



Heating the air inside a “hot-air” balloon raises the air’s temperature, causing it to expand, and forces some of the air out the opening at the bottom. The reduced amount of air inside means its density is lower than the outside air, so there is a net buoyant force upward on the balloon (Chapter 10). In this Chapter we study temperature and its effects on matter: thermal expansion and the gas laws. We examine the microscopic theory of matter as atoms or molecules that are continuously in motion, which we call kinetic theory. The temperature of a gas is directly related to the average translational kinetic energy of its molecules. We will consider ideal gases, but will also look at real gases and how they change phase, including evaporation, vapor pressure, and humidity.



Temperature and Kinetic Theory

CHAPTER-OPENING QUESTION—Guess now!

A hot-air balloon, open at one end (see photos above), rises when the air inside is heated by a flame. For the following properties, is the air inside the balloon higher, lower, or the same as for the air outside the balloon?

- (i) Temperature. (ii) Pressure. (iii) Density.

This Chapter is the first of three (Chapters 13, 14, and 15) devoted to temperature, heat, and thermodynamics. Much of this Chapter discusses the theory that matter is made up of atoms and that these atoms are in continuous random motion. This theory is called the *kinetic theory*. (“Kinetic,” you may recall from Chapter 6, is Greek for “moving.”)

We also discuss the concept of temperature and how it is measured, as well as the measured properties of gases which serve as a foundation for kinetic theory.

13-1 Atomic Theory of Matter

The idea that matter is made up of atoms dates back to the ancient Greeks. According to the Greek philosopher Democritus, if a pure substance—say, a piece of iron—were cut into smaller and smaller bits, eventually a smallest piece of that substance would be obtained which could not be divided further. This smallest piece was called an **atom**, which in Greek means “indivisible.” Today an atom is still the smallest piece of a substance, but we do not consider it indivisible. Rather it is viewed as consisting of a central nucleus (containing protons and neutrons) surrounded by electrons, Chapter 27.

CHAPTER 13

CONTENTS

- 13-1 Atomic Theory of Matter
- 13-2 Temperature and Thermometers
- 13-3 Thermal Equilibrium and the Zeroth Law of Thermodynamics
- 13-4 Thermal Expansion
- 13-5 The Gas Laws and Absolute Temperature
- 13-6 The Ideal Gas Law
- 13-7 Problem Solving with the Ideal Gas Law
- 13-8 Ideal Gas Law in Terms of Molecules: Avogadro’s Number
- 13-9 Kinetic Theory and the Molecular Interpretation of Temperature
- 13-10 Distribution of Molecular Speeds
- 13-11 Real Gases and Changes of Phase
- 13-12 Vapor Pressure and Humidity
- *13-13 Diffusion

Today the atomic theory is universally accepted. The experimental evidence in its favor, however, came mainly in the eighteenth, nineteenth, and twentieth centuries, and much of it was obtained from the analysis of chemical reactions.

We will often speak of the relative masses of individual atoms and molecules—what we call the **atomic mass** or **molecular mass**, respectively. (The terms *atomic weight* and *molecular weight* are sometimes used.) These masses are based on arbitrarily assigning the most abundant form of carbon atom, ^{12}C , the atomic mass of exactly 12.0000 **unified atomic mass units** (u). In terms of kilograms,

$$1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg.}$$

The average atomic mass of hydrogen is 1.0079 u, and the values for other atoms are as listed in the Periodic Table inside the back cover of this book, and also in Appendix B.[†] The molecular mass of a compound is the sum of atomic masses of the atoms making up the molecules of that compound.

[An **element** is a substance, such as neon, gold, iron, or copper, that cannot be broken down into simpler substances by chemical means. **Compounds** are substances made up of elements, and can be broken down into them; examples are carbon dioxide and water. The smallest piece of an element is an atom; the smallest piece of a compound is a **molecule**. Molecules are made up of atoms; a molecule of water, for example, is made up of two atoms of hydrogen and one of oxygen; its chemical formula is H_2O .]

An important piece of evidence for the atomic theory is called **Brownian motion**, named after the biologist Robert Brown, who is credited with its discovery in 1827. While he was observing tiny pollen grains suspended in water under his microscope, Brown noticed that the tiny grains moved about in erratic paths (Fig. 13–1), even though the water appeared to be perfectly still. The atomic theory easily explains Brownian motion if we assume that the atoms of any substance are continually in motion. Then Brown’s tiny pollen grains are jostled about by the vigorous barrage of rapidly moving molecules of water.

In 1905, Albert Einstein examined Brownian motion from a theoretical point of view and was able to calculate from the experimental data the approximate size and mass of atoms and molecules. His calculations showed that the diameter of a typical atom is about 10^{-10} m.

At the start of Chapter 10, we distinguished the three common phases (or states) of matter—solid, liquid, gas—based on **macroscopic**, or “large-scale,” properties. Now let us see how these three phases of matter differ, from the atomic or **microscopic** point of view. First of all, atoms and molecules must exert attractive forces on each other, because only this explains why a brick or a block of aluminum holds together in one piece. The attractive forces between molecules are of an electrical nature (more on this in later Chapters). When molecules come too close together, the force between them must become repulsive (electric repulsion between their outer electrons). We need this assumption to explain that matter takes up space. Thus molecules maintain a minimum distance from each other. In a solid material, the attractive forces are strong enough that the atoms or molecules move only slightly (oscillate) about relatively fixed positions, often in an array known as a crystal lattice, as shown in Fig. 13–2a. In a liquid, the atoms or molecules are moving more rapidly, or the forces between them are weaker, so that they are sufficiently free to pass around one another, as in Fig. 13–2b. In a gas, the forces are so weak, or

[†] The relative masses of different atoms came from analysis of chemical reactions, and the **law of definite proportions**. It states that when two or more elements combine to form a compound, they always do so in the same proportions by mass. For example, table salt is always formed from 23 parts sodium and 35 parts chlorine; and water from one part hydrogen and eight parts oxygen. A continuous theory of matter could not account for the law of definite proportions but atomic theory does: the proportions of each element that form a compound correspond to the relative masses of the combining atoms. One atom of sodium (Na) combines with one atom of chlorine (Cl) to form one molecule of salt (NaCl), and one atom of sodium has a mass 23/35 times as large as one of chlorine. Hydrogen, the lightest atom, was arbitrarily assigned the relative mass of 1. On this scale, carbon was about 12, oxygen 16, sodium 23, and so on. It was sometimes more complicated. For example, from the various compounds oxygen formed, its relative mass was judged to be 16; but this was inconsistent with the mass ratio in water of oxygen to hydrogen, only 8 to 1. This was explained by assuming two H atoms combine with one O atom to form a water molecule.

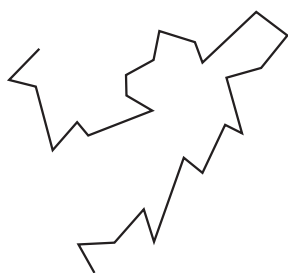
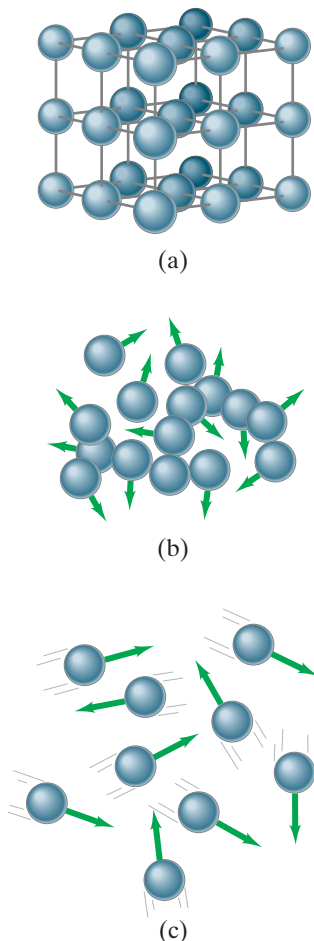


FIGURE 13–1 Path of a tiny particle (pollen grain, for example) suspended in water. The straight lines connect observed positions of the particle at equal time intervals.

FIGURE 13–2 Atomic arrangements in (a) a crystalline solid, (b) a liquid, and (c) a gas.



the speeds so high, that the molecules do not even stay close together. They move rapidly every which way, Fig. 13–2c, filling any container and occasionally colliding with one another. On average, the speeds are sufficiently high in a gas that when two molecules collide, the force of attraction is not strong enough to keep them close together and they fly off in new directions.

EXAMPLE 13–1 ESTIMATE Distance between atoms. The density of copper is $8.9 \times 10^3 \text{ kg/m}^3$, and each copper atom has a mass of 63 u. Estimate the average distance between the centers of neighboring copper atoms.

APPROACH We consider a cube of copper 1 m on a side. From the given density ρ we can calculate the mass m of a cube of volume $V = 1 \text{ m}^3$ ($m = \rho V$). We divide this mass m by the mass of one atom (63 u) to obtain the number of atoms in 1 m^3 . We assume the atoms are in a uniform array, and we let N be the number of atoms in a 1-m length; then $(N)(N)(N) = N^3$ equals the total number of atoms in 1 m^3 .

SOLUTION The mass of 1 copper atom is $63 \text{ u} = 63 \times 1.66 \times 10^{-27} \text{ kg} = 1.05 \times 10^{-25} \text{ kg}$. This means that in a cube of copper 1 m on a side (volume = 1 m^3), there are

$$\frac{8.9 \times 10^3 \text{ kg}}{1.05 \times 10^{-25} \text{ kg/atom}} = 8.5 \times 10^{28} \text{ atoms.}$$

The volume of a cube of side ℓ is $V = \ell^3$, so on one edge of the 1-m-long cube there are $(8.5 \times 10^{28})^{1/3} \text{ atoms} = 4.4 \times 10^9 \text{ atoms}$. Hence the distance between neighboring atoms is

$$\frac{1 \text{ m}}{4.4 \times 10^9 \text{ atoms}} = 2.3 \times 10^{-10} \text{ m.}$$

NOTE Watch out for units. Even though “atoms” is not a unit, it is helpful to include it to make sure you calculate correctly.

NOTE The distance between atoms is essentially what we mean when we speak of the size or diameter of an atom. So we have calculated the size of a copper atom.



FIGURE 13–3 Expansion joint on a bridge. Note center white line of highway.

FIGURE 13–4 Thermometers built by the Accademia del Cimento (1657–1667) in Florence, Italy, are among the earliest known. These sensitive and exquisite instruments contained alcohol, sometimes colored, like many thermometers today.



13–2 Temperature and Thermometers

In everyday life, **temperature** is a measure of how hot or cold something is. A hot oven is said to have a high temperature, whereas the ice of a frozen lake is said to have a low temperature.

Many properties of matter change with temperature. For example, most materials expand when their temperature is increased.[†] An iron beam is longer when hot than when cold. Concrete roads and sidewalks expand and contract slightly according to temperature, which is why compressible spacers or expansion joints (Fig. 13–3) are placed at regular intervals. The electrical resistance of matter changes with temperature (Chapter 18). So too does the color radiated by objects, at least at high temperatures: you may have noticed that the heating element of an electric stove glows with a red color when hot. At higher temperatures, solids such as iron glow orange or even white. The white light from an incandescent lightbulb comes from an extremely hot tungsten wire. The surface temperatures of the Sun and other stars can be measured by the predominant color (more precisely, wavelengths) of light they emit.

Instruments designed to measure temperature are called **thermometers**. There are many kinds of thermometers, but their operation always depends on some property of matter that changes with temperature. Many common thermometers rely on the expansion of a material with an increase in temperature. The first idea for a thermometer, by Galileo, made use of the expansion of a gas. Common thermometers today consist of a hollow glass tube filled with mercury or with alcohol colored with a red dye, as were the earliest usable thermometers (Fig. 13–4).

[†]Most materials expand when their temperature is raised, but not all. Water, for example, in the range 0°C to 4°C contracts with an increase in temperature (see Section 13–4).

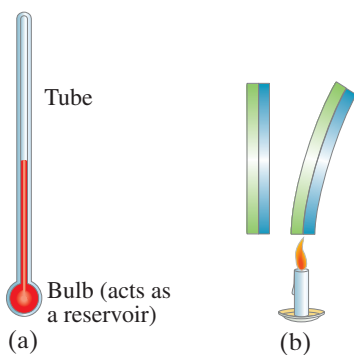


FIGURE 13-5 (a) Mercury- or alcohol-in-glass thermometer; (b) bimetallic strip.

FIGURE 13-6 Photograph of a thermometer using a coiled bimetallic strip.

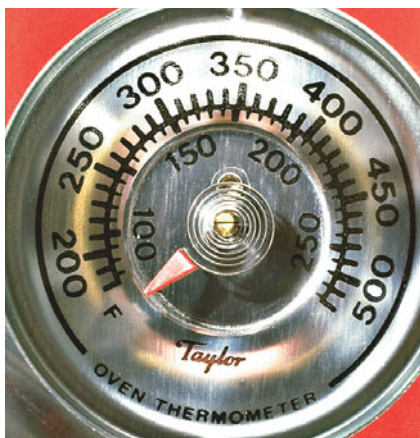
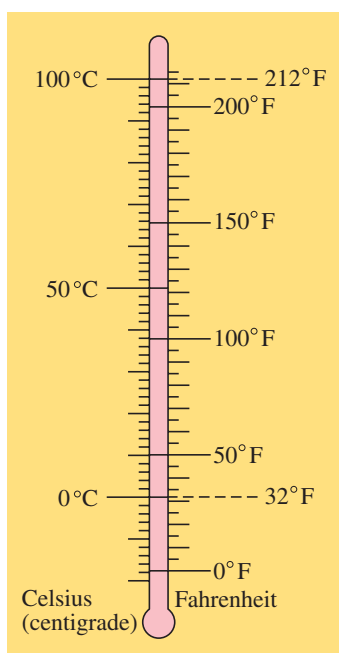


FIGURE 13-7 Celsius and Fahrenheit scales compared.



Inside a common liquid-in-glass thermometer, the liquid expands more than the glass when the temperature is increased, so the liquid level rises in the tube (Fig. 13–5a). Although metals also expand with temperature, the change in length of a metal rod, say, is generally too small to measure accurately for ordinary changes in temperature. However, a useful thermometer can be made by bonding together two different metals with different rates of expansion (Fig. 13–5b). When the temperature is increased, the different amounts of expansion cause the **bimetallic strip** to bend. Often the bimetallic strip is in the form of a coil, one end of which is fixed while the other is attached to a pointer, Fig. 13–6. Such thermometers are used as ordinary air thermometers, oven thermometers, automatic off switches in electric coffeepots, and in room thermostats for determining when the heater or air conditioner should go on or off. Very precise thermometers make use of electrical properties (Chapter 18), such as resistance thermometers, thermocouples, and thermistors, often with a digital readout.

Temperature Scales

In order to measure temperature quantitatively, some sort of numerical scale must be defined. The most common scale today is the **Celsius or centigrade** scale. In the United States, the **Fahrenheit** scale is common. The most important scale in scientific work is the absolute, or Kelvin, scale, and it will be discussed later in this Chapter.

One way to define a temperature scale is to assign arbitrary values to two readily reproducible temperatures. For both the Celsius and Fahrenheit scales these two fixed points are chosen to be the freezing point and the boiling point[†] of water, both taken at standard atmospheric pressure. On the Celsius scale, the freezing point of water is chosen to be 0°C (“zero degrees Celsius”) and the boiling point 100°C. On the Fahrenheit scale, the freezing point is defined as 32°F and the boiling point 212°F. A practical thermometer is calibrated by placing it in carefully prepared environments at each of the two temperatures and marking the position of the liquid or pointer. For a Celsius scale, the distance between the two marks is divided into one hundred equal intervals representing each degree between 0°C and 100°C (hence the name “centigrade scale” meaning “hundred steps”). For the Fahrenheit scale, the two points are labeled 32°F and 212°F and the distance between them is divided into 180 equal intervals. For temperatures below the freezing point of water and above the boiling point of water, the scales may be extended using the same equally spaced intervals. However, thermometers can be used only over a limited temperature range because of their own limitations—for example, an alcohol-in-glass thermometer is rendered useless above temperatures where the alcohol vaporizes. For very low or very high temperatures, specialized thermometers are required, some of which we will mention later.

