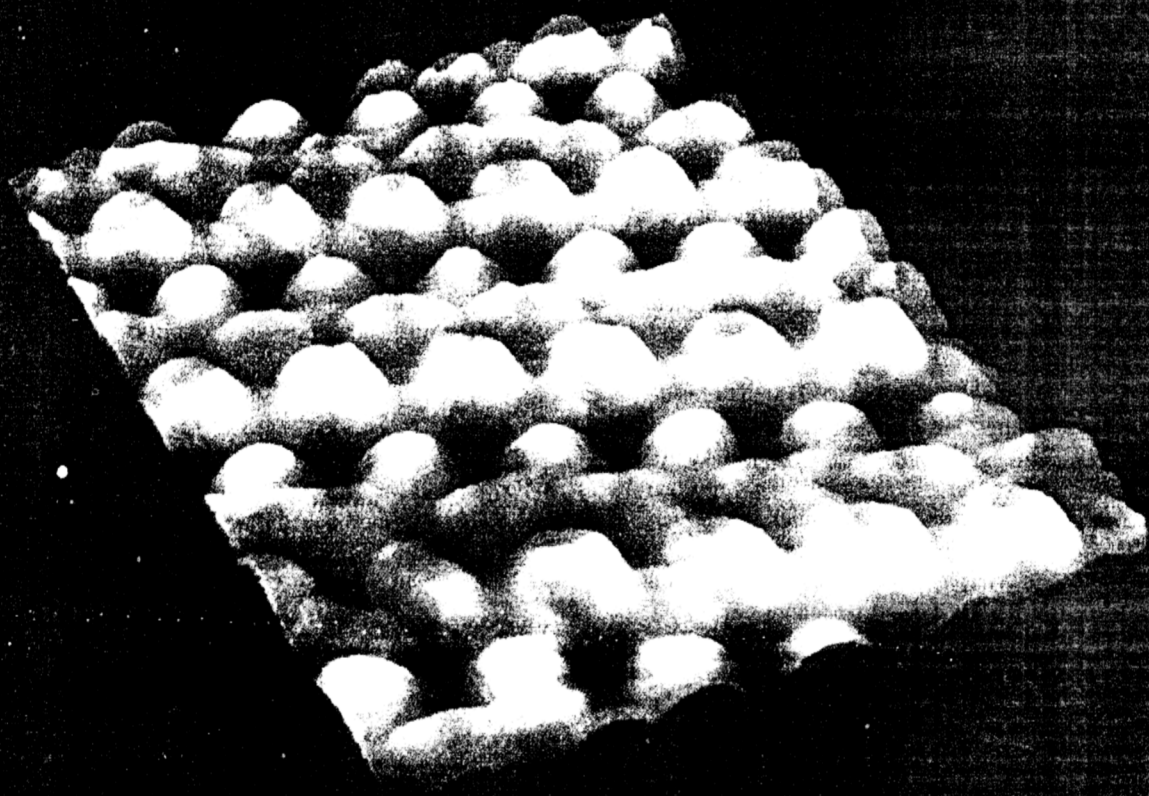


APPENDIX 1

**Chapter Two: “Atoms and The Atomic Theory”
(Petrucchi & Harwood 1993)**

2



Until about 20 years ago, there was no direct evidence for the existence of atoms. Now, with the modern technique called scanning tunneling microscopy, images of individual atoms can be obtained. Shown here are individual atoms on the surface of germanium, the different colors representing atoms at two different kinds of sites on the surface.

ATOMS AND THE ATOMIC THEORY

- 2-1 Early Chemical Discoveries and the Atomic Theory
- 2-2 Electrons and Other Discoveries in Atomic Physics
- 2-3 The Nuclear Atom
- 2-4 Chemical Elements

- 2-5 Atomic Masses
 - 2-6 The Avogadro Constant and the Concept of the Mole
 - 2-7 Using the Mole Concept in Calculations
- Focus On Occurrence and Abundances of the Elements*

Our current knowledge of the structure of atoms comes mostly from the field of physics. Beginning over 200 years ago, however, discoveries made by chemists led to the first theory of atomic structure. After a brief survey of these early chemical discoveries, we describe physical evidence leading to the modern picture of a *nuclear* atom: protons and neutrons combined into a nucleus with electrons found outside this nucleus.

Also, we introduce the Avogadro constant and the concept of the mole, which are the principal tools for counting atoms and molecules and measuring amounts of substances. We will use them throughout the text.

2-1 EARLY CHEMICAL DISCOVERIES AND THE ATOMIC THEORY

Chemistry is a rather mature science. Important chemicals such as sulfuric acid (oil of vitriol), nitric acid (aqua fortis), and sodium sulfate (Glauber's salt) were all well known and used several hundred years ago. Before the end of the eighteenth century, the principal gases of the atmosphere—nitrogen and oxygen—had been isolated, and natural laws had been proposed describing the physical behavior of gases. Yet, chemistry cannot be said to have entered the modern age until the process of combustion was explained. In this section we explore the direct link between the explanation of combustion and Dalton's atomic theory.

Law of Conservation of Mass

The process of combustion—burning—is so familiar it is hard to realize what a difficult riddle this posed for early scientists. Some of the difficult-to-explain observations are described in Figure 2-1.

In 1774, Antoine Lavoisier (1743–1794) performed an experiment in which he heated a sealed glass vessel containing a sample of tin and some air. He found that the mass before heating (glass vessel + tin + air) and after heating (glass vessel + tin calx + remaining air) were the same. Through further experiments he showed that the tin calx (we now call it tin oxide) consisted of the original tin together with a portion of the air. Experiments such as this proved to Lavoisier that oxygen from air is essential to combustion and also led him to formulate the **law of conservation of mass**: *The mass of substances formed by a chemical reaction is the same as the mass of substances entering into the reaction.* Stated another way, this law says that matter can neither be created nor destroyed in a chemical reaction.

To see just how precise were Lavoisier's measurements of mass, refer to Exercise 27.



Figure 2-1
Two combustion reactions.

The apparent product of the combustion of the match—the ash—weighs *less* than the match. The product of the combustion of the magnesium ribbon (the “smoke”) weighs *more* than the ribbon. Actually, in each case the total mass remains *unchanged*. To understand this requires knowing that oxygen gas enters into both combustions, and that water and carbon dioxide are also products of the combustion of the match.

EXAMPLE 2-1

Applying the Law of Conservation of Mass. A 0.455-g sample of magnesium is allowed to burn in 2.315 g oxygen gas. The sole product is magnesium oxide. After the reaction the mass of unreacted oxygen is 2.015 g. What mass of magnesium oxide was produced?

SOLUTION

To answer this question you need to identify the substances present before and after the reaction. The total mass is unchanged.

$$\text{mass before reaction} = 0.455 \text{ g magnesium} + 2.315 \text{ g oxygen} = 2.770 \text{ g}$$

$$\text{mass after reaction} = ? \text{ g magnesium oxide} + 2.015 \text{ g oxygen} = 2.770 \text{ g}$$

$$? \text{ g magnesium oxide} = 2.770 \text{ g} - 2.015 \text{ g} = 0.755 \text{ g}$$

PRACTICE EXAMPLE: A 7.12-g sample of magnesium was heated with 1.80 g bromine. All the bromine was used up, and 2.07 g magnesium bromide was the only product. What mass of magnesium remained *unreacted*?

Law of Constant Composition

In 1799, Joseph Proust (1754–1826) reported that “One hundred pounds of copper, dissolved in sulfuric or nitric acids and precipitated by the carbonates of soda or potash, invariably gives 180 pounds of green carbonate.”* This and similar observations became the basis of the **law of constant composition** or the **law of definite proportions**: *All samples of a compound have the same composition—the same proportions by mass of the constituent elements.*

To see how the law of constant composition works, consider the compound water. Water is made up of two atoms of hydrogen (H) for every atom of oxygen (O), a fact that can be represented symbolically by a *chemical formula*, the familiar H_2O . The two samples described below have the same proportions of the two elements, expressed as percentages by mass. To determine the percent by mass of hydrogen, for example, simply divide the mass of hydrogen by the sample mass and multiply by 100%. For each sample you will obtain the same result: 11.19% H.

SAMPLE A	COMPOSITION	SAMPLE B
10.0000 g		27.0000 g
1.1190 g H	% H = 11.19	3.0213 g H
8.8810 g O	% O = 88.81	23.9787 g O

EXAMPLE 2-2

Using the Law of Constant Composition. A 0.100-g sample of magnesium, when combined with oxygen, yields 0.166 g magnesium oxide. A second magnesium sample with a mass of 0.144 g is also combined with oxygen. What mass of magnesium oxide is produced from this second sample?

SOLUTION

We can use data from the first experiment to establish the proportion of magnesium in magnesium oxide.

$$\frac{0.100 \text{ g magnesium}}{0.166 \text{ g magnesium oxide}}$$

This proportion must be the same in *all* samples. Note that for the second sample we must invert the factor before we use it, because we must convert from mass of magnesium to mass of magnesium oxide.

$$0.144 \text{ g magnesium} \times \frac{0.166 \text{ g magnesium oxide}}{0.100 \text{ g magnesium}} = 0.239 \text{ g magnesium oxide}$$



The mineral *malachite* is basic copper carbonate and has the same composition (the very same percent copper, for example) as did the basic copper carbonate prepared by Proust in 1799.

□ The mass of magnesium oxide must be greater than the mass of magnesium. The conversion factor must have a value greater than 1.

*The substance Proust worked with is actually a combination of two compounds, copper carbonate and copper hydroxide. It is called *basic* copper carbonate. Proust's results were valid because, like all compounds, basic copper carbonate has a definite composition.



John Dalton (1766–1844)—developer of the atomic theory. Dalton has not been considered a particularly good experimenter, perhaps because of his color blindness (a condition now called daltonism). However, he did skillfully use the data of others in formulating his atomic theory.

One of the early successes of Dalton’s atomic theory was in explaining a law of chemical combination known as the law of multiple proportions. We consider this law in Section 3-4.

PRACTICE EXAMPLE: We wish to make exactly 2.00 g magnesium oxide. What masses of magnesium and oxygen must we combine to do this?

Dalton’s Atomic Theory

From 1803 to 1808, John Dalton, an English schoolteacher, used the two fundamental laws of chemical combination that we have just described as the basis of an atomic theory. His theory involved three assumptions.

- 1. Each chemical element is composed of minute, indestructible particles called atoms. Atoms can neither be created nor destroyed during a chemical change.
- 2. All atoms of an element are alike in mass (weight) and other properties, but the atoms of one element are different from those of all other elements.
- 3. In each of their compounds, different elements combine in a simple numerical ratio: for example, one atom of A to one of B (AB), or one atom of A to two of B (AB₂), or

If atoms of an element are indestructible (assumption 1), then the *same* atoms must be present after a chemical reaction as before. The total mass remains unchanged. Dalton’s theory explains the law of conservation of mass. If all atoms of an element are alike in mass (assumption 2), and if atoms unite in *fixed* numerical ratios (assumption 3), the percent composition of a compound must have a unique value, regardless of the origin of the sample analyzed. Dalton’s theory also explains the law of constant composition.

The characteristic masses of the atoms of an element became known as atomic weights, and throughout the nineteenth century chemists worked at establishing reliable values of relative atomic weights. Mostly, however, chemists directed their attention to discovering new elements, synthesizing new compounds, developing techniques for analyzing materials, and, in general, building up a vast body of chemical facts. Efforts to unravel the structure of the atom became the focus of physicists, as we see in the next several sections.

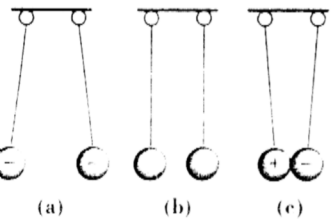


Figure 2-2
Forces between electrically charged objects.
The objects in (b) are electrically neutral and exert no forces on one another. The objects in (a) both carry a negative charge; they repel one another (the effect would be the same if both objects were positively charged). In (c) the objects carry opposite charges and attract one another.

2-2 ELECTRONS AND OTHER DISCOVERIES IN ATOMIC PHYSICS

Fortunately, we can acquire a qualitative understanding of atomic structure without having to retrace all the discoveries that preceded atomic physics. However, we do need a few key ideas about the interrelated phenomena of electricity and magnetism, which we briefly discuss with the help of Figures 2-2 and 2-3.

In the center of Figure 2-2 two small objects are shown suspended by thin threads from a support. The objects hang straight down because the force of gravity draws them as close to the center of Earth as possible. Certain objects may carry an electric charge, of which there are two types: *positive* and *negative*. Two electrically charged objects exert a force between them. Objects with like charges (either both positive or both negative) repel one another, as represented in Figure 2-2a. As shown in Figure 2-2c, objects with unlike charges (one positive and one negative) attract one another. The force (*F*) of attraction or repulsion is *directly* proportional to the magnitude or quantity of the charges (*Q*₁ and *Q*₂) and *inversely* proportional to the square of the distance between them (*r*²). In mathematical terms

$$F \propto \frac{Q_1 \cdot Q_2}{r^2}$$

A positive force is a force of repulsion, and a negative force is one of attraction.

As we learn in this section, all objects of matter are made up of electrically charged particles. An electrically *neutral* object has equal numbers of positive and negative charges. If the number of positive charges exceeds the number of negative charges, an object has a net *positive* charge. If negative charges exceed positive charges in number, an object has a net *negative* charge.

Figure 2-3 shows how electrically charged particles behave when they move through the field of a magnet. They are deflected from their straight-line path into a curved path perpendicular to the field. Think of the field or region of influence of the magnet as represented by a series of invisible lines ("lines of force") running from the north pole to the south pole of the magnet.

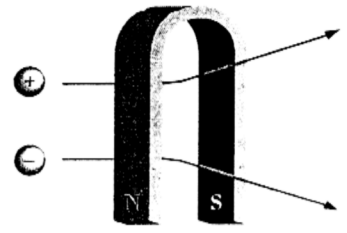


Figure 2-3
Effect of a magnetic field on charged particles.

Negatively charged particles are deflected in one direction when they travel at right angles through a magnetic field. Positively charged particles are deflected in the opposite direction. Several of the phenomena described in this section depend on this behavior.

The Discovery of Electrons

CRT, the abbreviation for cathode ray tube, has become an everyday expression. The CRT is the heart of the familiar computer monitor or TV set. The first cathode ray tube was made by Michael Faraday (1791–1867) about 150 years ago. In passing electricity through evacuated glass tubes, Faraday discovered **cathode rays**, a type of radiation emitted by the negative terminal or *cathode* that crossed the evacuated tube to the positive terminal or *anode*. Later scientists found that cathode rays travel in straight lines and have properties that are independent of the cathode material (i.e., whether it is iron, platinum, etc.). As suggested by Figure 2-4, cathode rays are invisible, and they can only be detected by the light emitted by materials that they strike. (*Fluorescence* is the term used to describe the emission of light by a material when it is struck by energetic radiation.) Another significant observation about cathode rays is that they are deflected by electric and magnetic fields in the manner expected for *negatively charged particles* (see Figure 2-5).

In 1897, by the method outlined in Figure 2-6, J. J. Thomson (1856–1940) established the ratio of mass (m) to electric charge (e) for cathode rays, that is, m/e . Also, Thomson concluded that cathode rays are negatively charged *fundamental* particles of matter found in *all* atoms. Cathode rays subsequently became known as **electrons**, a term first proposed by George Stoney in 1874.

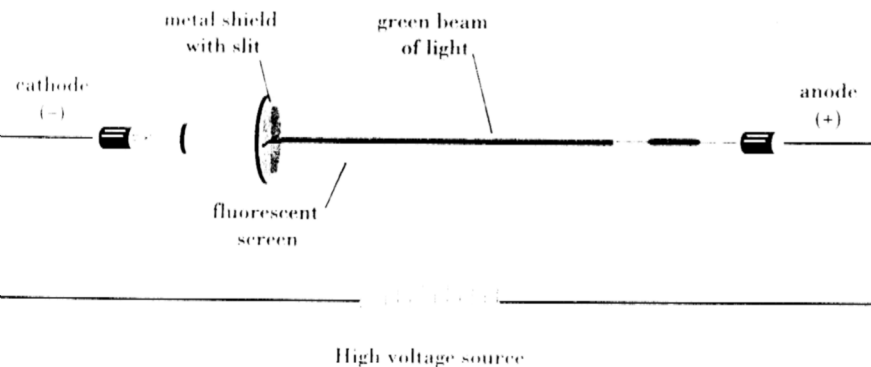
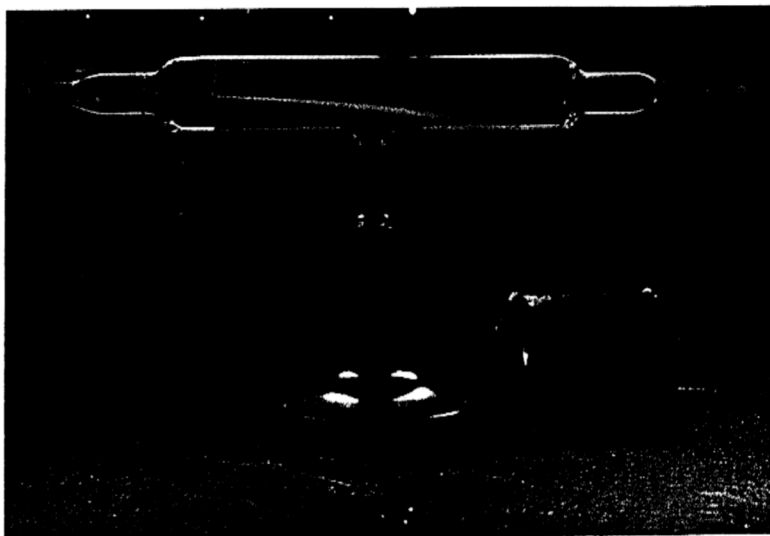


Figure 2-4
A cathode ray tube.

The high voltage source of electricity creates a negative charge on the electrode at the left (cathode) and a positive charge on the electrode at the right (anode). Cathode rays pass from the cathode, through the slit in the metal shield, and to the anode. The rays are visible only through the green fluorescence they produce along the zinc sulfide coated screen. They are invisible in other parts of the tube.

Figure 2-5
Deflection of cathode rays in a magnetic field.

The beam of cathode rays is deflected as it travels from left to right in the field of the magnet on the right. The deflection corresponds to that expected of negatively charged particles.



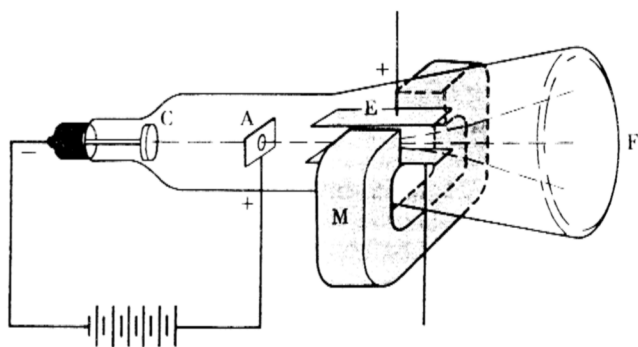
The coulomb (C) is the SI unit of electric charge (see also Appendix B).

Robert Millikan (1868–1953) determined the electronic charge e through a series of “oil drop” experiments (1906–1914), described in Figure 2-7. The currently accepted value of the electronic charge e (to five significant figures) is -1.6022×10^{-19} C. By combining this value with an accurate value of the mass-to-charge ratio for an electron we get the mass of an electron: 9.1094×10^{-28} g.

Once the electron was seen to be a fundamental particle of matter found in all atoms, atomic physicists began to speculate on how these particles were incorporated into atoms. The commonly accepted model was that proposed by J. J. Thomson. Thomson thought that the positive charge needed to counterbalance the negative charges of electrons in a neutral atom was in the form of a nebulous cloud (see Figure 2-8). Electrons, he suggested, floated in this diffuse cloud of positive charge (rather like a lump of Jello with electron “fruit” embedded in it). This model became known as the “plum pudding” model because of its similarity to a popular English dessert.

Figure 2-6
Determining the mass-to-charge ratio, m/e , for cathode rays.

The cathode ray beam strikes the end screen, undeflected, if the forces exerted on it by the electric and magnetic fields are unbalanced. By knowing the strengths of the electric and magnetic fields, together with other data, a value of m/e can be obtained. Precise measurements yield a value of -5.6857×10^{-18} gram per coulomb. (Because cathode rays carry a negative charge, the sign of the mass-to-charge ratio is also negative.)



C, cathode; A, anode (perforated to allow the passage of a narrow beam of cathode rays); E, electrically charged condenser plates; M, magnet; F, fluorescent screen.

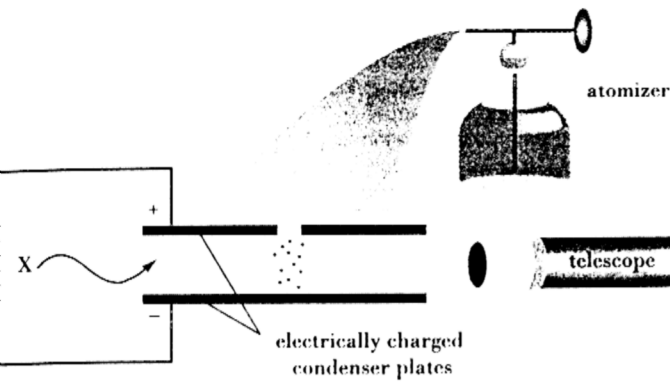


Figure 2-7

Millikan's oil drop experiment.

Ions (electrically charged atoms or molecules) are produced by energetic radiation such as X-rays (X). Some of these ions become attached to oil droplets, giving them a charge.

The fall of a droplet between the condenser plates is speeded up or slowed down, depending on the magnitude and sign of the charge on the droplet. By analyzing data from a large number of droplets, Millikan concluded that the magnitude of the charge, q , on a droplet is an *integral* multiple of the electronic charge, e . That is, $q = ne$ (where $n = 1, 2, 3, \dots$).

X-rays and Radioactivity

Cathode ray research had many important spin-offs. In particular, two natural phenomena of immense theoretical and practical significance were discovered in the course of other investigations.

In 1895, Wilhelm Roentgen (1845–1923) noticed that when cathode ray tubes were operating certain materials *outside* the tubes would glow or fluoresce. He showed that this fluorescence was caused by radiation emitted by the cathode ray tubes. Because of the unknown nature of this radiation, Roentgen coined the term X-ray. We now recognize the X-ray as a form of high-energy electromagnetic radiation, which is discussed in Chapter 9.

Antoine Becquerel (1852–1908) associated X-rays with fluorescence and wondered if naturally fluorescent materials produce X-rays. To test this idea he wrapped photographic plate with black paper, placed a coin on the paper, covered the coin with a uranium-containing fluorescent material, and exposed the entire assembly to daylight. When he developed the film, a clear image of the coin could be seen. The fluorescent material had emitted radiation (presumably X-rays) that penetrated the paper and exposed the film. On one occasion, because the sky was overcast, Becquerel placed the experimental assembly inside a desk drawer for a few days while waiting for the weather to clear. Upon resuming the experiment, Becquerel decided to replace the original photographic film, expecting that it may have become slightly exposed. He did develop the original film, however, and found that instead of the expected feeble image he got a very sharp one. The film had become strongly exposed. The material had emitted radiation continuously, even when it was not fluorescing. Becquerel had discovered **radioactivity**.

Ernest Rutherford (1871–1937) identified two types of radiation from radioactive materials, alpha (α) and beta (β). **Alpha rays** are particles carrying two fundamental units of positive charge and having the same mass as helium atoms. Alpha particles are identical to He^{2+} ions. **Beta rays** are negatively charged particles produced by changes occurring within the nuclei of radioactive atoms and have the same properties as electrons. A third form of radiation that is not affected by an electric field was discovered by Paul Villard (1900). This radiation, called **gamma rays** (γ), is electromagnetic radiation of extremely high penetrating power. These three forms of radioactivity are illustrated in Figure 2-9.

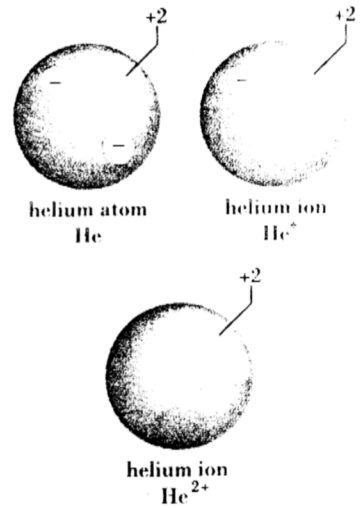


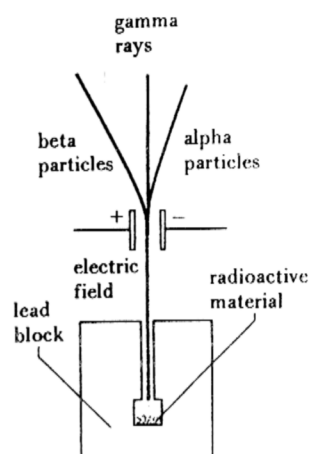
Figure 2-8

The "plum pudding" atomic model.

According to this model, a hydrogen atom consists of a "cloud" of positive charge (+1) and one electron (−1). Helium would have a +2 cloud and two electrons (−2). If a helium atom loses one electron, the atom becomes electrically charged and is called an *ion*. This ion, referred to as He^+ , has a net charge of +1. If the helium atom loses both electrons, the He^{2+} ion forms.

Figure 2-9
Three types of radiation from radioactive materials.

The radioactive material is enclosed in a lead block. All the radiation except that passing through the narrow opening is absorbed by the lead. When this radiation is passed through an electric field, it splits into three beams. One beam is undeflected—these are gamma (γ) rays. A second beam is attracted to the negatively charged plate. These are the positively charged alpha (α) particles. The third beam is deflected toward the positive plate. This is the beam of beta (β) particles.



By the early 1900s additional radioactive elements were discovered, principally by Marie and Pierre Curie. Rutherford and Frederick Soddy made another profound finding: The chemical properties of a radioactive element *change* as it undergoes radioactive decay. This observation suggests that radioactivity involves fundamental changes at the *subatomic* level—that in radioactive decay one element is changed into another, a process known as *transmutation*.

2-3 THE NUCLEAR ATOM

In 1909, Rutherford, with his assistant Hans Geiger, began a line of research using alpha particles as probes to study the inner structure of atoms. Based on Thomson's "plum pudding" model (recall Figure 2-8), Rutherford expected that a beam of alpha particles would pass through thin sections of matter largely undeflected. However, he believed that some alpha particles would be slightly scattered or deflected as they encountered electrons. By studying these scattering patterns, he hoped to deduce something about the distribution of electrons in atoms.

The apparatus used for these studies is pictured in Figure 2-10. Alpha particles were detected by the flashes of light they produced when they struck a zinc sulfide screen mounted on the end of a telescope. When Geiger and Ernest Marsden, a student, bombarded very thin foils of gold with alpha particles, here is what they observed.

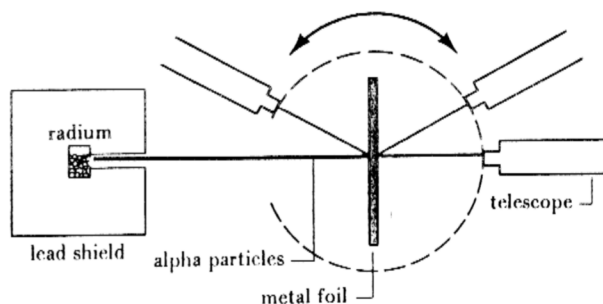


Figure 2-10
The scattering of alpha particles by metal foil.

