{1 \text{ mol Ca}(\text{OH})_2} \right) \\ &= 14.40 \text{ mol Ca}(\text{OCl})_2 \end{aligned}$$

From the number of moles and molar masses of reactants and products, the following desired masses are found:

$$\text{Mass NaOH reacting} = (28.80 \text{ mol})(40.00 \text{ g mol}^{-1}) = 1152 \text{ g}$$

$$\text{Mass Cl}_2 \text{ reacting} = (28.80 \text{ mol})(70.91 \text{ g mol}^{-1}) = 2042 \text{ g}$$

$$\text{Mass Ca}(\text{OCl})_2 \text{ produced} = (14.40 \text{ mol})(142.98 \text{ g mol}^{-1}) = 2059 \text{ g}$$

Related Problems: 33, 34, 35, 36

In calculations such as the one illustrated in Example 2.6, we are given a known mass of one substance and are asked to calculate the masses of one or more of the other reactants or products. Figure 2.4 summarizes the three-step process used. With experience, it is possible to write down the answers in a shorthand form so that all three conversions are conducted at the same time. The amount of NaOH reacting in the preceding example can be written as

$$\left(\frac{1067 \text{ g Ca(OH)}_2}{74.10 \text{ g mol}^{-1}} \right) \times \left(\frac{2 \text{ mol NaOH}}{1 \text{ mol Ca(OH)}_2} \right) \times 40.00 \text{ g mol}^{-1} = 1152 \text{ g NaOH}$$

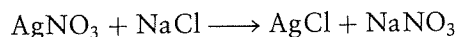
At first, however, it is better to follow a stepwise procedure for such calculations.

2.6 LIMITING REACTANT AND PERCENTAGE YIELD

In the cases we have considered so far, the reactants were present in the exact ratios necessary for them all to be completely consumed in forming products. This is not the usual case, however. It is necessary to have methods for describing cases in which one of the reactants may not be present in sufficient amount and in which conversion to products is less than complete.

Limiting Reactant

Suppose arbitrary amounts of reactants are mixed and allowed to react. The one that is used up first is called the **limiting reactant** (limiting reagent in some texts); some quantity of the other reactants remains after the reaction has gone to completion. These other reactants are present **in excess**. An increase in the amount of the limiting reactant leads to an increase in the amount of product formed. This is not true of the other reactants. In an industrial process, the limiting reactant is often the most expensive one, to ensure that none of it is wasted. For instance, the silver nitrate used in preparing silver chloride for photographic film by the reaction

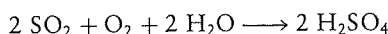


is far more expensive than the sodium chloride (ordinary salt). Thus, it makes sense to perform the reaction with an excess of sodium chloride to ensure that as much of the silver nitrate as possible reacts to form products.

There is a systematic method to find the limiting reactant and determine the maximum possible amounts of products. Take each reactant in turn, assume that it is used up completely in the reaction, and calculate the mass of one of the products that will be formed. Whichever reactant gives the *smallest* mass of this product is the limiting reactant. Once it has reacted fully, no further product can be formed.

EXAMPLE 2.7

Sulfuric acid (H_2SO_4) forms in the chemical reaction



Suppose 400 g SO_2 , 175 g O_2 , and 125 g H_2O are mixed and the reaction proceeds until one of the reactants is used up. Which is the limiting reactant? What mass of H_2SO_4 is produced, and what masses of the other reactants remain?

Solution

The number of moles of each reactant originally present is calculated by dividing each mass by the corresponding molar mass:

$$\frac{400 \text{ g SO}_2}{64.06 \text{ g mol}^{-1}} = 6.24 \text{ mol SO}_2$$

$$\frac{175 \text{ g O}_2}{32.00 \text{ g mol}^{-1}} = 5.47 \text{ mol O}_2$$

$$\frac{125 \text{ g H}_2\text{O}}{18.02 \text{ g mol}^{-1}} = 6.94 \text{ mol H}_2\text{O}$$

If all the SO₂ reacted, it would give

$$6.24 \text{ mol SO}_2 \times \left(\frac{2 \text{ mol H}_2\text{SO}_4}{2 \text{ mol SO}_2} \right) = 6.24 \text{ mol H}_2\text{SO}_4$$

If all the O₂ reacted, it would give

$$5.47 \text{ mol O}_2 \times \left(\frac{2 \text{ mol H}_2\text{SO}_4}{1 \text{ mol O}_2} \right) = 10.94 \text{ mol H}_2\text{SO}_4$$

Finally, if all the water reacted, it would give

$$6.94 \text{ mol H}_2\text{O} \times \left(\frac{2 \text{ mol H}_2\text{SO}_4}{2 \text{ mol H}_2\text{O}} \right) = 6.94 \text{ mol H}_2\text{SO}_4$$