Every temperature on the Celsius scale corresponds to a particular temperature on the Fahrenheit scale, Fig. 13–7. To convert from one to the other, remember that 0°C corresponds to 32°F and that a range of 100° on the Celsius scale corresponds to a range of 180° on the Fahrenheit scale. Thus, one Fahrenheit degree (1 F°) corresponds to $100/180 = \frac{5}{9}$ of a Celsius degree (1 C°). That is, $1 \text{ F}^\circ = \frac{5}{9} \text{ C}^\circ$. (Notice that when we refer to a specific temperature, we say “degrees Celsius,” as in 20°C; but when we refer to a *change* in temperature or a temperature *interval*, we say “Celsius degrees,” as in “2 C°.”) The conversion between the two temperature scales can be written

$$T(^{\circ}\text{C}) = \frac{5}{9}[T(^{\circ}\text{F}) - 32]$$

or

$$T(^{\circ}\text{F}) = \frac{9}{5}T(^{\circ}\text{C}) + 32.$$

Rather than memorizing these relations, it may be simpler to remember that 0°C = 32°F and that a change of 5 C° = a change of 9 F°.

[†]The freezing point of a substance is defined as that temperature at which the solid and liquid phases coexist in equilibrium—that is, without any net liquid changing into the solid or vice versa. Experimentally, this is found to occur at only one definite temperature, for a given pressure. Similarly, the boiling point is defined as that temperature at which the liquid and gas coexist in equilibrium. Since these points vary with pressure, the pressure must be specified (usually it is 1 atm).

EXAMPLE 13–2 **Taking your temperature.** Normal body temperature is 98.6°F . What is this on the Celsius scale?

APPROACH We recall that $0^{\circ}\text{C} = 32^{\circ}\text{F}$ and that a change of $5^{\circ}\text{C} = 9^{\circ}\text{F}$.

SOLUTION First we relate the given temperature to the freezing point of water (0°C). That is, 98.6°F is $98.6 - 32.0 = 66.6^{\circ}\text{F}$ above the freezing point of water. Since each F° is equal to $\frac{5}{9}\text{C}^{\circ}$, this corresponds to $66.6 \times \frac{5}{9} = 37.0$ Celsius degrees above the freezing point. The freezing point of water is 0°C , so normal body temperature is 37.0°C .

CAUTION

Convert temperature by remembering $0^{\circ}\text{C} = 32^{\circ}\text{F}$ and a change of $5^{\circ}\text{C} = 9^{\circ}\text{F}$

***Standard Temperature Scale**

Different materials do not expand in quite the same way over a wide temperature range. Consequently, if we calibrate different kinds of thermometers exactly as described above, they will not usually agree precisely.

Because of such discrepancies, some standard kind of thermometer must be chosen so that all temperatures can be precisely defined. The chosen standard for this purpose is the **constant-volume gas thermometer**. As shown in the simplified diagram of Fig. 13–8, this thermometer consists of a bulb filled with a low-pressure gas connected by a thin tube to a mercury manometer (Section 10–6). The volume of the gas is kept constant by raising or lowering the right-hand tube of the manometer so that the mercury in the left-hand tube coincides with the reference mark. An increase in temperature causes a proportional increase in pressure in the bulb. Thus the tube must be lifted higher to keep the gas volume constant. The height of the mercury in the right-hand column is then a measure of the temperature. This thermometer gives the same results for all gases in the limit of reducing the gas pressure in the bulb toward zero. The resulting scale serves as a basis for the **standard temperature scale**.

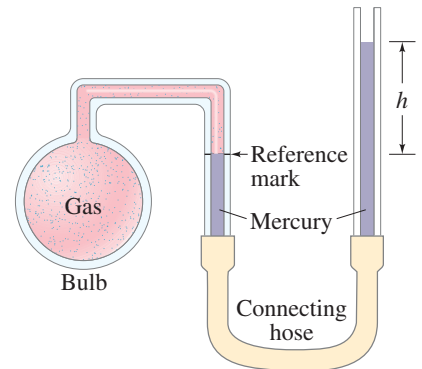


FIGURE 13–8 Constant-volume gas thermometer.

13–3 Thermal Equilibrium and the Zeroth Law of Thermodynamics

If two objects at different temperatures are placed in thermal contact (meaning thermal energy can transfer from one to the other), the two objects will eventually reach the same temperature. They are then said to be in **thermal equilibrium**. For example, you leave a fever thermometer in your mouth until it comes into thermal equilibrium with that environment; then you read it. Two objects are defined to be in thermal equilibrium if, when placed in thermal contact, no net energy flows from one to the other, and their temperatures don't change.

***The Zeroth Law of Thermodynamics**

Experiments indicate that

if two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

This postulate is called the **zeroth law of thermodynamics**. It has this unusual name because it was not until after the first and second laws of thermodynamics (Chapter 15) were worked out that scientists realized that this apparently obvious postulate needed to be stated first.

Temperature is a property of a system that determines whether the system will be in thermal equilibrium with other systems. When two systems are in thermal equilibrium, their temperatures are (by definition) equal, and no net thermal energy is exchanged between them. This is consistent with our everyday notion of temperature: when a hot object and a cold one are put into contact, they eventually come to the same temperature. Thus the importance of the zeroth law is that it allows a useful definition of temperature.

13-4 Thermal Expansion

Most substances expand when heated and contract when cooled. However, the amount of expansion or contraction varies, depending on the material.

Linear Expansion

Experiments indicate that the change in length $\Delta\ell$ of almost all solids is, to a good approximation, directly proportional to the change in temperature ΔT , as long as ΔT is not too large. The change in length is also proportional to the original length of the object, ℓ_0 . That is, for the same temperature increase, a 4-m-long iron rod will increase in length twice as much as a 2-m-long iron rod. We can write this proportionality as an equation:

$$\Delta\ell = \alpha\ell_0\Delta T, \quad (13-1a)$$

where α , the proportionality constant, is called the **coefficient of linear expansion** for the particular material and has units of $(\text{C}^\circ)^{-1}$. We write $\ell = \ell_0 + \Delta\ell$, Fig. 13-9, and rewrite this equation as

$$\ell = \ell_0(1 + \alpha\Delta T), \quad (13-1b)$$

where ℓ_0 is the length initially, at temperature T_0 , and ℓ is the length after heating or cooling to a temperature T . If the temperature change $\Delta T = T - T_0$ is negative, then $\Delta\ell = \ell - \ell_0$ is also negative; the length shortens as the temperature decreases.

The values of α for various materials at 20°C are listed in Table 13-1. Actually, α does vary slightly with temperature (which is why thermometers made of different materials do not agree precisely). However, if the temperature range is not too great, the variation can usually be ignored.

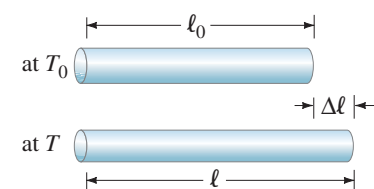


FIGURE 13-9 A thin rod of length ℓ_0 at temperature T_0 is heated to a new uniform temperature T and acquires length ℓ , where $\ell = \ell_0 + \Delta\ell$.

TABLE 13-1 Coefficients of Expansion, near 20°C

Material	Coefficient of Linear Expansion, α $(\text{C}^\circ)^{-1}$	Coefficient of Volume Expansion, β $(\text{C}^\circ)^{-1}$
<i>Solids</i>		
Aluminum	25×10^{-6}	75×10^{-6}
Brass	19×10^{-6}	56×10^{-6}
Copper	17×10^{-6}	50×10^{-6}
Gold	14×10^{-6}	42×10^{-6}
Iron or steel	12×10^{-6}	35×10^{-6}
Lead	29×10^{-6}	87×10^{-6}
Glass (Pyrex [®])	3×10^{-6}	9×10^{-6}
Glass (ordinary)	9×10^{-6}	27×10^{-6}
Quartz	0.4×10^{-6}	1×10^{-6}
Concrete and brick	$\approx 12 \times 10^{-6}$	$\approx 36 \times 10^{-6}$
Marble	$1.4\text{--}3.5 \times 10^{-6}$	$4\text{--}10 \times 10^{-6}$
<i>Liquids</i>		
Gasoline		950×10^{-6}
Mercury		180×10^{-6}
Ethyl alcohol		1100×10^{-6}
Glycerin		500×10^{-6}
Water		210×10^{-6}
<i>Gases</i>		
Air (and most other gases at atmospheric pressure)		3400×10^{-6}

EXAMPLE 13-3 Bridge expansion. The steel bed of a suspension bridge is 200 m long at 20°C. If the extremes of temperature to which it might be exposed are -30°C to +40°C, how much will it contract and expand?

APPROACH We assume the bridge bed will expand and contract linearly with temperature, as given by Eq. 13-1a.

SOLUTION From Table 13-1, we find that $\alpha = 12 \times 10^{-6}(\text{C}^\circ)^{-1}$ for steel. The increase in length when it is at 40°C will be

$\Delta l = \alpha l_0 \Delta T = (12 \times 10^{-6}/\text{C}^\circ)(200 \text{ m})(40^\circ\text{C} - 20^\circ\text{C}) = 4.8 \times 10^{-2} \text{ m}$,
or 4.8 cm. When the temperature decreases to -30°C, $\Delta T = -50 \text{ C}^\circ$. Then

$$\Delta l = (12 \times 10^{-6}/\text{C}^\circ)(200 \text{ m})(-50 \text{ C}^\circ) = -12.0 \times 10^{-2} \text{ m},$$

or a decrease in length of 12 cm. The total range the expansion joints must accommodate is 12 cm + 4.8 cm \approx 17 cm (Fig. 13-3).

CONCEPTUAL EXAMPLE 13-4 Do holes expand or contract? If you heat a thin, circular ring (Fig. 13-10a) in the oven, does the ring's hole get larger or smaller?

RESPONSE If you guessed that the metal expands into the hole, making the hole smaller, it is not so. Imagine the ring is solid, like a coin (Fig. 13-10b). Draw a circle on it with a pen as shown. When the metal expands, the material inside the circle will expand along with the rest of the metal; so the dashed circle expands. Cutting the metal where the circle is shows that the hole in Fig. 13-10a increases in diameter.

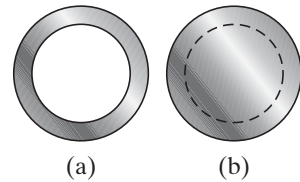


FIGURE 13-10 Example 13-4.

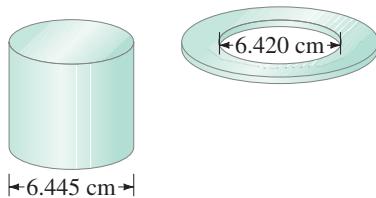


FIGURE 13-11
Example 13-5.

EXAMPLE 13-5 Ring on a rod. An iron ring is to fit snugly on a cylindrical iron rod (Fig. 13-11). At 20°C, the diameter of the rod is 6.445 cm and the inside diameter of the ring is 6.420 cm. To slip over the rod, the ring must be slightly larger than the rod diameter by about 0.008 cm. To what temperature must the ring be brought if its hole is to be large enough so it will slip over the rod?

APPROACH The hole in the ring must be increased from a diameter of 6.420 cm to 6.445 cm + 0.008 cm = 6.453 cm. The ring must be heated since the hole diameter will increase linearly with temperature (Example 13-4).

SOLUTION We solve for ΔT in Eq. 13-1a and find

$$\Delta T = \frac{\Delta l}{\alpha l_0} = \frac{6.453 \text{ cm} - 6.420 \text{ cm}}{(12 \times 10^{-6}/\text{C}^\circ)(6.420 \text{ cm})} = 430 \text{ C}^\circ.$$

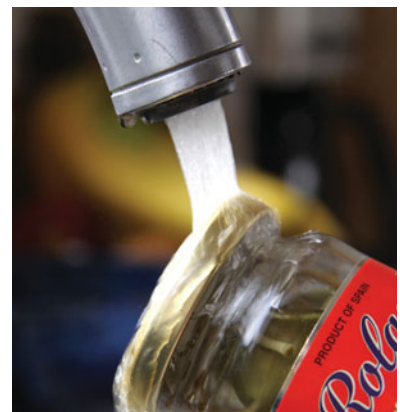
So the ring must be raised at least to $T = (20^\circ\text{C} + 430 \text{ C}^\circ) = 450^\circ\text{C}$.

NOTE In doing Problems, do not forget the last step, adding in the initial temperature (20°C here).

CONCEPTUAL EXAMPLE 13-6 Opening a tight jar lid. When the lid of a glass jar is tight, holding the lid under hot water for a short time will often make it easier to open (Fig. 13-12). Why?

RESPONSE The lid may be struck by the hot water more directly than the glass and so expand sooner. But even if not, metals generally expand more than glass for the same temperature change (α is greater—see Table 13-1).

FIGURE 13-12 Example 13-6.



Volume Expansion

The change in *volume* of a material which undergoes a temperature change is given by a relation similar to Eq. 13–1a, namely,

$$\Delta V = \beta V_0 \Delta T, \quad (13-2)$$

where V_0 is the original volume, ΔV is the change in volume when the temperature changes by ΔT , and β is the **coefficient of volume expansion**. The units of β are $(\text{C}^\circ)^{-1}$.

Values of β for various materials are given in Table 13–1. Notice that for solids, β is normally equal to approximately 3α . Note also that linear expansion has no meaning for liquids and gases because they do not have fixed shapes.

Equations 13–1 and 13–2 are accurate only if $\Delta \ell$ (or ΔV) is small compared to ℓ_0 (or V_0). This is of particular concern for liquids and even more so for gases because of the large values of β . Furthermore, β itself varies substantially with temperature for gases. Therefore, a more convenient way of dealing with gases is needed, and will be discussed starting in Section 13–5.



EXAMPLE 13–7 Gas tank in the Sun. The 70-liter (L) steel gas tank of a car is filled to the top with gasoline at 20°C . The car sits in the Sun and the tank reaches a temperature of 40°C (104°F). How much gasoline do you expect to overflow from the tank?

APPROACH Both the gasoline and the tank expand as the temperature increases, and we assume they do so linearly as described by Eq. 13–2. The volume of overflowing gasoline equals the volume increase of the gasoline minus the increase in volume of the tank.

SOLUTION The gasoline expands by

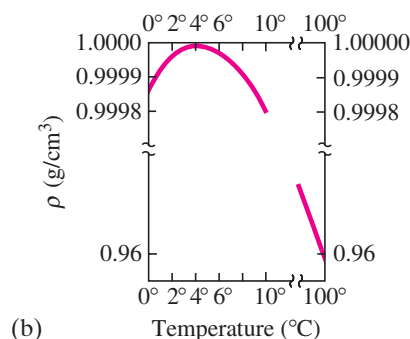
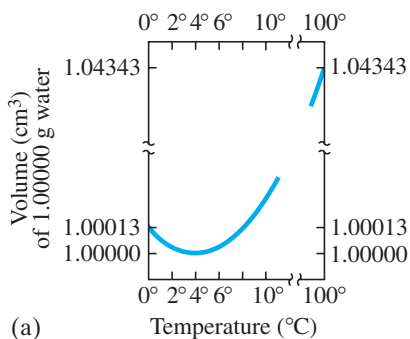
$$\begin{aligned} \Delta V &= \beta V_0 \Delta T = (950 \times 10^{-6}/\text{C}^\circ)(70 \text{ L})(40^\circ\text{C} - 20^\circ\text{C}) \\ &= 1.3 \text{ L.} \end{aligned}$$

The tank also expands. We can think of it as a steel shell that undergoes volume expansion ($\beta = 35 \times 10^{-6}/\text{C}^\circ \approx 3\alpha$). If the tank were solid, the surface layer (the shell) would expand just the same (as in Example 13–4). Thus the tank increases in volume by

$$\Delta V = (35 \times 10^{-6}/\text{C}^\circ)(70 \text{ L})(40^\circ\text{C} - 20^\circ\text{C}) = 0.049 \text{ L,}$$

so the tank expansion has little effect. More than a liter of gas could spill out.

FIGURE 13–13 Behavior of water as a function of temperature near 4°C . (a) Volume of 1.00000 gram of water as a function of temperature. (b) Density vs. temperature. [Note the break in each axis.]



Anomalous Behavior of Water Below 4°C

Most substances expand more or less uniformly with an increase in temperature, as long as no phase change occurs. Water, however, does not follow the usual pattern. If water at 0°C is heated, it actually *decreases* in volume until it reaches 4°C . Above 4°C water behaves normally and expands in volume as the temperature is increased, Fig. 13–13. Water thus has its greatest density at 4°C . This anomalous behavior of water is of great importance for the survival of aquatic life during cold winters. When water in a lake (or river) is above 4°C and begins to cool by contact with cold air, the water at the surface sinks because it is denser. It is replaced by warmer water from below. This mixing continues until the temperature of the entire lake reaches 4°C . As the surface water cools further, it remains on the surface because it is less dense than the 4°C water below. Water thus freezes first at the surface, and the ice remains on the surface since ice (specific gravity = 0.917) is less dense than water. The water at the bottom remains liquid unless it is so cold that the whole body of water freezes. If water were like most substances, becoming more dense as it cools, the water at the bottom of a lake would be frozen first.