The telescope travels in a circular track around an evacuated chamber containing the metal foil. Most α particles pass through the metal foil undeflected, but some are deflected through large angles.

- The majority of α particles penetrated the foil undeflected.
- Some α particles experienced slight deflections.
- A few (about one in every 20,000) suffered rather serious deflections as they penetrated the foil.
- A similar number did not pass through the foil at all but “bounced back” in the direction from which they had come.

The large-angle scattering greatly puzzled Rutherford. As he commented some years later, this observation was “about as credible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you.” By 1911, though, Rutherford had an explanation, outlined in Figure 2-11. The model of the atom he proposed is known as the *nuclear atom* and has these features.

- 1. Most of the mass and all of the positive charge of an atom are centered in a very small region called the *nucleus*. *The atom is mostly empty space.*
- 2. The magnitude of the positive charge is different for different atoms and is approximately one half the atomic weight of the element.
- 3. There exist as many electrons outside the nucleus as there are units of positive charge on the nucleus. The atom as a whole is electrically neutral.

Protons and Neutrons

Rutherford’s nuclear atom suggested the existence of positively charged fundamental particles of matter in the nuclei of atoms. Rutherford himself discovered these particles, called **protons**, in 1919, in studies involving the scattering of alpha particles by nitrogen atoms in air. The protons were freed as a result of collisions between alpha particles and the nuclei of nitrogen atoms. At about this same time, Rutherford predicted the existence in the nucleus of electrically neutral fundamental particles. In 1932, James Chadwick showed that a newly discovered penetrating radiation consisted of beams of *neutral* particles. These particles, called **neutrons**, originated from the nuclei of atoms. Thus, it has been only for about the past 60 years that we have had the atomic model suggested by Figure 2-12.

Fundamental Particles: A Summary

In this and the preceding section we have described three fundamental particles of matter: electrons, protons, and neutrons. Table 2-1 presents the electric charges and masses of these three fundamental particles in two ways.

Table 2-1

PROPERTIES OF THREE FUNDAMENTAL PARTICLES

	ELECTRIC CHARGE		MASS	
	SI (C)	ATOMIC	SI (g)	ATOMIC (u) ^a
Proton	$+1.602 \times 10^{-19}$	+1	1.673×10^{-24}	1.0073
Neutron	0	0	1.675×10^{-24}	1.0087
Electron	-1.602×10^{-19}	-1	9.109×10^{-28}	0.0005486

^a is the SI unit for atomic mass unit (abbreviated amu).

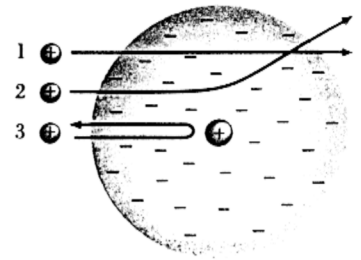


Figure 2-11

Rutherford’s interpretation of the scattering of α particles by thin metal foils.

In this model, alpha particles behave in one of three ways. They might

1. go through the atom undeflected, or only slightly deflected;
2. be severely deflected by passing close to the nucleus;
3. bounce back after approaching the nucleus “head-on.”

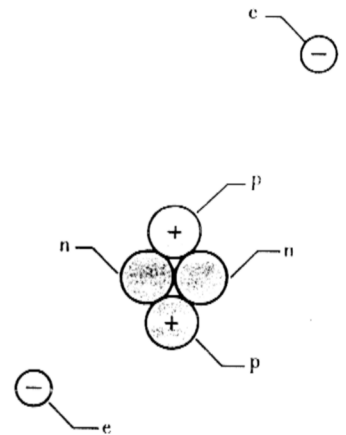


Figure 2-12

The nuclear atom—illustrated by the helium atom.

In this drawing electrons are shown much closer to the nucleus than is the case. The actual situation is more like this: If the entire atom were represented by a room, 5 m \times 5 m \times 5 m, the nucleus would only occupy about as much space as the period at the end of this sentence.

An electron carries an atomic unit of negative electric charge. A proton carries an atomic unit of positive charge. The **atomic mass unit** (see page 44) is defined as exactly 1/12 of the mass of the atom known as carbon-12 (“carbon twelve”). An atomic mass unit is referred to by the abbreviation, amu, and the unit, u. As we see from Table 2-1, the proton and neutron masses are just slightly greater than 1 u. By comparison the mass of an electron is seen to be only about 1/2000th the mass of the proton or neutron.

The number of protons in the nucleus of an atom is called the **atomic number**, or the **proton number**, **Z**. In an electrically neutral atom the number of electrons is also equal to **Z**, the proton number. The mass of an atom is determined by the total number of protons and neutrons in its nucleus. This total is called the **mass number**, **A**. The number of neutrons, the **neutron number**, is $A - Z$.

2-4 CHEMICAL ELEMENTS

Now that we have acquired some fundamental ideas about atomic structure, we can more thoroughly discuss the concept of chemical elements that we introduced in the opening pages of this text.

All the atoms of an element have the same atomic number, **Z**. At present the elements with atomic numbers ranging from $Z = 1$ to 109 are known. Each element has a name and a distinctive symbol. For most elements the **chemical symbol** is an abbreviation of the English name and consists of one or two letters. The first (but never the second) letter of the symbol is capitalized; for example: carbon, C; oxygen, O; nitrogen, N; sulfur, S; neon, Ne; and silicon, Si. Some elements known since ancient times have symbols based on their Latin names, such as Fe for iron (*ferrum*) and Pb for lead (*plumbum*). The element sodium has the symbol Na, based on the Latin *natrium* for sodium carbonate. Potassium has the symbol K, based on the Latin *kalium* for potassium carbonate. The symbol for tungsten, W, is based on the German *wolfram*.

Elements beyond uranium ($Z = 92$) do not occur naturally and must be synthesized in particle accelerators (described in Chapter 26), and elements of the very highest atomic numbers have only been produced on a limited number of occasions, a few atoms at a time. Inevitably, controversies have arisen about which research team discovered a new element and, in fact, whether a discovery was made at all. To resolve conflicts, the International Union of Pure and Applied Chemistry (IUPAC) has proposed that *provisional* names be used until discoveries are clearly confirmed. The IUPAC system for naming elements beyond $Z = 100$ uses an “ium” ending and relates numbers and names as follows.

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

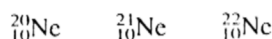
By this scheme element 106 is named “unnihexium” and has the symbol Unh. Some nuclear scientists do not care for this system and simply use atomic numbers in place of names for atoms with atomic number greater than 100.

Isotopes

To represent the composition of any particular atom we need to specify the number of protons (p), neutrons (n), and electrons (e) in the atom. We can do this with the symbolism

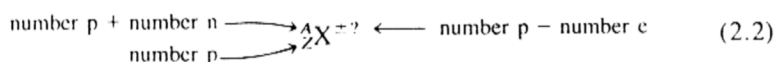


This symbolism indicates that the atom is of the element X . It has an atomic number Z and a mass number A . For example, an atom of aluminum represented as ${}^{27}_{13}\text{Al}$ has 13 protons and 14 neutrons in its nucleus and 13 electrons outside the nucleus. Contrary to what Dalton thought, we now know that atoms of an element do not necessarily all have the same mass. In 1912, J. J. Thomson measured the mass-to-charge ratios of positive ions formed in neon gas. He found that about 91% of the atoms had one mass and that the remaining atoms were about 10% heavier. All neon atoms have ten protons in their nuclei, and most have ten neutrons as well. A very few neon atoms, however, have 11 neutrons and some have 12. We can represent the three different types of neon atoms as



Two or more atoms having the *same* atomic number (Z) but *different* mass numbers are called **isotopes**. Of all Ne atoms on Earth, 90.9% are ${}^{20}_{10}\text{Ne}$. The percentages of ${}^{20}_{10}\text{Ne}$ and ${}^{22}_{10}\text{Ne}$ are 0.3% and 8.8%, respectively. These percentages—90.9%, 0.3%, 8.8%—are called the **percent natural abundances** of the three neon isotopes. Sometimes the mass numbers of isotopes are incorporated into the names of elements, such as neon-20 (read this as “neon twenty”). Some elements consist of a single type of atom and therefore do not have isotopes.* Aluminum, for example, consists only of aluminum-27 atoms.

An atom that has either lost or gained electrons is called an **ion** and carries a net electric charge. The number of protons never changes when an atom becomes an ion. ${}^{20}_{10}\text{Ne}^+$ and ${}^{22}_{10}\text{Ne}^{2+}$ are ions. The first one has ten protons, ten neutrons, and nine electrons. The second one has ten protons, 12 neutrons, and *eight* electrons. The charge on an ion is equal to the number of protons *minus* the number of electrons. That is



⌋ Percent natural abundances of isotopes are given on a *number* basis, not a mass basis. Thus, 909 out of every 1000 neon atoms are neon-20 atoms.

Nuclide is the general term used to describe an atom with a particular atomic number and mass number. If an element consists of two or more different nuclides, we can speak of these as being isotopes. If an element has but a single nuclide, it is improper to speak of this as being an isotope, but it can be done anyway. After all, you do not speak of someone as being a twin unless he or she actually has a twin brother or sister.

EXAMPLE 2-3

Relating the Numbers of Protons, Neutrons, and Electrons in Atoms and Ions.

(a) Indicate the number of protons, neutrons, and electrons in $^{35}_{17}\text{Cl}$. (b) Write an appropriate symbol for the species consisting of 29 protons, 34 neutrons, and 27 electrons.

SOLUTION

In using the symbolism ^A_ZX pay particular attention to whether the species is a neutral atom or an ion. If it is a neutral atom, number e = number p = Z (the atomic number). If the species is an ion, determine whether the number of electrons is smaller (positive ion) or larger (negative ion) than the number of protons. Whether the species is an atom or ion, the number of neutrons is equal to $A - Z$.

a. $^{35}_{17}\text{Cl}$: $Z = 17$, $A = 35$, a neutral atom.

$$\text{number } p = 17 \quad \text{number } e = 17 \quad \text{number } n = A - Z = 35 - 17 = 18$$

b. The element with $Z = 29$ is copper (Cu). The mass number A = number p + number n = $29 + 34 = 63$. Because the species has only 27 electrons, it must be an ion with a net charge = number p - number e = $29 - 27 = +2$. It should be represented as $^{63}_{29}\text{Cu}^{2+}$.

EXAMPLE: Determine the numbers of protons, neutrons, and electrons in an ion of sulfur-35 that carries a charge of -2 .

Isotopic Masses

Ordinarily we expect like-charged objects (such as protons) to repel one another (recall Example 2-2). The forces holding protons and neutrons together in the nucleus are very much stronger than ordinary electrical forces.

This definition also establishes that one atomic mass unit (1 u) is exactly $\frac{1}{12}$ the mass of a carbon-12 atom.

We cannot determine the mass of an individual atom just by adding up the masses of its fundamental particles. When an atomic nucleus is created from protons and neutrons, a small quantity of the original mass is converted to energy. This is the nuclear binding energy that holds the protons and neutrons together, and we cannot predict exactly how much this will be. Determining the masses of individual atoms, then, is something that must be done *by experiment*, in the following way:

We *arbitrarily* choose one atom and assign it a certain mass. By international agreement this standard is an atom of the isotope carbon-12, which is assigned a mass of *exactly* 12 atomic mass units, that is, 12 u. Next, we determine the masses of other atoms relative to the value of 12 u for carbon-12. To do this we use a **mass spectrometer**. In this device a beam of gaseous ions separates into components of differing mass as it passes through electric and magnetic fields. The separated ions are focused on a measuring instrument, which records their presence and amounts. Figure 2-13 illustrates mass spectrometry. A typical mass spectrum is pictured in Figure 2-14.

Although mass numbers are whole numbers, the *actual* masses of individual atoms (in atomic mass units, u) are never *exact* whole numbers, except for carbon-12. However, they are very close in value to the corresponding mass numbers. This means, for example, that we should expect the mass of oxygen-16 to be very nearly 16 u. In Example 2-4 we see that it is.

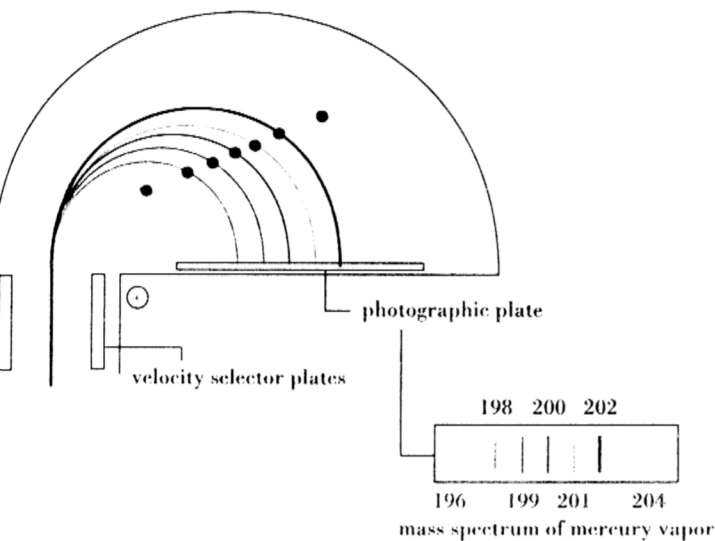


Figure 2-13
A mass spectrometer.

A gaseous sample is ionized by bombardment with electrons in the lower part of the apparatus (not shown). The positive ions thus formed are subjected to an electrical force by the electrically charged velocity selector plates and a magnetic force by a magnetic field perpendicular to the page. Only ions with a particular velocity pass through and are deflected into circular paths by the magnetic field. Ions with different masses strike the detector (here a photographic plate) in different regions. The more ions of a given type, the greater the response of the detector (depth of deposit on the photographic plate).

EXAMPLE 2-4

Establishing Isotopic Masses by Mass Spectrometry. With mass spectral data the ratio of the mass of ^{16}O to ^{12}C is found to be 1.33291. What is the mass of an ^{16}O atom?

SOLUTION

The ratio of the masses is $^{16}\text{O}/^{12}\text{C} = 1.33291$. The mass of the ^{16}O atom is 1.33291 times the mass of ^{12}C .

$$\text{mass of } ^{16}\text{O} = 1.33291 \times 12.00000 \text{ u} = 15.9949 \text{ u}$$

PRACTICE EXAMPLE: By mass spectrometry an atom of ^{16}O is found to have 1.06632 times the mass of ^{15}N . What is the mass of an ^{15}N atom, expressed in atomic mass units?

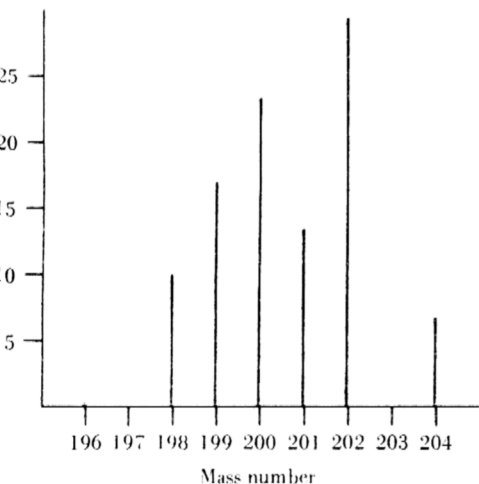


Figure 2-14
Mass spectrum for mercury.

The response of the ion detector in Figure 2-13 (depth of deposits on photographic plate) has been converted to a scale of relative numbers of atoms. The percent natural abundances of the mercury isotopes are ^{196}Hg , 0.146%; ^{198}Hg , 10.02%; ^{199}Hg , 16.84%; ^{200}Hg , 23.13%; ^{201}Hg , 13.22%; ^{202}Hg , 29.80%; ^{204}Hg , 6.85%.

2-5 ATOMIC MASSES

In a table of atomic masses the value listed for carbon is 12.011, yet the atomic mass standard is *exactly* 12. Why the difference? The atomic mass standard is based on a sample of carbon containing *only* atoms of carbon-12, whereas *naturally occurring* carbon contains some carbon-13 atoms as well. The existence of these two isotopes causes the *observed* atomic mass to be greater than 12. The **atomic mass (weight)*** of an element is the average of the isotopic masses, *weighted* according to the naturally occurring abundances of the isotopes of the element. In a "weighted" average we must assign greater importance—give greater weight—to the quantity that occurs more frequently. Since carbon-12 atoms are much more abundant than carbon-13, the weighted average must lie much closer to 12 than to 13. This is the result that we get by applying the following general equation.

$$\begin{array}{l} \text{at. mass} \\ \text{of an} \\ \text{element} \end{array} = \left(\begin{array}{cc} \text{fractional} & \text{mass of} \\ \text{abundance of} & \text{isotope} \\ \text{isotope (1)} & (1) \end{array} \right) + \left(\begin{array}{cc} \text{fractional} & \text{mass of} \\ \text{abundance of} & \text{isotope} \\ \text{isotope (2)} & (2) \end{array} \right) + \cdots \quad (2.3)$$

The mass spectrum of carbon shows that 98.892% of carbon atoms are carbon-12 with a mass of 12 u, *exactly*, and 1.108% are carbon-13 with a mass of 13.00335 u. In the setup below we calculate the contribution of each isotope to the weighted average separately and then add these contributions together, as required by equation (2.3).

$$\begin{array}{l} \text{contribution to} \\ \text{at. mass by } ^{12}\text{C} \end{array} = \begin{array}{l} \text{fraction of all} \\ \text{atoms that are } ^{12}\text{C} \end{array} \times \text{mass } ^{12}\text{C atom} \\ = 0.98892 \times 12.0000 \text{ u} = 11.867 \text{ u}$$

$$\begin{array}{l} \text{contribution to} \\ \text{at. mass by } ^{13}\text{C} \end{array} = \begin{array}{l} \text{fraction of all} \\ \text{atoms that are } ^{13}\text{C} \end{array} \times \text{mass } ^{13}\text{C atom} \\ = 0.01108 \times 13.00335 \text{ u} = 0.1441 \text{ u}$$

$$\begin{array}{l} \text{at. mass of naturally} \\ \text{occurring carbon} \end{array} = (\text{contribution by } ^{12}\text{C}) + (\text{contribution by } ^{13}\text{C}) \\ = 11.867 \text{ u} + 0.1441 \text{ u} \\ = 12.011 \text{ u}$$

To determine the atomic mass of an element having three naturally occurring isotopes, such as potassium, we would have to combine three contributions to the weighted average, and so on.

*Since the time of Dalton the atomic masses we describe in this section have been called "atomic weights." They still are by most chemists. Yet, from our discussion of mass and weight in Section 1-5 we see that what we are describing here is mass, not weight. Old habits die hard.

The percent natural abundances of the elements remain remarkably constant from sample to sample. For example, the proportions of ^{12}C and ^{13}C atoms are the same whether we analyze a sample of pure carbon (diamond), carbon dioxide gas, or a mineral form of calcium carbonate (calcite). We can treat all carbon-containing materials as if there were a single *hypothetical* type of carbon atom with a mass of 12.011 u. This means that once weighted-average atomic masses have been determined and tabulated,* we can simply use these values in all calculations requiring atomic masses.

Are You Wondering . . .

Whether weighted averages show up anywhere other than in the atomic masses of the elements? There is one weighted average that concerns almost every student: *grade-point average (GPA)*. If you need a "C" (2.0) average to remain in good academic standing, you know that one grade of "B" (3.0) and another "D" (1.0) won't necessarily assure an average of "C." The grades need to be "weighted" according to the number of units of credit for each course. The grade-point average will lie closer to the grade in the course carrying the greater number of units. If the course with the "B" grade has 4 units and the one with the "D" grade, 3 units, the GPA will exceed 2.0. The GPA will be less than 2.0 if the situation is the other way around. In fact, you can set up an equation for computing GPA that is very much like equation (2.3) (see Exercise 65).

In addition to being able to do calculations, it is also important to have a *qualitative* understanding of the relationship between isotopic masses, percent natural abundances, and weighted-average atomic masses, as illustrated in Example 2-5. Practice Example accompanying Example 2-5 provides another application of equation (2.3).

EXAMPLE 2-5

Understanding the Meaning of a Weighted-Average Atomic Mass. The two naturally occurring isotopes of lithium, lithium-6 and lithium-7, have masses of 6.01513 and 7.01601 u, respectively. Which of these two occurs in greater abundance?

*Atomic mass (atomic weight) values in tables are often written without units, especially if they are referred to as *relative* atomic masses. This simply means that the values listed are in relation to *exactly* 12 (rather than 12 u) for carbon-12. We will use the atomic mass unit (u) when referring to atomic masses (atomic weights). Most chemists do.

SOLUTION

From a table of atomic masses (inside the front cover) we see that of lithium is 6.941 u. Because this value—a weighted-average atomic mass—is much closer to 7 than to 6, lithium-7 must be the more abundant isotope.

PRACTICE EXAMPLE: Use the weighted-average atomic mass of 6.941 u in equation (2.3) to determine the percent natural abundances of lithium-6 and lithium-7. [Hint: Let x be the *fractional* abundance of one isotope and $1 - x$, the other. Solve the equation for x , and convert fractional to percent abundances (multiply by 100%).]

**Are You Wondering . . .**

Why some atomic masses (e.g., $F = 18.9984032$) are stated so much more precisely than others (e.g., $Kr = 83.80$)? There is *one* naturally occurring type of fluorine atom: fluorine-19. Determining the atomic mass of fluorine means establishing the mass of this type of atom as precisely as possible. Krypton has *six* naturally occurring isotopes. Because the percent distribution of the isotopes of krypton may differ very slightly from one sample to another, we can't state the weighted-average atomic mass of krypton with high precision.

2-6 THE AVOGADRO CONSTANT AND THE CONCEPT OF THE MOLE

Starting with Dalton, chemists have recognized the importance of relative numbers, such as in the statement that *two* hydrogen atoms and *one* oxygen atom combine to form *one* molecule of water. Yet, we cannot count atoms in the usual sense. We must resort to some other measurement, usually mass. This means that we need a relationship between the *measured* mass of an element and some *known* but *uncountable* number of atoms. Consider a practical example of mass substituting for a desired number of items: If you want to nail down new floor boards on the deck of a mountain cabin, you need a certain number of nails. However, you do not attempt to count out the number of nails you need—you buy them by the pound.

The SI quantity that describes an amount of substance by relating it to a number of particles of that substance is called the *mole*, and abbreviated *mol*.

A **mole** is an amount of substance that contains the same number of elementary entities as there are carbon-12 atoms in *exactly* 12 g of carbon-12.

The “number of elementary entities (atoms, molecules, . . .)” referred to in this definition is called the **Avogadro constant**, N_A (also known as Avogadro's num-

r). If we divide the mass of one mole of carbon-12 by the mass of a single carbon-12 atom (which can be determined experimentally by mass spectrometry), we obtain the number of “elementary entities” in a mole of carbon-12.

$$\begin{aligned}\text{Avogadro constant} &= \frac{\text{mass of } ^{12}\text{C per mole}}{\text{mass of } ^{12}\text{C atom}} = \frac{12.00000 \text{ g/mol}}{1.992648 \times 10^{-23} \text{ g}} \\ &= 6.022137 \times 10^{23} \text{ mol}^{-1}\end{aligned}$$

Then we will round off the value of N_A to $6.022 \times 10^{23} \text{ mol}^{-1}$, or even to $6.02 \times 10^{23} \text{ mol}^{-1}$. The unit “ mol^{-1} ” signifies that the entities being counted are those present in one mole.

If a substance contains atoms of a single isotope, we may write

$$1 \text{ mol } ^{12}\text{C} = 6.02214 \times 10^{23} \text{ } ^{12}\text{C atoms} = 12.0000 \text{ g}$$

$$1 \text{ mol } ^{16}\text{O} = 6.02214 \times 10^{23} \text{ } ^{16}\text{O atoms} = 15.9949 \text{ g} \quad \text{and so on.}$$

Most elements are composed of mixtures of two or more isotopes. The atoms to “counted out” to yield one mole are not all of the same mass. They must be taken in their naturally occurring proportions. Thus, in 1 mol of carbon most of the atoms are carbon-12 but some are carbon-13. In 1 mol of oxygen most of the atoms are oxygen-16 but some are oxygen-17 and some, oxygen-18. As a result,

$$1 \text{ mol of carbon} = 6.02214 \times 10^{23} \text{ C atoms} = 12.011 \text{ g}$$

$$1 \text{ mol of oxygen} = 6.02214 \times 10^{23} \text{ O atoms} = 15.9994 \text{ g} \quad \text{and so on.}$$

We can easily establish the mass of one mole of atoms, called the **molar mass**, from a table of atomic masses, e.g., 6.941 g Li/mol Li. Figure 2-15 illustrates

□ The most precise value for N_A is obtained by X-ray diffraction studies of crystals, as we will see in Chapter 13.

□ Note that molar mass has the unit g/mol.

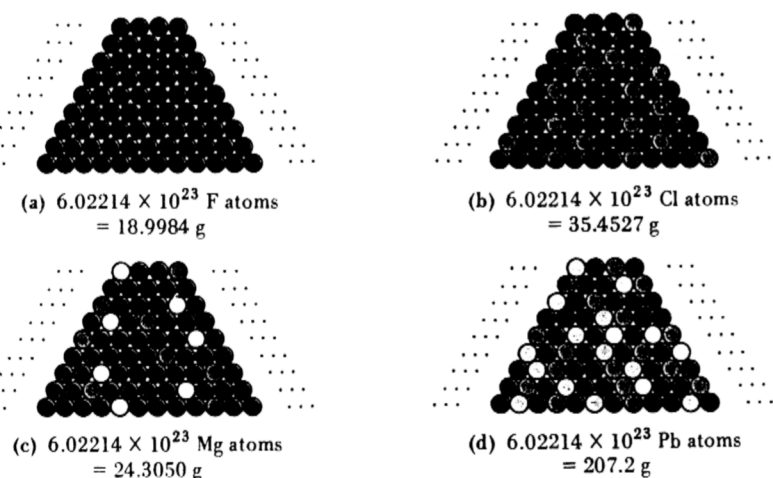


FIGURE 2-15

An attempt to picture one mole of atoms.

An enormously large number of atoms is needed to comprise one mole.

(a) There is only one type of fluorine atom, ^{19}F .

(b) In chlorine, 75.77% of the atoms are ^{35}Cl and the remainder are ^{37}Cl .

(c) Magnesium has a principal isotope, ^{24}Mg , and two minor ones, ^{25}Mg (10.00%) and ^{26}Mg (11.01%).

(d) Lead has four naturally occurring isotopes: ^{204}Pb (1.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%), and ^{208}Pb (52.4%).

the meaning of 1 mol of atoms of an element, and Figure 2-16 pictures one mole each of four common elements.

Thinking About the Avogadro Constant

Avogadro's constant (6.02214×10^{23}) is an enormously large number and practically inconceivable in terms of ordinary experience. Suppose that the piles of spheres in Figure 2-15 were garden peas instead of atoms. If the typical pea had a volume of about 0.1 cm^3 , the required pile to form "one mole of peas" would cover the United States to a depth of about 6 km (4 mi). Or, imagine that a mole of objects, say grains of wheat, could be counted at the rate of 100 per minute. A given individual might be able to count out about 4 billion objects in a lifetime. Even so, if all the people currently on Earth were to spend their lives counting grains of wheat they could not reach Avogadro's constant. In fact, if all the people who ever lived on Earth had spent their lifetimes counting grains of wheat, the total would still be far less than Avogadro's constant. (And one mole of grains of wheat is far more wheat than has been produced in human history.) Now consider a much more efficient counting method, a modern supercomputer; it is capable of counting about one billion per second. The task of counting out Avogadro's constant would still take about 20 million years!