In this case, SO₂ is the limiting reactant because the computation based on its amount produces the smallest amount of product (6.24 mol H₂SO₄). Oxygen and water are present in excess. After reaction, the amount of each reactant that remains is the original amount minus the amount reacted:

$$\begin{aligned} \text{mol O}_2 &= 5.47 \text{ mol O}_2 - \left(6.24 \text{ mol SO}_2 \times \frac{1 \text{ mol O}_2}{2 \text{ mol SO}_2} \right) \\ &= 5.47 - 3.12 \text{ mol O}_2 = 2.35 \text{ mol O}_2 \end{aligned}$$

$$\begin{aligned} \text{mol H}_2\text{O} &= 6.94 \text{ mol H}_2\text{O} - \left(6.24 \text{ mol SO}_2 \times \frac{2 \text{ mol H}_2\text{O}}{2 \text{ mol SO}_2} \right) \\ &= 6.94 - 6.24 \text{ mol H}_2\text{O} = 0.70 \text{ mol H}_2\text{O} \end{aligned}$$

The masses of reactants and products after the reaction are

$$\text{mass H}_2\text{SO}_4 \text{ produced} = (6.24 \text{ mol})(98.07 \text{ g mol}^{-1}) = 612 \text{ g}$$

$$\text{mass O}_2 \text{ remaining} = (2.35 \text{ mol})(32.00 \text{ g mol}^{-1}) = 75 \text{ g}$$

$$\text{mass H}_2\text{O remaining} = (0.70 \text{ mol})(18.02 \text{ g mol}^{-1}) = 13 \text{ g}$$

The total mass at the end is 612 g + 13 g + 75 g = 700 g, which is, of course, equal to the total mass originally present, 400 g + 175 g + 125 g = 700 g, as required by the law of conservation of mass.

Related Problems: 47, 48

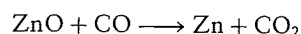
Percentage Yield

The amounts of products calculated so far have been **theoretical yields**, determined by assuming that the reaction goes cleanly and completely. The **actual yield** of a product (that is, the amount present after separating it from other products and reactants and purifying it) is less than the theoretical yield. There are several possible reasons for

this. The reaction may stop short of completion, so reactants remain unreacted. There may be competing reactions that give other products, and therefore reduce the yield of the desired one. Finally, in the process of separation and purification, some of the product is invariably lost, although that amount can be reduced by careful experimental techniques. The ratio of the actual yield to the theoretical yield (multiplied by 100%) gives the **percentage yield** for that product in the reaction.

EXAMPLE 2.8

The sulfide ore of zinc (ZnS) is reduced to elemental zinc by “roasting” it (heating it in air) to give ZnO, and then heating the ZnO with carbon monoxide. The two reactions can be written as



Suppose 5.32 kg ZnS is treated in this way and 3.30 kg pure Zn is obtained. Calculate the theoretical yield of zinc and its actual percentage yield.

Solution

From the molar mass of ZnS (97.46 g mol^{-1}), the number of moles of ZnS initially present is

$$\frac{5320 \text{ g ZnS}}{97.46 \text{ g mol}^{-1}} = 54.6 \text{ mol ZnS}$$

Because each mole of ZnS gives 1 mol of ZnO in the first chemical equation, and each mole of ZnO then gives 1 mol of Zn, the theoretical yield of zinc is 54.6 mol. In grams, this is

$$54.6 \text{ mol Zn} \times 65.39 \text{ g mol}^{-1} = 3570 \text{ g Zn}$$

The ratio of actual yield to theoretical yield, multiplied by 100%, gives the percentage yield of zinc:

$$\% \text{ yield} = \left(\frac{3.30 \text{ kg}}{3.57 \text{ kg}} \right) \times 100\% = 92.4\%$$

Related Problems: 49, 50

It is clearly desirable to achieve the highest percentage yield of product possible to reduce the consumption of raw materials. In some synthetic reactions (especially in organic chemistry), the final product is the result of many successive reactions. In such processes, the yields in the individual steps must be quite high if the synthetic method is to be a practical success. Suppose, for example, that ten consecutive reactions must be performed to reach the product, and that each has a percentage yield of only 50% (a fractional yield of 0.5). The overall yield is the product of the fractional yields of the steps:

$$(0.5) \times (0.5) \times \dots \times (0.5) = (0.5)^{10} = 0.001$$

10 terms

This overall percentage yield of 0.1% makes the process useless for synthetic purposes. If all the individual percentage yields could be increased to 90%, however, the overall yield would then be $(0.9)^{10} = 0.35$, or 35%. This is a much more reasonable result, and one that might make the process worth considering.