Lakes would freeze solid more easily because circulation would bring the warmer water to the surface to be efficiently cooled. The complete freezing of a lake would cause severe damage to its plant and animal life. Because of the unusual behavior of water below 4°C, it is rare for any large and deep body of water to freeze completely, and this is helped by the layer of ice on the surface which acts as an insulator to reduce the flow of heat out of the water into the cold air above. Without this peculiar but wonderful property of water, life on this planet as we know it might not have been possible.

Not only does water expand as it cools from 4°C to 0°C, it expands even more as it freezes to ice. This is why ice cubes float in water and pipes break when water inside them freezes.

*Thermal Stresses

In many situations, such as in buildings and roads, the ends of a beam or slab of material are rigidly fixed, which greatly limits expansion or contraction. If the temperature should change, large compressive or tensile stresses, called **thermal stresses**, will occur. The magnitude of such stresses can be calculated using the concept of elastic modulus developed in Chapter 9. To calculate the internal stress in a beam, we can think of this process as occurring in two steps: (1) the beam tries to expand (or contract) by an amount $\Delta\ell$ given by Eq. 13-1; (2) the solid in contact with the beam exerts a force to compress (or expand) it, keeping it at its original length. The force F required is given by Eq. 9-4:

$$\Delta\ell = \frac{1}{E} \frac{F}{A} \ell_0,$$

where E is Young's modulus for the material. To calculate the internal stress, F/A , we then set $\Delta\ell$ in Eq. 13-1a equal to $\Delta\ell$ in the equation above and find

$$\alpha\ell_0 \Delta T = \frac{1}{E} \frac{F}{A} \ell_0.$$

Hence, the stress is

$$\frac{F}{A} = \alpha E \Delta T.$$

For example, if 10-m-long concrete slabs are placed touching each other in a new park you are designing, a 30°C increase in temperature would produce a stress $F/A = \alpha E \Delta T = (12 \times 10^{-6}/\text{C}^\circ)(20 \times 10^9 \text{ N/m}^2)(30 \text{ C}^\circ) = 7.2 \times 10^6 \text{ N/m}^2$. That stress would exceed the shear strength of concrete (Table 9-2), no doubt causing fracture and cracks. This is why soft spacers (or expansion joints) are placed between slabs on sidewalks and highways.

13-5 The Gas Laws and Absolute Temperature

Equation 13-2 is not useful for describing the expansion of a gas, partly because the expansion can be so great, and partly because gases generally expand to fill whatever container they are in. Indeed, Eq. 13-2 is meaningful only if the pressure is kept constant. The volume of a gas depends very much on the pressure as well as on the temperature. It is therefore valuable to determine a relation between the volume, the pressure, the temperature, and the quantity of a gas. Such a relation is called an **equation of state**. (By the word *state*, we mean the physical condition of the system.)

If the state of a system is changed, we will always wait until the pressure and temperature have reached the same values throughout. We thus consider only **equilibrium states** of a system—when the variables that describe it (such as temperature and pressure) are the same throughout the system and are not changing in time. We also note that the results of this Section are accurate only for gases that are not too dense (the pressure is not too high, on the order of an atmosphere or less) and not close to the liquefaction (boiling) point.

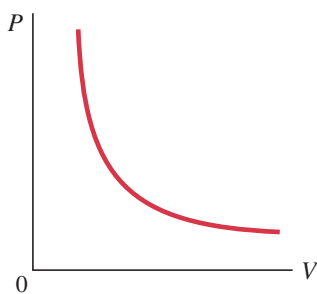


FIGURE 13-14 Pressure vs. volume of a fixed amount of gas at a constant temperature, showing the inverse relationship as given by Boyle's law: as the pressure decreases, the volume increases.

For a given quantity of gas it is found experimentally that, to a good approximation, *the volume of a gas is inversely proportional to the absolute pressure applied to it when the temperature is kept constant.* That is,

$$V \propto \frac{1}{P}, \quad [\text{constant } T]$$

where P is the absolute pressure (*not* “gauge pressure”—see Section 10-4). For example, if the pressure on a gas is doubled, the volume is reduced to half its original volume. This relation is known as **Boyle's law**, after the Englishman Robert Boyle (1627–1691), who first stated it on the basis of his own experiments. A graph of P vs. V for a fixed temperature is shown in Fig. 13-14. Boyle's law can also be written

$$PV = \text{constant} \quad [\text{constant } T]$$

for a fixed quantity of a gas kept at constant temperature. If either the pressure or volume of a fixed amount of gas is allowed to vary, the other variable also changes so that the product PV remains constant.

Temperature also affects the volume of a gas, but a quantitative relationship between V and T was not found until more than a century after Boyle's work. The Frenchman Jacques Charles (1746–1823) found that when the pressure is not too high and is kept constant, the volume of a gas increases with temperature at a nearly linear rate, as shown in Fig. 13-15a. However, all gases liquefy at low temperatures (for example, oxygen liquefies at -183°C), so the graph cannot be extended below the liquefaction point. Nonetheless, the graph is essentially a straight line and if projected to lower temperatures, as shown by the dashed line, it crosses the axis at about -273°C .

Such a graph can be drawn for any gas, and a straight line results which always projects back to -273°C at zero volume. This seems to imply that if a gas could be cooled to -273°C , it would have zero volume, and at lower temperatures a negative volume, which makes no sense. It could be argued that -273°C is the lowest temperature possible; indeed, many other more recent experiments indicate that this is so. This temperature is called the **absolute zero** of temperature. Its value has been determined to be -273.15°C .

Absolute zero forms the basis of a temperature scale known as the **absolute scale** or **Kelvin scale**, and it is used extensively in scientific work. On this scale the temperature is specified as degrees Kelvin or, preferably, simply as **kelvins (K)** without the degree sign. The intervals are the same as for the Celsius scale, but the zero on this scale (0 K) is chosen as absolute zero. Thus the freezing point of water (0°C) is 273.15 K, and the boiling point of water is 373.15 K. Indeed, any temperature on the Celsius scale can be changed to kelvins by adding 273.15 to it:

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15.$$

Now let us look at Fig. 13-15b, where the graph of the volume of a gas versus absolute temperature is a straight line that passes through the origin. Thus, to a good approximation, *the volume of a fixed quantity of gas is directly proportional to the absolute temperature when the pressure is kept constant.* This is known as **Charles's law**, and is written

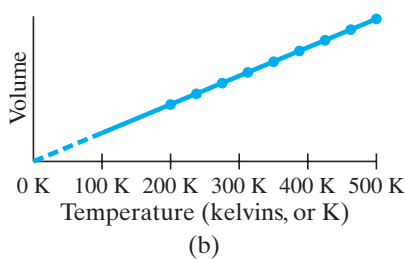
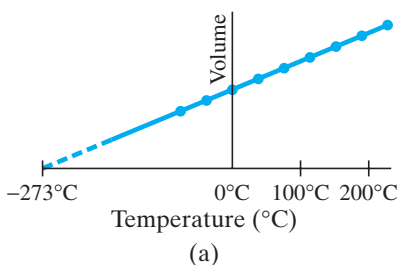
$$V \propto T. \quad [\text{constant } P]$$

A third gas law, known as **Gay-Lussac's law**, after Joseph Gay-Lussac (1778–1850), states that *at constant volume, the absolute pressure of a fixed quantity of a gas is directly proportional to the absolute temperature:*

$$P \propto T. \quad [\text{constant } V]$$

The laws of Boyle, Charles, and Gay-Lussac are not really laws in the sense that we use this term today (precise, deep, wide-ranging validity). They are really only approximations that are accurate for real gases only as long as the pressure and density of the gas are not too high, and the gas is not too close to liquefaction (condensation). The term *law* applied to these three relationships has become traditional, however, so we have stuck with that usage.

FIGURE 13-15 Volume of a fixed amount of gas as a function of (a) Celsius temperature, and (b) Kelvin temperature, when the pressure is kept constant.



CONCEPTUAL EXAMPLE 13–8 Why you should not put a closed glass

jar into a campfire. What could happen if you tossed an empty glass jar, with the lid on tight, into a fire, and why?

RESPONSE The inside of the jar is not empty. It is filled with air. As the fire heats the air inside, its temperature rises. The volume of the glass jar changes only slightly due to the heating. According to Gay-Lussac's law the pressure P of the air inside the jar can increase enough to cause the jar to explode, throwing glass pieces outward.

13–6 The Ideal Gas Law

The gas laws of Boyle, Charles, and Gay-Lussac were obtained by means of an important scientific technique: namely, *considering one quantity and how it is affected by changing only one other variable, keeping all other variables constant*. These laws can now be combined into a single more general relation among all three variables—absolute pressure, volume, and absolute temperature of a fixed amount of gas:

$$PV \propto T.$$

This relation indicates how any of the quantities P , V , or T will vary when the other two quantities change. This relation reduces to Boyle's, Charles's, or Gay-Lussac's law when either T , P , or V , respectively, is held constant.

Finally, we must incorporate the effect of the amount of gas present. For example, when more air is forced into a balloon, the balloon gets bigger (Fig. 13–16). Indeed, careful experiments show that at constant temperature and pressure, the volume V of an enclosed gas increases in direct proportion to the mass m of gas present. Hence we write

$$PV \propto mT.$$

This proportion can be made into an equation by inserting a constant of proportionality. Experiment shows that this constant has a different value for different gases. However, the constant of proportionality turns out to be the same for all gases if, instead of the mass m , we use the number of *moles*.

The “mole” is an official SI unit for the amount of substance. One **mole** (abbreviated mol) is the amount of substance that contains 6.02×10^{23} objects (usually atoms, molecules, or ions, etc.). This number is called *Avogadro's number*, as discussed in Section 13–8. Its value comes from measurements. The mole's precise definition is the number of atoms in exactly 12 grams of carbon-12 (page 360).

Equivalently, 1 mol is that amount of substance whose mass in grams is numerically equal to the molecular mass of the substance (Section 13–1). For example, the mass of 1 mole of CO_2 is $[12 + (2 \times 16)] = 44$ g because carbon has atomic mass of 12 and oxygen 16 (see Periodic Table inside the rear cover).

In general, the number of moles, n , in a given sample of a pure substance is equal to the mass of the sample in grams divided by the molecular mass specified as grams per mole:

$$n \text{ (mole)} = \frac{\text{mass (grams)}}{\text{molecular mass (g/mol)}}.$$

For example, the number of moles in 132 g of CO_2 (molecular mass 44 u) is

$$n = \frac{132 \text{ g}}{44 \text{ g/mol}} = 3.0 \text{ mol}.$$



FIGURE 13–16 Blowing up a balloon means putting more air (more air molecules) into the balloon, which increases its volume. The pressure is nearly constant, at atmospheric pressure, except for the small effect of the balloon's elasticity.

IDEAL GAS LAW

We can now write the proportion above ($PV \propto nT$) as an equation:

$$PV = nRT, \quad (13-3)$$

where n represents the number of moles and R is the constant of proportionality. R is called the **universal gas constant** because its value is found experimentally to be the same for all gases. The value of R , in several sets of units (only the first is the proper SI unit), is

$$\begin{aligned} R &= 8.314 \text{ J}/(\text{mol} \cdot \text{K}) && [\text{SI units}] \\ &= 0.0821 \text{ (L} \cdot \text{atm)} / (\text{mol} \cdot \text{K}) \\ &= 1.99 \text{ calories}/(\text{mol} \cdot \text{K}).^\dagger \end{aligned}$$

Equation 13-3 is called the **ideal gas law**, or the **equation of state for an ideal gas**. We use the term “ideal” because real gases do not follow Eq. 13-3 precisely, particularly at high pressure (and density) or when the gas is near the liquefaction point (= boiling point). However, at pressures less than an atmosphere or so, and when T is not close to the liquefaction point of the gas, Eq. 13-3 is quite accurate and useful for real gases.

Always remember, when using the ideal gas law, that temperatures must be given in kelvins (K) and that the pressure P must always be *absolute* pressure, not gauge pressure (Section 10-4).

 CAUTION

Always give T in kelvins and P as absolute (not gauge) pressure

EXERCISE A Return to the Chapter-Opening Question, page 359, and answer it again now. Try to explain why you may have answered differently the first time.

EXERCISE B An ideal gas is contained in a steel sphere at 27.0°C and 1.00 atm absolute pressure. If no gas is allowed to escape and the temperature is raised to 127°C , what will be the new pressure? (a) 0.21 atm ; (b) 0.75 atm ; (c) 1.00 atm ; (d) 1.33 atm ; (e) 4.7 atm .

13-7 Problem Solving with the Ideal Gas Law

The ideal gas law is an extremely useful tool, and we now consider some Examples. We will often refer to “standard conditions” or **standard temperature and pressure (STP)**, which means:

$$T = 273 \text{ K } (0^\circ\text{C}) \quad \text{and} \quad P = 1.00 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2 = 101.3 \text{ kPa.}$$

EXAMPLE 13-9 **Volume of one mole at STP.** Determine the volume of 1.00 mol of any gas, assuming it behaves like an ideal gas, at STP.

APPROACH We use the ideal gas law, solving for V with $n = 1.00 \text{ mol}$.

SOLUTION We solve for V in Eq. 13-3:

$$V = \frac{nRT}{P} = \frac{(1.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(273 \text{ K})}{(1.013 \times 10^5 \text{ N/m}^2)} = 22.4 \times 10^{-3} \text{ m}^3.$$

Since 1 liter (L) is $1000 \text{ cm}^3 = 1.00 \times 10^{-3} \text{ m}^3$, 1.00 mol of any (ideal) gas has volume $V = 22.4 \text{ L}$ at STP.

The value of 22.4 L for the volume of 1 mol of an ideal gas at STP is worth remembering, for it sometimes makes calculation simpler.

EXERCISE C What is the volume of 1.00 mol of ideal gas at 546 K ($= 2 \times 273 \text{ K}$) and 2.0 atm absolute pressure? (a) 11.2 L ; (b) 22.4 L ; (c) 44.8 L ; (d) 67.2 L ; (e) 89.6 L .

[†]Sometimes it is useful to use R as given in terms of calories; calories will be defined in Section 14-1.

 PROBLEM SOLVING

1 mol of gas at STP has $V = 22.4 \text{ L}$

EXAMPLE 13–10 Helium balloon. A helium party balloon, assumed to be a perfect sphere, has a radius of 18.0 cm. At room temperature (20°C), its internal pressure is 1.05 atm. Find the number of moles of helium in the balloon and the mass of helium needed to inflate the balloon to these values.

APPROACH We can use the ideal gas law to find n , since we are given P and T , and can find V from the given radius.

SOLUTION We get the volume V from the formula for a sphere:

$$\begin{aligned} V &= \frac{4}{3}\pi r^3 \\ &= \frac{4}{3}\pi (0.180 \text{ m})^3 = 0.0244 \text{ m}^3. \end{aligned}$$

The pressure is given as $1.05 \text{ atm} = 1.064 \times 10^5 \text{ N/m}^2$. The temperature must be expressed in kelvins, so we change 20°C to $(20 + 273)\text{K} = 293 \text{ K}$. Finally, we use the value $R = 8.314 \text{ J/(mol}\cdot\text{K)}$ because we are using SI units. Thus

$$n = \frac{PV}{RT} = \frac{(1.064 \times 10^5 \text{ N/m}^2)(0.0244 \text{ m}^3)}{(8.314 \text{ J/mol}\cdot\text{K})(293 \text{ K})} = 1.066 \text{ mol}.$$

The mass of helium (atomic mass = 4.00 g/mol as given in the Periodic Table or Appendix B) can be obtained from

$$\begin{aligned} \text{mass} &= n \times \text{molecular mass} = (1.066 \text{ mol})(4.00 \text{ g/mol}) = 4.26 \text{ g} \\ &\text{or } 4.26 \times 10^{-3} \text{ kg}. \end{aligned}$$

EXAMPLE 13–11 ESTIMATE Mass of air in a room. Estimate the mass of air in a room whose dimensions are 5 m \times 3 m \times 2.5 m high, at STP.

APPROACH First we determine the number of moles n using the given volume. Then we can multiply by the mass of one mole to get the total mass.