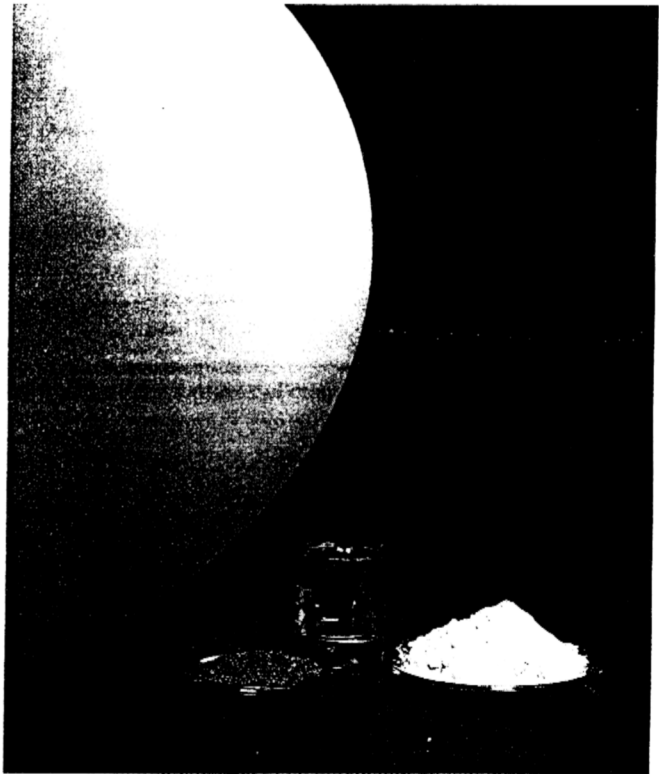


Figure 2-16
one mole of an element.
Two test glasses contain one mole of copper atoms (left) and one mole of sulfur atoms (right). The beaker contains one mole of liquid mercury, and the balloon contains one mole of hydrogen gas.

The Avogadro constant is clearly not a useful number for counting ordinary objects. However, when this inconceivably large number is used to count inconceivably small objects, such as atoms and molecules, the result is quantities of materials that are easily within our grasp.

2-7 USING THE MOLE CONCEPT IN CALCULATIONS

Throughout the text, the mole concept will provide us with conversion factors for problem-solving situations. As we encounter each new situation we will explore how the mole concept applies. For now, we will deal with the relationship between numbers of atoms and the mole. Consider the statement: $1 \text{ mol Mg} = 6.022 \times 10^{23} \text{ Mg atoms} = 24.31 \text{ g Mg}$. This allows us to write the conversion factors

$$\frac{1 \text{ mol Mg}}{6.022 \times 10^{23} \text{ Mg atoms}} \quad \text{and} \quad \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}}$$

We use these factors in Example 2-7. Example 2-6 is perhaps the simplest possible application of the mole concept: relating the number of atoms in a sample to the number of moles of atoms.

In calculations requiring the Avogadro constant, an often asked question concerns when to multiply and when to divide. One answer is always to use the constant so you get the proper cancellation of units. Another answer is to think in terms of the expected result. In calculating a number of atoms, the answer is expected to be a *very large* number, and certainly *never* smaller than 1. The number of *moles* of atoms, on the other hand, is generally a number of more modest size. It will often be smaller than 1.

EXAMPLE 2-6

Relating Number of Moles and Total Number of Atoms. A sample of iron metal is described as being 2.35 mol Fe. How many iron atoms are present in this sample?

SOLUTION

The conversion factor we need is based on the fact that $1 \text{ mol Fe} = 6.022 \times 10^{23} \text{ Fe atoms}$.

$$\begin{aligned} ? \text{ Fe atoms} &= 2.35 \text{ mol Fe} \times \frac{6.022 \times 10^{23} \text{ Fe atoms}}{1 \text{ mol Fe}} \\ &= 1.42 \times 10^{24} \text{ Fe atoms} \end{aligned}$$

From this point on we will not routinely show the cancellation of units. However, you should always assure yourself that the proper cancellation does occur.

PRACTICE EXAMPLE: How many magnesium-24 atoms are present in $8.27 \times 10^{-3} \text{ mol Mg}$? [Hint: What proportion of all Mg atoms are ^{24}Mg (see Figure 2-15)?]

EXAMPLE 2-7

Relating Number of Atoms of an Element to Its Amount in Moles and Its Mass in Grams. (a) How many moles of Mg are present in a sample containing 1.00×10^{22} Mg atoms? (b) What is the mass of this sample?

SOLUTION

To ensure the maximum precision allowable, we will express quantities known very precisely, such as the Avogadro constant, with at least one more significant figure than the number of significant figures in the least precisely measured quantity.

- a. As in Example 2-6, we need the Avogadro constant as a conversion factor, but here the factor is *inverted* from the form used there.

$$\begin{aligned} ? \text{ mol Mg} &= 1.00 \times 10^{22} \text{ Mg atoms} \times \frac{1 \text{ mol Mg}}{6.022 \times 10^{23} \text{ Mg atoms}} \\ &= 0.0166 \text{ mol Mg} \end{aligned}$$

- b. We can begin with the result of part (a)—0.0166 mol Mg—and use molar mass as a conversion factor.

$$? \text{ g Mg} = 0.0166 \text{ mol Mg} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = 0.404 \text{ g Mg}$$

Or, we can simply combine the setups for parts (a) and (b).

$$\begin{aligned} ? \text{ g Mg} &= 1.00 \times 10^{22} \text{ Mg atoms} \times \frac{1 \text{ mole Mg}}{6.022 \times 10^{23} \text{ Mg atoms}} \\ &\quad \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} \\ &= 0.404 \text{ g Mg} \end{aligned}$$

Figure 2-17 shows how we might weigh out the quantity of magnesium involved in this problem.

How many He atoms are present in a 22.6-g sample of He gas? [*Hint:* This calculation is the “inverse” of part (b).]



Figure 2-17
Measurement of 1.00×10^{22} Mg atoms (0.0166 mol Mg)—Example 2-7, as illustrated.

The balance is set to zero (tared) when just the weighing paper is present. The sample of magnesium weighs 0.404 g.

Example 2-8 is perhaps the most representative way in which the mole concept is used—as part of a larger problem that requires other, unrelated, conversion factors as well. One approach is to outline a series of conversions—chart a path—to get from the given to the desired information. The path in Example 2-8 is from mg K \rightarrow g K \rightarrow mol K \rightarrow K atoms \rightarrow ^{40}K atoms. The first step requires a conversion factor between SI mass units that you should know. The second step requires molar mass as a conversion factor. This number you can obtain from a table of atomic masses. In the third step you need Avogadro’s constant, a quantity that you should remember. In the fourth step the necessary conversion factor is the percent natural abundance of ^{40}K , which must be given in the statement of the problem.

EXAMPLE 2-8

Combining Several Factors in a Calculation—Molar Mass, the Avogadro Constant, Percent Abundances. Potassium-40 is one of the few naturally occurring radioactive isotopes of elements of low atomic number. Its percent natural abundance is 0.012%. How many ^{40}K atoms do you ingest by drinking one cup of whole milk containing 371 mg K?

SOLUTION

Following the path charted on page 52, convert the mass of K to number of moles of K. For this, use molar mass in the *inverse* manner to Example 2-7.

$$? \text{ mol K} = 371 \text{ mg K} \times \frac{1 \text{ g K}}{1000 \text{ mg K}} \times \frac{1 \text{ mol K}}{39.10 \text{ g K}} = 9.49 \times 10^{-3} \text{ mol K}$$

Then convert the number of moles of K to number of K atoms.

$$\begin{aligned} ? \text{ K atoms} &= 9.49 \times 10^{-3} \text{ mol K} \times \frac{6.022 \times 10^{23} \text{ K atoms}}{1 \text{ mol K}} \\ &= 5.71 \times 10^{21} \text{ K atoms} \end{aligned}$$

Finally, use the percent natural abundance of ^{40}K to formulate a factor to convert from number of K atoms to number of ^{40}K atoms.

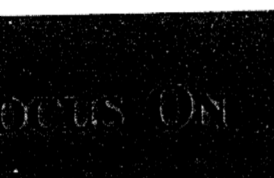
$$\begin{aligned} ? \text{ } ^{40}\text{K atoms} &= 5.71 \times 10^{21} \text{ K atoms} \times \frac{0.012 \text{ } ^{40}\text{K atoms}}{100 \text{ K atoms}} \\ &= 6.9 \times 10^{17} \text{ } ^{40}\text{K atoms} \end{aligned}$$

□ The radioactivity associated with milk is part of the natural background radiation to which we are all exposed and is not considered harmful.

Outlining an approach to a multistep problem, as we did on page 52, may also make it easier to see how to do a problem through a single setup. Thus, we can write

$$\begin{aligned} ? \text{ } ^{40}\text{K atoms} &= 371 \text{ mg K} \times \frac{1 \text{ g K}}{1000 \text{ mg K}} \times \frac{1 \text{ mol K}}{39.10 \text{ g K}} \\ &\quad \times \frac{6.022 \times 10^{23} \text{ K atoms}}{1 \text{ mol K}} \times \frac{0.012 \text{ } ^{40}\text{K atoms}}{100 \text{ K atoms}} \\ &= 6.9 \times 10^{17} \text{ } ^{40}\text{K atoms} \end{aligned}$$

PRACTICE EXAMPLE: How many Pb atoms are present in a small piece of lead with a volume of 0.105 cm^3 ? The density of Pb = 11.34 g/cm^3 .



Occurrence and Abundances of the Elements

What is the most abundant element? This seemingly simple question does not have a simple answer. If we consider the entire universe, hydrogen accounts for about 90% of all the atoms and 75% of the mass, and helium accounts for most of the rest. If we consider only the elements present on Earth, iron is probably the most abundant element. However, most of this iron is believed to be in Earth's core. The currently accessible elements are those present in Earth's atmosphere, oceans, and solid continental crust. The relative abundances of some elements and common materials containing these elements are listed in Table 2-2.

Not all the known elements exist in Earth's crust. Trace amounts of neptunium ($Z = 93$) and plutonium ($Z = 94$) are found in uranium minerals, but for practical

is one of the most abundant elements in Earth's crust. compounds give soils a characteristic red color, such as the Navajo Sandstone Paria Canyon Wilderness Area of Arizona.

Table 2-2
ABUNDANCES OF THE ELEMENTS IN EARTH'S CRUST^a

ELEMENT	ABUNDANCE, MASS %	PRINCIPAL MATERIALS CONTAINING THE ELEMENT
Oxygen	49.3	water; silica; silicates; metal oxides; the atmosphere
Silicon	25.8	silica (sand, quartz, agate, flint); silicates (feldspar, clay, mica)
Aluminum	7.6	silicates (clay, feldspar, mica); oxide (bauxite)
Iron	4.7	oxide (hematite, magnetite)
Calcium	3.4	carbonate (limestone, marble, chalk); sulfate (gypsum); fluoride (fluorite); silicates (feldspar, zeolites)
Sodium	2.7	chloride (rock salt, ocean waters); silicates (feldspar, zeolites)
Potassium	2.4	chloride; silicates (feldspar, mica)
Magnesium	1.9	carbonate; chloride (seawater); sulfate (Epsom salts)
Hydrogen	0.7	oxide (water); natural gas and petroleum; organic matter
Titanium	0.4	oxide
Chlorine	0.2	common salt (rock salt, ocean waters)
Phosphorus	0.1	phosphate rock; organic matter
All others ^b	0.8	

^aEarth's crust is taken to consist of the solid crust, terrestrial waters, and the atmosphere.

^bThis figure includes C, N, and S—all essential to life—and less abundant, although commercially important, elements such as B, Be, Cr, Cu, F, I, Pb, Sn, and Zn.

For purposes elements with atomic numbers higher than 82 can only be produced artificially by nuclear processes. Moreover, most of the elements do not occur free in nature, that is, as the uncombined element. Only about 20% of them do. The remaining elements occur only in chemical combination with other elements.

We cannot assume that the ease and cost of obtaining a pure element from its natural sources are necessarily related to the relative abundance of the element. Aluminum is the most abundant of the metals, but it cannot be produced as cheaply as iron. This is partly because concentrated deposits of iron-containing compounds—iron ores—are more common than are ores of aluminum. Some elements whose percent abundances are quite low are nevertheless widely used because their

ores are fairly common. This is the case with copper, for example, whose abundance is only 0.005%. On the other hand, some elements have a fairly high abundance but no characteristic ores of their own. They are not easily obtainable, as in the case of rubidium, the sixteenth most abundant element.

In later chapters we describe the ways in which elements are obtained from natural sources: oxygen, nitrogen, and argon from the atmosphere; hydrogen from natural gas; magnesium and bromine from seawater; sulfur from underwater deposits; sodium and chlorine from ordinary salt; and several metals from their ores.

SUMMARY

Modern chemistry began with 18th century discoveries that led to the formulation of the law of conservation of mass and the law of constant composition, followed by Dalton's atomic theory. Important 19th century developments leading to an understanding of the structure of the atom occurred mostly in the field of physics, however. Cathode ray research led to the discovery of the electron—a fundamental particle of all matter and the basic unit of negative electrical charge. The discoveries of X-rays and radioactivity were a consequence of cathode ray studies. The discovery of isotopes and the development of modern mass spectrometry also have their origins in cathode ray research. Studies on the scattering of particles by thin metal foils led to the concept of the nuclear atom. A more complete description of the atomic nucleus was made possible by the later discovery of the proton and neutron.

By assigning a mass of *exactly* 12 u to a carbon-12 atom, the masses of other atoms can be established by mass spectrometry. From the masses of the different isotopes of an element and their percent natural abundances, the weighted-average atomic mass (weight) of an element can be determined. It is these weighted averages that are listed in tables of atomic masses (weights).

The Avogadro constant, $N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$, represents the number of carbon-12 atoms in *exactly* 12 g of carbon-12. More generally, it is the number of elementary entities present in 1 mol of a substance. The mass of 1 mol of atoms of an element is called its molar mass. Molar mass and the Avogadro constant are used in a variety of calculations involving the mass, amount (in moles), or number of atoms in a sample of an element.

SUMMARIZING EXAMPLE

stainless steel ball bearing has a radius of 6.35 mm and a density of 7.75 g/cm³. Iron is the principal element in steel. Carbon is a key minor element. The ball bearing consists of 0.5% carbon, by mass.

Given that the percent natural abundance of the isotope ¹³C is 1.108%, how many ¹³C atoms are present in the ball bearing?

1. Determine the volume of the ball bearing, in cm³. The formula for the volume (V) of a sphere is $V = \frac{4}{3}\pi r^3$. The radius (r) must be expressed in cm. *Result:* 1.07 cm³.

2. Determine the mass of carbon present. (a) Use the density of steel and the volume of the ball bearing to calcu-

late its mass. (b) Use the percent carbon in the steel to convert from mass of steel to mass of carbon. *Result:* 0.021 g C.

3. Determine the total number of carbon atoms present. (a) Use the molar mass of carbon to convert the mass of carbon to the amount of carbon expressed in moles. (b) Use the Avogadro constant to establish the number of carbon atoms. *Result:* 1.1×10^{21} C atoms.

4. Determine the number of ¹³C atoms. The percent natural abundance leads to the conversion factor: 1.108 ¹³C atoms/100 C atoms. Multiply the result of step 3 by this factor to obtain the number of ¹³C atoms.

Answer: 1.2×10^{19} ¹³C atoms.

KEY TERMS

alpha (α) ray (2-2)

atomic mass unit (u) (2-3)

atomic number (proton number), Z (2-3)

atomic mass (weight) (2-5)

Avogadro constant, N_A (2-6)

beta (β) ray (2-2)

cathode ray (2-2)

chemical symbol (2-4)

electron (2-2)

gamma (γ) ray (2-2)

ion (2-4)

isotope (2-4)

law of conservation of mass (2-1)

law of constant composition
(definite proportions) (2-1)

mass number, A (2-3)

mass spectrometer (2-4)

molar mass, M (2-6)

mole (2-6)

neutron (2-3)

neutron number (2-3)

nuclide (2-4)

percent natural abundance (2-4)

proton (2-2)

radioactivity (2-2)

REVIEW QUESTIONS

1. In your own words define or explain the following terms or symbols: (a) Z ; (b) β particle; (c) isotope; (d) ¹⁶O; (e) molar mass.

2. Briefly describe each of the following ideas: (a) law of conservation of mass; (b) Rutherford's nuclear atom; (c) weighted-average atomic mass; (d) radioactivity.

3. Explain the important distinctions between each of the following terms: (a) cathode rays and beta rays; (b) protons and neutrons; (c) nuclear charge and ionic charge; (d) Avogadro's constant and the mole.

4. A 0.255-g sample of magnesium reacts with oxygen, producing 0.423 g magnesium oxide as the only product. What mass of oxygen was consumed in the reaction?

5. A 0.750-g sample of sodium reacts with 2.050 g chlorine to produce sodium chloride as the only product. For the reaction 0.893 g chlorine remains unreacted. What mass of sodium chloride was formed?

6. If sodium and chlorine atoms combine in the proportions 1:1 in sodium chloride, what must be the percent

by mass of sodium in the compound? (*Hint:* Use the tabulated atomic masses of Na and Cl.)

7. When an iron object rusts its mass increases. When a match burns its mass decreases. Do these observations violate the law of conservation of mass? Explain.

8. In Example 2-2 we established that the proportion of magnesium to magnesium oxide was 0.100 g magnesium/0.166 g magnesium oxide.

(a) What is the proportion of oxygen to magnesium oxide?

(b) What is the proportion of oxygen to magnesium (i.e., g O/g Mg)?

(c) What is the percent by mass of magnesium in magnesium oxide?

9. Samples of pure carbon weighing 1.48, 2.06, and 3.17 g were burned in an excess of air. The masses of carbon dioxide obtained (the sole product in each case) were 5.42, 7.55, and 11.62 g, respectively.

(a) Do these data establish that carbon dioxide has a fixed composition?

- (b) What is the composition of carbon dioxide, expressed in % C and % O, by mass?
10. When 5.00 g magnesium and 80.0 g bromine react, find that (1) all the magnesium is used up, (2) some bromine remains unreacted, and (3) magnesium bromide is the only product. With this information alone, is it possible to calculate the mass of magnesium bromide produced? Explain.
11. Complete the table below. What minimum amount of information is required to characterize completely an element or ion?

Element	Symbol	Number of protons	Number of electrons	Number of neutrons	Mass number
Sodium	$^{23}_{11}\text{Na}$	11	11	12	23
Carbon	_____	_____	_____	14	_____
_____	_____	37	_____	_____	85
_____	$^{40}_{19}\text{K}$	_____	_____	_____	_____
_____	_____	_____	33	42	_____
_____	$^{20}\text{Ne}^{2+}$	_____	_____	_____	_____
_____	_____	_____	_____	_____	80
_____	_____	_____	_____	126	_____

12. Arrange the following species in order of increasing (a) number of electrons; (b) number of neutrons; (c) mass.

Sn $^{40}_{18}\text{Ar}$ $^{122}_{52}\text{Te}$ $^{59}_{29}\text{Cu}$ $^{120}_{48}\text{Cd}$ $^{58}_{27}\text{Co}$ $^{39}_{19}\text{K}$

13. All of these radioactive isotopes have applications in medicine. Write their symbols in the form ^A_ZX . (a) cobalt-60; (b) phosphorus-32; (c) iodine-131; (d) sulfur-35.

14. For the nuclide $^{133}_{55}\text{Cs}$, express the percentage, by mass, of the fundamental particles in the nucleus that are (a) protons; (b) neutrons.

15. There are two principal isotopes of indium (atomic mass = 114.82 u). One of these, ^{113}In , has a mass of 112.9043 u. Which of these must be the second isotope: ^{111}In , ^{112}In , ^{114}In , ^{115}In ? Explain.

16. An isotope with mass number 63 has five more neutrons than protons. This is an isotope of what element?

17. The following data on isotopic masses are given in a handbook. What is the ratio of each of these masses to that of $^{12}_6\text{C}$? (a) $^{27}_{13}\text{Al}$, 26.98153 u; (b) $^{40}_{20}\text{Ca}$, 39.96259 u; (c) $^{197}_{79}\text{Au}$, 196.9666 u.

18. The following ratios of masses were obtained with a mass spectrometer: $^{19}\text{F}/^{12}\text{C} = 1.5832$; $^{35}\text{Cl}/^{19}\text{F} = 1.8406$; $^{81}\text{Br}/^{35}\text{Cl} = 2.3140$. Determine the mass of a ^{81}Br atom in atomic mass units. (Hint: What is the mass of a ^{12}C atom?)

19. In naturally occurring uranium, 99.27% of the atoms are $^{238}_{92}\text{U}$ with mass 238.05 u; 0.72%, $^{235}_{92}\text{U}$ with mass 235.04 u; and 0.006%, $^{234}_{92}\text{U}$ with mass 234.04 u. Calculate the atomic mass of naturally occurring uranium.

20. What is the total number of atoms in each of the following samples? (a) 34.5 mol Mg; (b) 0.0123 mol He; (c) 6.1×10^{-12} mol Np.

21. Calculate the quantities indicated.

- the number of moles represented by 9.32×10^{25} Zn atoms
- the mass, in grams, of 3.27 mol Ar
- the mass, in mg, of a sample containing 3.07×10^{20} Ag atoms
- the number of atoms in 46.5 cm³ of Fe ($d = 7.86 \text{ g/cm}^3$)

22. Without doing detailed calculations, indicate which of the following quantities contains the greatest number of atoms: 6.02×10^{23} Fe atoms, 50.0 g sulfur, 55.0 g Fe, 5.0 cm³ Fe ($d = 7.86 \text{ g/cm}^3$). Explain your reasoning.

23. How many ^{204}Pb atoms are present in a piece of lead weighing 1.57 g? The percent natural abundance of ^{204}Pb is 1.4%.

24. A particular lead-cadmium alloy is 92.0% lead by mass. What mass of this alloy, in grams, must you weigh out to obtain a sample containing 1.50×10^{23} Cd atoms?

EXERCISES

Law of Conservation of Mass

25. When a strip of magnesium metal is burned in air (see Figure 2-1), it produces a white powder that weighs more than the original metal. When a strip of magnesium is burned in a photoflash bulb, the bulb weighs the same before and after it is flashed. Explain the difference in these observations.

26. Within the limits of experimental error, show that the law of conservation of mass was obeyed in the following experiment: 10.00 g calcium carbonate (found in limestone) was dissolved in 100.0 mL hydrochloric acid ($d = 1.148 \text{ g/mL}$). The products were 120.40 g solution (a mixture of hydrochloric acid and calcium chloride) and 2.22 L carbon dioxide gas ($d = 1.9769 \text{ g/L}$).

27. The data Lavoisier obtained in the experiment described on page 34 are as follows.

Before heating: glass vessel + tin + air =
13 ounces, 2 gros, 2.50 grains
After heating: glass vessel + tin calx + remaining air =
13 ounces, 2 gros, 5.62 grains

How closely did Lavoisier's results conform to the law of conservation of mass? What must have been the sensitivity of Lavoisier's balance? That is, how small a mass do you think the balance would have detected? 1 livre = 16 ounces; 1 ounce = 8 gros; 1 gros = 72 grains. In modern terms, 1 livre = 30.59 g.

Law of Constant Composition

28. In one experiment 2.18 g sodium was allowed to react with 16.12 g chlorine. All the sodium was used up, and 5.54 g sodium chloride (salt) was produced. In a second experiment 2.10 g chlorine was allowed to react with 0.00 g sodium. All the chlorine was used up, and 3.46 g sodium chloride was produced. Show that these results are consistent with the law of constant composition.

29. When 3.06 g hydrogen was allowed to react with an excess of oxygen, 27.35 g water was obtained. In a second experiment a sample of water was decomposed by electrolysis, resulting in 1.45 g hydrogen and 11.51 g oxygen. Are these results consistent with the law of constant composition? Demonstrate why or why not.

30. In one experiment the burning of 0.312 g sulfur produced 0.623 g sulfur dioxide as the sole product. In a second experiment 0.842 g sulfur dioxide was obtained. What mass of sulfur must have been burned in the second experiment?

31. In one experiment the reaction of 1.00 g mercury and an excess of sulfur yielded 1.16 g of a sulfide of mercury as the sole product. In a second experiment the same sulfide was produced in the reaction of 1.50 g mercury and 0.00 g sulfur.

- What mass of the sulfide of mercury was produced in the second experiment?
- What mass of which element (mercury or sulfur) remained *unreacted*?

Fundamental Particles

32. Cite the evidence that most convincingly established that electrons are fundamental particles of all matter.

33. Why could not the same methods that had been used to characterize electrons be used to isolate and detect neutrons?

34. Investigation of electrical discharge in gases led to the discovery of both negative and positive particles of matter. Explain why the negative particles *all* proved to be fundamental particles of matter but most of the positive particles did not.

Fundamental Charges and Mass-to-Charge Ratios

35. These observations were made for a series of 10 oil drops in an experiment similar to Millikan's (see Figure 2-7). Drop 1 carried a charge of 1.28×10^{-18} C; drops 2 and 3 each carried $\frac{1}{2}$ the charge of drop 1; drop 4 carried $\frac{1}{4}$ the charge of drop 1; drop 5 had a charge four times that of drop 1; drops 6 and 7 had charges three times that of drop 1; drops 8 and 9 had charges twice that of drop 1; and drop 10 had the same charge as drop 1. Are these data consistent with the value of the electronic charge given in the text? Could Millikan have inferred the charge on the electron from this particular series of data? Explain.

36. Use data from Table 2-1 to verify the following statements.

- The mass of electrons is about 1/2000 that of hydrogen atoms.
- The mass-to-charge ratio, m/e , for positive ions is considerably larger than for the electron.

37. Determine the approximate value of the mass-to-charge ratio, m/e , in coulombs/gram, for the ions $^{127}_{53}\text{I}^-$ and $^{32}_{16}\text{S}^{2-}$. Why are these values only approximate?

Atomic Number, Mass Number, and Isotopes

38. Describe the significance of each term in the symbol ^A_ZX .

39. For the atom $^{138}_{56}\text{Ba}$, with a mass of 137.9050 u, determine

- the numbers of protons, neutrons, and electrons in the atom;
- the ratio of the mass of this atom to that of an atom of $^{12}_6\text{C}$;
- the ratio of the mass of this atom to that of an atom of $^{16}_8\text{O}$ (refer to Example 2-4).

40. An isotope of silver has a mass that is 6.68374 times that of oxygen-16. What is the mass (in u) of this isotope? What is the ratio of its mass to that of carbon-12? (*Hint*: Refer to Example 2-4.)

41. Explain why the symbols $^{35}_{17}\text{Cl}$ and ^{35}Cl actually convey the same information. Do the symbols $^{35}_{17}\text{Cl}$ and $^{35}_{17}\text{Cl}$ have the same meaning?

42. Given the following species: $^{24}\text{Mg}^{2+}$, ^{47}Cr , $^{59}\text{Co}^{2+}$, $^{35}\text{Cl}^-$, $^{124}\text{Sn}^{2+}$, ^{226}Th , ^{90}Sr . Which of these species

- has equal numbers of neutrons and electrons?
- has protons contributing more than 50% of the mass?