CHAPTER SUMMARY

We have shown you how chemists count molecules by weighing macroscopic quantities of substances. Avogadro's number connects the nanoscopic world of atoms and molecules to the macroscopic scale of the laboratory: $1 \text{ mol} = 6.02 \times 10^{23}$ atoms or molecules. The relative number of atoms in a molecule or solid is given by its empirical or its molecular formula, and we have shown how these formulas are determined experimentally. The principle of conservation of mass has been sharpened a bit in our discussion of balancing chemical reactions. Not only is the total mass conserved in ordinary (as opposed to nuclear) chemical reactions, but the total number of atoms of every element is also conserved. Balancing a chemical reaction requires nothing more than assuring that the same numbers of atoms (or moles of atoms) of each element appear on each side of the balanced equation. Because chemists weigh macroscopic quantities of reactants and products, it is important to understand how mass ratios relate to mole ratios in chemical reactions. Finally, we point out that not every reactant is completely consumed in a chemical reaction, and that the limiting reactant determines the maximum theoretical yield; the percentage yield may be somewhat less.

CONCEPTS AND SKILLS



Interactive versions of these problems are assignable in OWL.

Section 2.1 – The Mole: Weighing and Counting Molecules

Interconvert mass, number of moles, number of molecules, and (using density) the molar volume of a substance (Problems 1–12).

- Avogadro's number (6.02×10^{23}) is the conversion factor between moles and numbers of molecules. The molar mass is the conversion factor between moles and mass. Setting up calculations to convert any of these quantities can be done by inspection, using dimensional analysis to guide you. Molar volumes are calculated by dividing the molar mass by the density.

Section 2.2 – Empirical and Molecular Formulas

Distinguish between empirical and molecular formulas.

Section 2.3 – Chemical Formula and Percentage Composition

Given the percentages by mass of the elements in a compound, determine its empirical formula and vice versa (Problems 13–24).

- Determine the number of moles of each element in a compound by dividing the mass of each element (from mass percentages) by the molar mass of the element and then take ratios, reducing them to the smallest ratio of integers.

Use the masses of products obtained in combustion train measurements to determine empirical formulas (Problems 24 and 25).

Use ratios of gas densities to estimate molar mass and determine molecular formulas (Problems 27–30).

- The ratio of the density of an unknown gas to that of a known gas (using Avogadro's hypothesis) gives an approximate molar mass.

Section 2.4 – Writing Balanced Chemical Equations

Balance simple chemical equations (Problems 31 and 32).

- Choose the substance with the most elements and assign it a stoichiometric coefficient of 1.
- Choose an element that appears in only one other substance in the reaction and balance it with respect to the first substance. Continue in this way until all of the elements have been balanced.

Section 2.5 – Mass Relationships in Chemical Reactions

Given the mass of a reactant or product in a chemical reaction, use a balanced chemical equation to calculate the masses of other reactants consumed and other products formed (Problems 33–46).

- Use the flowchart (Figure 2.4).
- Convert masses of reactants to moles of reactants using their molar masses.
- Convert moles of reactants to moles of products using stoichiometry.
- Convert moles of reactants to moles of products using their molar masses.

Section 2.6 – Limiting Reactant and Percentage Yield

Given a set of initial masses of reactants and a balanced chemical equation, determine the limiting reactant and calculate the masses of reactants and products after the reaction has gone to completion (Problems 47 and 48).

- Calculate the number of moles of each reactant and determine which one would produce the smallest amount of product if the reaction went to completion.
- Calculate the number of moles of reactants consumed and products produced using the number of moles of this limiting reactant and the reaction stoichiometry.

CUMULATIVE EXERCISE

Titanium in Industry

Metallic titanium and its alloys (especially those with aluminum and vanadium) combine the advantages of high strength and light weight and are therefore used widely in the aerospace industry for the bodies and engines of airplanes. The major natural source for titanium is the ore rutile, which contains titanium dioxide (TiO_2).

- An intermediate in the preparation of elemental titanium from TiO_2 is a volatile chloride of titanium (boiling point 136°C) that contains 25.24% titanium by mass. Determine the empirical formula of this compound.
- At 136°C and atmospheric pressure, the density of this gaseous chloride is 5.6 g L^{-1} . Under the same conditions, the density of gaseous nitrogen (N_2 , molar mass 28.0 g mol^{-1}) is 0.83 g L^{-1} . Determine the molecular formula of this compound.
- The titanium chloride dealt with in parts (a) and (b) is produced by the reaction of chlorine with a hot mixture of titanium dioxide and coke (carbon), with carbon dioxide generated as a by-product. Write a balanced chemical equation for this reaction.
- What mass of chlorine is needed to produce 79.2 g of the titanium chloride?
- The titanium chloride then reacts with liquid magnesium at 900°C to give titanium and magnesium chloride (MgCl_2). Write a balanced chemical equation for this step in the refining of titanium.
- Suppose the reaction chamber for part (e) contains 351 g of the titanium chloride and 63.2 g liquid magnesium. Which is the limiting reactant? What maximum mass of titanium could result?
- Isotopic analysis of the titanium from a particular ore gave the following results:

Isotope	Relative Mass	Abundance (%)
^{46}Ti	45.952633	7.93
^{47}Ti	46.95176	7.28
^{48}Ti	47.947948	73.94
^{49}Ti	48.947867	5.51
^{50}Ti	49.944789	5.34



A jet engine fan blade made of a single crystal titanium alloy.