SOLUTION Example 13–9 told us that 1 mol of a gas at 0°C has a volume of $22.4 \text{ L} = 22.4 \times 10^{-3} \text{ m}^3$. The room's volume is $5 \text{ m} \times 3 \text{ m} \times 2.5 \text{ m}$, so

$$n = \frac{(5 \text{ m})(3 \text{ m})(2.5 \text{ m})}{22.4 \times 10^{-3} \text{ m}^3/\text{mol}} \approx 1700 \text{ mol}.$$

Air is a mixture of about 20% oxygen (O_2) and 80% nitrogen (N_2). The molecular masses are $2 \times 16 \text{ u} = 32 \text{ u}$ and $2 \times 14 \text{ u} = 28 \text{ u}$, respectively, for an average of about 29 u. Thus, 1 mol of air has a mass of about $29 \text{ g} = 0.029 \text{ kg}$, so our room has a mass of air

$$m \approx (1700 \text{ mol})(0.029 \text{ kg/mol}) \approx 50 \text{ kg}.$$

NOTE That is roughly 100 lb of air!

 **PHYSICS APPLIED**
The mass of the air
in a room is significant

EXERCISE D At 20°C , would there be (a) more, (b) less, or (c) the same mass of air in a room than at 0°C ?

Frequently, volume is specified in liters and pressure in atmospheres. Rather than convert these to SI units, we can instead use the value of R given in Section 13–6 as $0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$.

In many situations it is not necessary to use the value of R at all. For example, many problems involve a change in the pressure, temperature, and volume of a fixed amount of gas. In this case, $PV/T = nR = \text{constant}$, since n and R remain constant. If we now let P_1 , V_1 , and T_1 represent the appropriate variables initially, and P_2 , V_2 , T_2 represent the variables after the change is made, then we can write

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad [\text{fixed } n]$$

If we know any five of the quantities in this equation, we can solve for the sixth. Or, if one of the three variables is constant ($V_1 = V_2$, or $P_1 = P_2$, or $T_1 = T_2$) then we can use this equation to solve for one unknown when given the other three quantities.

 **PROBLEM SOLVING**
Using the ideal gas law as a ratio



FIGURE 13-17 Example 13-12.

EXAMPLE 13-12 Check tires cold. An automobile tire is filled (Fig. 13-17) to a gauge pressure of 210 kPa (= 30 psi) at 10°C. After a drive of 100 km, the temperature within the tire rises to 40°C. What is the pressure within the tire now?

APPROACH We do not know the number of moles of gas, or the volume of the tire, but we assume they are constant. We use the ratio form of the ideal gas law.

SOLUTION Since $V_1 = V_2$, then

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

This is, incidentally, a statement of Gay-Lussac's law. Since the pressure given is the gauge pressure (Section 10-4), we must add atmospheric pressure (= 101 kPa) to get the absolute pressure $P_1 = (210 \text{ kPa} + 101 \text{ kPa}) = 311 \text{ kPa}$. We convert temperatures to kelvins by adding 273 and solve for P_2 :

$$P_2 = P_1 \left(\frac{T_2}{T_1} \right) = (3.11 \times 10^5 \text{ Pa}) \left(\frac{313 \text{ K}}{283 \text{ K}} \right) = 344 \text{ kPa}.$$

Subtracting atmospheric pressure, we find the resulting gauge pressure to be 243 kPa, which is a 16% increase (= 35 psi).

NOTE This Example shows why car manuals emphasize checking tire pressure when the tires are cold.

13-8 Ideal Gas Law in Terms of Molecules: Avogadro's Number

The fact that the gas constant, R , has the same value for all gases is a remarkable reflection of simplicity in nature. It was first recognized, although in a slightly different form, by the Italian scientist Amedeo Avogadro (1776–1856). Avogadro stated that *equal volumes of gas at the same pressure and temperature contain equal numbers of molecules*. This is sometimes called **Avogadro's hypothesis**. That this is consistent with R being the same for all gases can be seen as follows. From Eq. 13-3, $PV = nRT$, we see that for the same number of moles, n , and the same pressure and temperature, the volume will be the same for all gases as long as R is the same. Second, the number of molecules in 1 mole is the same for all gases (see page 369). Thus Avogadro's hypothesis is equivalent to R being the same for all gases.

The number of molecules in one mole of any pure substance is known as **Avogadro's number**, N_A . Although Avogadro conceived the notion, he was not able to actually determine the value of N_A . Indeed, precise measurements were not done until the twentieth century.

A number of methods have been devised to measure N_A , and the accepted value today is (see inside front cover for more precise value)

Avogadro's number

$$N_A = 6.02 \times 10^{23} \quad [\text{molecules/mole}]$$

Since the total number of molecules, N , in a gas is equal to N_A times the number of moles ($N = nN_A$), then the ideal gas law, Eq. 13-3, can be written in terms of the number of molecules present:

$$PV = nRT = \frac{N}{N_A} RT,$$

or

$$PV = NkT, \quad (13-4)$$

IDEAL GAS LAW
(in terms of molecules)

where $k = R/N_A$ is called the **Boltzmann constant** and has the value

$$k = \frac{R}{N_A} = \frac{8.314 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} / \text{mol}} = 1.38 \times 10^{-23} \text{ J/K}.$$

EXAMPLE 13–13 Hydrogen atom mass. Use Avogadro's number to determine the mass of a hydrogen atom.

APPROACH The mass of one atom equals the mass of 1 mol divided by the number of atoms in 1 mol, N_A .

SOLUTION One mole of hydrogen atoms (atomic mass = 1.008 u, Section 13–1 or Appendix B) has a mass of 1.008×10^{-3} kg and contains 6.02×10^{23} atoms. Thus one atom has a mass

$$m = \frac{1.008 \times 10^{-3} \text{ kg}}{6.02 \times 10^{23}} = 1.67 \times 10^{-27} \text{ kg}.$$

NOTE Historically, the reverse was done: a precise value of N_A was obtained from a precise measurement of the mass of the hydrogen atom.

EXAMPLE 13–14 ESTIMATE **How many molecules in one breath?** Estimate how many molecules you breathe in with a 1.0-L breath of air.

APPROACH We determine what fraction of a mole 1.0 L is using the result of Example 13–9 that 1 mole has a volume of 22.4 L at STP, and then multiply that by N_A to get the number of molecules in this number of moles.

SOLUTION One mole corresponds to 22.4 L at STP, so 1.0 L of air is $(1.0 \text{ L})/(22.4 \text{ L/mol}) = 0.045 \text{ mol}$. Then 1.0 L of air contains

$$(0.045 \text{ mol})(6.02 \times 10^{23} \text{ molecules/mole}) \approx 3 \times 10^{22} \text{ molecules}.$$



13–9 Kinetic Theory and the Molecular Interpretation of Temperature

The analysis of matter in terms of atoms in continuous random motion is called **kinetic theory**. We now investigate the properties of a gas from the point of view of kinetic theory, which is based on the laws of classical mechanics. But to apply Newton's laws to each one of the vast number of molecules in a gas ($>10^{25}/\text{m}^3$ at STP) is far beyond the capability of any present computer. Instead we take a statistical approach and determine averages of certain quantities, and connect these averages to macroscopic variables. We will demand that our microscopic description correspond to the macroscopic properties of gases; otherwise our theory would be of little value. Most importantly, we will arrive at an important relation between the average kinetic energy of molecules in a gas and the absolute temperature.

We make the following assumptions about the molecules in a gas. These assumptions reflect a simple view of a gas, but nonetheless the results they predict correspond well to the essential features of real gases that are at low pressure and are far from the liquefaction point. Under these conditions real gases follow the ideal gas law quite closely, and indeed the gas we now describe is referred to as an **ideal gas**. The assumptions representing the basic postulates of kinetic theory for an ideal gas are:

1. There are a large number of molecules, N , each of mass m , moving in random directions with a variety of speeds. This assumption agrees with our observation that a gas fills its container and, in the case of air on Earth, is kept from escaping only by the force of gravity.
2. The molecules are, on average, far apart from one another. That is, their average separation is much greater than the diameter of each molecule.
3. The molecules are assumed to obey the laws of classical mechanics, and are assumed to interact with one another only when they collide. Although molecules exert weak attractive forces on each other between collisions, the potential energy associated with these forces is small compared to the kinetic energy.
4. Collisions with another molecule or the wall of the vessel are assumed to be perfectly elastic, like the collisions of perfectly elastic billiard balls (Chapter 7). We assume the collisions are of very short duration compared to the time between collisions. Then we can ignore the potential energy associated with collisions in comparison to the kinetic energy between collisions.

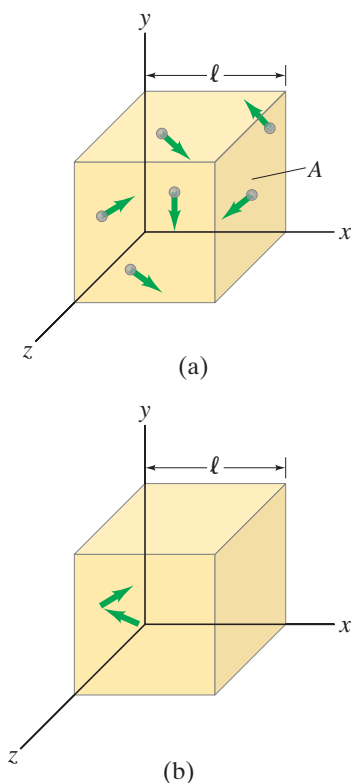


FIGURE 13-18 (a) Molecules of a gas moving about in a rectangular container. (b) Arrows indicate the momentum of one molecule as it rebounds from the end wall.

We can see how this kinetic view of a gas can explain Boyle's law (Section 13-5). The pressure exerted on a wall of a container of gas is due to the constant bombardment of molecules. If the volume is reduced by (say) half, the molecules are closer together and twice as many will be striking a given area of the wall per second. Hence we expect the pressure to be twice as great, in agreement with Boyle's law.

Now let us calculate quantitatively the pressure a gas exerts on its container in terms of microscopic quantities. We imagine that the molecules are inside a rectangular container (at rest) whose ends have area A and whose length is ℓ , as shown in Fig. 13-18a. The pressure exerted by the gas on the walls of its container is, according to our model, due to the collisions of the molecules with the walls. Let us focus our attention on the wall, of area A , at the left end of the container and examine what happens when one molecule strikes this wall, as shown in Fig. 13-18b. This molecule exerts a force on the wall, and according to Newton's third law the wall exerts an equal and opposite force back on the molecule. The magnitude of this force on the molecule, according to Newton's second law, is equal to the molecule's rate of change of momentum, $F = \Delta(mv)/\Delta t$ (Eq. 7-2). Assuming the collision is elastic, only the x component of the molecule's momentum changes, and it changes from $-mv_x$ (it is moving in the negative x direction) to $+mv_x$. Thus the change in the molecule's momentum, $\Delta(mv)$, which is the final momentum minus the initial momentum, is

$$\Delta(mv) = mv_x - (-mv_x) = 2mv_x$$

for one collision. This molecule will make many collisions with the wall, each separated by a time Δt , which is the time it takes the molecule to travel across the container and back again, a distance (x component) equal to 2ℓ . Thus $2\ell = v_x \Delta t$, or

$$\Delta t = \frac{2\ell}{v_x}.$$

The time Δt between collisions with a wall is very small, so the number of collisions per second is very large. Thus the average force—averaged over many collisions—will be equal to the momentum change during one collision divided by the time between collisions (Newton's second law, Eq. 7-2):

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2\ell/v_x} = \frac{mv_x^2}{\ell}. \quad [\text{due to one molecule}]$$

During its passage back and forth across the container, the molecule may collide with the tops and sides of the container, but this does not alter its x component of momentum and thus does not alter our result. [It may also collide with other molecules, which may change its v_x . However, any loss (or gain) of momentum is acquired by other molecules, and because we will eventually sum over all the molecules, this effect will be included. So our result above is not altered.]

The actual force due to one molecule is intermittent, but because a huge number of molecules are striking the wall per second, the force is, on average, nearly constant. To calculate the force due to *all* the molecules in the container, we have to add the contributions of each. If all N molecules have the same mass m , the net force on the wall is

$$F = \frac{m}{\ell}(v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2),$$

where v_{x1} means v_x for molecule number 1 (we arbitrarily assign each molecule a number) and the sum extends over the total number of molecules N in the container. The average value of the square of the x component of velocity is

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2}{N}, \quad (13-5)$$

where the overbar ($\overline{\quad}$) means "average." Thus we can write the force as

$$F = \frac{m}{\ell} N \overline{v_x^2}. \quad (i)$$

We know that the square of any vector is equal to the sum of the squares of its components (theorem of Pythagoras). Thus $v^2 = v_x^2 + v_y^2 + v_z^2$ for any velocity v .

Taking averages, we obtain

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}. \quad \text{(ii)}$$

Since the velocities of the molecules in our gas are assumed to be random, there is no preference to one direction or another. Hence

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}. \quad \text{(iii)}$$

Combining Eqs. (iii) and (ii), we get

$$\overline{v^2} = 3\overline{v_x^2}. \quad \text{(iv)}$$

We substitute Eq. (iv) into Eq. (i) for net force F (bottom of previous page):

$$F = \frac{m}{\ell} N \frac{\overline{v^2}}{3}.$$

The pressure on the wall is then

$$P = \frac{F}{A} = \frac{1}{3} \frac{Nm\overline{v^2}}{A\ell}$$

or

$$P = \frac{1}{3} \frac{Nm\overline{v^2}}{V}, \quad \left[\begin{array}{l} \text{pressure in an} \\ \text{ideal gas} \end{array} \right] \quad \text{(13-6)}$$

where $V = \ell A$ is the volume of the container. This is the result we wanted, the pressure exerted by a gas on its container expressed in terms of molecular properties.

Equation 13-6 can be rewritten in a clearer form by multiplying both sides by V and rearranging the right-hand side:

$$PV = \frac{2}{3} N \left(\frac{1}{2} m\overline{v^2} \right). \quad \text{(13-7)}$$

The quantity $\frac{1}{2} m\overline{v^2}$ is the average translational kinetic energy ($\overline{\text{KE}}$) of the molecules in the gas. If we compare Eq. 13-7 with Eq. 13-4, the ideal gas law $PV = NkT$, we see that the two agree if

$$\frac{2}{3} \left(\frac{1}{2} m\overline{v^2} \right) = kT,$$

or

$$\overline{\text{KE}} = \frac{1}{2} m\overline{v^2} = \frac{3}{2} kT. \quad \text{[ideal gas]} \quad \text{(13-8)}$$

TEMPERATURE RELATED TO
AVERAGE KINETIC ENERGY
OF MOLECULES

This equation tells us that

the average translational kinetic energy of molecules in random motion in an ideal gas is directly proportional to the absolute temperature of the gas.

The higher the temperature, according to kinetic theory, the faster the molecules are moving on average. This relation is one of the triumphs of kinetic theory.

EXAMPLE 13-15 **Molecular kinetic energy.** What is the average translational kinetic energy of molecules in an ideal gas at 37°C ?

APPROACH We use the absolute temperature in Eq. 13-8.

SOLUTION We change 37°C to 310 K and insert into Eq. 13-8:

$$\overline{\text{KE}} = \frac{3}{2} kT = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K})(310 \text{ K}) = 6.42 \times 10^{-21} \text{ J}.$$

NOTE A mole of molecules would have a total translational kinetic energy equal to $(6.42 \times 10^{-21} \text{ J})(6.02 \times 10^{23}) = 3860 \text{ J}$, which equals the kinetic energy of a 1-kg stone traveling almost 90 m/s.

EXERCISE E If molecules of hydrogen gas and oxygen gas were placed in the same balloon at room temperature, how would the average kinetic energies of the molecules compare?
(a) They would be the same. (b) The hydrogen molecules would have greater kinetic energy.
(c) The oxygen molecules would have greater kinetic energy. (d) Need more information.

Equation 13-8 holds not only for gases, but also applies reasonably accurately to liquids and solids. Thus the result of Example 13-15 would apply to molecules within living cells at body temperature (37°C).

We can use Eq. 13–8 to calculate how fast molecules are moving on average. Notice that the average in Eqs. 13–5 through 13–8 is over the *square* of the speed. The square root of $\overline{v^2}$ is called the **root-mean-square** speed, v_{rms} (since we are taking the square *root* of the *mean* of the *square* of the speed):

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}. \quad (13-9)$$

EXAMPLE 13–16 **Speeds of air molecules.** What is the rms speed of air molecules (O_2 and N_2) at room temperature (20°C)?

APPROACH To obtain v_{rms} , we need the masses of O_2 and N_2 molecules and then apply Eq. 13–9 to oxygen and nitrogen separately, since they have different masses.