- (c) has a number of neutrons equal to the number of protons plus one-half the number of electrons?

Mass Units, Atomic Masses

What is the mass, in grams, corresponding to 1 u? (Hint: Refer to Table 2-1.)

The mass of a carbon-12 atom is taken to be *exactly* 12 u. Are there likely to be any other atoms with an *exact* (whole number) mass, expressed in u? Explain.

Which statement is probably true concerning the masses of individual copper atoms: that *all*, *some*, or *none* have a mass of 63.546 u? Explain.

There are *three* naturally occurring isotopes of magnesium. Their masses and percent natural abundances are 24.0030 u, 78.99%; 24.985837 u, 10.00%; and 25.982593 u, 11.01%. Calculate the weighted-average atomic mass of magnesium.

There are *two* naturally occurring isotopes of silver. Their masses and percent natural abundances are 106.905092 u, 51.84%; 107.905092 u, 48.16%. The mass of ^{107}Ag is 106.905092 u. What is the mass of ^{109}Ag ? (Hint: What is the weighted-average atomic mass of Ag?)

Bromine has *two* naturally occurring isotopes. One isotope, bromine-79, has a mass of 78.918336 u and a natural abundance of 50.69%. What must be the mass and natural abundance of the other, bromine-81?

The three isotopes of naturally occurring potassium are ^{39}K , 38.963707 u; ^{40}K , 39.963999 u; and ^{41}K . The percent natural abundances of ^{39}K and ^{41}K are 93.2581% and 6.7399%, respectively. Determine the isotopic mass of ^{40}K .

Mass Spectrometry

The masses of the naturally occurring mercury isotopes are ^{196}Hg , 195.9658 u; ^{198}Hg , 197.9668 u; ^{199}Hg , 198.9683 u; ^{200}Hg , 199.9683 u; ^{201}Hg , 200.9703 u; ^{202}Hg , 201.9706 u; and ^{204}Hg , 203.9735 u. Use these data, together with data from Figure 2-14, to calculate the atomic mass of mercury.

Use the data suggested by the mass spectrum at the bottom of the page to *estimate* the atomic mass of germanium. State two reasons why this result is only approximately correct.

The three isotopes of hydrogen, ^1H , ^2H , and ^3H , all combine with chlorine to form simple diatomic molecules with H and Cl in a 1:1 ratio, that is, HCl. The percent natural abundances of the chlorine isotopes are ^{35}Cl , 75.78%, and ^{37}Cl , 24.22%. The percent natural abundances of ^1H and ^3H are 99.985% and less than 0.0001%, respectively.

- (a) How many HCl molecules of different masses are possible?

- (b) What are the mass numbers of these different molecules (i.e., the sum of the mass numbers of the two atoms in each molecule)?
- (c) Which is the most abundant of the possible HCl molecules? Which is the second most abundant?
- (d) In the manner of Figure 2-14, sketch the mass spectrum you would expect to obtain for HCl molecules.

The Avogadro Constant and the Mole

53. Use fundamental definitions and statements from the text to establish the fact that $6.022 \times 10^{23} \text{ u} = 1.000 \text{ g}$. (Hint: Recall how 1 mole of carbon-12 and the mass of a carbon-12 atom are defined.)

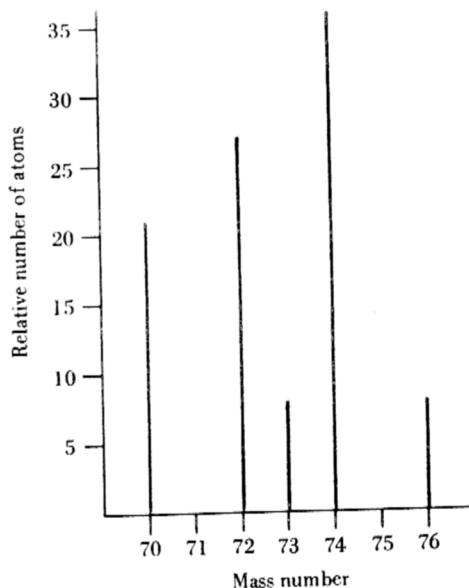
54. Determine

- (a) the number of moles of Na in a 135.0-g sample;
- (b) the number of S atoms in 245.0 kg sulfur;
- (c) the mass of a one-trillion (1.0×10^{12}) atom sample of copper.

55. How many Ag atoms are present in a piece of sterling silver jewelry weighing 38.7 g? Sterling silver contains 92.5% Ag, by mass.

56. Refer to Figure 2-15 and determine the number of magnesium-24 atoms in one mole of magnesium produced from naturally occurring sources.

57. Medical experts generally consider a lead level of $30 \mu\text{g Pb}$ per dL of blood to pose a significant health risk (1 dL = 0.1 L). Express this lead level (a) in the unit mol Pb/L blood; (b) as the number of Pb atoms per mL blood.



58. During a severe air pollution episode the concentration of lead in air was observed to be $3.01 \mu\text{g Pb/m}^3$. How many Pb atoms would be present in a 0.500-L sample of air (the approximate lung capacity of a human adult)?
59. Gold occurs in seawater to the extent of 0.15 mg/g of seawater. How many Au atoms are present in a glassful

(300 g) of seawater? (1 ton = 2000 lb, 1 lb = 453.6 g).

60. An alloy that melts at about the boiling point of water has Bi, Pb, and Sn atoms in the ratio 10:6:5, respectively. What is the mass of a sample of this alloy containing a total of one mole of atoms?

ADVANCED EXERCISES

1. Prout (1815) advanced the hypothesis that all other elements are built up of hydrogen atoms, suggesting that all elements should have integral atomic masses based on an atomic mass of 1 for hydrogen. This hypothesis appeared discredited by the discovery of atomic masses such as 24.3 for magnesium and 35.5 for chlorine. In terms of modern knowledge, explain why Prout's hypothesis is actually quite reasonable.

2. Fluorine has a single atomic species, fluorine-19. Determine the atomic mass of fluorine-19 by adding together the masses of its protons, neutrons, and electrons, and compare with the value listed inside the front cover. Explain why the agreement is not better.

3. Use 1×10^{-13} cm as the approximate diameter of a spherical nucleus of the hydrogen-1 atom, together with data from Table 2-1, to estimate the density of matter in a nucleus.

4. Osmium metal (used in catalysts) has about the highest density known: 22 g/cm^3 . What does a comparison of this value and the density of the proton estimated in Exercise 63 suggest about the amount of empty space in matter?

5. The Are You Wondering feature on page 47 compares determining weighted-average atomic masses to evaluating grade-point averages. Set up the equation for grade-point average referred to there, and compute the GPA for a student earning 5 units of A (4.0), 3 units of B (3.0), and 2 units of C (2.0).

6. The atomic mass of oxygen listed in this book is 15.9994. A textbook printed 30 years ago lists a value of 16.0000. This is based on an earlier atomic mass standard, based on exactly 16 for the naturally occurring mixture of isotopes ^{16}O , ^{17}O , and ^{18}O . Would you expect other atomic masses listed in the older text to be the same, generally higher, or generally lower than in this text? Explain.

7. Suppose we redefined the atomic mass scale by arbitrarily assigning to the naturally occurring mixture of three isotopes an atomic mass of 35.00000 u.

- (a) What would be the atomic masses of helium, sodium, and iodine on this new atomic mass scale?

- (b) Why do these three elements have nearly integral (whole number) atomic masses based on carbon-12 but not based on naturally occurring chlorine?

68. In each case, identify the element in question if (Hint: You will find it helpful to use algebra for some of these.)

- (a) an atom has a *total* of 60 protons, neutrons, and electrons, with *equal* numbers of all three.
- (b) the mass number of an atom is 234 and the atom has 60.0% more neutrons than protons.
- (c) an ion with a 2+ charge has 10.0% more protons than electrons.
- (d) an ion with a mass number of 110 and a 2+ charge has 25.0% more neutrons than electrons.

69. Identify the isotope X if its nucleus contains one more neutron than protons and the mass number is 9 times larger than the charge on the ion X^{3+} .

70. Determine the only possible 2+ ion for which the following two conditions are both satisfied.

- the net ionic charge is *one-tenth* the nuclear charge, and
- the number of neutrons is *four* more than the number of electrons.

71. Determine the only possible isotope (X) for which the following conditions are met.

- The mass number of X is 2.50 times its atomic number.
- The atomic number of X is equal to the mass number of another isotope (Y). In turn, the isotope Y has a neutron number that is 1.33 times the atomic number of Y and equal to the neutron number of selenium-82.

72. The two naturally occurring isotopes of nitrogen have masses of 14.0031 and 15.0001 u, respectively. Determine the percentage of nitrogen-15 atoms in naturally occurring nitrogen. (Hint: What is the weighted-average atomic mass of nitrogen?)

73. Silicon has one major isotope, ^{28}Si (27.97693 u, 92.21% natural abundance), and two minor ones, ^{29}Si (28.97649 u) and ^{30}Si (29.97376 u). What are the percent natural abundances of the two minor isotopes? Comment on the limitation of the precision of this calculation.

4. Deuterium, ^2H , is sometimes used to replace ordinary ^1H atoms in chemical studies. The percent natural abundance of ^2H is 0.015%. What mass of hydrogen gas would have to be processed to extract 1.00 g of pure ^2H ?

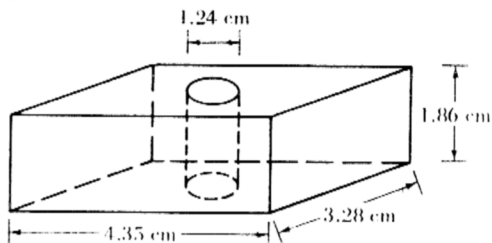
5. A particular silver solder (used in the electronics industry to join electrical components) is to be prepared having the *atom* ratio 5.00 Ag/4.00 Cu/1.00 Zn. What masses of the three metals must be melted together to prepare 1.00 kg of the solder?

6. A low-melting Sn-Pb-Cd alloy called *eutectic* is analyzed. The *mole* ratio of tin to lead is found to be 1.00, and the *mass* ratio of lead to cadmium is found to be 1.78:1.00.

- What is the percent composition of this alloy, by mass?
- What is the mass of a sample of this alloy containing a *total* of 1.00 mol of atoms?

77. How many Cu atoms are present in a 1.00-m length of 20-gauge copper wire? (A 20-gauge wire has a diameter of 0.03196 in.; density of Cu = 8.92 g/cm^3 .)

78. Monel metal is a corrosion-resistant Ni-Cu alloy used in the electronics industry. The object pictured below is made of a particular Monel metal having a density of 8.80 g/cm^3 and containing 0.022% Si, by mass. What is the total mass of silicon-30 in this object? The percent natural abundance of silicon-30 is 3.10%, and its mass is 29.97376 u.

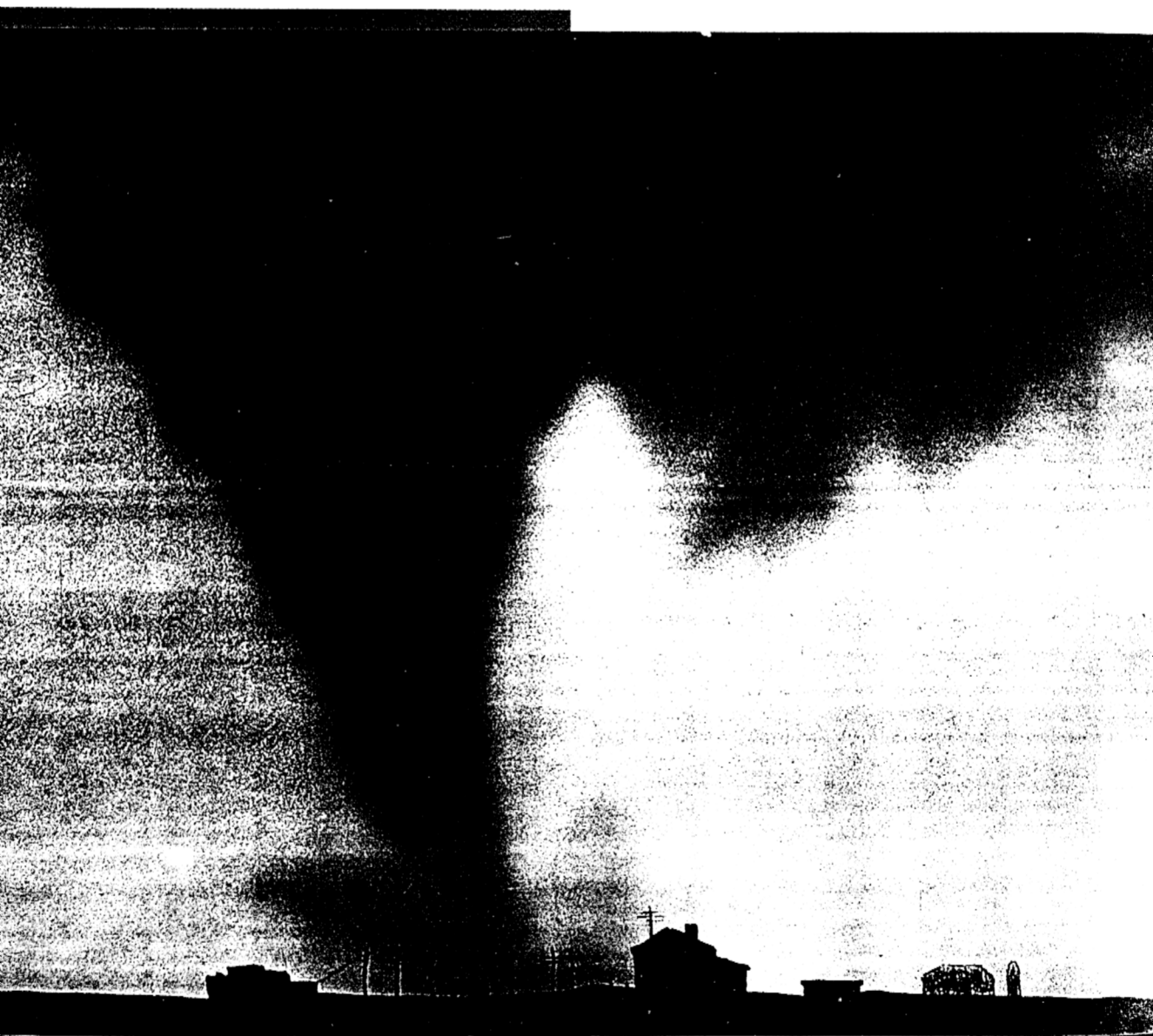


APPENDIX 2

**Chapter Ten: “Gases”
(Brown & Le May 1988)**

CHAPTER *10*

Gases





In the past several chapters we have learned about the electronic structures of atoms and about how atoms come together to form molecules or ionic substances. We commonly observe matter, however, on the atomic and molecular level, but as a solid, liquid, or gas. In the next few chapters we will be considering some of the important characteristics of these states of matter. We will be interested in learning what substances are found in one or the other state; what forces operate between atoms, ions, or molecules in these states; what transitions may occur between states; and about some of the characteristic properties of matter in each state.

10.1 CHARACTERISTICS OF GASES

Many familiar substances exist at ordinary temperature and pressure as gases. These include several elements (H_2 , N_2 , O_2 , F_2 , Cl_2 , and the noble gases) and a great variety of compounds. Table 10.1 lists a few of the more common gaseous compounds. Under appropriate conditions, substances that are ordinarily liquids or solids can also exist in the gaseous state, where they are often referred to as *vapors*. The substance H_2O , for example, is familiar to us as liquid water, ice, or water vapor. Frequently, a substance exists in all three separate states of matter, or phases, at the same time. A Thermos flask containing a mixture of ice and water at $0^\circ C$ has a certain pressure of water vapor in the gas phase over the liquid and solid phases.

Normally, the three states of matter differ very obviously from one another. Gases differ dramatically from solids and liquids in several respects. A gas expands to fill its container. Consequently, the volume of a gas is given simply by specifying the volume of the container in which it is held. Volumes of solids and liquids, on the other hand, are not determined by the container. The corollary of this is that gases are highly compressible. When pressure is applied to a gas, its volume readily contracts. Liquids and solids, on the other hand, are not very compressible at all. Great pressures must be applied to cause the volume of a liquid or solid to diminish by even as little as 5 percent.

Two or more gases form homogeneous mixtures in all proportions, regardless of how different the gases may be. Liquids, on the other hand, often do not form homogeneous mixtures. For example, when water and gasoline are poured into a bottle, the water vapor and gasoline vapors above the liquids form a homogeneous gas mixture. The two liquids, by

CONTENTS

- 10.1 Characteristics of Gases
- 10.2 Pressure
- 10.3 The Gas Laws
- 10.4 The Ideal-Gas Equation
- 10.5 Dalton's Law of Partial Pressures
- 10.6 Molecular Weights and Gas Densities
- 10.7 Quantities of Gases Involved in Chemical Reactions
- 10.8 Kinetic-Molecular Theory
- 10.9 Molecular Effusion and Diffusion; Graham's Law
- 10.10 Nonideal Gases: Departures from the Ideal-Gas Equation

A tornado is one of the most destructive manifestations of the gaseous state of matter. Tornadoes form when moist, warm air at lower levels converges with cooler dry air aloft. The resultant air flows lead to winds that can attain speeds of 200 to 300 miles per hour, with updraft speeds in the range of 200 miles per hour. (Dr. E. R. Degginger)

TABLE 10.1 Some common compounds that are gases

Formula	Name	Characteristics
HCN	Hydrogen cyanide	Very toxic, slight odor of bitter almonds
HCl	Hydrogen chloride	Toxic, corrosive, choking odor
H ₂ S	Hydrogen sulfide	Very toxic, odor of rotten eggs
CO	Carbon monoxide	Toxic, colorless, odorless
CO ₂	Carbon dioxide	Colorless, odorless
CH ₄	Methane	Colorless, odorless, flammable
N ₂ O	Nitrous oxide	Colorless, sweet odor, "laughing gas"
NO ₂	Nitrogen dioxide	Red-brown, irritating odor
NH ₃	Ammonia	Colorless, pungent odor
SO ₂	Sulfur dioxide	Colorless, irritating odor

contrast, remain largely separate; each dissolves in the other to only a slight extent.

The characteristic properties of gases arise because the individual molecules are relatively far apart. For example, in the air we breathe, the molecules take up only about 0.1 percent of the volume. The average distance between molecules in air is about 10 times as great as the sizes of the molecules themselves. Thus each molecule behaves largely as though the others weren't present; different gases behave similarly, even though they are made up of different molecules. By contrast, the individual molecules in a liquid are close together and occupy perhaps 70 percent of the total space. The attractive forces among the molecules keep the liquid together. Because these forces differ from one substance to another, different liquids behave differently.

2 PRESSURE

Among the most readily measured properties of a gas are its temperature, volume, and pressure. It is not surprising, therefore, that many early studies of gases focused on relationships among these properties. We have already discussed volume and temperature (Section 1.3). Let us now consider the concept of pressure.

In general terms, **pressure** carries with it the idea of a force, something that tends to move something else in a given direction. Pressure is, in fact, the force that acts on a given area ($P = F/A$). Gases exert a pressure on any surface with which they are in contact. For example, the gas in an inflated balloon exerts a pressure on the inside surface of the balloon.

To understand better the concept of pressure and the units in which it is expressed, consider the aluminum cylinder illustrated in Figure 10.1. Because of the gravitational force, this cylinder exerts a downward force upon the surface on which it rests. According to Newton's second law of motion, the force exerted by an object is the product of its mass, m , times its acceleration, a : $F = ma$. The acceleration due to the gravitational force of earth is 9.81 m/s^2 . The mass of the cylinder is 1.06 kg . Thus the force with which the earth attracts it is

$$(1.06 \text{ kg})(9.81 \text{ m/s}^2) = 10.4 \text{ kg}\cdot\text{m/s}^2 = 10.4 \text{ N}$$

A $\text{kg}\cdot\text{m/s}^2$ is the SI unit for force; it is called the **newton**, abbreviated N: $1 \text{ N} = 1 \text{ kg}\cdot\text{m/s}^2$. The cylinder has a cross-sectional area of $7.85 \times$

3 m^2 ; thus the pressure exerted by the cylinder is

$$P = \frac{F}{A} = \frac{10.4 \text{ N}}{7.85 \times 10^{-3} \text{ m}^2} = 1.32 \times 10^3 \text{ N/m}^2$$

N/m^2 is the standard unit of pressure in SI units. It is given the name **pascal** (abbreviated Pa) after Blaise Pascal (1623–1662), a French mathematician and scientist: $1 \text{ Pa} = 1 \text{ N/m}^2$.

Like the aluminum cylinder in our example above, the earth's atmosphere is also attracted toward earth by gravitational attraction. A column of air 1 m^2 in cross section extending through the atmosphere has a mass of roughly 10,000 kg and produces a resultant pressure of about 101 kPa (Figure 10.2):

$$P = \frac{F}{A} = \frac{(10,000 \text{ kg})(9.81 \text{ m/s}^2)}{1 \text{ m}^2} = 1 \times 10^5 \text{ Pa} = 1 \times 10^2 \text{ kPa}$$

Of course, the actual atmospheric pressure at any location depends on altitude and weather conditions.

Atmospheric pressure can be measured by use of a mercury **barometer**, like that illustrated in Figure 10.3. Such a barometer is formed by taking a glass tube more than 76 cm long, which is closed on one end, filling it with mercury and inverting it in a dish of mercury. Care must be taken that no air gets into the tube. When the tube is inverted in this manner, some of the mercury runs out, but a column remains.

The mercury surface outside the tube experiences the full force of the earth's atmosphere over each unit area. However, the atmosphere is not in contact with the mercury surface within the tube. The atmosphere pushes the mercury up the tube until the pressure due to the mass of the mercury column balances the atmospheric pressure. Thus the height of the mercury column fluctuates as the atmospheric pressure fluctuates. The **standard atmospheric pressure**, which corresponds to the typical pressure at sea level, is defined as the pressure sufficient to support

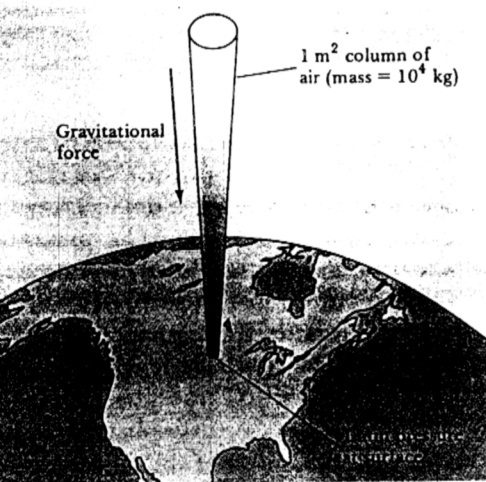


FIGURE 10.2 Illustration of the manner in which earth's atmosphere exerts pressure at the surface of the planet. The mass of a column of atmosphere 1 m^2 in cross-sectional area and extending to the top of the atmosphere exerts a force of $1.01 \times 10^5 \text{ N}$. Thus the pressure is 101 kPa, corresponding to 760 mm Hg.

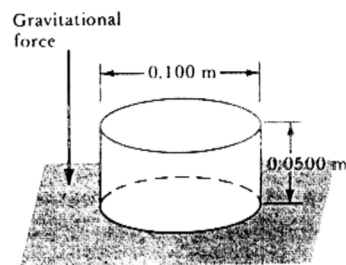
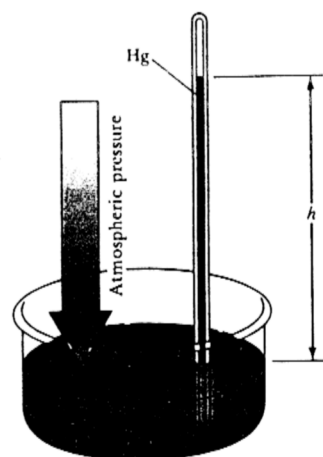


FIGURE 10.1 Aluminum cylinder resting on a flat surface. The diameter of the cylinder is 0.100 m and its height is 0.0500 m. The area of its base is thus $A = \pi r^2 = \pi(0.0500 \text{ m})^2 = 7.85 \times 10^{-3} \text{ m}^2$. Its volume is $V = \pi r^2 h = \pi(0.0500 \text{ m})^2(0.0500 \text{ m}) = 3.93 \times 10^{-4} \text{ m}^3$. The density of aluminum is $2.70 \text{ g/cm}^3 = 2.70 \times 10^3 \text{ kg/m}^3$. The mass of the cylinder is then $M = d \times V = (2.70 \times 10^3 \text{ kg/m}^3) \times (3.93 \times 10^{-4} \text{ m}^3) = 1.06 \text{ kg}$. Calculation of the pressure exerted by this cylinder on the surface upon which it rests is described in the text.

FIGURE 10.3 Mercury barometer invented by Torricelli. The space in the tube above mercury is nearly a vacuum; a negligible amount of mercury vapor occupies it.



a column of mercury 760 mm in height. This pressure, which corresponds to 1.01325×10^5 Pa, is used to define another unit in common use, the atmosphere (abbreviated **atm**):

$$1 \text{ atm} = 760 \text{ mm Hg} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa}$$

One mm Hg pressure is also referred to as a **torr**, after the Italian scientist Evangelista Torricelli (1608–1647), who invented the barometer: $1 \text{ mm Hg} = 1 \text{ torr}$.

In this text we will ordinarily express gas pressure in units of atm or mm Hg. However, you should be able to convert gas pressures from one set of units to another.

EXAMPLE EXERCISE 10.1

Convert 0.605 atm to millimeters of mercury (mm Hg). (b) Convert 3.5×10^{-4} mm Hg to atmospheres.

Solution: (a) Because $1 \text{ atm} = 760 \text{ mm Hg}$, conversion of atm to mm Hg is made by multiplying the number of atm by the factor 760 mm Hg/1 atm:

$$(0.605 \text{ atm}) \left(\frac{760 \text{ mm Hg}}{1 \text{ atm}} \right) = 460 \text{ mm Hg}$$

Notice that the units cancel in the required manner.

(b) To convert from mm Hg to atm, we must multiply by the conversion factor $1 \text{ atm}/760 \text{ mm Hg}$:

$$(3.5 \times 10^{-4} \text{ mm Hg}) \left(\frac{1 \text{ atm}}{760 \text{ mm Hg}} \right) = 4.6 \times 10^{-7} \text{ atm}$$

PRACTICE EXERCISE

What is the pressure, in atmospheres, exerted by a mercury column 1340 cm in height?

Answer: 17.6 atm

EXAMPLE EXERCISE 10.2

Some countries that use the metric system—for example, Canada—express atmospheric pressure in units of kPa. Convert a pressure of 735 mm Hg to kPa.

Solution: From the material discussed earlier we know that $1 \text{ atm} = 101.3 \text{ kPa} = 760 \text{ mm Hg}$. Thus the conversion factor we want is of the form $101.3 \text{ kPa}/760 \text{ mm Hg}$. We use this conversion factor

to convert the pressure given:

$$(735 \text{ mm Hg}) \left(\frac{101.3 \text{ kPa}}{760 \text{ mm Hg}} \right) = 98.0 \text{ kPa}$$

PRACTICE EXERCISE

A pressure of 1.0 kPa corresponds to how many mm Hg?

Answer: 7.5 mm Hg

We can use a device called a **manometer**, whose principle of operation is similar to that of a barometer, to measure the pressures of enclosed gases. Figure 10.4(a) shows a closed-tube manometer, a device normally used to measure pressures below atmospheric pressure. The pressure is just the difference in the heights of the mercury levels in the two arms.