Wolfgang Kumm/Corbis

Calculate the mass of a single ^{48}Ti atom and the *average* mass of the titanium atoms in this ore sample.

Answers

- (a) TiCl_4
- (b) TiCl_4
- (c) $\text{TiO}_2 + \text{C} + 2 \text{Cl}_2 \longrightarrow \text{TiCl}_4 + \text{CO}_2$
- (d) 59.2 g
- (e) $\text{TiCl}_4 + 2 \text{Mg} \longrightarrow \text{Ti} + 2 \text{MgCl}_2$
- (f) Mg; 62.3 g
- (g) 7.961949×10^{-23} g; 7.950×10^{-23} g

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

The Mole: Weighing and Counting Molecules

- Compute the mass (in grams) of a single iodine atom if the relative atomic mass of iodine is 126.90447 on the accepted scale of atomic masses (based on 12 as the relative atomic mass of ^{12}C).
- Determine the mass (in grams) of exactly 100 million atoms of fluorine if the relative atomic mass of fluorine is 18.998403 on a scale on which exactly 12 is the relative atomic mass of ^{12}C .
- Compute the relative molecular masses of the following compounds on the ^{12}C scale:
 - (a) P_4O_{10} (b) BrCl
 - (c) $\text{Ca}(\text{NO}_3)_2$ (d) KMnO_4
 - (e) $(\text{NH}_4)_2\text{SO}_4$
- Compute the relative molecular masses of the following compounds on the ^{12}C scale:
 - (a) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ (b) $\text{Ca}_3[\text{Co}(\text{CO}_3)_3]_2$
 - (c) OsO_4 (d) H_2SO_4
 - (e) $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$
- Suppose that a person counts out gold atoms at the rate of one each second for the entire span of an 80-year life. Has the person counted enough atoms to be detected with an ordinary balance? Explain.
- A gold atom has a diameter of 2.88×10^{-10} m. Suppose the atoms in 1.00 mol of gold atoms are arranged just touching their neighbors in a single straight line. Determine the length of the line.
- The vitamin A molecule has the formula $\text{C}_{20}\text{H}_{30}\text{O}$, and a molecule of vitamin A₂ has the formula $\text{C}_{20}\text{H}_{28}\text{O}$. Determine how many moles of vitamin A₂ contain the same number of atoms as 1.000 mol vitamin A.
- Arrange the following in order of increasing mass: 1.06 mol SF_4 ; 117 g CH_4 ; 8.7×10^{23} molecules of Cl_2O_7 ; and 417×10^{23} atoms of argon (Ar).

- Mercury is traded by the “flask,” a unit that has a mass of 34.5 kg. Determine the volume of a flask of mercury if the density of mercury is 13.6 g cm^{-3} .
- Gold costs \$400 per troy ounce, and 1 troy ounce = 31.1035 g. Determine the cost of 10.0 cm^3 gold if the density of gold is 19.32 g cm^{-3} at room conditions.
- Aluminum oxide (Al_2O_3) occurs in nature as a mineral called corundum, which is noted for its hardness and resistance to attack by acids. Its density is 3.97 g cm^{-3} . Calculate the number of atoms of aluminum in 15.0 cm^3 corundum.
- Calculate the number of atoms of silicon (Si) in 415 cm^3 of the colorless gas disilane at 0°C and atmospheric pressure, where its density is $0.00278 \text{ g cm}^{-3}$. The molecular formula of disilane is Si_2H_6 .

Chemical Formula and Percentage Composition

- A newly synthesized compound has the molecular formula $\text{ClF}_2\text{O}_2\text{PtF}_6$. Compute, to four significant figures, the mass percentage of each of the four elements in this compound.
- Acetaminophen is the generic name of the pain reliever in Tylenol and some other headache remedies. The compound has the molecular formula $\text{C}_8\text{H}_9\text{NO}_2$. Compute, to four significant figures, the mass percentage of each of the four elements in acetaminophen.
- Arrange the following compounds from left to right in order of increasing percentage by mass of hydrogen: H_2O , $\text{C}_{12}\text{H}_{26}$, N_4H_6 , LiH .
- Arrange the following compounds from left to right in order of increasing percentage by mass of fluorine: HF , C_6HF_5 , BrF , UF_6 .
- “Q-gas” is a mixture of 98.70% helium and 1.30% butane (C_4H_{10}) by mass. It is used as a filling for gas-flow Geiger counters. Compute the mass percentage of hydrogen in Q-gas.
- A pharmacist prepares an antiulcer medicine by mixing 286 g Na_2CO_3 with water, adding 150 g glycine ($\text{C}_2\text{H}_5\text{NO}_2$),

and stirring continuously at 40°C until a firm mass results. The pharmacist heats the mass gently until all the water has been driven away. No other chemical changes occur in this step. Compute the mass percentage of carbon in the resulting white crystalline medicine.