SOLUTION The masses of one molecule of O_2 (molecular mass = 32 u) and N_2 (molecular mass = 28 u) are (where $1 \text{ u} = 1.66 \times 10^{-27} \text{ kg}$)

$$m(\text{O}_2) = (32)(1.66 \times 10^{-27} \text{ kg}) = 5.3 \times 10^{-26} \text{ kg},$$

$$m(\text{N}_2) = (28)(1.66 \times 10^{-27} \text{ kg}) = 4.6 \times 10^{-26} \text{ kg}.$$

Thus, for oxygen

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{(3)(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{(5.3 \times 10^{-26} \text{ kg})}} = 480 \text{ m/s},$$

and for nitrogen the result is $v_{\text{rms}} = 510 \text{ m/s}$.

NOTE These speeds are more than 1700 km/h or 1000 mi/h, and are greater than the speed of sound, $\approx 340 \text{ m/s}$ at 20°C (Chapter 12).

EXERCISE F By what factor must the absolute temperature change to double v_{rms} ? (a) $\sqrt{2}$; (b) 2; (c) $2\sqrt{2}$; (d) 4; (e) 16.

* Kinetic Energy Near Absolute Zero

Equation 13–8, $\overline{KE} = \frac{3}{2}kT$, implies that as the temperature approaches absolute zero, the kinetic energy of molecules approaches zero. Modern quantum theory, however, tells us this is not quite so. Instead, as absolute zero is approached, the kinetic energy approaches a very small nonzero minimum value. Even though all real gases become liquid or solid near 0 K, molecular motion does not cease, even at absolute zero.

13–10 Distribution of Molecular Speeds

The molecules in a gas are assumed to be in random motion, which means that many molecules have speeds less than the rms speed and others have greater speeds. In 1859, James Clerk Maxwell (1831–1879) derived, on the basis of kinetic theory, that the speeds of molecules in a gas are distributed according to the graph shown in Fig. 13–19. This is known as the **Maxwell distribution of speeds**.[†] The speeds vary from zero to many times the rms speed, but as the graph shows, most molecules have speeds that are not far from the average. Less than 1% of the molecules exceed four times v_{rms} .

Experiments to determine the distribution of molecular speeds in real gases, starting in the 1920s, confirmed with considerable accuracy the Maxwell distribution and the direct proportion between average kinetic energy and absolute temperature, Eq. 13–8.

[†] Mathematically, the distribution is given by $\Delta N = Cv^2 \exp(-\frac{1}{2}mv^2/kT)\Delta v$, where ΔN is the number of molecules with speed between v and $v + \Delta v$, C is a constant, and \exp means the expression in parentheses is an exponent on the “natural number” $e = 2.718\dots$

FIGURE 13–19 Distribution of speeds of molecules in an ideal gas. Note that v_{rms} is not at the peak of the curve (that speed is called the “most probable speed,” v_p). This is because the curve is skewed to the right: it is not symmetrical.

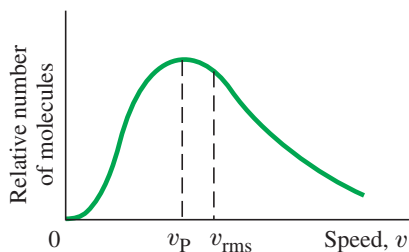


Figure 13–20 shows the Maxwell distribution for two different temperatures. Just as v_{rms} increases with temperature, so the whole distribution curve shifts to the right at higher temperatures. Kinetic theory can be applied approximately to liquids and solutions. Figure 13–20 illustrates how kinetic theory can explain why many chemical reactions, including those in biological cells, take place more rapidly as the temperature increases. Most chemical reactions occur in a liquid solution, and the molecules have a speed distribution close to the Maxwell distribution. Two molecules may chemically react only if their kinetic energy is above some particular minimum value (called the *activation energy*), E_A , so that when they collide, they penetrate into each other somewhat. Figure 13–20 shows that at a higher temperature, many more molecules have a speed and kinetic energy KE above the needed threshold E_A .

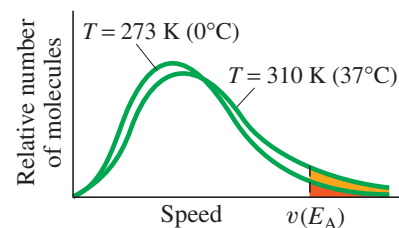


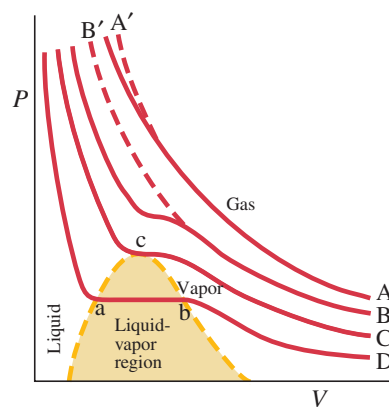
FIGURE 13–20 Distribution of molecular speeds for two different temperatures. Color shading shows proportions of molecules above a certain speed (corresponding to an activation energy $E_A = \frac{1}{2}mv^2$).

13–11 Real Gases and Changes of Phase

The ideal gas law, $PV = NkT$, is an accurate description of the behavior of a real gas as long as the pressure is not too high and the temperature is far from the liquefaction point. But what happens when these two criteria are not satisfied? First we discuss real gas behavior, and then we examine how kinetic theory can help us understand this behavior.

Let us look at a graph of pressure plotted against volume for a given amount of gas. On such a **PV diagram**, Fig. 13–21, each point represents the pressure and volume of an equilibrium state of the given substance. The various curves (labeled A, B, C, and D) show how the pressure varies as a function of volume for four different values of constant temperature T_A , T_B , T_C , and T_D . The red dashed curve A' represents the behavior of a gas as predicted by the ideal gas law; that is, $PV = \text{constant}$. The solid curve A represents the behavior of a real gas at the same temperature. Notice that at high pressure, the volume of a real gas is less than that predicted by the ideal gas law. The curves B and C in Fig. 13–21 represent the gas at successively lower temperatures, and we see that the behavior deviates even more from the curves predicted by the ideal gas law (for example, B'), and the deviation is greater the closer the gas is to liquefying.

FIGURE 13–21 PV diagram for a real substance. Curves A, B, C, and D represent the same substance at different temperatures ($T_A > T_B > T_C > T_D$).



To explain this behavior, note that at higher pressure we expect the molecules to be closer together. And at lower temperatures, the potential energy associated with attractive forces between the molecules (which we ignored before) is no longer negligible. These attractive forces tend to pull the molecules closer together so the volume is less than expected from the ideal gas law. At still lower temperatures, these forces cause liquefaction, and the molecules become very close together.

Curve D represents the situation when liquefaction occurs. At low pressure on curve D (on the right in Fig. 13–21), the substance is a gas and occupies a large volume. As the pressure is increased, the volume decreases until point b is reached. From point b to point a, the volume decreases with no change in pressure; the substance is gradually changing from the gas to the liquid phase. At point a, all of the substance has changed to liquid. Further increase in pressure reduces the volume only slightly—liquids are nearly incompressible—so on the left the curve is very steep as shown. The shaded area under the gold dashed line represents the region where the gas and liquid phases exist together in equilibrium.

Curve C in Fig. 13–21 represents the behavior of the substance at its **critical temperature**; the point c (the one point where curve C is horizontal) is called the **critical point**. At temperatures less than the critical temperature, a gas will change to the liquid phase if sufficient pressure is applied. Above the critical temperature (and this is the definition of the term), no amount of pressure can cause a gas to change phase and become a liquid. (Thus curves A and B represent the substance at temperatures where it can only be a gas.) The critical temperatures for various gases are given in Table 13–2. Scientists tried for many years to liquefy oxygen without success, which led to the idea that there must be a critical point. Oxygen can be liquefied only if first cooled below its critical temperature of -118°C .

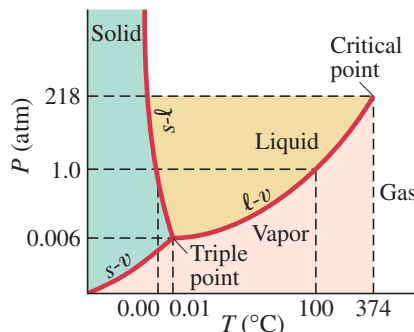
TABLE 13–2 Critical Temperatures and Pressures

Substance	Critical Temperature		Critical Pressure (atm)
	$^\circ\text{C}$	K	
Water	374	647	218
CO_2	31	304	72.8
Oxygen	-118	155	50
Nitrogen	-147	126	33.5
Hydrogen	-239.9	33.3	12.8
Helium	-267.9	5.3	2.3

Often a distinction is made between the terms “gas” and “vapor”: a substance below its critical temperature in the gaseous state is called a **vapor**; above the critical temperature, it is called a **gas**.

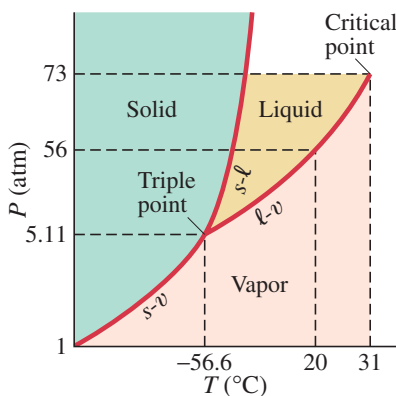
The behavior of a substance can be diagrammed not only on a PV diagram but also on a PT diagram. A **PT diagram**, often called a **phase diagram**, is particularly convenient for comparing the different phases of a substance. Figure 13–22 is the phase diagram for water. The curve labeled $l-v$ represents those points where the liquid and vapor phases are in equilibrium—it is thus a graph of the boiling point versus pressure. Note that the curve correctly shows that at a pressure of 1 atm the boiling point is 100°C and that the boiling point is lowered for a decreased pressure. The curve $s-l$ represents points where solid and liquid exist in equilibrium and thus is a graph of the freezing point versus pressure.

FIGURE 13–22 Phase diagram for water (note that the scales are not linear).



At 1 atm, the freezing point of water is 0°C , as shown. Notice also in Fig. 13–22 that at a pressure of 1 atm, the substance is in the liquid phase if the temperature is between 0°C and 100°C , but is in the solid or vapor phase if the temperature is below 0°C or above 100°C . The curve labeled $s-v$ is the *sublimation point* versus pressure curve. **Sublimation** refers to the process whereby at low pressures a solid changes directly into the vapor phase without passing through the liquid phase. For water, sublimation occurs if the pressure of the water vapor is less than 0.0060 atm. Carbon dioxide, which in the solid phase is called dry ice, sublimates even at atmospheric pressure (Fig. 13–23).

FIGURE 13–23 Phase diagram for carbon dioxide.



The intersection of the three curves (in Fig. 13–22) is the **triple point**. For water this occurs at $T = 273.16\text{ K}$ and $P = 6.03 \times 10^{-3}\text{ atm}$. It is only at the triple point that the three phases can exist together in equilibrium. Because the triple point corresponds to a unique value of temperature and pressure, it is precisely reproducible and is often used as a point of reference. For example, the standard of temperature is usually specified as exactly 273.16 K at the triple point of water, rather than 273.15 K at the freezing point of water at 1 atm.

Notice that the solid-liquid ($s-l$) curve for water (Fig. 13–22) slopes upward to the left. This is true only of substances that *expand* upon freezing; at a higher pressure, a lower temperature is needed to cause the liquid to freeze. More commonly, substances contract upon freezing and the $s-l$ curve slopes upward to the right, as shown for carbon dioxide (CO_2) in Fig. 13–23.

The phase transitions we have been discussing are the common ones. Some substances, however, can exist in several forms in the solid phase. A transition from one phase to another occurs at a particular temperature and pressure, just like ordinary phase changes. For example, ice has been observed in at least eight forms at very high pressure. Ordinary helium has two distinct liquid phases, called helium I and II. They exist only at temperatures within a few degrees of absolute zero. Helium II exhibits very unusual properties referred to as **superfluidity**. It has essentially zero viscosity and exhibits strange properties such as climbing up the sides of an open container. Also interesting are **liquid crystals** (used for computer and TV monitors, Section 24–11) which can be considered to be in a phase between liquid and solid.

13–12 Vapor Pressure and Humidity

Evaporation

If a glass of water is left out overnight, the water level will have dropped by morning. We say the water has evaporated, meaning that some of the water has changed to the vapor or gas phase.

This process of **evaporation** can be explained on the basis of kinetic theory. The molecules in a liquid move past one another with a variety of speeds that follow, approximately, the Maxwell distribution. There are strong attractive forces between these molecules, which is what keeps them close together in the liquid phase. A molecule near the surface of the liquid may, because of its speed, leave the liquid momentarily. But just as a rock thrown into the air returns to the Earth, so the attractive forces of the other molecules can pull the vagabond molecule back to the liquid surface—that is, if its velocity is not too large. A molecule with a high enough velocity, however, will escape the liquid entirely, like a rocket escaping the Earth, and become part of the gas phase. Only those molecules that have kinetic energy above a particular value can escape to the gas phase. We have already seen that kinetic theory predicts that the relative number of molecules with kinetic energy above a particular value (such as E_A in Fig. 13–20) increases with temperature. This is in accord with the well-known observation that the evaporation rate is greater at higher temperatures.

Because it is the fastest molecules that escape from the surface, the average speed of those remaining is less. When the average speed is less, the absolute temperature is less. Thus kinetic theory predicts that *evaporation is a cooling process*. You may have noticed this effect when you stepped out of a warm shower and felt cold as the water on your body began to evaporate; and after working up a sweat on a hot day, even a slight breeze makes you feel cool through evaporation. Try licking your finger and then blow on it.

Vapor Pressure

Air normally contains water vapor (water in the gas phase), and it comes mainly from evaporation. To look at this process in a little more detail, consider a closed container that is partially filled with water (or another liquid) and from which the air has been removed (Fig. 13–24). The fastest moving molecules quickly evaporate into the empty space above the liquid's surface. As they move about, some of these molecules strike the liquid surface and again become part of the liquid phase: this is called **condensation**. The number of molecules in the vapor increases until the number of molecules returning to the liquid equals the number leaving in the same time interval. Equilibrium then exists, and the space above the liquid surface is said to be *saturated*. The pressure of the vapor when it is saturated is called the **saturated vapor pressure** (or simply the vapor pressure).

The saturated vapor pressure of any substance depends on the temperature. At higher temperatures, more molecules have sufficient kinetic energy to break from the liquid surface into the vapor phase. Hence equilibrium will be reached at a higher vapor pressure. The saturated vapor pressure of water at various temperatures is given in Table 13–3. Notice that even solids—for example, ice—have a measurable saturated vapor pressure.

In everyday situations, evaporation from a liquid takes place into the air above it rather than into a vacuum. This does not materially alter the discussion above relating to Fig. 13–24. Equilibrium will still be reached when there are sufficient molecules in the gas phase that the number reentering the liquid equals the number leaving. The concentration of particular molecules (such as water) in the gas phase is not affected by the presence of air, although collisions with air molecules may lengthen the time needed to reach equilibrium. Thus equilibrium occurs at the same value of the saturated vapor pressure as if air were not there.

If the container is large or is not closed, all the liquid may evaporate before saturation is reached. And if the container is not sealed—as, for example, a room in your house—it is not likely that the air will become saturated with water vapor (unless it is raining outside).

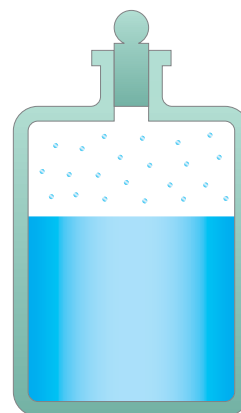


FIGURE 13–24 Vapor appears above a liquid in a closed container.

PHYSICS APPLIED

Evaporation cools

TABLE 13–3 Saturated Vapor Pressure of Water

Temperature (°C)	Saturated Vapor Pressure	
	torr (= mm-Hg)	Pa (= N/m ²)
–50	0.030	4.0
–10	1.95	2.60×10^2
0	4.58	6.11×10^2
5	6.54	8.72×10^2
10	9.21	1.23×10^3
15	12.8	1.71×10^3
20	17.5	2.33×10^3
25	23.8	3.17×10^3
30	31.8	4.24×10^3
40	55.3	7.37×10^3
50	92.5	1.23×10^4
60	149	1.99×10^4
70 [†]	234	3.12×10^4
80	355	4.73×10^4
90	526	7.01×10^4
100 [‡]	760	1.01×10^5
120	1489	1.99×10^5
150	3570	4.76×10^5

[†] Boiling point on summit of Mt. Everest.