An open-tube manometer, like that pictured in Figure 10.4(b) and (c), is often employed to measure gas pressures that are near atmospheric pressure. The difference in the heights of the mercury levels in the two arms of the manometer relates the gas pressure to atmospheric pressure. If the pressure of the enclosed gas is the same as atmospheric pressure, the levels in the two arms are equal. If the pressure of the enclosed gas is

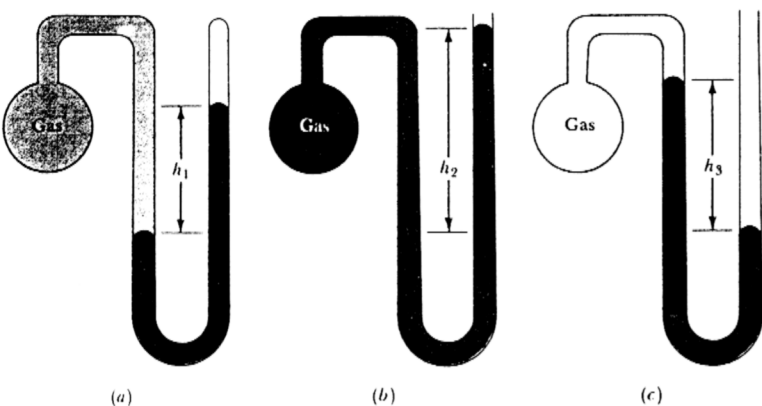


FIGURE 10.4 Closed-end manometer (a) and open-end manometers (b) and (c). In (b) gas pressure exceeds atmospheric pressure; in (c) gas pressure is less than atmospheric pressure.

greater than atmospheric pressure, mercury is forced higher in the arm exposed to the atmosphere, as in Figure 10.4(b). Conversely, if atmospheric pressure exceeds the gas pressure, the mercury is higher in the arm exposed to the gas, as in Figure 10.4(c).

Although mercury is most often used as the liquid in a manometer, other liquids can be employed. For a given pressure difference, the difference in heights of the liquid levels in the two arms of the manometer is inversely proportional to the density of the liquid. That is, the less dense the liquid, the greater the difference in column heights.

SAMPLE EXERCISE 10.3

Consider a container of gas with an attached open-tube manometer. The manometer is not filled with mercury but rather with another nonvolatile liquid, dibutylphthalate. The density of mercury is 13.6 g/mL; that of dibutylphthalate is 1.05 g/mL. If the conditions are as shown in Figure 10.4(b) with $h = 12.2$ cm when atmospheric pressure is 0.964 atm, what is the pressure of the enclosed gas in mm Hg?

Solution: Converting atmospheric pressure to mm Hg, we have

$$(0.964 \text{ atm}) \left(\frac{760 \text{ mm Hg}}{1 \text{ atm}} \right) = 733 \text{ mm Hg}$$

The pressure associated with a 12.2-cm column of

dibutylphthalate is equivalent to a mercury column of

$$(12.2 \text{ cm}) \left(\frac{1.05 \text{ g/mL}}{13.6 \text{ g/mL}} \right) = 0.94 \text{ cm} = 9.4 \text{ mm}$$

If the situation is like that in Figure 10.4(b), the pressure of the enclosed gas exceeds atmospheric pressure by this amount:

$$P = 733 \text{ mm Hg} + 9 \text{ mm Hg} = 742 \text{ mm Hg}$$

PRACTICE EXERCISE

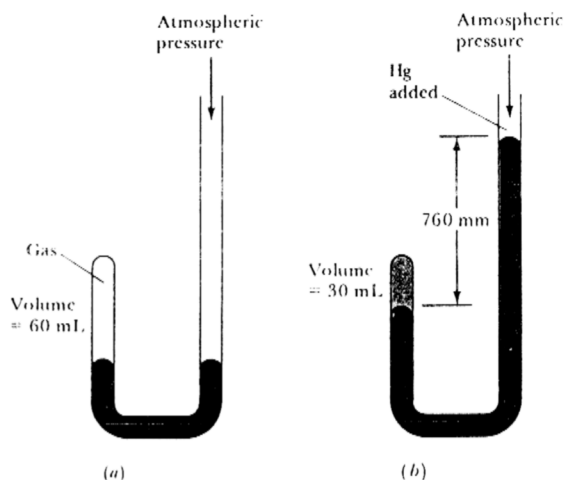
What height of a dibutylphthalate column would be supported by 1 atm pressure?

Answer: 9.84×10^3 mm

Experiments with a large number of gases reveal that the four variables temperature (T), pressure (P), volume (V), and quantity of gas in moles (n) are sufficient to define the state, or condition, of many gaseous substances. The first relationship between these variables was found in 1662 by Robert Boyle (1627–1691). **Boyle's law** states that *the volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the gas pressure*.

10.3 THE GAS LAWS

FIGURE 10.5 An illustration of Boyle's experiment. In (a) the volume of the gas trapped in the J-tube is 60 mL when the gas pressure is 760 mm Hg, corresponding to a balance in the two columns of mercury between the trapped gas and the atmospheric pressure. When additional mercury is added, as shown in (b), the trapped gas is compressed. The volume is 30 mL when its total pressure is 1520 mm Hg, corresponding to atmospheric pressure plus the pressure exerted by the 760-mm column of mercury.



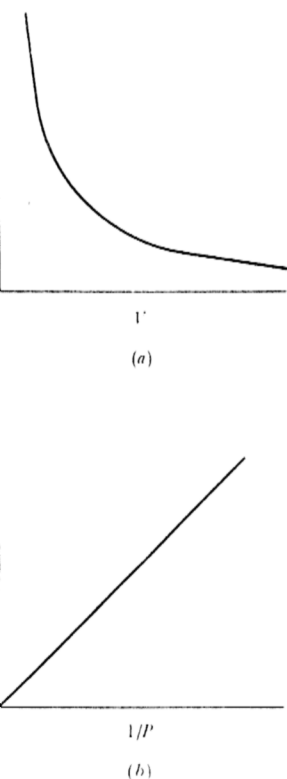
Boyle was interested in determining how the volume of a fixed quantity of gas varies with pressure. To perform his experiments he used a J-shaped tube in which a quantity of gas was trapped behind a column of mercury (see Figure 10.5). Boyle measured changes in the gas volume as he added mercury to the column to increase the pressure. He found that the volume of gas decreased as pressure increased, as shown in Figure 10.5. Doubling the pressure results in the gas volume decreasing to one half its original value. The product of pressure times volume is constant for a given quantity of gas: $PV = c$. The value for c depends on the temperature and amount of gas in the sample. A graph of Boyle's pressure versus volume data is shown in Figure 10.6(a).

Boyle's relationship can be rearranged to yield $V = c/P$. This is the equation for a straight line with slope c and zero intercept (Appendix A.4). Figure 10.6(b) shows a graph of V versus $1/P$ for Boyle's data. Notice that a linear relationship is obtained.

The relationship between gas volume and temperature was discovered in 1787 by Jacques Charles (1746–1823), a French scientist. Charles found that the volume of a fixed quantity of gas at constant pressure increases in a linear fashion with temperature. Some typical data are shown in Figure 10.7. Notice that the extrapolated (extended) line (which is dashed) through the data points passes through -273.15°C . Note also that the gas is predicted to have zero volume at this temperature. Of course, this condition is never fulfilled, because all gases liquefy or solidify before reaching this temperature. In 1848, William Thomson (1824–1907), a British physicist whose title was Lord Kelvin, proposed the idea of an absolute temperature scale, now known as the Kelvin scale, with $-273^\circ\text{C} = 0\text{ K}$. In terms of this scale, **Charles's law** can be stated as follows: *The volume of a fixed amount of gas maintained at constant pressure is directly proportional to absolute temperature.* This relationship can be expressed as $V \propto T$ or as $V = cT$, where the proportionality constant, c , depends on the pressure and amount of gas. Thus doubling absolute temperature, say from 200 K to 400 K, causes the gas volume to double.

The relationship between gas volume and the quantity of gas follows from the work of the French scientist Joseph Louis Gay-Lussac (1778

FIGURE 10.6 Graphs based on Boyle's law: (a) pressure versus volume; (b) volume versus $1/P$.



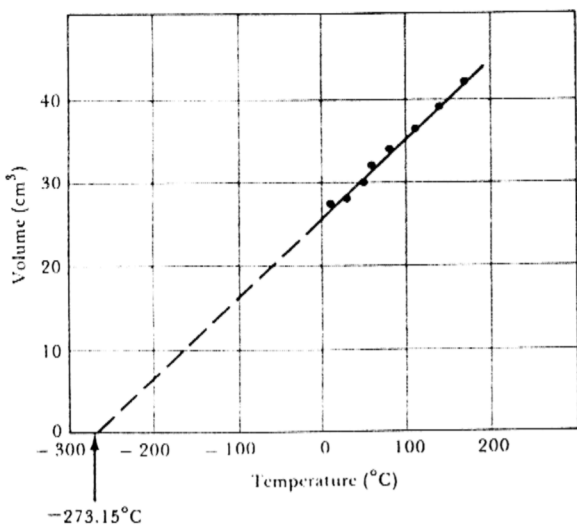


FIGURE 10.7 Volume of an enclosed gas as a function of temperature at constant pressure.

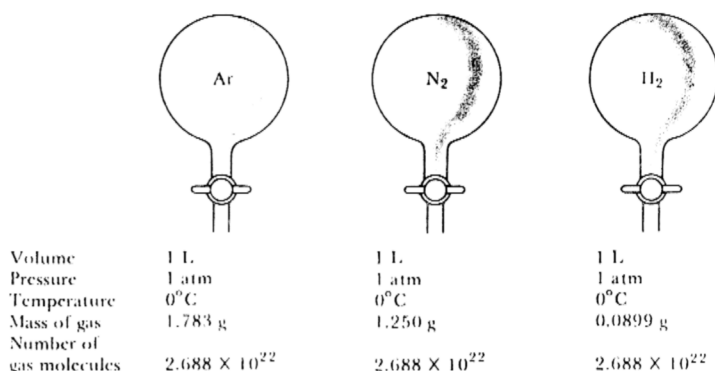
1850) and the Italian scientist Amedeo Avogadro (1776- 1856). Gay-Lussac is one of those extraordinary figures in the early history of modern science who can truly be called an adventurer. He was interested in lighter-than-air balloons and in 1804 made an ascent to 23,000 ft (Figure 10.8). This exploit set the altitude record for several decades, but Gay-Lussac had other reasons for making the flight: He tested the variation of the earth's magnetic field and sampled the composition of the atmosphere as a function of elevation.

To control lighter-than-air balloons properly, Gay-Lussac needed to know more about the properties of gases. He therefore carried out several



FIGURE 10.8 A representation of Gay-Lussac's 1804 balloon ascent, taken from *Appleton's Beginner's Handbook of Chemistry*, a popular nineteenth-century chemistry text.

FIGURE 10.9 Comparison illustrating Avogadro's hypothesis. Note that argon gas consists of argon atoms; we can regard these as one-atom molecules. Each gas has the same volume, temperature, and pressure and thus contains the same number of molecules. Because a molecule of one substance differs in mass from a molecule of another, the masses of gas in the three containers differ.



experiments. The most important of these led to his discovery in 1808 of the law of combining volumes (Section 3.3). Recall that this law states that the volumes of gases that react with one another at the same pressure and temperature are in the ratios of small whole numbers.

Gay-Lussac's work led Avogadro in 1811 to propose what is known as **Avogadro's hypothesis**: *Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.* We saw in Chapter 3 the importance of both Gay-Lussac's and Avogadro's work in setting the stage for a correct appreciation of atomic weights. Let us now consider how their results can help us understand the nature of the gaseous state. Suppose that we have three 1-L bulbs containing Ar, N₂, and H₂, respectively (Figure 10.9), and that each gas is at the same pressure and temperature. According to Avogadro's hypothesis, those bulbs contain *equal numbers of gaseous particles*, although the masses of the substances in the bulbs differ greatly.

Avogadro's law follows from Avogadro's hypothesis: *The volume of a gas maintained at constant temperature and pressure is directly proportional to the quantity of gas: $V \propto n$ or $V = cn$.* Thus doubling the number of moles of gas will cause the volume to double if T and P remain constant.

10.4 THE IDEAL-GAS EQUATION

In the preceding section, we examined three historically important gas laws:

Boyle's law: $V \propto \frac{1}{P}$ (constant n , T)

Charles's law: $V \propto T$ (constant n , P)

Avogadro's law: $V \propto n$ (constant P , T)

We can combine these relationships to make a more general gas law:

$$V \propto \frac{nT}{P}$$

If we call the proportionality constant R , we have

$$V = R \left(\frac{nT}{P} \right)$$

Rearranging, we have this relationship in its more familiar form:

$$PV = nRT \quad [10.1]$$

This equation is known as the **ideal-gas equation**. The term R is called the **gas constant**. The numerical value of R depends on the units chosen for the four variables in the equation. Temperature, T , must be expressed in an absolute temperature scale, normally the Kelvin scale. The quantity of gas, n , is normally expressed in moles. The units chosen for pressure, P , and volume, V , are most often atm and liters, respectively. However, other units could be used. Table 10.2 shows the numerical values for R in a few of the more important units. The last two values given, which include calories and joules among the units, arise because the product $P \times V$ has energy units (Section 4.3).

The ideal-gas equation is called an *equation of state* for a gas because it contains all the variables needed to describe completely the condition, or state, of any gas sample. Knowledge of any three of the variables (temperature, pressure, volume, and number of moles of gas) is enough to specify the system completely, because the fourth variable can be calculated from the other three using the ideal-gas equation.

TABLE 10.2 Numerical values of the gas constant, R , in various units

Units	Numerical value
Liter-atm/K-mol	0.08206
Calories/K-mol	1.987
Joules/K-mol*	8.314
* SI units.	

SAMPLE EXERCISE 10.4

Using the ideal-gas equation, calculate the volume of exactly 1 mol of gas at 0°C (273.15 K) and exactly 1 atm pressure.

Solution: Rearranging Equation 10.1 to solve for V gives

$$V = \frac{nRT}{P}$$

Inserting the numerical values for each term gives

$$\begin{aligned} V &= \frac{(1 \text{ mol})(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273.15 \text{ K})}{1 \text{ atm}} \\ &= 22.41 \text{ L} \end{aligned}$$

PRACTICE EXERCISE

What is the pressure exerted by 2.0 mol of an ideal gas when it occupies a volume of 12.0 L at 100°C (373 K)?

Answer: 5.1 atm

The conditions 0°C and 1 atm are referred to as the **standard temperature and pressure** (abbreviated **STP**). Many properties of gases are tabulated for these conditions. The volume calculated in Sample Exercise 10.4, 22.41 L, is known as the *molar volume* of an ideal gas at STP.

SAMPLE EXERCISE 10.5

A flashbulb of volume 2.6 cm³ contains O₂ gas at a pressure of 2.3 atm and a temperature of 26°C. How many moles of O₂ does the flashbulb contain?

Solution: Because we know volume, temperature, and pressure, the only unknown quantity in the ideal-gas equation (Equation 10.1) is the number of moles, n . Solving Equation 10.1 for n gives

$$n = \frac{PV}{RT}$$

The values of all quantities involved are tabulated and changed to units consistent with those for R :

$$\begin{aligned} P &= 2.3 \text{ atm} \\ V &= 2.6 \text{ cm}^3 = 2.6 \times 10^{-3} \text{ L} \end{aligned}$$

$$n = ?$$

$$R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$$

$$T = 26^\circ\text{C} = 299 \text{ K}$$

us we have

$$\begin{aligned} n &= \frac{(2.3 \text{ atm})(2.6 \times 10^{-3} \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(299 \text{ K})} \\ &= 2.4 \times 10^{-4} \text{ mol} \end{aligned}$$

PRACTICE EXERCISE

We may make an exotic—but quite accurate—thermometer by measuring the volume of a known quantity of gas at a known pressure. If 0.200 mol of helium, He, occupies a volume of 64.0 L at a pressure of 0.150 atm, what is the temperature of the gas?

Answer: 585 K

The fact that Equation 10.1 is called the *ideal-gas* equation correctly suggests that there may be conditions where gases don't exactly obey this equation. For example, we might calculate the quantity of a gas, n , for given conditions of P , V , and T and find it to differ somewhat from the measured quantity under these conditions. Ordinarily, however, the difference between ideal and real behavior is so small that we may ignore it. We will examine deviations from ideal behavior later, in Section 10.9.

Relationship between the Ideal-Gas Equation and the Gas Laws

The simple gas laws, such as Boyle's law, which we discussed in Section 10.3, are special cases of the ideal-gas equation. For example, when the temperature and quantity of gas are held constant, n and T have fixed values. Thus the product nRT is the product of three constants and must itself be a constant:

$$PV = nRT = \text{constant} = c \quad \text{or} \quad PV = c \quad [10.2]$$

Thus we have Boyle's law. Equation 10.2 expresses the fact that even though the individual values of P and V can change, their product PV remains constant.

Similarly, when n and P are constant, the ideal-gas equation gives the following relationship:

$$V = \left(\frac{nR}{P}\right)T = \text{constant} \times T \quad \text{or} \quad \frac{V}{T} = c \quad [10.3]$$

As we have noted earlier, this relationship was first observed by Charles and is known as Charles's law.

EXAMPLE EXERCISE 10.6

The pressure of nitrogen gas in a 12.0-L tank at 27°C is 2300 lb/in.². What volume would the gas in this tank have at 1 atm pressure (14.7 lb/in.²) if the temperature remains unchanged?

Solution: Let us begin by making a table that lists initial and final values for the pressure, temperature, and volume of the gas. (Always convert temperature to the Kelvin scale.)

	Temperature (K)	Pressure (lb/in. ²)	Volume (L)
Initial	300	2300	12.0
Final	300	14.7	?

If the quantity of gas (n) and the temperature (T) do not change, the product PV must remain constant (see Equation 10.2). Thus, if we have two

different sets of conditions for the same quantity of gas at constant temperature, we can write

$$P_1 V_1 = P_2 V_2$$

In our example, P_1 is 2300 lb/in.², P_2 is 14.7 lb/in.², V_1 is 12 L, and V_2 is unknown. Inserting all the known quantities and solving for V_2 , we obtain

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{(2300 \text{ lb/in.}^2)(12.0 \text{ L})}{14.7 \text{ lb/in.}^2} = 1880 \text{ L}$$

You can see from this expression that we have multiplied the initial volume (V_1) by a ratio of pres-

ures (P_1/P_2). You can check that the result makes sense. If the pressure is to decrease in going from the initial state to the final state, volume should increase, as it does.

PRACTICE EXERCISE

A large natural-gas storage tank is arranged so that the pressure is maintained at 2.2 atm. On a cold day in December, when the temperature is -15°C (4°F), the volume of gas in the tank is 28,500 ft³. What is the volume of the same quantity of gas on a warm July day when the temperature is 31°C (88°F)?

Answer: 33,600 ft³

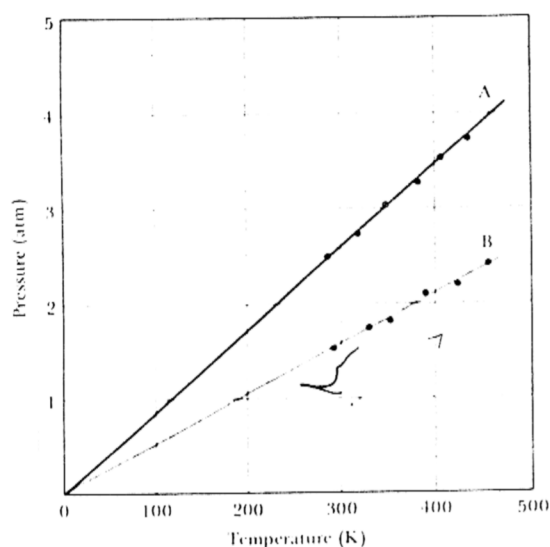


FIGURE 10.10 Variation of gas pressure with temperature under constant-volume conditions.

We know that when a confined gas is heated at constant volume, the pressure increases. For example, a popcorn kernel bursts open under the pressure of steam that forms within the kernel when it is heated in oil. We could make quantitative measurements of the change in pressure of a confined gas by placing the gas in a steel container fitted with a pressure gauge and then varying the temperature. We would find that the pressure increases linearly with absolute temperature, perhaps as shown by the sample data labeled A in Figure 10.10. If the experiment were repeated with a different-sized sample of the same gas, we might obtain the results labeled B in the figure. Note that in both cases the extrapolated pressure at 0 K is zero.

If both n and V in Equation 10.1 are fixed, the pressure varies with temperature as expressed in the equation

$$P = \left(\frac{nR}{V} \right) T = \text{constant} \times T \quad [10.4]$$

Thus the ideal-gas equation predicts a linear relationship between pressure and absolute temperature, extrapolating to zero pressure at 0 K. Again, we must remind ourselves that real gases lose their gaseous properties before absolute zero is reached.

SAMPLE EXERCISE 10.7

Why do the two samples of gas for which data are shown in Figure 10.10 show different linear relationships?

Solution: Inspection of Equation 10.4 shows us that the linear relationship between P and T passes through the origin and has slope nR/V . (You may wish to review linear equations, Appendix A.4.) In our example, both R and V are the same for the two samples, but the number of moles of gas, n , is different.

SAMPLE EXERCISE 10.8

The gas pressure in an aerosol can is 1.5 atm at 25°C. Assuming that the gas inside obeys the ideal-gas equation, what would the pressure be if the can were heated to 450°C?

Solution: Let us proceed, as in Sample Exercise 10.6, by writing down the initial and final conditions (temperature, pressure, and volume) that the problem gives us. (Remember that we must convert temperatures to kelvin.)

	Volume	Pressure (atm)	Temperature (K)
Initial	V_1	1.5	298
Final	V_1	P_2	723

From Equation 10.1 we can see that $P/T = nR/V$. In this problem the quantity of gas (n) and volume (V) are constant. Thus, if we have two different sets of

conditions for the same quantity of gas at constant volume, we have

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Rearranging gives us

$$P_2 = \left(\frac{T_2}{T_1}\right)P_1$$

$$P_2 = (1.5 \text{ atm})\left(\frac{723 \text{ K}}{298 \text{ K}}\right) = 3.6 \text{ atm}$$

It is evident from this example why aerosol cans carry the warning not to incinerate.

PRACTICE EXERCISE

An inflatable raft is filled with gas at a pressure of 800 mm Hg at 16°C. When the raft is left in the sun, the gas heats up to 44°C. Assuming no volume change, what is the gas pressure in the raft under these conditions?

Answer: 878 mm Hg

Combined Gas Law

The three variables P , V , and T may all change for a given sample of gas. Under these circumstances we have, from the ideal gas law,

$$\frac{PV}{T} = nR = \text{constant}$$

Thus as long as the total quantity of gas, n , is constant, PV/T is a constant. If we represent the initial and final conditions of pressure, temper-

ature, and volume by subscripts 1 and 2, respectively, we can write the following expression:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad [10.5]$$

SAMPLE EXERCISE 10.9

A quantity of helium gas occupies a volume of 16.5 L at 78°C and 45.6 atm. What is its volume at STP?

Solution: It is best to begin problems of this sort by writing down all we know of the initial and final values of temperature, pressure, and volume. (Remember that you must always convert temperatures to the absolute temperature scale, K.)

	Pressure (atm)	Volume (L)	Temperature (K)
Initial	45.6	16.5	351
Final	1 (exactly)	V_2	273

Putting the quantities into Equation 10.5, we have

$$V_2 = \left(\frac{45.6 \text{ atm}}{1 \text{ atm}} \right) \left(\frac{273 \text{ K}}{351 \text{ K}} \right) (16.5 \text{ L}) = 585 \text{ L}$$

Does this answer make sense? Notice that the initial volume, 16.5 L, is multiplied by a ratio of temperatures and by a ratio of pressures. The temperature of the gas decreases; this should cause a decrease in volume. Thus the temperature ratio should be less than 1. The decrease in pressure from 45.6 atm to 1 atm will cause expansion of the gas. Thus the pressure ratio should be greater than 1. Our intuitive sense of what should happen is in accord with the expression we have used. It is always a good idea in checking your work to ask whether the answer makes sense.

PRACTICE EXERCISE

A pocket of gas is discovered in a deep drilling operation. The gas has a temperature of 480°C and is at a pressure of 12.8 atm. Assume ideal behavior. What volume of the gas is required to provide 18.0 L at the surface at 1.00 atm and 22°C?

Answer: 3.59 L

The pressure of a gas under conditions of constant volume and temperature is directly proportional to the number of moles of gas:

$$P = \left(\frac{RT}{V} \right) n = \text{constant} \times n \quad [10.6]$$

Suppose that the gas with which we are concerned is not made up of a single kind of gas particle but is rather a mixture of two or more different substances. We expect that the total pressure exerted by the gas mixture is the sum of pressures due to the individual components. Each of the individual components, if present alone under the same temperature and volume conditions as the mixture, would exert a pressure that we term the **partial pressure**. John Dalton was the first to observe that the *total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone*:

$$P_t = P_1 + P_2 + P_3 + \cdots \quad [10.7]$$

Each of the gases obeys the ideal-gas equation. Thus we can write

10.5 DALTON'S LAW OF PARTIAL PRESSURES

$$P_1 = n_1 \left(\frac{RT}{V} \right), \quad P_2 = n_2 \left(\frac{RT}{V} \right), \quad P_3 = n_3 \left(\frac{RT}{V} \right), \quad \text{etc.}$$

All of the gases experience the same temperature and volume. Therefore, by substituting into Equation 10.7, we obtain

$$P_t = \frac{RT}{V} (n_1 + n_2 + n_3 + \cdots) \quad [10.8]$$

That is, the total pressure at constant temperature and volume is determined by the total number of moles of gas present, whether that total represents just one substance or a mixture.

EXAMPLE EXERCISE 10.10

From data gathered by *Voyager 1*, scientists estimate that methane, CH_4 , constitutes 6.0 mol percent of the atmosphere of Titan, Saturn's largest moon. The total pressure at the surface of Titan is 1.6 earth atmospheres. Calculate the partial pressure of methane, in earth units.

Solution: Let's first calculate the total pressure on Titan in units of mm Hg:

$$P_t = (1.6 \text{ atm}) \left(\frac{760 \text{ mm Hg}}{1 \text{ atm}} \right) = 1216 \text{ mm Hg}$$

The total pressure of the atmosphere on Titan is the sum of the pressures exerted by each of the components. The pressure exerted by each component is proportional to its mol fraction, f , in the gas mixture. We can see this by using Equation 10.8 to set up the following ratio:

$$\begin{aligned} \frac{P_1}{P_t} &= \frac{(RT/V)n_1}{(RT/V)(n_1 + n_2 + n_3 + \cdots)} \\ &= \frac{n_1}{n_1 + n_2 + n_3 + \cdots} = f_1 \end{aligned}$$

Thus $P_1 = P_t f_1$ and $P_t = P_t f_1 + P_t f_2 + P_t f_3 + \cdots$. The sum of the mol fractions must, of course, equal 1.

$$f_1 + f_2 + f_3 + \cdots = 1$$

Mol percent is just mol fraction times 100. Thus for CH_4 we have $f = 0.060$.

$$\begin{aligned} P_{\text{CH}_4} &= 1216 \times 0.060 = 73 \text{ mm Hg} \\ &= 0.096 \text{ earth atm} \end{aligned}$$

PRACTICE EXERCISE

If a 0.20-L sample of O_2 at 0°C and 1.0 atm pressure and a 0.10-L sample of N_2 at 0°C and 2.0 atm pressure are both placed in a 0.40-L container at 0°C , what is the total pressure in the container?