19. Zinc phosphate is used as a dental cement. A 50.00-mg sample is broken down into its constituent elements and gives 16.58 mg oxygen, 8.02 mg phosphorus, and 25.40 mg zinc. Determine the empirical formula of zinc phosphate.
20. Bromoform is 94.85% bromine, 0.40% hydrogen, and 4.75% carbon by mass. Determine its empirical formula.
21. Fulgurites are the products of the melting that occurs when lightning strikes the earth. Microscopic examination of a sand fulgurite shows that it is a globule with variable composition that contains some grains of the definite chemical composition Fe 46.01%, Si 53.99%. Determine the empirical formula of these grains.
22. A sample of a "suboxide" of cesium gives up 1.6907% of its mass as gaseous oxygen when gently heated, leaving pure cesium behind. Determine the empirical formula of this binary compound.
23. Barium and nitrogen form two binary compounds containing 90.745% and 93.634% barium, respectively. Determine the empirical formulas of these two compounds.
24. Carbon and oxygen form no fewer than five different binary compounds. The mass percentages of carbon in the five compounds are as follows: A, 27.29; B, 42.88; C, 50.02; D, 52.97; and E, 65.24. Determine the empirical formulas of the five compounds.
25. A sample of 1.000 g of a compound containing carbon and hydrogen reacts with oxygen at elevated temperature to yield 0.692 g H₂O and 3.381 g CO₂.
 - (a) Calculate the masses of C and H in the sample.
 - (b) Does the compound contain any other elements?
 - (c) What are the mass percentages of C and H in the compound?
 - (d) What is the empirical formula of the compound?
26. Burning a compound of calcium, carbon, and nitrogen in oxygen in a combustion train generates calcium oxide (CaO), carbon dioxide (CO₂), nitrogen dioxide (NO₂), and no other substances. A small sample gives 2.389 g CaO, 1.876 g CO₂, and 3.921 g NO₂. Determine the empirical formula of the compound.
27. The empirical formula of a gaseous fluorocarbon is CF₂. At a certain temperature and pressure, a 1-L volume holds 8.93 g of this fluorocarbon, whereas under the same conditions, the 1-L volume holds only 1.70 g gaseous fluorine (F₂). Determine the molecular formula of this compound.
28. At its boiling point (280°C) and at atmospheric pressure, phosphorus has a gas density of 2.7 g L⁻¹. Under the same conditions, nitrogen has a gas density of 0.62 g L⁻¹. How many atoms of phosphorus are there in one phosphorus molecule under these conditions?
29. A gaseous binary compound has a vapor density that is 1.94 times that of oxygen at the same temperature and pressure. When 1.39 g of the gas is burned in an excess of oxygen, 1.21 g water is formed, removing all the hydrogen originally present.

- (a) Estimate the molecular mass of the gaseous compound.
- (b) How many hydrogen atoms are there in a molecule of the compound?
- (c) What is the maximum possible value of the atomic mass of the second element in the compound?
- (d) Are other values possible for the atomic mass of the second element? Use a table of atomic masses to identify the element that best fits the data.
- (e) What is the molecular formula of the compound?

30. A gaseous binary compound has a vapor density that is 2.53 times that of nitrogen at 100°C and atmospheric pressure. When 8.21 g of the gas reacts with AlCl₃ at 100°C, 1.62 g gaseous nitrogen is produced, removing all of the nitrogen originally present.

- (a) Estimate the molecular mass of the gaseous compound.
- (b) How many nitrogen atoms are there in a molecule of the compound?
- (c) What is the maximum possible value of the atomic mass of the second element?
- (d) Are other values possible for the atomic mass of the second element? Use a table of atomic masses to identify the element that best fits the data.
- (e) What is the molecular formula of the compound?

Writing Balanced Chemical Equations

31. Balance the following chemical equations:

- (a) $\text{H}_2 + \text{N}_2 \longrightarrow \text{NH}_3$
- (b) $\text{K} + \text{O}_2 \longrightarrow \text{K}_2\text{O}_2$
- (c) $\text{PbO}_2 + \text{Pb} + \text{H}_2\text{SO}_4 \longrightarrow \text{PbSO}_4 + \text{H}_2\text{O}$
- (d) $\text{BF}_3 + \text{H}_2\text{O} \longrightarrow \text{B}_2\text{O}_3 + \text{HF}$
- (e) $\text{KClO}_3 \longrightarrow \text{KCl} + \text{O}_2$
- (f) $\text{CH}_3\text{COOH} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
- (g) $\text{K}_2\text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{KOH} + \text{O}_2$
- (h) $\text{PCl}_5 + \text{AsF}_3 \longrightarrow \text{PF}_5 + \text{AsCl}_3$