[‡] Boiling point at sea level.



FIGURE 13–25 Boiling: bubbles of water vapor float upward from the bottom (where the temperature is highest).

Boiling

The saturated vapor pressure of a liquid increases with temperature. When the temperature is raised to the point where the saturated vapor pressure at that temperature equals the external pressure, **boiling** occurs (Fig. 13–25). As the boiling point is approached, tiny bubbles tend to form in the liquid, which indicate a change from the liquid to the gas phase. However, if the vapor pressure inside the bubbles is less than the external pressure, the bubbles immediately are crushed. As the temperature is increased, the saturated vapor pressure inside a bubble eventually becomes equal to or exceeds the external air pressure. The bubble will then not collapse but can rise to the surface. Boiling has then begun. *A liquid boils when its saturated vapor pressure equals the external pressure.* This occurs for water at a pressure of 1 atm (760 torr) at 100°C, as can be seen from Table 13–3.

The boiling point of a liquid depends on the external pressure. At high elevations, the boiling point of water is somewhat less than at sea level because the air pressure is less up there. For example, on the summit of Mt. Everest (8850 m) the air pressure is about one-third of what it is at sea level, and from Table 13–3 we can see that water will boil at about 70°C. Cooking food by boiling takes longer at high elevations, because the boiling water is cooking at a lower temperature. Pressure cookers reduce cooking time because they build up a pressure as high as 2 atm, allowing a higher boiling (and cooking) temperature to be attained (Problem 64 and Fig. 13–32).

Partial Pressure and Humidity

When we refer to the weather as being dry or humid, we are referring to the water vapor content of the air. In a gas such as air, which is a mixture of several types of gases, the total pressure is the sum of the *partial pressures* of each gas present.[†] By **partial pressure**, we mean the pressure each gas would exert if it alone were present. The partial pressure of water in the air can be as low as zero and can vary up to a maximum equal to the saturated vapor pressure of water at the given temperature. Thus, at 20°C, the partial pressure of water cannot exceed 17.5 torr (see Table 13–3) or about 0.02 atm. The **relative humidity** is defined as the ratio of the partial pressure of water vapor to the saturated vapor pressure at a given temperature. It is usually expressed as a percentage:

$$\text{Relative humidity} = \frac{\text{partial pressure of H}_2\text{O}}{\text{saturated vapor pressure of H}_2\text{O}} \times 100\%.$$

Thus, when the humidity is close to 100%, the air holds nearly all the water vapor it can.

EXAMPLE 13–17 **Relative humidity.** On a particular hot day, the temperature is 30°C and the partial pressure of water vapor in the air is 21.0 torr. What is the relative humidity?

APPROACH From Table 13–3, we see that the saturated vapor pressure of water at 30°C is 31.8 torr.

SOLUTION The relative humidity is thus

$$\frac{21.0 \text{ torr}}{31.8 \text{ torr}} \times 100\% = 66\%.$$



Humans are sensitive to humidity. A relative humidity of 40–50% is generally optimum for both health and comfort. High humidity, particularly on a hot day, reduces the evaporation of moisture from the skin, which is one of the body's vital mechanisms for regulating body temperature. Very low humidity, on the other hand, can dry the skin and mucous membranes.

[†]For example, 78% (by volume) of air molecules are nitrogen and 21% oxygen, with much smaller amounts of water vapor, argon, carbon dioxide, and other gases. At an air pressure of 1 atm, oxygen exerts a partial pressure of 0.21 atm and nitrogen 0.78 atm.

Air is saturated with water vapor when the partial pressure of water in the air is equal to the saturated vapor pressure at that temperature. If the partial pressure of water exceeds the saturated vapor pressure, the air is said to be **supersaturated**. This situation can occur when a temperature decrease occurs. For example, suppose the temperature is 30°C and the partial pressure of water is 21 torr, which represents a humidity of 66% as we saw in Example 13–17. Suppose now that the temperature falls to, say, 20°C, as might happen at nightfall. From Table 13–3 we see that the saturated vapor pressure of water at 20°C is 17.5 torr. Hence the relative humidity would be greater than 100%, and the supersaturated air cannot hold this much water vapor. The excess water may condense and appear as dew, clouds, or as fog or rain (Fig. 13–26).

When air containing a given amount of water is cooled, a temperature is reached where the partial pressure of water equals the saturated vapor pressure. This is called the **dew point**. Measurement of the dew point is the most accurate means of determining the relative humidity. One method uses a polished metal surface which is gradually cooled down while in contact with air. The temperature at which moisture begins to appear on the surface is the dew point, and the partial pressure of water can then be obtained from saturated vapor pressure Tables. If, for example, on a given day the temperature is 20°C and the dew point is 5°C, then the partial pressure of water (Table 13–3) in the 20°C air is 6.54 torr, whereas its saturated vapor pressure is 17.5 torr; hence the relative humidity is $6.54/17.5 = 37\%$.

CONCEPTUAL EXAMPLE 13–18 Dryness in winter. Why does the air inside heated buildings seem very dry on a cold winter day?

RESPONSE Suppose the relative humidity outside on a -10°C day is 50%. Table 13–3 tells us the partial pressure of water in the air is about 1.0 torr. If this air is brought indoors and heated to $+20^\circ\text{C}$, the relative humidity is $(1.0 \text{ torr})/(17.5 \text{ torr}) = 5.7\%$. Even if the outside air were saturated at a partial pressure of 1.95 torr, the inside relative humidity would still be at a low 11%.

* 13–13 Diffusion

If you carefully place a few drops of food coloring in a glass of water as in Fig. 13–27, you will find that the color spreads throughout the water. The process may take some time (assuming you do not shake the glass), but eventually the color will become uniform. This mixing, known as **diffusion**, is readily explained by kinetic theory as due to the random movement of the molecules. Diffusion occurs in gases too. Common examples include perfume or smoke (or the odor of something cooking on a stove) diffusing in air, although convection (moving air currents) often plays a greater role in spreading odors than does diffusion. Diffusion depends on concentration, by which we mean the number of molecules or moles per unit volume. In general, *the diffusing substance moves from a region where its concentration is high to a region where its concentration is low.*

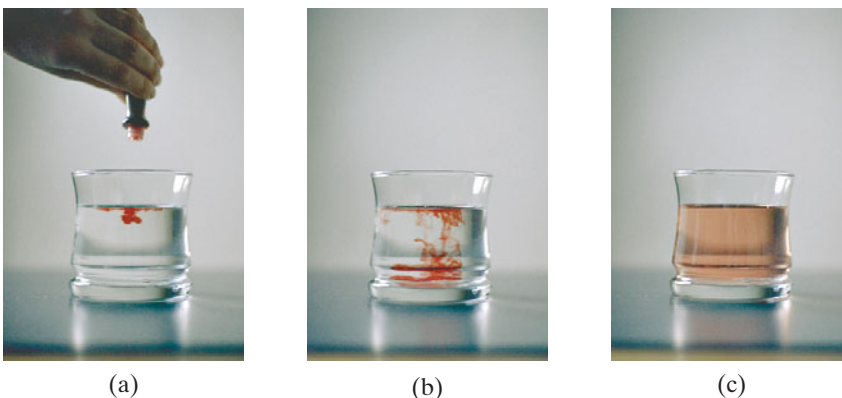


FIGURE 13–27 A few drops of food coloring (a) dropped into water, (b) spreads slowly throughout the water, eventually (c) becoming uniform.

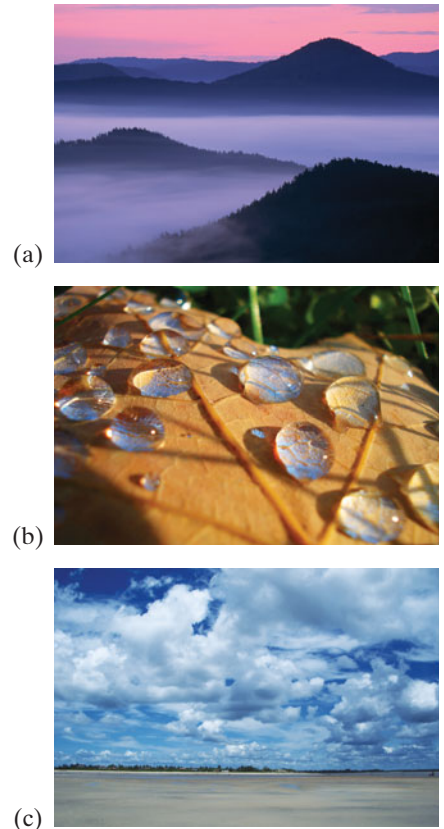


FIGURE 13–26 (a) Fog or mist settling in a valley where the temperature has dropped below the dew point. (b) Dew drops on a leaf. (c) Clouds form on a sunny day at the beach due to air, nearly saturated with water vapor, rising to an altitude where the cooler temperature is at the dew point.

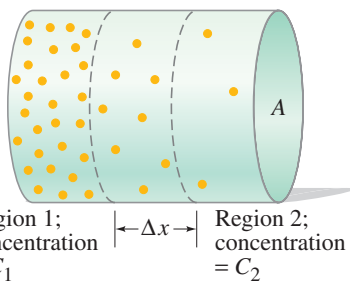


FIGURE 13–28 Diffusion occurs from a region of high concentration to one of lower concentration (only one type of molecule is shown).

TABLE 13–4 Diffusion Constants, D (20°C, 1 atm)

Diffusing Molecules	Medium	D (m ² /s)
H ₂	Air	6.3×10^{-5}
O ₂	Air	1.8×10^{-5}
O ₂	Water	100×10^{-11}
Glycine (an amino acid)	Water	95×10^{-11}
Blood hemoglobin	Water	6.9×10^{-11}
DNA (mass 6×10^6 u)	Water	0.13×10^{-11}

PHYSICS APPLIED
Diffusion time

Diffusion can be readily understood on the basis of kinetic theory and the random motion of molecules. Consider a tube of cross-sectional area A containing molecules in a higher concentration on the left than on the right, Fig. 13–28. We assume the molecules are in random motion. Yet there will be a net flow of molecules to the right. To see why, let us consider the small section of tube of length Δx as shown. Molecules from both regions 1 and 2 cross into this central section as a result of their random motion. The more molecules there are in a region, the more will strike a given area or cross a boundary. Since there is a greater concentration of molecules in region 1 than in region 2, more molecules cross into the central section from region 1 than from region 2. There is, then, a net flow of molecules from left to right, from high concentration (C_1) toward low concentration (C_2). The net flow becomes zero only when the concentrations become equal.

We might expect that the greater the difference in concentration, the greater the flow rate. Indeed, the rate of diffusion, J (number of molecules or moles or kg per second), is directly proportional to the difference in concentration per unit distance, $(C_1 - C_2)/\Delta x$ (which is called the **concentration gradient**), and to the cross-sectional area A (see Fig. 13–28):

$$J = DA \frac{C_1 - C_2}{\Delta x} \quad (13-10)$$

D is a constant of proportionality called the **diffusion constant**. Equation 13–10 is known as the **diffusion equation**, or **Fick's law**. If the concentrations are given in mol/m³, then J is the number of moles passing a given point per second. If the concentrations are given in kg/m³, then J is the mass movement per second (kg/s). The length Δx is given in meters, and area A in m². The values of D for a variety of substances diffusing in a particular medium are given in Table 13–4.

EXAMPLE 13–19 ESTIMATE Diffusion of ammonia in air. To get an idea of the time required for diffusion, estimate how long it might take for ammonia (NH₃) to be detected 10 cm from a bottle after it is opened, assuming only diffusion is occurring.

APPROACH This will be an order-of-magnitude calculation. The rate of diffusion J can be set equal to the number of molecules N diffusing across area A in a time t : $J = N/t$. Then the time $t = N/J$, where J is given by Eq. 13–10. We will have to make some assumptions and rough approximations about concentrations to use Eq. 13–10.

SOLUTION Using Eq. 13–10, we find

$$t = \frac{N}{J} = \frac{N \Delta x}{DA \Delta C}$$

The average concentration (midway between bottle and nose) can be approximated by $\bar{C} \approx N/V$, where V is the volume over which the molecules move and is roughly on the order of $V \approx A \Delta x$, where Δx is 10 cm = 0.10 m. We substitute $N = \bar{C}V = \bar{C}A \Delta x$ into the above equation:

$$t \approx \frac{(\bar{C}A \Delta x) \Delta x}{DA \Delta C} = \frac{\bar{C}}{\Delta C} \frac{(\Delta x)^2}{D}$$

The concentration of ammonia is high near the bottle (C) and low near the detecting nose (≈ 0), so $\bar{C} \approx C/2 \approx \Delta C/2$, or $(\bar{C}/\Delta C) \approx \frac{1}{2}$. Since NH₃ molecules have a size somewhere between H₂ and O₂, from Table 13–4 we can estimate $D \approx 4 \times 10^{-5}$ m²/s. Then

$$t \approx \frac{1}{2} \frac{(0.10 \text{ m})^2}{(4 \times 10^{-5} \text{ m}^2/\text{s})} \approx 100 \text{ s,}$$

or about a minute or two.

NOTE This result seems rather long from experience, suggesting that air currents (convection) are more important than diffusion for transmitting odors.

Diffusion is extremely important for living organisms. For example, molecules produced in certain chemical reactions within cells diffuse to other areas where they take part in other reactions.

Gas diffusion is important too. Plants require carbon dioxide for photosynthesis. The CO_2 diffuses into leaves from the outside air through tiny openings (stomata). As CO_2 is utilized by the cells, its concentration drops below that in the air outside, and more diffuses inward. Water vapor and oxygen produced by the cells diffuse outward into the air.

Animals also exchange oxygen and CO_2 with the environment. Oxygen is required for energy-producing reactions and must diffuse into cells. CO_2 is produced as an end product of many metabolic reactions and must diffuse out of cells. But diffusion is slow over longer distances, so only the smallest organisms in the animal world could survive without having developed complex respiratory and circulatory systems. In humans, oxygen is taken into the lungs, where it diffuses short distances across lung tissue and into the blood. Then the blood circulates it to cells throughout the body. The blood also carries CO_2 produced by the cells back to the lungs, where it diffuses outward.

Summary

The atomic theory of matter postulates that all matter is made up of tiny entities called **atoms**, which are typically 10^{-10} m in diameter.

Atomic and **molecular masses** are specified on a scale where the most common form of carbon (^{12}C) is arbitrarily given the value 12.0000 u (atomic mass units), exactly.

The distinction between solids, liquids, and gases can be attributed to the strength of the attractive forces between the atoms or molecules and to their average speed.

Temperature is a measure of how hot or cold something is. **Thermometers** are used to measure temperature on the **Celsius** ($^{\circ}\text{C}$), **Fahrenheit** ($^{\circ}\text{F}$), and **Kelvin** (K) scales. Two standard points on each scale are the freezing point of water (0°C , 32°F , 273.15 K) and the boiling point of water (100°C , 212°F , 373.15 K). A one-kelvin change in temperature equals a change of one Celsius degree or $\frac{9}{5}$ Fahrenheit degrees. Kelvins are related to $^{\circ}\text{C}$ by

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15.$$

When two objects at different temperatures are placed in contact, they eventually reach the same temperature and are then said to be in **thermal equilibrium**.

The change in length, $\Delta\ell$, of a solid, when its temperature changes by an amount ΔT , is directly proportional to the temperature change and to its original length ℓ_0 . That is,

$$\Delta\ell = \alpha\ell_0\Delta T, \quad (13-1a)$$

where α is the *coefficient of linear expansion*.

The change in volume of most solids, liquids, and gases is proportional to the temperature change and to the original volume V_0 :

$$\Delta V = \beta V_0\Delta T. \quad (13-2)$$

The *coefficient of volume expansion*, β , is approximately equal to 3α for uniform solids.

Water is unusual because, unlike most materials whose volume increases with temperature, its volume in the range from 0°C to 4°C actually decreases as the temperature increases.

The **ideal gas law**, or **equation of state for an ideal gas**, relates the pressure P , volume V , and temperature T (in kelvins) of n moles of gas by the equation

$$PV = nRT, \quad (13-3)$$

where $R = 8.314\text{ J/mol}\cdot\text{K}$ for all gases. Real gases obey the

ideal gas law quite accurately if they are not at too high a pressure or near their liquefaction point.

One **mole** is that amount of a substance whose mass in grams is numerically equal to the atomic or molecular mass of that substance.

Avogadro's number, $N_A = 6.02 \times 10^{23}$, is the number of atoms or molecules in 1 mol of any pure substance.