Answer: 1.0 atm

EXAMPLE EXERCISE 10.11

What pressure, in atm, is exerted by a mixture of 10.0 g of H_2 and 8.00 g of N_2 at 273 K in a 10.0-L vessel?

Solution: The pressure depends on the total moles of gas (Equation 10.8). Calculating the moles of H_2 and N_2 , we have

$$n_{\text{H}_2} = (2.00 \text{ g H}_2) \left(\frac{1 \text{ mol H}_2}{2.02 \text{ g H}_2} \right) = 0.990 \text{ mol H}_2$$

$$n_{\text{N}_2} = (8.00 \text{ g N}_2) \left(\frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2} \right) = 0.286 \text{ mol N}_2$$

Using Equation 10.8 gives us

$$\begin{aligned} P_t &= \frac{RT}{V} (n_{\text{H}_2} + n_{\text{N}_2}) \\ &= \frac{(0.0821 \text{ L-atm/mol-K})(273 \text{ K})}{10.0 \text{ L}} \\ &\quad \times (0.990 \text{ mol} + 0.286 \text{ mol}) \\ &= 2.86 \text{ atm} \end{aligned}$$

This total pressure is the sum of the partial pressures of H_2 and N_2 .

PRACTICE EXERCISE

A study of the effects of certain gases on plant growth requires a synthetic atmosphere in a 120-L space at 745 mm Hg and 295 K. This atmosphere is to be composed of 1.5 mol percent CO_2 , 18.0 mol percent O_2 , and 80.5 mol percent Ar. Calculate the partial

pressure of each gas in the mixture, and compute the volume of each gas, measured at atmospheric pressure and 295 K, required to form the 120 L of mixture.

Answers: CO_2 , 11.2 mm Hg, 1.76 L; O_2 , 134 mm Hg, 21.2 L; Ar, 600 mm Hg, 94.7 L

We can make many applications of the ideal-gas equation in measuring and calculating gas density. Density has the units of mass per unit volume. We can arrange the gas equation to obtain

$$\frac{n}{V} = \frac{P}{RT}$$

Now n/V has the units of moles per liter. Suppose that we multiply both sides of this equation by molecular weight (\mathcal{M}), which is the number of grams in 1 mol of a substance:

$$\frac{n \cdot \mathcal{M}}{V} = \frac{P \cdot \mathcal{M}}{RT} \quad [10.9]$$

But the product of the quantities n/V and \mathcal{M} equals density, because the units multiply as follows:

$$\frac{\text{Moles}}{\text{Liter}} \times \frac{\text{grams}}{\text{mole}} = \frac{\text{grams}}{\text{liter}}$$

Thus the density of the gas is given by the expression on the right in Equation 10.9:

$$d = \frac{P \cdot \mathcal{M}}{RT} \quad [10.10]$$

or, rearranging, we obtain

$$\mathcal{M} = \frac{dRT}{P} \quad [10.11]$$

SAMPLE EXERCISE 10.12

What is the density of carbon dioxide gas at 745 mm Hg and 65°C?

Solution: The molecular weight of carbon dioxide, CO_2 , is $12.0 + (2)(16.0) = 44.0$ g/mol. If we are to use 0.0821 L·atm/K·mol for R , we must convert pressure to atmospheres. Using Equation 10.10, we have then

$$\begin{aligned} d &= \frac{\left(\frac{745}{760} \text{ atm}\right) (44.0 \text{ g/mol})}{(0.0821 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(338 \text{ K})} \\ &= 1.55 \text{ g/L} \end{aligned}$$

The problem can be turned around a bit to determine the molecular weight of a gas from its density, as shown in Sample Exercise 10.13.

10.6 MOLECULAR WEIGHTS AND GAS DENSITIES

PRACTICE EXERCISE

The mean molecular weight of the atmosphere of Titan at the surface is 28.6 amu. The surface temperature is 95 K, and the pressure is 1.6 earth atm.

Assuming ideal behavior, calculate the density of Titan's atmosphere.

Answer: 5.9 g/L

SAMPLE EXERCISE 10.13

A large flask fitted with a stopcock is evacuated and weighed; its mass is found to be 134.567 g. It is then filled to a pressure of 735 mm Hg at 31°C with a gas of unknown molecular weight and then reweighed; its mass is 137.456 g. The flask is then filled with water and again weighed; its mass is now 1067.9 g. Assuming that the ideal-gas equation applies, what is the molecular weight of the unknown gas? (The density of water at 31°C is 0.997 g/cm³.)

Solution: First we must determine the volume of the flask. This is given by the difference in weights of the empty flask and the flask filled with water, divided by the density of water at 31°C, which is 0.997 g/cm³:

$$V = \frac{1067.9 \text{ g} - 134.6 \text{ g}}{0.997 \text{ g/cm}^3} = 936 \text{ cm}^3$$

Because the mass of the gas is 137.456 g – 134.567 g =

2.889 g, its density is 2.889 g/0.936 L = 3.087 g/L. Using Equation 10.11, we have

$$\begin{aligned} M &= \frac{dRT}{P} \\ &= \frac{(3.087 \text{ g/L})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(304 \text{ K})}{(735/760) \text{ atm}} \\ &= 79.7 \text{ g/mol} \end{aligned}$$

PRACTICE EXERCISE

One method for accurately determining the molecular weight of a gas is to measure its density as a function of pressure. The graph of the quantity d/P against pressure is extrapolated to zero pressure to obtain a limiting value. In one set of experiments a certain gas was shown to have a limiting value d/P of 2.86 at 0°C. Calculate the molecular weight.

Answer: 64.1 g/mol

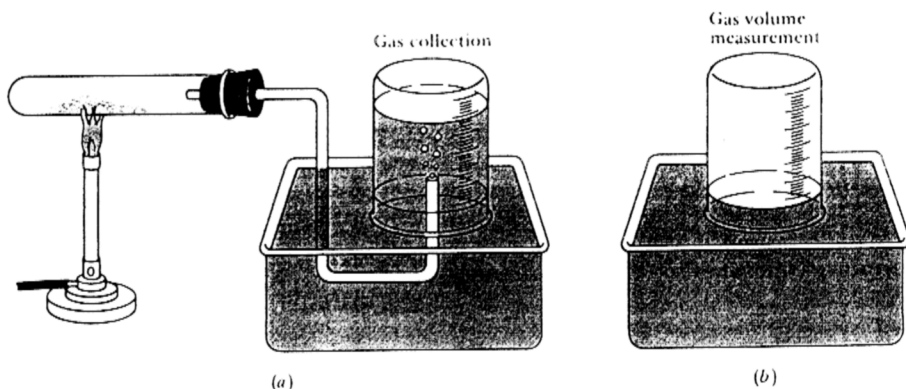
10.7 QUANTITIES OF GASES INVOLVED IN CHEMICAL REACTIONS

A knowledge of the properties of gases is important for chemists because gases are so often reactants or products in chemical reactions. We are thus often faced with calculating the volumes of gases required as reactants or yielded as products, or with calculating pressure changes in reaction vessels of fixed volume. In this context the gas laws are a part of chemical stoichiometry, a subject discussed in Chapter 3.

An experiment that often comes up in the course of laboratory work is the determination of the number of moles of gas collected from a chemical reaction. Sometimes this gas is collected over water. For example, solid potassium chlorate (KClO₃) may be decomposed by heating it in a

FIGURE 10.11

(a) Collection of gas over water. (b) When the gas has been collected, the bottle is raised or lowered to equalize pressures inside and outside before measuring the volume of the gas collected.



test tube in an arrangement shown in Figure 10.11. The balanced equation for the reaction is



The oxygen gas is collected in a bottle that is initially filled with water and inverted in a water pan.

The volume of gas collected is measured by raising or lowering the bottle as necessary until the water levels inside and outside the bottle are the same. When this condition is met, the pressure inside the bottle is equal to the atmospheric pressure outside. The total pressure inside is the sum of the pressure of gas collected and the pressure of water vapor in equilibrium with liquid water:

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{H}_2\text{O}} \quad [10.12]$$

The pressure exerted by water vapor, $P_{\text{H}_2\text{O}}$, at various temperatures is shown in Appendix C.

SAMPLE EXERCISE 10.14

Suppose that 0.200 L of oxygen gas is collected over water, as shown in Figure 10.10. The temperature of the water and gas is 26°C, and the atmospheric pressure is 750 mm Hg. **(a)** How many moles of O_2 are collected? **(b)** What volume would the O_2 gas collected occupy when dry, at the same temperature and pressure?

Solution: **(a)** The pressure of O_2 gas in the vessel is the difference between the total pressure, 750 mm Hg, and the vapor pressure of water at 26°C, 25 mm (Appendix C):

$$P_{\text{O}_2} = 750 - 25 = 725 \text{ mm Hg}$$

Solving the ideal-gas equation for n , we have

$$\begin{aligned} n &= \frac{PV}{RT} = \frac{\left(\frac{725}{760} \text{ atm}\right)(0.200 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(299 \text{ K})} \\ &= 7.77 \times 10^{-3} \text{ mol} \end{aligned}$$

(b) Suppose that we dried the water from the gas sample while maintaining the same total pressure. The O_2 pressure after drying would be 750 mm Hg. The corrected O_2 volume would thus be less for the dry gas, because its partial pressure is greater than for the wet gas:

$$V_{\text{O}_2} = (0.200 \text{ L}) \left(\frac{725 \text{ mm Hg}}{750 \text{ mm Hg}} \right) = 0.193 \text{ L}$$

PRACTICE EXERCISE

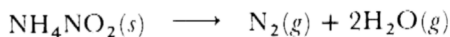
Assume that 260 mL of dry nitrogen at 20°C and 760 mm Hg are bubbled through water and stored in an inverted beaker, as shown in Figure 10.10(b). What is the volume of the stored gas at a pressure of 740 mm Hg and a temperature of 26°C?

Answer: 282 mL.

We often collect a gas over water in an experiment to determine the amount of gaseous product. To compute the number of moles of gas collected, a correction must be applied for the partial pressure of water vapor in the collection bottle. We shall go through a complete analysis of such an experiment in Sample Exercise 10.15 to show how the stoichiometric relationships come together.

SAMPLE EXERCISE 10.15

A 2.55-g sample of ammonium nitrite (NH_4NO_2) is heated in a test tube, as shown in Figure 10.11. The ammonium nitrite is expected to decompose according to the equation



If it does decompose in this way, what volume of N_2 will be collected in the flask? The water and gas

temperature are 26°C, and the barometric pressure is 745 mm Hg.

Solution: We begin by calculating the number of moles of N₂ gas formed:

$$5 \text{ g NH}_4\text{NO}_2 \left(\frac{1 \text{ mol NH}_4\text{NO}_2}{64.0 \text{ g NH}_4\text{NO}_2} \right) \times \left(\frac{1 \text{ mol N}_2}{1 \text{ mol NH}_4\text{NO}_2} \right) = 0.0398 \text{ mol N}_2$$

To predict the volume of N₂ gas that is to be collected, we might be tempted simply to calculate the volume that would be occupied by 0.0398 mol of N₂ at 745 mm Hg. But we must also take into account the partial pressure of water vapor at 26°C, because the gas within the bottle is saturated with water vapor. From a table of water-vapor pressure versus temperature (see Appendix C), we can determine that the vapor pressure of water at 26°C is 25 mm Hg. The pressure of nitrogen gas in the flask when the water levels inside and out have been equalized is thus 745 – 25 = 720 mm Hg. We must calculate the predicted volume of gas using this pres-

sure (720/760 = 0.947 atm). (Pressure must be expressed in atm when we employ the value for the gas constant, *R*, expressed in L-atm/mol-K.) Rearranging Equation 10.2, we obtain

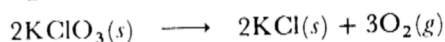
$$V = \frac{nRT}{P}$$

Inserting all known quantities in correct units, we obtain

$$V = \frac{(0.0398 \text{ mol})(0.0821 \text{ L-atm/K-mol})(299 \text{ K})}{0.947 \text{ atm}} = 1.03 \text{ L}$$

PRACTICE EXERCISE

A 1.60-g sample of KClO₃ is heated to produce O₂ according to the equation



Assume complete decomposition and ideal-gas behavior. What volume of O₂ collects over water at 26°C, 740 mm Hg pressure?

Answer: 511 mL

10.8 KINETIC-MOLECULAR THEORY

The ideal-gas equation describes *how* gases behave, but it doesn't explain *why* they behave as they do. For example, why does a gas expand when heated at constant pressure, or why does its pressure increase when the gas is compressed at constant temperature? To understand the physical properties of gases, we need a model that helps us picture what happens to gas particles as experimental conditions such as pressure or temperature change. Such a model, known as the **kinetic-molecular theory**, was developed over a period of about 100 years, culminating in 1857 when Rudolf Clausius (1822–1888) published a complete and satisfactory form of the theory.

The kinetic-molecular theory is summarized by the following statements:

1. Gases consist of large numbers of molecules that are in continuous, random motion. (The word "molecule" is used here to designate the smallest particle of any gas; some gases, such as the noble gases, consist of uncombined atoms.)
2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained.
3. Attractive and repulsive forces between gas molecules are negligible.
4. Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant. In other words, the collisions are perfectly elastic.
5. The average kinetic energy of the molecules is proportional to absolute temperature. At any given temperature the molecules of all gases have the same average kinetic energy.

The kinetic-molecular theory gives us an understanding of both pressure and temperature at the molecular level. The pressure of a gas is caused by collisions of the molecules with the walls of the container; it is determined both by the frequency of collisions per unit area and by the impulse imparted per collision (that is, by how frequently and by how “hard” the molecules strike the walls). The absolute temperature of a substance is a measure of the average kinetic energy of its molecules; absolute zero is the temperature at which the average kinetic energy of the molecules would be zero.

The idea that average kinetic energy and temperature are proportional provides a particularly important insight into matter. Let’s consider this idea further. The molecules of a gas move at varying speeds. At one instant some of them are moving rapidly, others slowly. Figure 10.11 illustrates the distribution of molecular speeds within nitrogen gas at 0°C (red line) and at 100°C (blue line). Notice that at higher temperatures the distribution curve has shifted toward higher speeds.

Figure 10.12 also shows the value of the **root-mean-square** (rms) speed, u , of the molecules at each temperature. This quantity is the square root of the average squared speeds of the molecules. The rms speed is not the same as the average speed. The difference between the two, however, is so small that for most purposes they can be considered equal.* The rms speed is important because the average kinetic energy of the gas molecules, ϵ , is related directly to u^2 :

$$\epsilon = \frac{1}{2}mu^2 \tag{10.13}$$

where m is the mass of the molecule. When the temperature of a gas increases, the average kinetic energy of the gas molecules increases

* To illustrate the difference between rms speed and average speed, suppose that we have four objects with speeds of 4.0, 6.0, 10.0, and 12.0 m/s. Their average speed is $\frac{1}{4}(4.0 + 6.0 + 10.0 + 12.0) = 8.0$ m/s. However, the rms speed, u , is

$$\sqrt{\frac{1}{4}(4.0^2 + 6.0^2 + 10.0^2 + 12.0^2)} = \sqrt{74.0} = 8.6 \text{ m/s}$$

In general, the average speed equals $0.921 \times u$. Thus the average speed is directly proportional to the rms speed, and the two are in fact nearly equal.

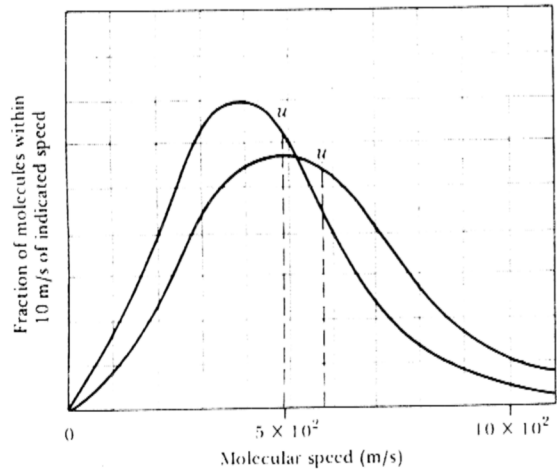


FIGURE 10.12
Distribution of molecular speeds for nitrogen at 0°C (red line) and 100°C (blue line).

proportionally. The relationship between average kinetic energy and temperature that is obtained from kinetic-molecular theory is given in Equation 10.14, where R is the ideal gas constant, N is Avogadro's number, and T is the absolute temperature:

$$\epsilon = \frac{1}{2} mu^2 = \frac{3RT}{2N} \quad [10.14]$$

AMPLE EXERCISE 10.16

What is the average kinetic energy of a nitrogen molecule at 27°C?

olution: Using Equation 10.14, we have

$$\begin{aligned} \epsilon &= \frac{3RT}{2N} = \frac{3(8.314 \text{ J/K}\cdot\text{mol})(300 \text{ K})}{2(6.022 \times 10^{23}/\text{mol})} \\ &= 6.21 \times 10^{-21} \text{ J} \end{aligned}$$

The average kinetic energy of a gas molecule at 27°C will have this same value for any other gaseous substance.

PRACTICE EXERCISE

Without repeating the foregoing calculation, give the average kinetic energy of gaseous argon atoms at 600 K.

Answer: $1.24 \times 10^{-20} \text{ J}$

The empirical observations of gas properties as expressed in the various gas laws are readily understood in terms of the kinetic-molecular theory. The following examples are illustrative.

1. *Effect of a volume increase at constant temperature:* The fact that temperature remains constant means that the average kinetic energy of the gas molecules remains unchanged. This in turn means that the rms speed of the molecules, u , is unchanged. However, if the volume is increased, the molecules must move a longer distance between collisions. Consequently, there are fewer collisions per unit time with the container walls, and pressure decreases. Thus the model accounts in a simple way for Boyle's law.
2. *Effect of a temperature increase at constant volume:* An increase in temperature means an increase in the average kinetic energy of the molecules, and thus an increase in u . If there is no change in volume, there will be more collisions with the walls per unit time. Furthermore, the change in momentum in each collision increases (the molecules strike the walls harder). Hence the model explains the observed pressure increase.

AMPLE EXERCISE 10.17

A sample of O_2 gas initially at STP is transferred from a 2-L container to a 1-L container at constant temperature. What effect does this change have on (a) the average kinetic energy of O_2 molecules; (b) the average speed of the O_2 molecules; (c) the total number of collisions of O_2 molecules with the container walls in a unit time; (d) the number of collisions of O_2 molecules with a unit area of container wall in a unit time?

olution: (a) The average kinetic energy of O_2 molecules is determined only by temperature. The

average kinetic energy is not changed by the compression of O_2 from 2 L to 1 L at constant temperature.

(b) If the average kinetic energy of the O_2 molecules doesn't change, neither does u (see Equation 10.14). Both the average and rms speeds remain constant.

(c) The total number of collisions with the container walls in a unit time must increase, because the molecules are moving within a smaller volume but with the same average speed as before. Under these conditions they must encounter a wall more frequently.

(d) The number of collisions with a unit area of wall increases, because the total number of collisions with

the walls is higher and the area of wall is smaller than before.

PRACTICE EXERCISE

How is the rms speed of N_2 molecules in a gas sample

changed by (a) an increase in temperature; (b) an increase in volume of sample; (c) mixing with an Ar sample at the same temperature?

Answers: (a) increases; (b) no effect; (c) no effect

Beginning with the postulates of the kinetic-molecular theory it is possible to derive the ideal-gas equation. Rather than proceed through a derivation, let's consider in somewhat qualitative terms how the ideal-gas equation might follow. As we have seen (Section 10.2), pressure is force per unit area. The total force of the molecular collisions on the walls, and hence the pressure produced by these collisions, depend both on how strongly the molecules strike the walls (impulse imparted per collision) and on the rate at which these collisions occur:

$$P \propto \text{impulse imparted per collision} \times \text{rate of collisions} \quad [10.15]$$

The impulse imparted by a collision of a molecule with a wall depends on the momentum of the molecule; that is, it depends on the product of its mass and speed, mu . The rate of collisions is proportional to both the number of molecules per unit volume, n/V , and their speed, u . If there are more molecules in a container, there will be more frequent collisions with the container walls. As the molecular speed increases or the volume of the container decreases, the time required for molecules to traverse the distance from one wall to another is reduced, and the molecules collide more frequently with the walls. Thus we have

$$P \propto mu \times \frac{n}{V} \times u \propto \frac{nm u^2}{V} \quad [10.16]$$

From Equation 10.14 we have that $mu^2 \propto T$. (This proportionality also follows from the basic idea that the average kinetic energy is proportional to temperature.) Making this substitution into Equation 10.16, we have

$$P \propto \frac{n(mu^2)}{V} \propto \frac{nT}{V} \quad [10.17]$$

Let us now convert the proportionality sign to an equal sign by expressing n as the number of moles of gas; we then insert a proportionality constant R , the molar gas constant:

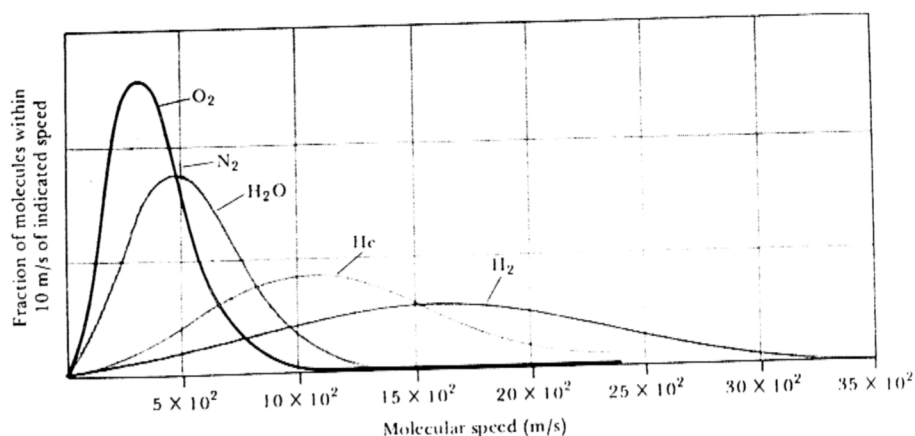
$$P = \frac{nRT}{V} \quad [10.18]$$

This expression, of course, is the familiar ideal-gas equation.

The Ideal-Gas Equation

FIGURE 10.13

Distribution of molecular speeds for different gases at 0°C.



10.9 MOLECULAR EFFUSION AND DIFFUSION; GRAHAM'S LAW

We have already made reference to the fact that the molecules of a gas do not all move at the same speed. Instead, the molecules are distributed over a range of speeds, as shown for nitrogen at two different temperatures in Figure 10.12. The distribution of molecular speeds depends on the mass of the gas molecules and on temperature. The average kinetic energy of the molecules in any gas is determined only by temperature; thus the quantity $\frac{1}{2}mu^2$, which is kinetic energy, must have the same value for two gases at the same temperature, though their masses may differ. This in turn means that molecules of larger mass must have smaller average speeds. From the kinetic-molecular theory it can be shown that the rms speed, u , is given by Equation 10.19. Note that u is proportional to the square root of the absolute temperature and *inversely* proportional to the square root of the molecular weight, \mathcal{M} :

$$u = \sqrt{\frac{3RT}{\mathcal{M}}} \quad [10.19]$$

This relationship tells us that at any given temperature lighter molecules have higher rms speeds. In fact, the entire distribution of molecular speeds is skewed to higher values for gases of lower molecular weights, as shown for several gases in Figure 10.13.

The dependence of molecular speeds on mass has several interesting consequences. For example, the rate at which a gas is able to escape through a tiny hole, as when a gas escapes through a hole in a balloon, depends on the molecular mass of the gas. This process is known as **effusion**. Effusion is related to, but is not quite the same as, **diffusion**. The latter term refers to the spread of one substance throughout a space, or throughout a second substance. For example, the molecules of a perfume diffuse through a room.

Graham's Law of Effusion

In about 1830, Thomas Graham discovered that the effusion rates of gases are inversely related to the square roots of their molecular weights. Assume that we have two gases at the same initial pressure contained in identical containers, each with an identical pinhole in one wall. Let the rate of effusion be called r . **Graham's law** states that

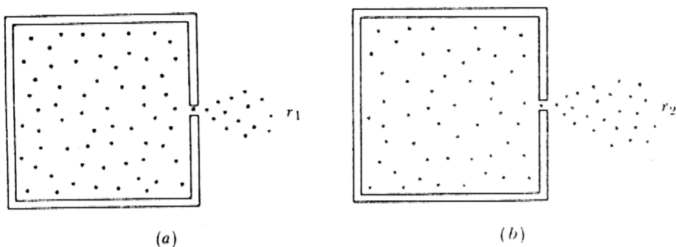


FIGURE 10.14 Effusion of gases through a pinhole leak. In this illustration the molecular weight of gas molecules in (a) is higher than in (b). The rate of effusion r_1 , from box (a), is slower than r_2 , from box (b), in accordance with Equation 10.20.

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad [10.20]$$

Equation 10.20 compares the *rates* of effusion of two different gases; the lighter gas effuses more rapidly (see Figure 10.14).

Graham's law follows from our previous discussion if we assume that the rate of effusion is proportional to the rms speed of the molecules. Because R and T are constant, we have from Equation 10.19:

$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \frac{\sqrt{3RT/\mathcal{M}_1}}{\sqrt{3RT/\mathcal{M}_2}} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad [10.21]$$

SAMPLE EXERCISE 10.18

(a) Calculate the rms speed, in m/s, of an O_2 molecule at 27°C . (b) If an unknown gas effuses at a rate that is only 0.468 times that of O_2 at the same temperature, what is the molecular weight of the unknown gas?

Solution: (a) Using Equation 10.19, we have

$$\begin{aligned} u &= \sqrt{\frac{3RT}{\mathcal{M}}} \\ &= \sqrt{\frac{(3)(8.314 \text{ J/K}\cdot\text{mol})(300 \text{ K})}{32.0 \text{ g/mol}}} \times \frac{10^3 \text{ g}}{1 \text{ kg}} \\ &= 484 \text{ m/s} \end{aligned}$$

The factor 10^3 g/kg is needed to convert mass to SI units consistent with the rest of the units in the problem. Recall (Section 4.1) that $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$.

(b) Using Equation 10.20, we have

$$\frac{r_x}{r_{\text{O}_2}} = \sqrt{\frac{\mathcal{M}_{\text{O}_2}}{\mathcal{M}_x}}$$

Thus

$$\frac{r_x}{r_{\text{O}_2}} = 0.468 = \sqrt{\frac{32.0 \text{ g/mol}}{x}}$$

Solving for x yields

$$\begin{aligned} \frac{32.0 \text{ g/mol}}{x} &= (0.468)^2 = 0.219 \\ x &= \frac{32.0 \text{ g/mol}}{0.219} = 146 \text{ g/mol} \end{aligned}$$

PRACTICE EXERCISE

Calculate the ratio of effusion rates of N_2 and O_2 , $r_{\text{N}_2}/r_{\text{O}_2}$.

Answer: $r_{\text{N}_2}/r_{\text{O}_2} = 1.07$

The explanation for diffusive flow is more complicated than that for effusion, because diffusion, unlike effusion, involves the effects of molecular collisions. Nevertheless, the dependence of diffusion rate on molecular mass is also given by Equation 10.20: The ratio of the rates of diffusion of two gases under identical experimental conditions is inversely proportional to the square root of the ratio of molecular masses.