32. Balance the following chemical equations:

- (a) $\text{Al} + \text{HCl} \longrightarrow \text{AlCl}_3 + \text{H}_2$
- (b) $\text{NH}_3 + \text{O}_2 \longrightarrow \text{NO} + \text{H}_2\text{O}$
- (c) $\text{Fe} + \text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{Fe}(\text{OH})_2$
- (d) $\text{HSbCl}_4 + \text{H}_2\text{S} \longrightarrow \text{Sb}_2\text{S}_3 + \text{HCl}$
- (e) $\text{Al} + \text{Cr}_2\text{O}_3 \longrightarrow \text{Al}_2\text{O}_3 + \text{Cr}$
- (f) $\text{XeF}_4 + \text{H}_2\text{O} \longrightarrow \text{Xe} + \text{O}_2 + \text{HF}$
- (g) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + \text{H}_2\text{O}$
- (h) $\text{NaBH}_4 + \text{H}_2\text{O} \longrightarrow \text{NaBO}_2 + \text{H}_2$

Mass Relationships in Chemical Reactions

33. For each of the following chemical reactions, calculate the mass of the underlined reactant that is required to produce 1.000 g of the underlined product.

- (a) $\text{Mg} + 2 \text{HCl} \longrightarrow \underline{\text{H}_2} + \text{MgCl}_2$
- (b) $2 \underline{\text{CuSO}_4} + 4 \text{KI} \longrightarrow 2 \text{CuI} + \underline{\text{I}_2} + 2 \text{K}_2\text{SO}_4$
- (c) $\underline{\text{NaBH}_4} + 2 \text{H}_2\text{O} \longrightarrow \text{NaBO}_2 + 4 \underline{\text{H}_2}$

34. For each of the following chemical reactions, calculate the mass of the underlined product that is produced from 1.000 g of the underlined reactant.

- (a) $\underline{\text{CaCO}_3} + \text{H}_2\text{O} \longrightarrow \underline{\text{Ca}(\text{OH})_2} + \text{CO}_2$
- (b) $\underline{\text{C}_3\text{H}_8} + 5 \text{O}_2 \longrightarrow 3 \underline{\text{CO}_2} + 4 \text{H}_2\text{O}$
- (c) $2 \underline{\text{MgNH}_4\text{PO}_4} \longrightarrow \underline{\text{Mg}_2\text{P}_2\text{O}_7} + 2 \text{NH}_3 + \text{H}_2\text{O}$

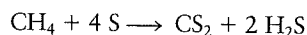
35. An 18.6-g sample of K₂CO₃ was treated in such a way that all of its carbon was captured in the compound K₂Zn₃[Fe(CN)₆]₂. Compute the mass (in grams) of this product.

36. A chemist dissolves 1.406 g pure platinum (Pt) in an excess of a mixture of hydrochloric and nitric acids and then, after a series of subsequent steps involving several other chemicals, isolates a compound of molecular formula $\text{Pt}_2\text{C}_{10}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_6$. Determine the maximum possible yield of this compound.
37. Disilane (Si_2H_6) is a gas that reacts with oxygen to give silica (SiO_2) and water. Calculate the mass of silica that would form if 25.0 cm^3 disilane (with a density of $2.78 \times 10^{-3} \text{ g cm}^{-3}$) reacted with excess oxygen.
38. Tetrasilane (Si_4H_{10}) is a liquid with a density of 0.825 g cm^{-3} . It reacts with oxygen to give silica (SiO_2) and water. Calculate the mass of silica that would form if 25.0 cm^3 tetrasilane reacted completely with excess oxygen.
39. Cryolite (Na_3AlF_6) is used in the production of aluminum from its ores. It is made by the reaction



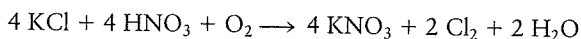
Calculate the mass of cryolite that can be prepared by the complete reaction of 287 g Al_2O_3 .

40. Carbon disulfide (CS_2) is a liquid that is used in the production of rayon and cellophane. It is manufactured from methane and elemental sulfur via the reaction



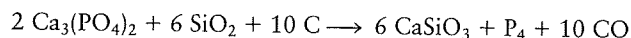
Calculate the mass of CS_2 that can be prepared by the complete reaction of 67.2 g sulfur.

41. Potassium nitrate (KNO_3) is used as a fertilizer for certain crops. It is produced through the reaction



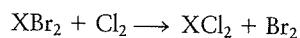
Calculate the minimum mass of KCl required to produce 567 g KNO_3 . What mass of Cl_2 will be generated as well?