The ideal gas law can be written in terms of the number of molecules N in the gas as

$$PV = NkT, \quad (13-4)$$

where $k = R/N_A = 1.38 \times 10^{-23}\text{ J/K}$ is Boltzmann's constant.

According to the **kinetic theory** of gases, which is based on the idea that a gas is made up of molecules that are moving rapidly and randomly, the average translational kinetic energy of molecules is proportional to the Kelvin temperature T :

$$\overline{KE} = \frac{1}{2}m\overline{v}^2 = \frac{3}{2}kT, \quad (13-8)$$

where k is Boltzmann's constant. At any moment, there exists a wide distribution of molecular speeds within a gas.

The behavior of real gases at high pressure, and/or when near their liquefaction point, deviates from the ideal gas law due to the attractive forces between molecules. Below the **critical temperature**, a gas can change to a liquid if sufficient pressure is applied; but if the temperature is higher than the critical temperature, no amount of pressure will cause a liquid surface to form. The **triple point** of a substance is that unique temperature and pressure at which all three phases—solid, liquid, and gas—can coexist in equilibrium.

Evaporation of a liquid is the result of the fastest moving molecules escaping from the surface. **Saturated vapor pressure** refers to the pressure of the vapor above a liquid when the two phases are in equilibrium. The vapor pressure of a substance (such as water) depends strongly on temperature, and at the boiling point is equal to atmospheric pressure. **Relative humidity** of air is the ratio of the actual partial pressure of water vapor in the air to the saturated vapor pressure at that temperature; it is usually expressed as a percentage.

[***Diffusion** is the process whereby molecules of a substance move (on average) from one area to another because of a difference in that substance's concentration.]

Questions

- Which has more atoms: 1 kg of lead or 1 kg of copper? (See the Periodic Table or Appendix B.) Explain why.
- Name several properties of materials that could be used to make a thermometer.
- Which is larger, 1 C° or 1 F°? Explain why.
- In the relation $\Delta l = \alpha l_0 \Delta T$, should l_0 be the initial length, the final length, or does it matter?
- A flat bimetallic strip consists of a strip of aluminum riveted to a strip of iron. When heated, the strip will bend. Which metal will be on the outside of the curve? Why? [Hint: See Table 13–1.]
- Long steam pipes that are fixed at the ends often have a section in the shape of a U. Why?
- Figure 13–29 shows a diagram of a simple bimetallic **thermostat** used to control a furnace (or other heating or cooling system). The electric switch (attached to the bimetallic strip) is a glass vessel containing liquid mercury that conducts electricity when it touches both contact wires. Explain how this device controls the furnace and how it can be set at different temperatures.

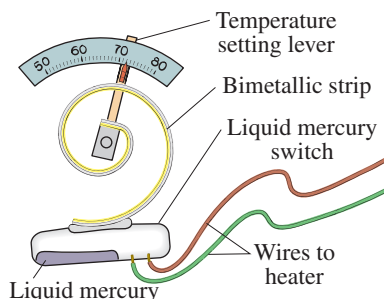


FIGURE 13–29
A thermostat (Question 7).

- A glass container may break if one part of it is heated or cooled more rapidly than adjacent parts. Explain.
- Explain why it is advisable to add water to an overheated automobile engine only slowly, and only with the engine running.
- The units for the coefficient of linear expansion α are $(\text{C}^\circ)^{-1}$, and there is no mention of a length unit such as meters. Would the expansion coefficient change if we used feet or millimeters instead of meters? Explain.
- When a cold alcohol-in-glass thermometer is first placed in a hot tub of water, the alcohol initially descends a bit and then rises. Explain.
- The principal virtue of Pyrex glass is that its coefficient of linear expansion is much smaller than that for ordinary glass (Table 13–1). Explain why this gives rise to the higher heat resistance of Pyrex.
- Will a clock using a pendulum supported on a long thin brass rod that is accurate at 20°C run fast or slow on a hot day (30°C)? Explain.
- Freezing a can of soda will cause its bottom and top to bulge so badly the can will not stand up. What has happened?
- Will the buoyant force on an aluminum sphere submerged in water increase, decrease, or remain the same, if the temperature is increased from 20°C to 40°C? Explain.
- Can you determine the temperature of a vacuum? Explain.
- Escape velocity from the Earth refers to the minimum speed an object must have to leave the Earth and never return. (a) The escape velocity from the Moon is about one-fifth what it is for the Earth, due to the Moon's smaller mass. Explain why the Moon has practically no atmosphere. (b) If hydrogen was once in the Earth's atmosphere, why would it have probably escaped?
- What exactly does it mean when we say that oxygen boils at -183°C ?
- A length of thin wire is placed over a block of ice (or an ice cube) at 0°C. The wire hangs down both sides of the ice, and weights are hung from the ends of the wire. It is found that the wire cuts its way through the ice cube, but leaves a solid block of ice behind it. This process is called *regelation*. Explain how this happens by inferring how the freezing point of water depends on pressure.
- (a) Why does food cook faster in a pressure cooker? (b) Why does pasta or rice need to boil longer at high altitudes? (c) Is it harder to boil water at high altitudes?
- Is it possible to boil water at room temperature (20°C) without heating it? Explain.
- Why does exhaled air appear as a little white cloud in the winter (Fig. 13–30)?



FIGURE 13–30
Question 22.

- Explain why it is dangerous to open the radiator cap of an overheated automobile engine.

MisConceptual Questions

- Rod A has twice the diameter of rod B, but both are made of iron and have the same initial length. Both rods are now subjected to the same change in temperature (but remain solid). How would the change in the rods' lengths compare?
 - Rod A > rod B.
 - Rod B > rod A.
 - Rod A = rod B.
 - Need to know whether the rods were cooled or heated.
- The linear expansion of a material depends on which of the following?
 - The length of the material.
 - The change in temperature of the material.
 - The type of material.
 - All of the above.
 - Both (b) and (c).

3. A steel plate has a hole in it with a diameter of exactly 1.0 cm when the plate is at a temperature of 20°C. A steel ring has an inner diameter of exactly 1.0 cm at 20°C. Both the plate and the ring are heated to 100°C. Which statement is true?
 - (a) The hole in the plate gets smaller, and the opening in the ring gets larger.
 - (b) The opening in the ring gets larger, but we need the relative size of the plate and the hole to know what happens to the hole.
 - (c) The hole in the plate and the opening in the ring get larger.
 - (d) The hole in the plate and the opening in the ring get smaller.
 - (e) The hole in the plate gets larger, and the opening in the ring gets smaller.
4. One mole of an ideal gas in a sealed rigid container is initially at a temperature of 100°C. The temperature is then increased to 200°C. The pressure in the gas
 - (a) remains constant.
 - (b) increases by about 25%.
 - (c) doubles.
 - (d) triples.
5. When an ideal gas is warmed from 20°C to 40°C, the gas's temperature T that appears in the ideal gas law increases by a factor
 - (a) of 2.
 - (b) of 1.07.
 - (c) that depends on the temperature scale you use.
6. Two identical bottles at the same temperature contain the same gas. If bottle B has twice the volume and contains half the number of moles of gas as bottle A, how does the pressure in B compare with the pressure in A?
 - (a) $P_B = \frac{1}{2} P_A$.
 - (b) $P_B = 2 P_A$.
 - (c) $P_B = \frac{1}{4} P_A$.
 - (d) $P_B = 4 P_A$.
 - (e) $P_B = P_A$.
7. The temperature of an ideal gas increases. Which of the following is true?
 - (a) The pressure must decrease.
 - (b) The pressure must increase.
 - (c) The pressure must increase while the volume decreases.
 - (d) The volume must increase while the pressure decreases.
 - (e) The pressure, the volume, or both, may increase.
8. An ideal gas is in a sealed rigid container. The average kinetic energy of the gas molecules depends most on
 - (a) the size of the container.
 - (b) the number of molecules in the container.
 - (c) the temperature of the gas.
 - (d) the mass of the molecules.
9. Two ideal gases, A and B, are at the same temperature. If the molecular mass of the molecules in gas A is twice that of the molecules in gas B, the molecules' root-mean-square speed is
 - (a) the same in both gases.
 - (b) twice as great in A.
 - (c) 1.4 times greater in A.
 - (d) twice as great in B.
 - (e) 1.4 times greater in B.
10. In a mixture of the gases oxygen and helium, which statement is valid?
 - (a) The helium atoms will be moving faster than the oxygen molecules, on average.
 - (b) Both will be moving at the same speed.
 - (c) The oxygen molecules will, on average, be moving more rapidly than the helium atoms.
 - (d) The kinetic energy of helium atoms will exceed that of oxygen molecules.
 - (e) None of the above.
11. Which of the following is *not* true about an ideal gas?
 - (a) The average kinetic energy of the gas molecules increases as the temperature increases.
 - (b) The volume of an ideal gas increases with temperature if the pressure is held constant.
 - (c) The pressure of an ideal gas increases with temperature if the volume is held constant.
 - (d) All gas molecules have the same speed at a particular temperature.
 - (e) The molecules are assumed to be far apart compared to their size.
12. When using the ideal gas law, which of the following rules must be obeyed?
 - (a) Always use temperature in kelvins and absolute pressure.
 - (b) Always use volume in m^3 and temperature in kelvins.
 - (c) Always use gauge pressure and temperature in degrees Celsius.
 - (d) Always use gauge pressure and temperature in kelvins.
 - (e) Always use volume in m^3 and gauge pressure.
13. The rms speed of the molecules of an ideal gas
 - (a) is the same as the most probable speed of the molecules.
 - (b) is always equal to $\sqrt{2}$ times the maximum molecular speed.
 - (c) will increase as the temperature of a gas increases.
 - (d) All of the above.

For assigned homework and other learning materials, go to the MasteringPhysics website.



Problems

13-1 Atomic Theory

1. (I) How does the number of atoms in a 27.5-gram gold ring compare to the number in a silver ring of the same mass?
2. (I) How many atoms are there in a 3.4-g copper coin?

13-2 Temperature and Thermometers

3. (I) (a) "Room temperature" is often taken to be 68°F. What is this on the Celsius scale? (b) The temperature of the filament in a lightbulb is about 1900°C. What is this on the Fahrenheit scale?
4. (I) Among the highest and lowest natural air temperatures claimed are 136°F in the Libyan desert and -129°F in Antarctica. What are these temperatures on the Celsius scale?
5. (I) A thermometer tells you that you have a fever of 38.9°C. What is this in Fahrenheit?
6. (I) (a) 18° below zero on the Celsius scale is what Fahrenheit temperature? (b) 18° below zero on the Fahrenheit scale is what Celsius temperature?

7. (II) Determine the temperature at which the Celsius and Fahrenheit scales give the same numerical reading ($T_C = T_F$).
8. (II) In an alcohol-in-glass thermometer, the alcohol column has length 12.61 cm at 0.0°C and length 22.79 cm at 100.0°C. What is the temperature if the column has length (a) 18.70 cm, and (b) 14.60 cm?

13-4 Thermal Expansion

9. (I) The Eiffel Tower (Fig. 13-31) is built of wrought iron approximately 300 m tall. Estimate how much its height changes between January (average temperature of 2°C) and July (average temperature of 25°C). Ignore the angles of the iron beams and treat the tower as a vertical beam.

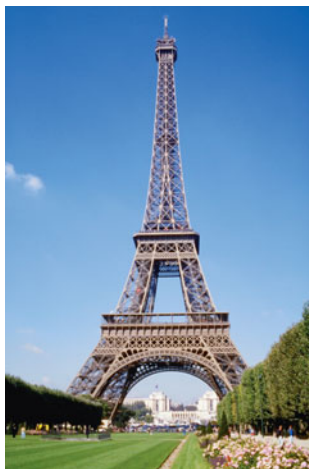


FIGURE 13-31 Problem 9. The Eiffel Tower in Paris.

10. (I) A concrete highway is built of slabs 12 m long (15°C). How wide should the expansion cracks between the slabs be (at 15°C) to prevent buckling if the range of temperature is -30°C to +50°C?
11. (I) Super Invar™, an alloy of iron and nickel, is a strong material with a very low coefficient of thermal expansion ($0.20 \times 10^{-6}/\text{C}^\circ$). A 1.8-m-long tabletop made of this alloy is used for sensitive laser measurements where extremely high tolerances are required. How much will this alloy table expand along its length if the temperature increases 6.0 C°? Compare to tabletops made of steel.
12. (II) To what temperature would you have to heat a brass rod for it to be 1.5% longer than it is at 25°C?
13. (II) To make a secure fit, rivets that are larger than the rivet hole are often used and the rivet is cooled (usually in dry ice) before it is placed in the hole. A steel rivet 1.872 cm in diameter is to be placed in a hole 1.870 cm in diameter in a metal at 22°C. To what temperature must the rivet be cooled if it is to fit in the hole?
14. (II) An ordinary glass is filled to the brim with 450.0 mL of water at 100.0°C. If the temperature of glass and water is decreased to 20.0°C, how much water could be added to the glass?
15. (II) An aluminum sphere is 8.75 cm in diameter. What will be its % change in volume if it is heated from 30°C to 160°C?
16. (II) It is observed that 55.50 mL of water at 20°C completely fills a container to the brim. When the container and the water are heated to 60°C, 0.35 g of water is lost. (a) What is the coefficient of volume expansion of the container? (b) What is the most likely material of the container? Density of water at 60°C is 0.98324 g/mL.
17. (II) A brass plug is to be placed in a ring made of iron. At 15°C, the diameter of the plug is 8.755 cm and that of the inside of the ring is 8.741 cm. They must both be brought to what common temperature in order to fit?

18. (II) A certain car has 14.0 L of liquid coolant circulating at a temperature of 93°C through the engine's cooling system. Assume that, in this normal condition, the coolant completely fills the 3.5-L volume of the aluminum radiator and the 10.5-L internal cavities within the aluminum engine. When a car overheats, the radiator, engine, and coolant expand and a small reservoir connected to the radiator catches any resultant coolant overflow. Estimate how much coolant overflows to the reservoir if the system goes from 93°C to 105°C. Model the radiator and engine as hollow shells of aluminum. The coefficient of volume expansion for coolant is $\beta = 410 \times 10^{-6}/\text{C}^\circ$.
- *19. (II) An aluminum bar has the desired length when at 12°C. How much stress is required to keep it at this length if the temperature increases to 35°C? [See Table 9-1.]
20. (III) The pendulum in a grandfather clock is made of brass and keeps perfect time at 17°C. How much time is gained or lost in a year if the clock is kept at 29°C? (Assume the frequency dependence on length for a simple pendulum applies.) [Hint: See Chapter 8.]

13-5 Gas Laws; Absolute Temperature

21. (I) Absolute zero is what temperature on the Fahrenheit scale?
22. (II) Typical temperatures in the interior of the Earth and Sun are about 4000°C and 15×10^6 °C, respectively. (a) What are these temperatures in kelvins? (b) What percent error is made in each case if a person forgets to change °C to K?

13-6 and 13-7 Ideal Gas Law

23. (I) If 3.50 m³ of a gas initially at STP is placed under a pressure of 3.20 atm, the temperature of the gas rises to 38.0°C. What is the volume?
24. (I) In an internal combustion engine, air at atmospheric pressure and a temperature of about 20°C is compressed in the cylinder by a piston to $\frac{1}{9}$ of its original volume (compression ratio = 9.0). Estimate the temperature of the compressed air, assuming the pressure reaches 40 atm.
25. (II) If 16.00 mol of helium gas is at 10.0°C and a gauge pressure of 0.350 atm, calculate (a) the volume of the helium gas under these conditions, and (b) the temperature if the gas is compressed to precisely half the volume at a gauge pressure of 1.00 atm.
26. (II) A storage tank contains 21.6 kg of nitrogen (N₂) at an absolute pressure of 3.45 atm. What will the pressure be if the nitrogen is replaced by an equal mass of CO₂ at the same temperature?
27. (II) A storage tank at STP contains 28.5 kg of nitrogen (N₂). (a) What is the volume of the tank? (b) What is the pressure if an additional 32.2 kg of nitrogen is added without changing the temperature?
28. (II) A scuba tank is filled with air to a gauge pressure of 204 atm when the air temperature is 29°C. A diver then jumps into the ocean and, after a short time on the ocean surface, checks the tank's gauge pressure and finds that it is only 191 atm. Assuming the diver has inhaled a negligible amount of air from the tank, what is the temperature of the ocean water?
29. (II) What is the pressure inside a 38.0-L container holding 105.0 kg of argon gas at 21.6°C?