That both effusion and diffusion rates are greater for lighter gases has many interesting applications. One popular lecture demonstration,

FIGURE 10.15 Hydrogen-fountain demonstration of the greater rate of diffusion of hydrogen compared with diffusion of air. A container filled with H_2 gas is placed over the porous cup containing air. Hydrogen diffuses into the cup more rapidly than the molecules of air diffuse outward. As a result the pressure inside the vessel increases and water is pushed out of the tube, which is open to the outside. (Donald Clegg and Roxy Wilson)

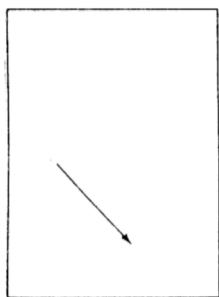


FIGURE 10.16 Schematic illustration of the diffusion of a gas molecule. For the sake of clarity all the other gas molecules in the container are not shown. The path of the molecule of interest begins at the dot. Each short segment of the line represents travel between collisions. The path traveled by the molecule is often described as a “random walk.” The red arrow indicates the net distance traveled by the molecule.

Mean Free Path and Thermal Conductivity

the hydrogen fountain, is illustrated in Figure 10.15. The diffusion of hydrogen through the walls of the porous cup is faster than diffusion of atmospheric gases out of the cup through the wall. Excess pressure builds up in the enclosure, forcing water through the tube.

The effort during World War II to develop the atomic bomb necessitated separating the relatively low-abundance uranium isotope ^{235}U (0.7 percent) from the much more abundant ^{238}U (99.3 percent). This was done by converting the uranium into a volatile compound, UF_6 , which boils at 56°C . The gaseous UF_6 was allowed to diffuse from one chamber into a second through a porous barrier. Because of the slight difference in molecular weights, the relative rates of passage through the barrier for $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ are not exactly the same. The ratio of diffusion rates is given by the square root of the ratio of molecular weights, Equation 10.20:

$$\frac{r_{235}}{r_{238}} = \sqrt{\frac{352.04}{349.03}} = 1.0043$$

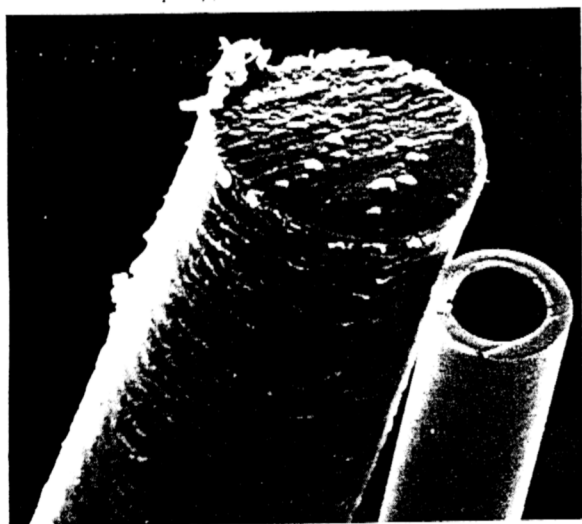
Thus the gas initially appearing on the opposite side of the barrier would be very slightly enriched in the lighter molecule. The diffusion process was repeated thousands of times, leading to a nearly complete separation of the two nuclides of uranium.

We can see from the horizontal scale of Figure 10.13 that the speeds of molecules are quite high. The average speed of N_2 at room temperature, 515 m/s, corresponds to 1850 km/hr, or 1150 mi/hr. Yet we know that if a vial of perfume is opened at one end of a room, some time elapses, perhaps a few minutes, before the odor is detected at the other end. The diffusion of gases is much slower than molecular speeds because of molecular collisions. These collisions occur quite frequently for a gas at atmospheric pressure—about 10^{10} times per second for each molecule. The paths of the gas molecules are therefore interrupted very often. Diffusion of gas molecules, depicted in Figure 10.16, thus consists of a random mo-

The rate of diffusion of a gas through a porous medium is not always determined solely by the molecular mass of the gas molecules. Even weak interactions between the molecules of gas and the molecules of the porous medium will affect the rate. Attractive intermolecular interactions, which we will discuss in more detail in the next chapter, slow the rate at which a gas molecule passes through the narrow passages of the porous medium.

The medium's molecules may attract one substance in a mixture more than another. Thus the rates of diffusion of a mixture's components through a medium are not uniform. Dow Chemical Company has recently developed a method of separating gaseous mixtures into their components by using the difference in the rates at which molecules pass through a porous membrane. Figure 10.17 shows Dow's tiny hollow fiber made of polyolefin, an organic polymer. The fiber is smaller than a human hair. Its walls are permeable to the passage of N_2 and O_2 . However, O_2 and water vapor diffuse through the fiber walls considerably more readily than does N_2 . To take advantage of this property, thousands of the fibers are formed into bundles.

FIGURE 10.17 Polyolefin fibers used to carry out gas separations. The solid cylinder is human hair. Gases such as nitrogen and oxygen differ significantly in the rate at which they pass through the wall of the hollow fiber. This difference in permeability provides the basis for gas separations, as shown in Figure 10.18. (Dow Chemical Company)



Compressed air is introduced around the outside of the bundles, as shown schematically in Figure 10.18. The gas stream taken from inside the fibers is selectively enriched in O_2 . The gas stream on the outside of the fibers is correspondingly enriched in N_2 .

The Dow process, called the Generon system, makes available a stream of gas containing O_2 up to 35 percent by volume (air is 20 percent O_2 by volume) at substantially less cost than previous methods of O_2 enrichment. The oxygen-rich gas stream can be used both to speed up many chemical oxidation processes and to replace other, more expensive chemicals—such as hydrogen peroxide—that might otherwise be used to bring about oxidation.

FIGURE 10.18 A diagrammatic illustration of gas separation that takes advantage of the difference in ease of diffusion of gases through polyolefin fiber walls. The gas that enters under pressure (feed air) passes from the distribution core all around the outsides of the tiny hollow fibers. Oxygen and water vapor preferentially pass through the fiber walls, are collected at the ends of the fibers, and pass out as oxygen-enriched air. The gas that has not passed through the fibers exits the assembly as nitrogen-enriched gas. (Dow Chemical Company)

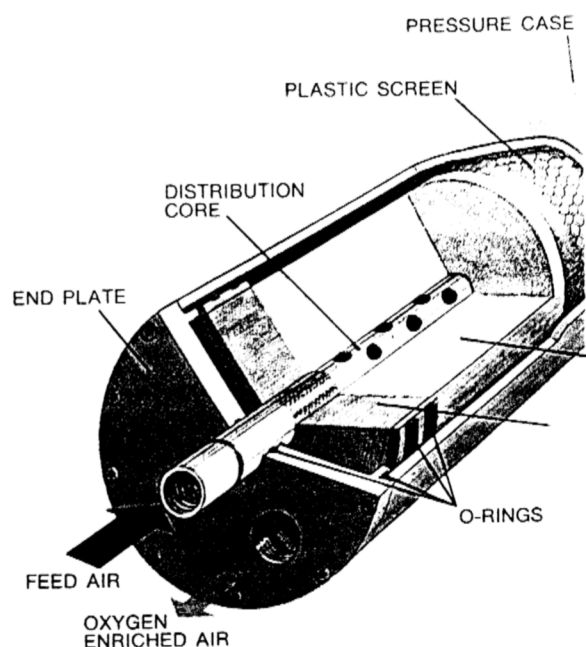


TABLE 10.3 Mean free paths for several gases at 0°C, 1 atm

Gas	Mean free path (nm)
Carbon dioxide	39.7
Carbon monoxide	58.1
Nitrogen	60.0
Argon	63.5
Oxygen	64.7
Hydrogen	112.3
Helium	179.8

tion, first in one direction, then in another, at one instant at high speed, the next at low speed.

The average distance traveled by a molecule between collisions is called the **mean free path**. This distance depends on the effective radius of the molecules, because larger molecules are more likely to undergo a collision. It depends also on the number of molecules in a unit volume—the larger the number of molecules per unit volume, the more likely is collision. Table 10.3 lists some values of experimentally determined mean free paths for several gases at STP. As you can see from these values, the molecules of a gas at STP do not travel very far before undergoing collision. By contrast, at an elevation of about 100 km in the earth's atmosphere, the mean free paths of nitrogen and oxygen molecules are on the order of 10 cm, more than a million times longer than at the earth's surface.

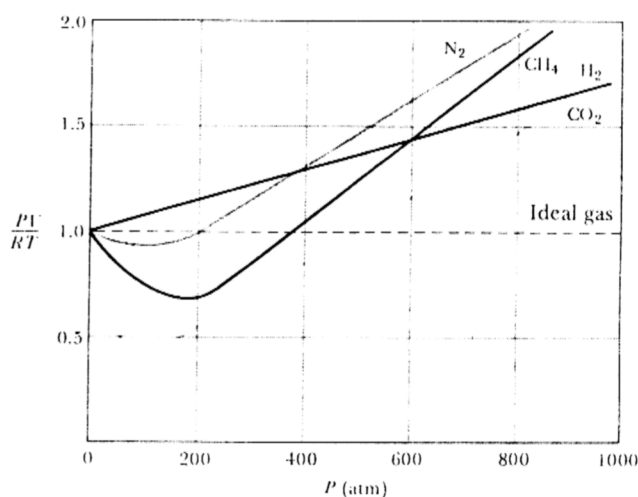
The **thermal conductivity** of a gas—the rate at which heat energy can be transferred through the gas—depends on the average speed of its molecules and on their mean free path. Those gases whose molecules move fastest and with the largest mean free path have the highest thermal conductivities. Among the gases in Table 10.3, carbon dioxide has the highest molecular weight and thus has the lowest average speed per molecule for a given temperature. It also has the shortest mean free path of the gases listed. We can conclude that carbon dioxide has the lowest thermal conductivity of any of the gases in the table. Helium has the highest thermal conductivity.

10.10 NONIDEAL GASES: DEPARTURES FROM THE IDEAL-GAS EQUATION

Although the ideal-gas equation is a very useful description of gases, all real gases fail to obey the relationship to a greater or lesser degree. The extent to which a real gas departs from ideal behavior may be seen by slightly rearranging the ideal-gas equation:

$$\frac{PV}{RT} = n \quad [10.22]$$

FIGURE 10.19 PV/RT versus pressure for several gases at 300 K. The data for CO_2 pertain to a temperature of 313 K, because CO_2 liquefies under high pressure at 300 K.



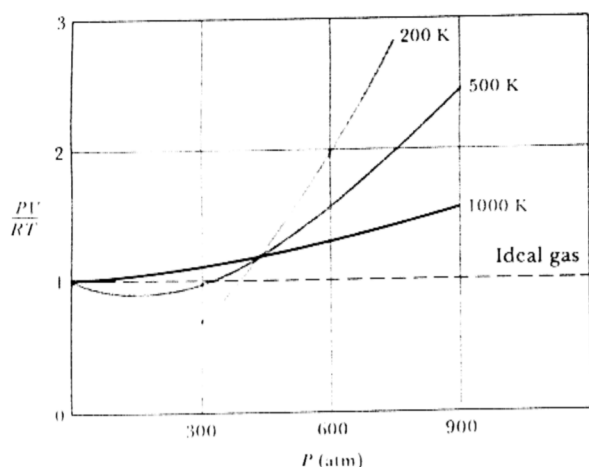


FIGURE 10.20 PV/RT for nitrogen gas at three different temperatures. As temperature increases, the gas more closely approaches ideal behavior.

For a mole of ideal gas ($n = 1$) the quantity PV/RT equals 1 at all pressures. Figure 10.19 shows the quantity PV/RT plotted as a function of pressure for a few gaseous substances, compared with the expected behavior of an ideal gas. Clearly, real gases are simply not ideal. However, the pressures shown are very high; at more ordinary pressures, below 10 atm, the deviations from ideal behavior are not so large, and the ideal-gas equation can be used without serious error.

Thus we see that deviations from ideal behavior tend to be larger at higher pressures than at lower ones. Temperature also has an effect.

Figure 10.20 shows graphs of PV/RT for N_2 at three different temperatures. As temperature increases, the properties of the gas more nearly approach the ideal gas behavior. In general, gases tend to show significant deviations from ideal behavior at temperatures near their liquefaction points; that is, the deviations increase as temperature decreases, becoming significant near the temperature at which the gas is converted into a liquid.

We can understand these pressure and temperature effects on non-ideality by considering two factors that are considered negligible in the kinetic-molecular theory: (1) the molecules of a gas possess finite volumes, and (2) at short distances of approach they exert attractive forces upon one another.

When gases are contained at relatively low pressure, say 1 atm, the volume of the space they occupy is very large in comparison with the volumes of the gas molecules themselves. At increasingly high pressures, however, the volume taken up by the molecules becomes a larger fraction of the total. This effect is illustrated in Figure 10.21. Thus, at pressures of several hundred atmospheres, the free volume in which the gas molecules can move is considerably smaller than the volume of the container. As a result, the value of V that *should* be used in the product PV is smaller than the volume of the container. Hence, when we use the container volume in the ideal-gas equation we obtain a product PV that is larger than it should be. The data for H_2 in Figure 10.19 illustrate this situation. Notice that PV/RT increases steadily with increasing pressure. This is due entirely to the finite volume of the H_2 molecules.

FIGURE 10.21 Illustration of the effect of the finite volume of gas molecules on the properties of a real gas at high pressure. In (a), at low pressure, the volume of the gas molecules is small compared with the container volume. In (b), at high pressure, the volume of the gas molecules themselves is a large fraction of the total space available.

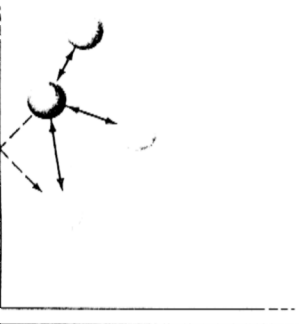
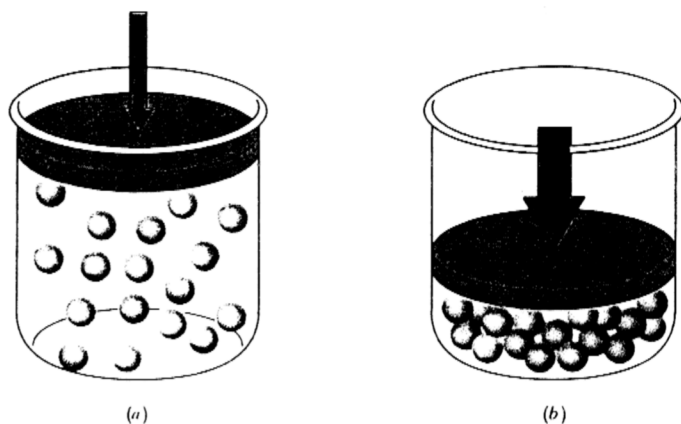


FIGURE 10.22 Effect of attractive intermolecular forces on the pressure exerted by a gas on its container walls. The pressure is determined by the change in momentum when molecules strike the container wall. The molecule that is about to strike the wall in the figure experiences attractive forces from nearby molecules, and its impact on the wall is thereby lessened. The attractive forces become noticeable only under high-pressure conditions, when the average distance between molecules is small.

The attractive forces between molecules come into play at short distances, when the molecules undergo collisions or pass very close to one another. Because of these attractive forces, the impact of a given molecule with the wall of the container is lessened. If we could stop the action in a gas, we might see something like that illustrated in Figure 10.22. The molecule about to make contact with the wall experiences the attractive forces of nearby adjacent molecules, and thus the change of momentum when it hits the wall is lessened. As a result the quantity PV/RT is less than we would expect on the basis of the ideal-gas equation. The effect of such intermolecular attractive forces becomes more significant as the pressure of the gas increases and the average distance between gas molecules correspondingly decreases.

From the data illustrated in Figure 10.19 we can guess that the attractive forces between molecules are greatest for CO_2 among the sample gases. The product PV shows a substantial negative departure from the ideal-gas relationship over a wide range of pressure. The attractive forces are less important for CH_4 , and less important still for N_2 . Because there is very little attractive interaction between H_2 molecules, the quantity PV/RT for this gas is continuously larger than that expected for an ideal gas.

Temperature determines how effective attractive forces between gas molecules are. As the gas is cooled, the motional energies decrease while intermolecular attractions remain constant. In a sense, cooling a gas deprives molecules of the energy they need to overcome their mutual attractive influence.

The effects of temperature shown in Figure 10.20 illustrate this point very well. Notice that as temperature increases, the negative departure of PV/RT from the ideal-gas behavior disappears. What difference remains at high temperature stems mainly from the effect of volume.

the van der Waals equation

Engineers and scientists who work with gases at high pressures often cannot use the ideal-gas equation to predict the pressure-volume properties of gas, because departures from the ideal-gas behavior are too large. Various equations of state have been developed to predict more realistically the pressure-volume behavior of real gases. These equations, though more realistic, are also considerably more complicated than the simple

TABLE 10.4 Van der Waals constants
for gas molecules

Substance	a (L ² -atm/mol ²)	b (L/mol)
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
CO ₂	3.59	0.0427
CH ₄	2.25	0.0428
CCl ₄	20.4	0.1383

ideal-gas equation (Equation 10.1). Equation 10.23 shows the **van der Waals equation**, named after Johannes van der Waals, who presented it in 1873.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad [10.23]$$

This equation differs from the ideal-gas equation by the presence of two correction terms; one corrects the volume, the other modifies the pressure. The term nb in the expression $(V - nb)$ is a correction for the finite volume of the gas molecules; the van der Waals constant b , different for each gas, has units of liters/mole. It is a measure of the actual volume occupied by the gas molecules. Values of b for several gases are listed in Table 10.4. Note that b increases with an increase in mass of the molecule or in the complexity of its structure.

The correction to the pressure takes account of the intermolecular attractions between molecules. Notice that it consists of the constant a , different for each gas, times the quantity $(n/V)^2$. The units of n/V are moles/liter. This quantity is squared because the number of molecular-molecular interactions, as illustrated in Figure 10.22, is proportional to the square of the number of molecules per unit volume. Values of the van der Waals constant a are listed in Table 10.4 for several gases. Notice that a , like b , increases with an increase in molecular weight and with an increase in complexity of molecular structure.

To get some feeling for the magnitudes of the departures from ideal behavior, let's calculate these departures for CO₂ at STP.

SAMPLE EXERCISE 10.19

Calculate the correction terms to pressure and volume for CO₂ at STP, using the data in Table 10.4. Compare these terms with the ideal-gas values for P and V .

Solution: From Equation 10.23 we see that the volume correction term is given by nb . Since $n = 1$, nb equals 0.0427 L, which is to be compared with

22.4 L, the molar volume of an ideal gas at STP. The correction to volume is thus

$$\frac{0.0427}{22.4} \times 100 = 0.191\% \approx 0.2\%$$

The correction to pressure is given by an^2/V^2 . Inserting the value of a from Table 10.4, $n = 1$, and $V = 22.4$ L, we obtain

$$\frac{an^2}{V^2} = \frac{\left(\frac{3.59 \text{ L}^2\text{-atm}}{\text{mol}^2}\right) 1 \text{ mol}^2}{(22.4 \text{ L})^2} = 0.007 \text{ atm}$$

The required correction to pressure is thus $0.007 \times 100 = 0.7\%$. We conclude that the ideal-gas law is

obeyed by CO_2 at STP conditions to within 1 percent.

PRACTICE EXERCISE

Which of the following molecules would you expect to have the largest values for a and b : CO_2 , Ar, SO_2 ?

Answer: SO_2



FOR REVIEW

SUMMARY

Many substances are capable of existing in any one of the three states of matter—solid, liquid, or gas. This chapter has been concerned with the gaseous state. To describe the state or condition of a gas, we must specify four variables: pressure, temperature, volume, and quantity of gas. Volume is usually measured in liters (L), and temperature in the Kelvin scale. Pressure is defined as the force per unit area. It is expressed in SI units as pascals, Pa ($1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg/m}\cdot\text{s}^2$), or more commonly in millimeters of mercury (mm Hg) or in atmospheres (atm). One **standard atmosphere** pressure equals 101.325 kPa, or 760 mm Hg. A **barometer** is often used to measure the atmospheric pressure. A **manometer** can be used to measure the pressure of enclosed gases.

The **ideal-gas equation**, $PV = nRT$, is the equation of state for an ideal gas. Most gases at pressures of about 1 atm and temperatures of 300 K and above obey the ideal-gas equation reasonably well. We can use the ideal-gas equation to calculate variations in one variable when one or more of the others are changed. For example, for a constant quantity of gas at constant temperature, the volume of the gas is inversely proportional to the pressure (**Boyle's law**). Similarly, for a constant quantity of gas at constant pressure, the volume of a gas is directly proportional to temperature (**Charles's law**). **Avogadro's law** states that at constant temperature and pressure the volume of a gas is directly proportional to the quantity of gas, that is, to the number of gas molecules. In gas mixtures, the total pressure is the sum of the partial pressures that each gas would exert if it were present alone under the same conditions (**Dalton's law of partial pressures**). In all applications of the ideal-gas equation we must remember to convert temperatures to the absolute temperature scale, Kelvin.

We use the ideal-gas equation to solve problems involving gases as reactants or products in chemical reactions. From the gas density, d , under given conditions of pressure and temperature, we may calculate the molecular weight of the gas: $M = dRT/P$. In calculating the quantity of gas collected over water, correction must be made for the partial pressure of water vapor in the container.

The **kinetic-molecular theory** accounts for the properties of an ideal gas in terms of a set of assumptions about the nature of gases. Briefly these assumptions are that molecules are in ceaseless, chaotic motion; that the volume of gas molecules is negligible in relation to the volume of their container; that the gas molecules have no attractive forces for one another; that the average kinetic energy does not change; and that the average kinetic energy of the gas molecules is proportional to absolute temperature.

The molecules of a gas do not all have the same kinetic energy at a given instant. Their speeds are distributed over a wide range; the distribution varies with the molecular weight of the gas and with temperature. The root-mean-square (rms) speed, u , varies in proportion to the square root of absolute temperature and inversely with the square root of molecular weight: $u = (3RT/M)^{1/2}$. It follows that the rate at which a gas escapes (effuses) through a tiny hole is inversely proportional to the square root of its molecular weight (**Graham's law**). Molecules in a real gas possess finite volume and thus undergo frequent collisions with one another. Because of these collisions, the mean free path—the mean distance traveled between collisions—is short. Collisions between molecules limit the rate at which a gas molecule can diffuse through the space occupied by other gas molecules and influence the thermal conductivity of a gas.

Departures from ideal behavior increase in mag-

nitude as pressure increases and as temperature decreases. The extent of nonideality of a real gas can be seen by examining the quantity PV/RT for 1 mol of the gas as a function of pressure; for an ideal gas this quantity is exactly 1 at all pressures. Real gases depart from the ideal behavior because the molecules possess finite volume (leads to $PV/RT > 1$), or be-

cause the molecules experience attractive forces for one another upon collision (leads to $PV/RT < 1$). The van der Waals equation is an equation of state for gases that modifies the ideal-gas equation to more faithfully represent the pressure and volume behavior of real gases.

LEARNING GOALS

Having read and studied this chapter, you should be able to:

1. Describe the general characteristics of gases as compared with other states of matter, and list the ways in which gases are distinctly different.
2. List the variables that are required to define the state of a gas.
3. Define atmosphere, millimeters of mercury, and kilopascals, the most important units in which pressure is expressed. You should also understand the principle of operation of a barometer and manometer.
4. Explain the way in which pressure, volume, and temperature are related in the ideal-gas equation. That is, you should remember $PV = nRT$ and be able to solve for one unknown given the other quantities.
5. Solve problems involving changes in the condition or state of a gas. You should be able to explain how one variable is affected by a change in another, when the other variables are maintained constant.
6. Calculate the quantity of a gas under a given set of conditions that is required as a reactant or formed as product in a chemical reaction.
7. Correct for the effects of water vapor pressure in calculating the quantity of a gas collected over water.
8. Explain the concept of gas density and describe how it is related to temperature, pressure, and molecular weight.
9. Calculate molecular weight, given gas density under defined conditions of temperature and pressure. You should also be able to calculate gas density under stated conditions, knowing molecular weight.
10. List and explain the assumptions on which the kinetic theory of gases is based.
11. Describe graphically how gas molecules are distributed over a range of speeds and how that distribution changes with temperature.
12. Describe how the relative rates of diffusion or effusion of two gases depend on their relative molecular weights (Graham's law).
13. Explain the concept of mean free path and how it relates to the rates of diffusion of molecules in the gas state and to thermal conductivity.
14. Explain the origin of deviations shown by real gases from the relationship $PV/RT = 1$ for 1 mole of ideal gas.
15. List the two major factors responsible for deviations of gases from ideal behavior.
16. Explain the origins of the correction terms to a and b that appear in the van der Waals equation of state for a gas.

KEY TERMS

Among the more important terms and expressions used for the first time in this chapter are the following:

According to **Avogadro's hypothesis** (Section 10.3), equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. Avogadro's law follows from this: At constant temperature and pressure, the volume of a gas is directly proportional to the quantity of gas.

A **barometer** (Section 10.2) is a device for measuring atmospheric pressure in terms of the height of a liquid column sustained by that pressure.

According to **Boyle's law** (Section 10.3), at constant temperature, the product of the volume and pressure of a given amount of gas is a constant.

According to **Charles's law** (Section 10.3), at constant pressure, the volume of a given quantity of

gas is proportional to absolute temperature.

Dalton's law of partial pressures (Section 10.5) states that the total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone.

Diffusion (Section 10.9) refers to the rate at which a substance speeds into and throughout a space. Thus a gas might diffuse throughout a room, or atmospheric oxygen might diffuse through the waters of a lake.

Effusion refers to the rate at which a gas escapes through an orifice or hole.

The **gas constant**, R (Section 10.4), is the constant of proportionality in the ideal-gas equation.

Graham's law (Section 10.9) states that the relative rate of effusion of two gases is inversely proportional to the square root of the ratio of their molecular weights.

The **ideal-gas equation** (Section 10.4) is an equation of state for gases that embodies Boyle's law, Charles's law, and Avogadro's hypothesis in the form $PV = nRT$.

The **kinetic-molecular theory of gases** (Section 10.8) consists of a set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation.

A **manometer** (Section 10.2) is a device for measuring gas pressure by measuring the difference in heights of the mercury columns in a U-tube.

The **mean free path** (Section 10.9) in a gas sample is the average distance traveled by a gas molecule between collisions.

Pressure (Section 10.2) is a measure of the force exerted on a unit area. In work with gases, pressure is most commonly expressed in units of atmospheres (atm) or of millimeters of mercury (mm Hg)—760 mm Hg = 1 atm; in SI units, pressure is expressed in pascal (Pa).

The **root-mean-square (rms) speed**, u (Section 10.8), of a gas is given by the square root of the average of the squared speeds of the gas molecules.

The **standard atmospheric pressure** (Section 10.2) is defined as 760 mm Hg or, in SI units, 101.325 kPa.

Standard temperature and pressure (STP) (Section 10.4), 0°C and 1 atm pressure, are frequently used reference conditions for a gas.

The **thermal conductivity** of a gas (Section 10.9) is a measure of the rate at which heat energy can be transferred through it.

The **torr** (Section 10.2) is a unit of pressure (1 torr = 1 mm Hg).

The **van der Waals equation** (Section 10.10) is an equation of state for real gases containing terms that correct for the existence of attractive forces between molecules and for their finite volumes.