42. Elemental phosphorus can be prepared from calcium phosphate via the overall reaction



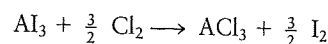
Calculate the minimum mass of $\text{Ca}_3(\text{PO}_4)_2$ required to produce 69.8 g P_4 . What mass of CaSiO_3 is generated as a by-product?

43. An element X has a dibromide with the empirical formula XBr_2 and a dichloride with the empirical formula XCl_2 . The dibromide is completely converted to the dichloride when it is heated in a stream of chlorine according to the reaction



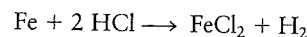
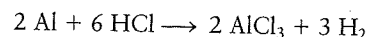
When 1.500 g XBr_2 is treated, 0.890 g XCl_2 results.

- (a) Calculate the atomic mass of the element X.
 (b) By reference to a list of the atomic masses of the elements, identify the element X.
- * 44. An element A has a triiodide with the formula AI_3 and a trichloride with the formula ACl_3 . The triiodide is quantitatively converted to the trichloride when it is heated in a stream of chlorine, according to the reaction



If 0.8000 g Al_3 is treated, 0.3776 g AlCl_3 is obtained.

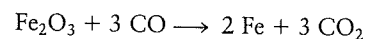
- (a) Calculate the atomic mass of the element A.
 (b) Identify the element A.
- * 45. A mixture consisting of only sodium chloride (NaCl) and potassium chloride (KCl) weighs 1.0000 g. When the mixture is dissolved in water and an excess of silver nitrate is added, all the chloride ions associated with the original mixture are precipitated as insoluble silver chloride (AgCl). The mass of the silver chloride is found to be 2.1476 g. Calculate the mass percentages of sodium chloride and potassium chloride in the original mixture.
- * 46. A mixture of aluminum and iron weighing 9.62 g reacts with hydrogen chloride in aqueous solution according to the parallel reactions



A 0.738-g quantity of hydrogen is evolved when the metals react completely. Calculate the mass of iron in the original mixture.

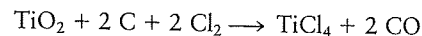
Limiting Reactant and Percentage Yield

47. When ammonia is mixed with hydrogen chloride (HCl), the white solid ammonium chloride (NH_4Cl) is produced. Suppose 10.0 g ammonia is mixed with the same mass of hydrogen chloride. What substances will be present after the reaction has gone to completion, and what will their masses be?
48. The poisonous gas hydrogen cyanide (HCN) is produced by the high-temperature reaction of ammonia with methane (CH_4). Hydrogen is also produced in this reaction.
 (a) Write a balanced chemical equation for the reaction that occurs.
 (b) Suppose 500.0 g methane is mixed with 200.0 g ammonia. Calculate the masses of the substances present after the reaction is allowed to proceed to completion.
49. The iron oxide Fe_2O_3 reacts with carbon monoxide (CO) to give iron and carbon dioxide:



The reaction of 433.2 g Fe_2O_3 with excess CO yields 254.3 g iron. Calculate the theoretical yield of iron (assuming complete reaction) and its percentage yield.

50. Titanium dioxide, TiO_2 , reacts with carbon and chlorine to give gaseous TiCl_4 :



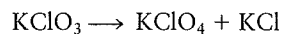
The reaction of 7.39 kg titanium dioxide with excess C and Cl_2 gives 14.24 kg titanium tetrachloride. Calculate the theoretical yield of TiCl_4 (assuming complete reaction) and its percentage yield.