30. (II) A sealed metal container contains a gas at 20.0°C and 1.00 atm. To what temperature must the gas be heated for the pressure to double to 2.00 atm? (Ignore expansion of the container.)
31. (II) A tire is filled with air at 15°C to a gauge pressure of 230 kPa. If the tire reaches a temperature of 38°C, what fraction of the original air must be removed if the original pressure of 230 kPa is to be maintained?
32. (II) If 61.5 L of oxygen at 18.0°C and an absolute pressure of 2.45 atm are compressed to 38.8 L and at the same time the temperature is raised to 56.0°C, what will the new pressure be?
33. (II) You buy an “airtight” bag of potato chips packaged at sea level, and take the chips on an airplane flight. When you take the potato chips out of your “carry-on” bag, you notice it has noticeably “puffed up.” Airplane cabins are typically pressurized at 0.75 atm, and assuming the temperature inside an airplane is about the same as inside a potato chip processing plant, by what percentage has the bag “puffed up” in comparison to when it was packaged?
34. (II) A helium-filled balloon escapes a child’s hand at sea level and 20.0°C. When it reaches an altitude of 3600 m, where the temperature is 5.0°C and the pressure only 0.68 atm, how will its volume compare to that at sea level?
35. (II) Compare the value for the density of water vapor at exactly 100°C and 1 atm (Table 10–1) with the value predicted from the ideal gas law. Why would you expect a difference?
36. (III) A sealed test tube traps 25.0 cm³ of air at a pressure of 1.00 atm and temperature of 18°C. The test tube’s stopper has a diameter of 1.50 cm and will “pop off” the test tube if a net upward force of 10.0 N is applied to it. To what temperature would you have to heat the trapped air in order to “pop off” the stopper? Assume the air surrounding the test tube is always at a pressure of 1.00 atm.
37. (III) An air bubble at the bottom of a lake 41.0 m deep has a volume of 1.00 cm³. If the temperature at the bottom is 5.5°C and at the top 18.5°C, what is the radius of the bubble just before it reaches the surface?

13–8 Ideal Gas Law in Terms of Molecules; Avogadro’s Number

38. (I) Calculate the number of molecules/m³ in an ideal gas at STP.
39. (I) How many moles of water are there in 1.000 L at STP? How many molecules?
40. (II) Estimate the number of (a) moles and (b) molecules of water in all the Earth’s oceans. Assume water covers 75% of the Earth to an average depth of 3 km.
41. (II) The lowest pressure attainable using the best available vacuum techniques is about 10⁻¹² N/m². At such a pressure, how many molecules are there per cm³ at 0°C?
42. (II) Is a gas mostly empty space? Check by assuming that the spatial extent of the gas molecules in air is about $\ell_0 = 0.3$ nm so one gas molecule occupies an approximate volume equal to ℓ_0^3 . Assume STP.

13–9 Molecular Interpretation of Temperature

43. (I) (a) What is the average translational kinetic energy of a nitrogen molecule at STP? (b) What is the total translational kinetic energy of 1.0 mol of N₂ molecules at 25°C?
44. (I) Calculate the rms speed of helium atoms near the surface of the Sun at a temperature of about 6000 K.

45. (I) By what factor will the rms speed of gas molecules increase if the temperature is increased from 20°C to 160°C?
46. (I) A gas is at 20°C. To what temperature must it be raised to triple the rms speed of its molecules?
47. (I) What speed would a 1.0-g paper clip have if it had the same kinetic energy as a molecule at 22°C?
48. (II) The rms speed of molecules in a gas at 20.0°C is to be increased by 4.0%. To what temperature must it be raised?
49. (II) If the pressure in a gas is tripled while its volume is held constant, by what factor does v_{rms} change?
50. (II) Show that the rms speed of molecules in a gas is given by $v_{\text{rms}} = \sqrt{3P/\rho}$, where P is the pressure in the gas and ρ is the gas density.
51. (II) Show that for a mixture of two gases at the same temperature, the ratio of their rms speeds is equal to the inverse ratio of the square roots of their molecular masses, $v_1/v_2 = \sqrt{M_2/M_1}$.
52. (II) What is the rms speed of nitrogen molecules contained in an 8.5-m³ volume at 2.9 atm if the total amount of nitrogen is 2100 mol?
53. (II) Two isotopes of uranium, ²³⁵U and ²³⁸U (the superscripts refer to their atomic masses), can be separated by a gas diffusion process by combining them with fluorine to make the gaseous compound UF₆. Calculate the ratio of the rms speeds of these molecules for the two isotopes, at constant T . Use Appendix B for masses.
54. (III) Calculate (a) the rms speed of an oxygen molecule at 0°C and (b) determine how many times per second it would move back and forth across a 5.0-m-long room on average, assuming it made no collisions with other molecules.

13–11 Real Gases; Phase Changes

55. (I) CO₂ exists in what phase when the pressure is 35 atm and the temperature is 35°C (Fig. 13–23)?
56. (I) (a) At atmospheric pressure, in what phases can CO₂ exist? (b) For what range of pressures and temperatures can CO₂ be a liquid? Refer to Fig. 13–23.
57. (I) Water is in which phase when the pressure is 0.01 atm and the temperature is (a) 90°C, (b) –20°C?
58. (II) You have a sample of water and are able to control temperature and pressure arbitrarily. (a) Using Fig. 13–22, describe the phase changes you would see if you started at a temperature of 85°C, a pressure of 180 atm, and decreased the pressure down to 0.004 atm while keeping the temperature fixed. (b) Repeat part (a) with the temperature at 0.0°C. Assume that you held the system at the starting conditions long enough for the system to stabilize before making further changes.

13–12 Vapor Pressure and Humidity

59. (I) What is the partial pressure of water vapor at 30°C if the humidity is 75%?
60. (I) What is the air pressure at a place where water boils at 80°C?
61. (II) What is the dew point if the humidity is 65% on a day when the temperature is 25°C?
62. (II) If the air pressure at a particular place in the mountains is 0.80 atm, estimate the temperature at which water boils.

63. (II) What is the mass of water in a closed room $5.0\text{ m} \times 6.0\text{ m} \times 2.4\text{ m}$ when the temperature is 25°C and the relative humidity is 55%?
64. (II) A **pressure cooker** is a sealed pot designed to cook food with the steam produced by boiling water somewhat above 100°C . The pressure cooker in Fig. 13–32 uses a weight of mass m to allow steam to escape at a certain pressure through a small hole (diameter d) in the cooker's lid. If $d = 3.0\text{ mm}$, what should m be in order to cook food at 120°C ? Assume that atmospheric pressure outside the cooker is $1.01 \times 10^5\text{ Pa}$.

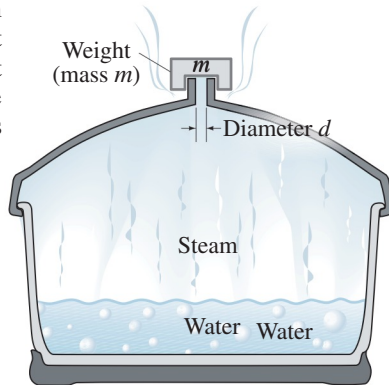


FIGURE 13–32
Problem 64.

65. (II) If the humidity in a sealed room of volume 420 m^3 at 20°C is 65%, what mass of water can still evaporate from an open pan?
66. (III) Air that is at its dew point of 5°C is drawn into a building where it is heated to 22°C . What will be the relative humidity at this temperature? Assume constant pressure of 1.0 atm. Take into account the expansion of the air.

67. (III) When using a mercury barometer (Section 10–6), the vapor pressure of mercury is usually assumed to be zero. At room temperature mercury's vapor pressure is about 0.0015 mm-Hg. At sea level, the height h of mercury in a barometer is about 760 mm. (a) If the vapor pressure of mercury is neglected, is the true atmospheric pressure greater or less than the value read from the barometer? (b) What is the percent error? (c) What is the percent error if you use a water barometer and ignore water's saturated vapor pressure at STP?

*13–13 Diffusion

- *68. (II) Estimate the time needed for a glycine molecule (see Table 13–4) to diffuse a distance of $25\text{ }\mu\text{m}$ in water at 20°C if its concentration varies over that distance from 1.00 mol/m^3 to 0.50 mol/m^3 ? Compare this "speed" to its rms (thermal) speed. The molecular mass of glycine is about 75 u.
- *69. (II) Oxygen diffuses from the surface of insects to the interior through tiny tubes called tracheae. An average trachea is about 2 mm long and has cross-sectional area of $2 \times 10^{-9}\text{ m}^2$. Assuming the concentration of oxygen inside is half what it is outside in the atmosphere, (a) show that the concentration of oxygen in the air (assume 21% is oxygen) at 20°C is about 8.7 mol/m^3 , then (b) calculate the diffusion rate J , and (c) estimate the average time for a molecule to diffuse in. Assume the diffusion constant is $1 \times 10^{-5}\text{ m}^2/\text{s}$.

General Problems

70. A Pyrex measuring cup was calibrated at normal room temperature. How much error will be made in a recipe calling for 375 mL of cool water, if the water and the cup are hot, at 95°C , instead of at room temperature? Neglect the glass expansion.
71. A precise steel tape measure has been calibrated at 14°C . At 37°C , (a) will it read high or low, and (b) what will be the percentage error?
72. A cubic box of volume $6.15 \times 10^{-2}\text{ m}^3$ is filled with air at atmospheric pressure at 15°C . The box is closed and heated to 165°C . What is the net force on each side of the box?
73. The gauge pressure in a helium gas cylinder is initially 32 atm. After many balloons have been blown up, the gauge pressure has decreased to 5 atm. What fraction of the original gas remains in the cylinder?
74. If a scuba diver fills his lungs to full capacity of 5.5 L when 9.0 m below the surface, to what volume would his lungs expand if he quickly rose to the surface? Is this advisable?
75. A house has a volume of 1200 m^3 . (a) What is the total mass of air inside the house at 15°C ? (b) If the temperature drops to -15°C , what mass of air enters or leaves the house?
76. Estimate the number of air molecules in a room of length 6.0 m, width 3.0 m, and height 2.5 m. Assume the temperature is 22°C . How many moles does that correspond to?
77. An iron cube floats in a bowl of liquid mercury at 0°C . (a) If the temperature is raised to 25°C , will the cube float higher or lower in the mercury? (b) By what percent will the fraction of volume submerged change? [Hint: See Chapter 10.]
78. A helium balloon, assumed to be a perfect sphere, has a radius of 24.0 cm. At room temperature (20°C), its internal pressure is 1.08 atm. Determine the number of moles of helium in the balloon, and the mass of helium needed to inflate the balloon to these values.
79. A standard cylinder of oxygen used in a hospital has gauge pressure = 2000 psi (13,800 kPa) and volume = 14 L (0.014 m^3) at $T = 295\text{ K}$. How long will the cylinder last if the flow rate, measured at atmospheric pressure, is constant at 2.1 L/min?
80. A brass lid screws tightly onto a glass jar at 15°C . To help open the jar, it can be placed into a bath of hot water. After this treatment, the temperatures of the lid and the jar are both 55°C . The inside diameter of the lid is 8.0 cm. Find the size of the gap (difference in radius) that develops by this procedure.
81. The density of gasoline at 0°C is $0.68 \times 10^3\text{ kg/m}^3$. (a) What is the density on a hot day, when the temperature is 33°C ? (b) What is the percent change in density?
82. The first real length standard, adopted more than 200 years ago, was a platinum bar with two very fine marks separated by what was defined to be exactly one meter. If this standard bar was to be accurate to within $\pm 1.0\text{ }\mu\text{m}$, how carefully would the trustees have needed to control the temperature? The coefficient of linear expansion is $9 \times 10^{-6}/^\circ\text{C}$.
83. If a steel band were to fit snugly around the Earth's equator at 25°C , but then was heated to 55°C , how high above the Earth would the band be (assume equal everywhere)?

84. In outer space the density of matter is about one atom per cm^3 , mainly hydrogen atoms, and the temperature is about 2.7 K. Calculate the rms speed of these hydrogen atoms, and the pressure (in atmospheres).
85. (a) Estimate the rms speed of an amino acid, whose molecular mass is 89 u, in a living cell at 37°C. (b) What would be the rms speed of a protein of molecular mass 85,000 u at 37°C?
86. The escape speed from the Earth is $1.12 \times 10^4 \text{ m/s}$, so that a gas molecule traveling away from Earth near the outer boundary of the Earth's atmosphere would, at this speed, be able to escape from the Earth's gravitational field and be lost to the atmosphere. At what temperature is the rms speed of (a) oxygen molecules, and (b) helium atoms equal to $1.12 \times 10^4 \text{ m/s}$? (c) Can you explain why our atmosphere contains oxygen but not helium?
87. Consider a container of oxygen gas at a temperature of 23°C that is 1.00 m tall. Compare the gravitational potential energy of a molecule at the top of the container (assuming the potential energy is zero at the bottom) with the average kinetic energy of the molecules. Is it reasonable to neglect the potential energy?
88. A space vehicle returning from the Moon enters the Earth's atmosphere at a speed of about 42,000 km/h. Molecules (assume nitrogen) striking the nose of the vehicle with this speed correspond to what temperature? (Because of this high temperature, the nose of a space vehicle must be made of special materials; indeed, part of it does vaporize, and this is seen as a bright blaze upon reentry.)
89. A sauna has 8.5 m^3 of air volume, and the temperature is 85°C. The air is perfectly dry. How much water (in kg) should be evaporated if we want to increase the relative humidity from 0% to 10%? (See Table 13–3.)
90. A 0.50-kg trash-can lid is suspended against gravity by tennis balls thrown vertically upward at it. How many tennis balls per second must rebound from the lid elastically, assuming they have a mass of 0.060 kg and are thrown at 15 m/s?
91. In humid climates, people constantly **dehumidify** their cellars to prevent rot and mildew. If the cellar in a house (kept at 20°C) has 105 m^2 of floor space and a ceiling height of 2.4 m, what is the mass of water that must be removed from it in order to drop the humidity from 95% to a more reasonable 40%?

Search and Learn

- This Chapter gives two ways to calculate the thermal expansion of a gas at a constant pressure of 1.0 atm. Use both methods to calculate the volume change of 1000 L of an ideal gas as it goes from -100°C to 0°C and from 0°C to 100°C . Why are the answers different?
- A scuba tank when fully charged has a pressure of 180 atm at 18°C . The volume of the tank is 11.3 L. (a) What would the volume of the air be at 1.00 atm and at the same temperature? (b) Before entering the water, a person consumes 2.0 L of air in each breath, and breathes 12 times a minute. At this rate, how long would the tank last? (c) At a depth of 23.0 m in sea water at a temperature of 10°C , how long would the same tank last assuming the breathing rate does not change?
- A 28.4-kg solid aluminum cylindrical wheel of radius 0.41 m is rotating about its axle in frictionless bearings with angular velocity $\omega = 32.8 \text{ rad/s}$. If its temperature is then raised from 15.0°C to 95.0°C , what is the fractional change in ω ?
- A hot-air balloon achieves its buoyant lift by heating the air inside the balloon, which makes it less dense than the air outside. Suppose the volume of a balloon is 1800 m^3 and the required lift is 3300 N (rough estimate of the weight of the equipment and passenger). Calculate the temperature of the air inside the balloon which will produce the required lift. Assume the outside air is an ideal gas at 0°C . What factors limit the maximum altitude attainable by this method for a given load? [Hint: See Chapter 10.]
- Estimate how many molecules of air are in each 2.0-L breath you inhale that were also in the last breath Galileo took. Assume the atmosphere is about 10 km high and of constant density. What other assumptions did you make?
- (a) The second postulate of kinetic theory is that the molecules are, on average, far apart from one another. That is, their average separation is much greater than the diameter of each molecule. Is this assumption reasonable? To check, calculate the average distance between molecules of a gas at STP, and compare it to the diameter of a typical gas molecule, about 0.3 nm. (b) If the molecules were the diameter of ping-pong balls, say 4 cm, how far away would the next ping-pong ball be on average? (c) Repeat part a, but now assume the gas has been compressed so that the pressure is now 3 atm but still at 273 K. (d) Estimate what % of the total volume of gas is taken up by molecules themselves in parts a and c. [Note that the volume of the molecules themselves can become a significant part of the total volume at lower temperatures and higher pressures. Hence the actual volume the molecules have to bounce around in is less than the total volume. This contributes to the effect shown in Fig. 13–21 at high pressures where real gases (solid red lines) deviate from ideal gas behavior (dashed lines A' and B').]

ANSWERS TO EXERCISES

- A:** (i) Higher, (ii) same, (iii) lower.
B: (d).
C: (b).

- D:** (b) Less.
E: (a).
F: (d).