EXERCISES

Introduction; Pressure

10.1 Compressibility, which is the change in volume of a substance in response to a change in pressure, is much greater for gases than for liquids or solids. Explain.

10.2 The mass of Venus is 0.82 times that of the earth; the atmospheric pressure at the surface of Venus is about 90 earth atmospheres. The atmosphere is 96 percent CO_2 , and the surface temperature is over 700 K. Given these facts, explain how it is possible for the atmospheric pressure on Venus to be so much greater than that on the earth.

10.3 Perform the following conversions: (a) 0.910 atm to kPa; (b) 730 mm Hg to kPa; (c) 29.86 in Hg to atm; (d) 1.06 atm to mm Hg.

10.4 Perform the following conversions: (a) 607 mm Hg to atm; (b) 636 kPa to atm; (c) 615 mm Hg to torr; (d) 0.393 atm to mm Hg.

10.5 (a) If the weather report for Montreal states that the temperature is 11°C and the barometric pressure is 98.8 kPa, what is the temperature in degrees Fahrenheit

and pressure in inches of mercury? (b) If the weather in Chicago is reported to be 89°F with a barometric pressure of 29.32 in. Hg, what is the temperature in degrees Celsius and pressure in kilopascals?

10.6 (a) On Titan, the largest moon of Saturn, atmospheric pressure is 1.6 earth atmospheres. What is the Titan atmosphere in kPa? (b) On Venus the surface atmospheric pressure is about 90 earth atmospheres. What is the Venusian atmosphere in kPa?

10.7 (a) A plastic bucket has a flat bottom of area $4.6 \times 10^3 \text{ cm}^2$. When filled with water it weighs 12.8 kg. What pressure, in pascals, does the bucket exert on a flat surface on which it rests? (b) A phonograph stylus resting on a record has an effective mass of 2.5 g. The area of the stylus making contact with the record averages $2.7 \times 10^{-4} \text{ mm}^2$. What pressure, in pascals, does the stylus exert on the record?

10.8 (a) Calculate the pressure in pascals exerted on a tabletop by an iron cube (density 7.87 g/cm^3) measuring 8.0 cm on an edge. (b) Suppose that a woman weighing 130 lb and wearing high-heeled shoes momentarily places all her weight on the heel of one foot. If the area of the

heel is 0.50 in.^2 , calculate the pressure exerted on the underlying surface, in atm and in kPa.

- 10.9** An open-tube manometer containing mercury is connected to a container of gas. What is the pressure of the enclosed gas, in mm Hg, in each of the following situations? **(a)** The mercury in the arm attached to the gas is 6.5 cm higher than the one open to the atmosphere; atmospheric pressure is 0.960 atm. **(b)** The mercury in the arm attached to the gas is 4.8 cm lower than the one open to the atmosphere; atmospheric pressure is 1.02 atm.
- 10.10** Suppose that the mercury in the barometer of Figure 10.2 were replaced by a liquid metal alloy with a density of 6.28 g/cm^3 . The density of mercury is 13.6 g/cm^3 . What height of column of liquid alloy would be supported by 1.00 atm pressure?

The Gas Laws

- 10.11** What are the variables that make up the equation of state for an ideal gas? How many of these variables need to be specified to completely determine the state of an ideal gas?
- 10.12** Which of the variables in the ideal-gas equation is *not* a variable in **(a)** Boyle's law; **(b)** Charles's law; **(c)** Avogadro's law.
- 10.13** Write an equation or proportionality expression that expresses each of the following statements: **(a)** for a given quantity of gas at constant temperature, the product of pressure times volume is constant; **(b)** for a given temperature and pressure, the volume of a gas is proportional to the number of moles of gas present; **(c)** for a given volume and quantity of gas, the pressure is proportional to the absolute temperature; **(d)** for a given quantity of gas, the product of pressure and volume is proportional to absolute temperature.
- 10.14** Which of the following statements, if any, are false? Correct any false statements. **(a)** At constant temperature and volume, pressure is inversely proportional to the number of moles of gas. **(b)** At constant volume the pressure of a given amount of gas increases in proportion to the absolute temperature. **(c)** An increase in volume of a given quantity of gas at constant pressure arises from an increase in absolute temperature. **(d)** At constant volume the pressure of a gas is inversely proportional to temperature.
- 10.15** Assuming a gas to behave ideally, calculate **(a)** its pressure if $7.25 \times 10^{-2} \text{ mol}$ occupies 184 mL at -14°C ; **(b)** its volume if 3.28 mol has a pressure of 0.688 atm and a temperature of 27°C ; **(c)** the quantity of gas, in moles, if 2.00 L at -25°C has a pressure of 2.48 atm; **(d)** the temperature, in kelvin, at which $9.87 \times 10^{-2} \text{ mol}$ occupies 164 mL at 722 mm Hg.
- 10.16** For an ideal gas, calculate **(a)** the pressure of the gas if 1.34 mol occupies 3.28 L at 28°C ; **(b)** the volume occupied by 0.150 mol at -14°C and 60.0 atm; **(c)** the number of moles in 1.50 L at 37°C and 725 mm Hg;

(d) the temperature at which 0.270 mol occupies 15.0 L at 2.54 atm.

- 10.17** Many gases are shipped in high-pressure containers. If a steel tank whose volume is 42.0 L contains O_2 gas at a total pressure of 18,000 kPa at 23°C , what mass of oxygen does it contain? What volume would the gas occupy at STP?
- 10.18** Fluorine gas, which is dangerously reactive, is shipped in steel cylinders of 30.0 L capacity, at a pressure of 160 lb/in.² at 26°C . What mass of F_2 is contained in such a tank?

The Ideal-Gas Equation

- 10.19** Starting with the ideal-gas equation, derive Avogadro's law.
- 10.20** Starting with the ideal-gas equation, show that at constant volume the pressure of a given quantity of gas is proportional to absolute temperature.
- 10.21** **(a)** A fixed quantity of gas is compressed at constant temperature from a volume of 368 mL to 108 mL. If the initial pressure was 522 mm Hg, what is the final pressure? **(b)** A fixed quantity of gas is allowed to expand at constant temperature from 2.45 L to 3.40 L. If the initial pressure was 1.05 atm, what is the final pressure? **(c)** What is the final volume of a gas if a 1.20-L sample is heated from 32°C to 450°C at constant pressure?
- 10.22** **(a)** A gas originally at 15°C and having a volume of 182 mL is reduced in volume to 82.0 mL while its pressure is held constant. What is its final temperature? **(b)** A gas exerts a pressure of 187 kPa at 27°C . The temperature is increased to 108°C with no volume change. What is the gas pressure at the higher temperature? **(c)** The helium in a 0.75-L tank at 105 atm, 27°C , is expanded to 54.5 L, -10°C . What is the final pressure of the gas?
- 10.23** At 36°C and 1.00 atm pressure, a gas occupies a volume of 0.600 L. How many liters will it occupy **(a)** at 0°C and 0.205 atm; **(b)** at STP?
- 10.24** Chlorine is widely used to purify municipal water supplies and to treat swimming pool waters. Suppose that the volume of a particular sample of Cl_2 is 6.18 L at 740 torr and 33°C . **(a)** What volume will the Cl_2 occupy at 107°C and 680 torr? **(b)** What volume will the Cl_2 occupy at STP? **(c)** At what temperature will the volume be 3.00 L if the pressure is $8.00 \times 10^2 \text{ mm Hg}$? **(d)** At what pressure will the volume be 5.00 L if the temperature is 67°C ?
- 10.25** In an experiment recently reported in the scientific literature, male cockroaches were made to run at different speeds on a miniature treadmill while their oxygen consumption was measured. The average cockroach running at 0.08 km/hr consumed 0.8 mL of O_2 at 1 atm pressure

and 24°C per gram of insect weight per hour. (a) On this basis, how many moles of O_2 would be consumed in 1 hr by a 5.2-g cockroach moving at this speed? (b) This same cockroach is caught by a child and placed in a 1-qt fruit jar with a tight lid. Assuming the same level of continuous activity as in the research, will the cockroach consume more than 20 percent of the available O_2 in a 48-hr period? (Air is 21 mol percent O_2 .)

10.26 After the large eruption of Mount St. Helens in 1980, gas samples from the volcano were taken by sampling the downwind gas plume. The unfiltered gas samples were passed over a gold-coated wire coil to absorb mercury, Hg, present in the gas. The mercury was recovered from the coil by heating it, then analyzed. In one particular set of experiments, scientists found a mercury vapor level of 1800 ng of Hg per cubic meter in the plume, at a gas temperature of 10°C . Calculate (a) the partial pressure of Hg vapor in the plume; (b) the number of Hg atoms per m^3 in the gas; (c) the total mass of Hg emitted per day by the volcano if the daily plume volume is 1600 km^3 .

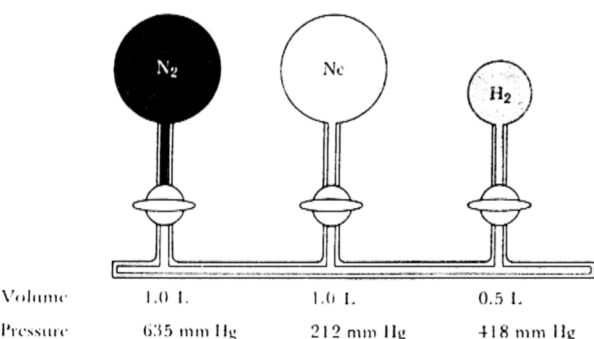
Dalton's Law of Partial Pressures

10.27 Consider a mixture composed of 2.10 g of H_2 , 65.2 g of O_2 , and 12.5 g of Ar confined to a volume of 4.10 m^3 at 88°C . Calculate (a) the partial pressure of H_2 ; (b) the total pressure in the vessel.

10.28 A mixture of cyclopropane gas, C_3H_6 , and oxygen, O_2 , is widely used as an anesthetic. (a) How many moles of each gas are present in a 16.5-L container at 23°C if the partial pressure of cyclopropane is 140 mm Hg and that of oxygen is 605 mm Hg? (b) What is the partial pressure of C_3H_6 in a mixture of 3.00 g of C_3H_6 and 20.0 g of O_2 if the total pressure in the vessel is 850 mm Hg?

10.29 Consider the arrangement of bulbs shown in Figure 10.23. Each of the bulbs contains a gas at the pressure shown. What is the pressure of the system when all the stopcocks are opened, assuming that the temperature remains constant? (We can neglect the volume of the capillary tubing connecting the bulbs.)

FIGURE 10.23



10.30 A quantity of N_2 gas originally held at 4.60 atm pressure in a 1.00-L container at 26°C is transferred to a 10.0-L container at 20°C . A quantity of O_2 gas orig-

inally at 3.50 atm and 26°C in a 5.00-L container is transferred to this same container. What is the total pressure in the new container?

Density and Molecular Weight

10.31 (a) Calculate the density of argon gas at STP. (b) Calculate the density of a gas at 37°C and 700 mm Hg if the gas has a molecular weight of 64.1 g/mol.

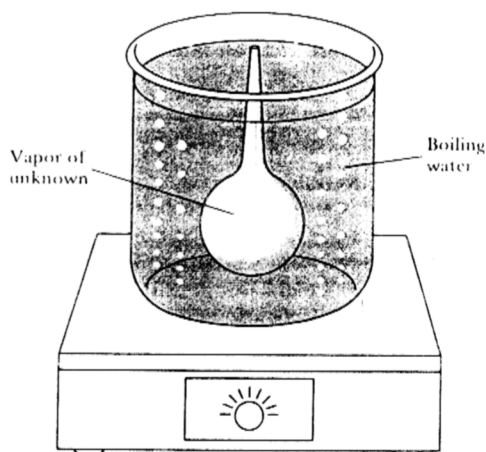
10.32 (a) Calculate the molecular weight of a gas if 0.835 g occupies 800 mL at 400 mm Hg and 34°C . (b) Calculate the molecular weight of a gas that has a density of 2.18 g/L at 66°C and 720 mm Hg.

10.33 (a) Cyanogen is 46.2 percent carbon and 53.8 percent nitrogen by mass. At 25°C and 750 mm Hg, 1.05 g of cyanogen occupies 0.500 L. What is the molecular formula of cyanogen? (b) Benzene is 92.3 percent carbon and 7.7 percent hydrogen by mass. At 120°C and 698 mm Hg, 0.555 g of benzene occupies 0.250 L. What is the molecular formula of benzene?

10.34 The atmosphere of Titan is believed to consist of 82 mol percent N_2 , 12 mol percent Ar, and 6.0 mol percent CH_4 , as its principal constituents. Calculate the average molecular weight. At the surface the temperature is 95 K, and the pressure is 1.6 earth atmospheres. Calculate the density of Titan's atmosphere at the surface, assuming ideal-gas behavior.

10.35 In the Dumas bulb technique for determining the molecular weight of an unknown liquid, one vaporizes the sample of a liquid that boils below 100°C in a boiling-water bath and determines the mass of vapor required to just fill the bulb (see Figure 10.24). From the following data, calculate the molecular weight of the unknown liquid; mass of unknown vapor, 1.012 g; volume of bulb, 354 cm^3 ; pressure, 742 mm Hg; temperature, 99°C .

FIGURE 10.24



10.36 The molecular weight of a volatile substance was determined by the Dumas bulb method described in Exercise 10.35. The unknown vapor had a mass of 0.846 g; the volume of the bulb was 354 cm^3 , pressure 752 mm Hg,

temperature 100°C. Calculate the molecular weight of the unknown vapor.

[10.37] A gaseous mixture of He and N₂ has a density of 0.550 g/L at 25°C and 715 mm Hg. What is the percent He (by mass) in the mixture?

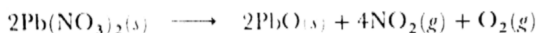
[10.38] A gaseous mixture of O₂ and Kr has a density of 1.104 g/L at 435 mm Hg and 300 K. What is the mole percent O₂ in the mixture?

Quantities of Gases in Chemical Reactions

10.39 Magnesium can be used as a "getter" in evacuated enclosures, to react with the last traces of oxygen. (The magnesium is usually heated by passing an electric current through a wire or ribbon of the metal.) If an enclosure of 0.382 L has a partial pressure of O₂ of 3.5×10^{-6} mm Hg at 27°C, what mass of magnesium will react according to the following equation?

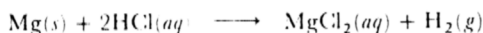


10.40 A 2.16-g sample of lead nitrate, Pb(NO₃)₂, is heated in an evacuated cylinder with a volume of 1.18 L. The salt decomposes when heated:



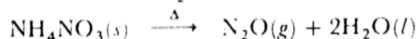
Assuming complete decomposition, what is the pressure in the cylinder after decomposition and cooling to a final temperature of 30°C?

10.41 A piece of solid magnesium is reacted with dilute hydrochloric acid to form hydrogen gas:



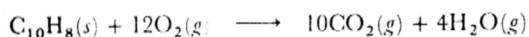
What volume of H₂ is collected over water at 28°C (see Appendix C) by reaction of 1.25 g of Mg with 50.0 mL of 0.10 M HCl? The barometer records an atmospheric pressure of 748 mm Hg.

10.42 Ammonium nitrate can be decomposed thermally to form nitrous oxide, N₂O:



In one experiment 860 cm³ of N₂O was collected over mineral oil, which has no appreciable vapor pressure, at 22°C, and 740 mm Hg pressure, using the experimental arrangement shown in Figure 10.10. **(a)** Assuming complete decomposition, how much NH₄NO₃ was decomposed? **(b)** What reason can you give for why mineral oil rather than water would be used in this case?

10.43 Recall from Chapter 4 that heats of combustion are often measured in a bomb calorimeter (Figure 4.13). Let's assume that we want to measure the heat of combustion of naphthalene, C₁₀H₈:



The bomb is loaded with 0.202 g of C₁₀H₈. It has a gas volume of 132 cm³. The bomb is pressurized with

completely with the naphthalene? If yes, what pressure of O₂ remains at the end of the reaction, when the temperature has returned to 25°C?

10.44 Assume that a single cylinder of an automobile engine has a volume of 600 cm³. **(a)** If the cylinder is full of air at 80°C and 0.980 atm, how many moles of O₂ are present? (The mole fraction of O₂ in dry air is 0.2095.) **(b)** How many grams of C₈H₁₈ could be combusted by this quantity of O₂ assuming complete combustion with formation of CO and H₂O?

Kinetic-Molecular Theory; Graham's Law

10.45 Suppose that we have two 1-L flasks, one containing N₂ at STP, the other containing SF₆ at STP. How do these systems differ with respect to **(a)** the average kinetic energies of the molecules; **(b)** the total number of collisions occurring per unit time with the container walls; **(c)** the shapes of the distribution curves of molecular speeds; **(d)** the relative rates of effusion through a pinhole leak?

10.46 Vessel A contains H₂ gas at 0°C and 1 atm. Vessel B contains O₂ gas at 20°C and 0.5 atm. The two vessels have the same volume. **(a)** Which vessel contains more molecules? **(b)** Which contains more mass? **(c)** In which vessel is the average kinetic energy of molecules higher? **(d)** In which vessel is the average speed of molecules higher?

10.47 Indicate which of the following statements regarding the kinetic-molecular theory of gases are correct. For those that are false, formulate a correct version of the statement. **(a)** The average kinetic energy of a collection of gas molecules at a given temperature is proportional to M^{1/2}. **(b)** The gas molecules are assumed to exert no forces on each other. **(c)** All the molecules of a gas at a given temperature have the same kinetic energy. **(d)** The volume of the gas molecules is negligible in comparison to the total volume in which the gas is contained.

10.48 What change or changes in the state of a gas bring about each of the following effects? **(a)** The number of impacts per unit time on a given container wall increases. **(b)** The average energy of impact of molecules with the wall of the container decreases. **(c)** The average distance between gas molecules increases. **(d)** The average speed of molecules in the gas mixture is increased.

10.49 Calculate the rms speed, in m/s, for each of the following: **(a)** H₂ at 400 K; **(b)** Cl₂ at 400 K; **(c)** Ar at 100 K.

10.50 **(a)** What is the ratio of the average kinetic energies of H₂ and N₂ molecules at 300 K? **(b)** What is the ratio of the rms speeds of the molecules in the two gases at 300 K?

10.51 Which gas will effuse faster, NH₃ or CO? What are their relative rates of effusion?

10.52 Calculate the ratio of rates of effusion of **(a)** H₂ and Ne; **(b)** CO and CO₂; **(c)** XeF₄ and XeF₆.

10.53 A gas of unknown molecular mass is allowed to effuse through a small opening under constant pressure conditions. It required 72 s for 1 L of the gas to effuse. Under identical experimental conditions it required 28 s

for 1 L of O_2 gas to effuse. Calculate the molecular weight of the unknown gas. (Remember that the faster the rate of effusion, the shorter the time required for effusion of 1 L; that is, rate and time are inversely proportional.)

- 10.54** Arsenic(III) sulfide sublimes readily, even below its melting point of $320^\circ C$. The molecules of the vapor phase are found to effuse through a tiny hole at 0.28 times the rate of effusion of Ar atoms under the same conditions of temperature and pressure. What is the molecular formula of arsenic(III) sulfide in the gas phase?

Departures from Ideal-Gas Behavior

- 10.55** Describe two respects in which the ideal-gas law is not obeyed by real gases. How do these departures from ideal behavior show up in the behavior of real gases?

- 10.56** The planet Jupiter has a mass of 318 earth masses, and its surface temperature is 140 K. Mercury has a mass of 0.05 earth mass, and its surface temperature is between 600 and 700 K. On which planet is the atmosphere more likely to obey the ideal-gas law? Explain.

- 10.57** Which of the following gases would you expect to show the largest negative departure from the PV/RT relationship expected for an ideal gas: SO_2 , Ar, H_2 , CH_4 ? For which of these gases should the correction for finite volume be largest?

- 10.58** For each of the following pairs of gases, indicate which you would expect to deviate more from the PV/RT relationship expected for an ideal gas: (a) N_2 and SF_6 ; (b) BF_3 and $SiCl_4$; (c) Ar and HCl. In each case indicate the reason for your choice.

- 10.59** It turns out that the van der Waals constant b is equal to four times the total volume actually occupied by the molecules of a mole of gas. Using this figure, calculate the fraction of the volume in a container actually occupied by Ar atoms (a) at STP; (b) at 100 atm pressure and $0^\circ C$. (Assume for simplicity that the ideal-gas equation still holds.)

- 10.60** Calculate the pressure that CCl_4 will exert at $40^\circ C$ if 1.00 mol occupies 28.0 L, assuming that (a) CCl_4 obeys the ideal-gas equation; (b) CCl_4 obeys the van der Waals equation. (Values for the van der Waals constants are given in Table 10.4.)

Additional Exercises

- 10.61** Atmospheric pressure is usually given in weather reports in units of inches of mercury. What is 1 atm pressure in inches of mercury?

- 10.62** At $25^\circ C$, the density of mercury is 13.6 g/ml and that of water is 1.00 g/mL. On a day when the atmospheric pressure is 735 mm Hg, how high would a column in a water-filled barometer be? (a) Ignore the vapor pressure of water. (b) Include the vapor pressure of water.

- 10.63** Suppose that the manometer illustrated in Figure 10.4(c) contains mineral oil (density 0.752 g/cm^3) as fluid in place of mercury, which has a density of 13.6 g/cm^3 .

The oil has no significant partial pressure of its own. When h is 36.5 cm and the atmospheric pressure is 742 mm Hg, what is the pressure of the enclosed gas?

- 10.64** A large lighter-than-air craft similar to the Good-year blimp has a gas capacity of $5.0 \times 10^7 \text{ L}$. Assume that this volume is filled with He at 1.0 atm pressure, $20^\circ C$. What lifting capacity does the craft possess? That is, what is the maximum mass that it can carry, including the gas bag itself, and still be lighter than air? (Air has a mean molecular mass of 28.7 g/mol.)

- 10.65** A bubble of helium gas is trapped in a cavity of 0.132 cm^3 volume inside a mineral sample at a pressure of 75 atm at $18^\circ C$. What pressure does the helium exert after release from the mineral and storage in a bulb of 90-cm^3 volume at $23^\circ C$?

- 10.66** The atmosphere of Venus at the surface consists of 96 mol percent CO_2 , 3 mol percent N_2 , 1 mol percent SO_2 , and traces of other gases. (a) Calculate the average molecular weight of the Venusian atmosphere. (b) The surface atmospheric pressure on Venus is 90 earth atmospheres. The temperature is about 750 K. Calculate the density of the Venusian atmosphere at the surface.

- 10.67** Under British law the maximum level of tetraethyllead, $Pb(C_2H_5)_4$, allowable in the work environment is 0.10 mg/m^3 . To what partial pressure of $Pb(C_2H_5)_4$ does this correspond?

- 10.68** Some of Robert Boyle's data from his experiments in 1662 with air trapped in a J-tube follow. (These were pre-SI-unit days; pressure was measured in inches of mercury. The gas volume units are arbitrary.)

Gas volume	48	40	32	24	20	16	12
Difference in Hg levels (in.)	0	6.2	15.1	29.7	41.6	58.1	88.4

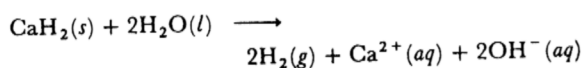
Atmospheric pressure on that day was recorded at 29.1 in. Show whether the hypothesis that pressure is inversely related to gas volume is supported by Boyle's data.

- [10.69]** A mixture of methane, CH_4 , and acetylene, C_2H_2 , occupies a certain volume at a total pressure of 70.5 mm Hg. The sample is burned, forming CO_2 and H_2O . The H_2O is removed and the remaining CO_2 found to have a pressure of 96.4 mm Hg at the same volume and temperature as the original mixture. What fraction of the gas was acetylene?

- 10.70** Anhydrous copper(II) nitrate, $Cu(NO_3)_2$, is a sublimable solid. The vapor at a temperature of $182^\circ C$ and a pressure of 0.32 mm Hg has a density of 2.11 mg/L. Is $Cu(NO_3)_2$ monomeric or dimeric in the gas phase?

- 10.71** Boron forms a gaseous compound with hydrogen with empirical formula BH_3 . A 1.05-L sample of this compound at a pressure of 88 mm Hg at $22^\circ C$ has a mass of 0.138 g. What is the molecular formula of the compound?

- 10.72** Calcium hydride, CaH_2 , reacts with water to produce H_2 gas:



This reaction is used to generate H_2 to inflate life rafts and for similar uses where a simple compact means of H_2 generation is desired. Assuming complete reaction with water, how many grams of CaH_2 are required to fill a balloon to a total pressure of 1.08 atm at 15°C if its volume is 6.16 L?

10.73 Nickel carbonyl, $\text{Ni}(\text{CO})_4$, is one of the most toxic substances known. The present maximum allowable concentration in laboratory air during an 8-hr workday is 1 part in 10^9 . Assume 24°C at 1 atm pressure. What mass of $\text{Ni}(\text{CO})_4$ is allowable in a laboratory that is 110 m^2 in area, with a ceiling height of 2.7 m ?

10.74 A glass vessel fitted with a stopcock has a mass of 337.428 g when evacuated. When filled with Ar it has a mass of 339.712 g. When evacuated and refilled with a mixture of Ne and Ar, under the same conditions of temperature and pressure, it weighs 339.218 g. What is the mole percentage of Ne in the gas mixture?

10.75 Derive Equation 10.19, $u = \sqrt{3RT/M}$, starting with Equation 10.14.

10.76 A balloon made of rubber permeable to small molecules is filled with helium. This balloon is then placed in a box that contains pure hydrogen, H_2 . Will the balloon expand or contract? Explain.

10.77 It is very difficult to obtain uniform gas samples from a tank containing a mixture of gases. After the tank has been in place for a time, the gas that initially flows when the tank is first opened is enriched in the lowest-molecular-weight components. Is this result predicted by the kinetic-molecular theory of gases? Suggest an explanation for the behavior.

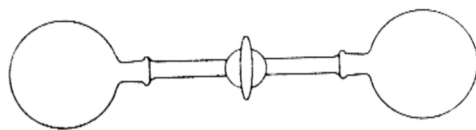
10.78 Suppose that a relatively rare isotope of carbon, ^{13}C , could be separated from the more abundant ^{12}C by using a diffusion process similar to that described in the

text for separating uranium isotopes. The uranium diffusion requires UF_6 . The carbon diffusion requires CO or CO_2 . Calculate the relative rates of diffusion for ^{12}CO and ^{13}CO and similarly for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$. Which substance would give the greater degree of separation?

10.79 Scandium metal reacts with excess hydrochloric acid to produce H_2 gas. When 2.25 g of scandium is treated in this way, it is found that 2.41 L of H_2 measured at 100°C and 722 mm Hg pressure is liberated. Write the balanced chemical equation for the reaction that occurred.

10.80 Consider the experiment illustrated in Figure 10.25. A gas is confined in the leftmost cylinder under 1 atm pressure, and the other cylinder is evacuated. When the stopcock is opened, the gas expands to fill both cylinders. Only a very small temperature change is noted when this expansion occurs. Explain how this observation relates to assumption 4 of the kinetic-molecular theory (Section 10.8.)

FIGURE 10.25



10.81 The density of a gas of unknown molecular mass was measured as a function of pressure at 0°C :

Pressure (atm)	1.00	0.666	0.500	0.333	0.250
Density (g/L)	2.3074	1.5263	1.1401	0.7571	0.5660

(a) Determine a precise molecular weight for the gas. (Hint: Graph d/P versus P .) (b) Why is d/P not a constant as a function of pressure?