ADDITIONAL PROBLEMS

51. Human parathormone has the impressive molecular formula $C_{691}H_{898}N_{125}O_{164}S_{11}$. Compute the mass percentages of all the elements in this compound.
52. A white oxide of tungsten is 79.2976% tungsten by mass. A blue tungsten oxide also contains exclusively tungsten and oxygen, but it is 80.8473% tungsten by mass. Determine the empirical formulas of white tungsten oxide and blue tungsten oxide.
53. A dark brown binary compound contains oxygen and a metal. It is 13.38% oxygen by mass. Heating it moderately drives off some of the oxygen and gives a red binary compound that is 9.334% oxygen by mass. Strong heating drives off more oxygen and gives still another binary compound, which is only 7.168% oxygen by mass.
- Compute the mass of oxygen that is combined with 1.000 g of the metal in each of these three oxides.
 - Assume that the empirical formula of the first compound is MO_2 (where M represents the metal). Give the empirical formulas of the second and third compounds.
 - Name the metal.
54. A binary compound of nickel and oxygen contains 78.06% nickel by mass. Is this a stoichiometric or a non-stoichiometric compound? Explain.
55. Two binary oxides of the element manganese contain, respectively, 30.40% and 36.81% oxygen by mass. Calculate the empirical formulas of the two oxides.
- * 56. A sample of a gaseous binary compound of boron and chlorine weighing 2.842 g occupies 0.153 L. This sample is decomposed to give 0.664 g solid boron and enough gaseous chlorine (Cl_2) to occupy 0.688 L at the same temperature and pressure. Determine the molecular formula of the compound.
57. A possible practical way to eliminate oxides of nitrogen (such as NO_2) from automobile exhaust gases uses cyanuric acid, $C_3N_3(OH)_3$. When heated to the relatively low temperature of 625°F, cyanuric acid converts to gaseous isocyanic acid (HNCO). Isocyanic acid reacts with NO_2 in the exhaust to form nitrogen, carbon dioxide, and water, all of which are normal constituents of the air.
- Write balanced equations for these two reactions.
 - If the process described earlier became practical, how much cyanuric acid (in kilograms) would be required to absorb the 1.7×10^{10} kg NO_2 generated annually in auto exhaust in the United States?
58. Aspartame (molecular formula $C_{14}H_{18}N_2O_5$) is a sugar substitute in soft drinks. Under certain conditions, 1 mol of aspartame reacts with 2 mol of water to give 1 mol of aspartic acid (molecular formula $C_4H_7NO_4$), 1 mol of methanol (molecular formula CH_3OH), and 1 mol of phenylalanine. Determine the molecular formula of phenylalanine.
59. 3'-Methylphthalanilic acid is used commercially as a "fruit set" to prevent premature drop of apples, pears, cherries, and peaches from the tree. It is 70.58% carbon, 5.13% hydrogen, 5.49% nitrogen, and 18.80% oxygen. If eaten, the fruit set reacts with water in the body to produce an innocuous product, which contains carbon, hydrogen, and oxygen only, and *m*-toluidine ($NH_2C_6H_4CH_3$), which causes anemia and kidney damage. Compute the mass of the fruit set that would produce 5.23 g *m*-toluidine.
60. Aluminum carbide (Al_4C_3) reacts with water to produce gaseous methane (CH_4). Calculate the mass of methane formed from 63.2 g Al_4C_3 .
61. Citric acid ($C_6H_8O_7$) is made by fermentation of sugars such as sucrose ($C_{12}H_{22}O_{11}$) in air. Oxygen is consumed and water generated as a by-product.
- Write a balanced equation for the overall reaction that occurs in the manufacture of citric acid from sucrose.
 - What mass of citric acid is made from 15.0 kg sucrose?
62. A sample that contains only $SrCO_3$ and $BaCO_3$ weighs 0.800 g. When it is dissolved in excess acid, 0.211 g carbon dioxide is liberated. What percentage of $SrCO_3$ did the sample contain? Assume all the carbon originally present is converted to carbon dioxide.
63. A sample of a substance with the empirical formula XBr_2 weighs 0.5000 g. When it is dissolved in water and all its bromine is converted to insoluble $AgBr$ by addition of an excess of silver nitrate, the mass of the resulting $AgBr$ is found to be 1.0198 g. The chemical reaction is
- $$XBr_2 + 2 AgNO_3 \longrightarrow 2 AgBr + X(NO_3)_2$$
- Calculate the molecular mass (that is, formula mass) of XBr_2 .
 - Calculate the atomic mass of X and give its name and symbol.
64. A newspaper article about the danger of global warming from the accumulation of greenhouse gases such as carbon dioxide states that "reducing driving your car by 20 miles a week would prevent release of over 1000 pounds of CO_2 per year into the atmosphere." Is this a reasonable statement? Assume that gasoline is octane (molecular formula C_8H_{18}) and that it is burned completely to CO_2 and H_2O in the engine of your car. Facts (or reasonable guesses) about your car's gas mileage, the density of octane, and other factors will also be needed.
65. In the Solvay process for producing sodium carbonate (Na_2CO_3), the following reactions occur in sequence:
- $$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$
- $$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$
- $$2 NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + H_2O + CO_2$$

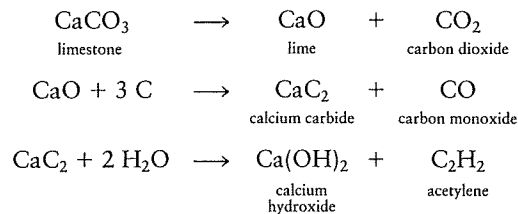
How many metric tons of sodium carbonate would be produced per metric ton of NH_3 if the process were 100% efficient (1 metric ton = 1000 kg)?

66. A yield of 3.00 g KClO_4 is obtained from the (unbalanced) reaction



when 4.00 g of the reactant is used. What is the percentage yield of the reaction?

67. An industrial-scale process for making acetylene consists of the following sequence of operations:



What is the percentage yield of the overall process if 2.32 metric tons C_2H_2 is produced from 10.0 metric tons limestone (1 metric ton = 1000 kg)?

68. Silicon nitride (Si_3N_4), a valuable ceramic, is made by the direct combination of silicon and nitrogen at high temperature. How much silicon must react with excess nitrogen to prepare 125 g silicon nitride if the yield of the reaction is 95.0%?