

13 TEMPERATURE, KINETIC THEORY, AND THE GAS LAWS



Figure 13.1 The welder's gloves and helmet protect him from the electric arc that transfers enough thermal energy to melt the rod, spray sparks, and burn the retina of an unprotected eye. The thermal energy can be felt on exposed skin a few meters away, and its light can be seen for kilometers. (credit: Kevin S. O'Brien/U.S. Navy)

Chapter Outline

13.1. Temperature

- Define temperature.
- Convert temperatures between the Celsius, Fahrenheit, and Kelvin scales.
- Define thermal equilibrium.
- State the zeroth law of thermodynamics.

13.2. Thermal Expansion of Solids and Liquids

- Define and describe thermal expansion.
- Calculate the linear expansion of an object given its initial length, change in temperature, and coefficient of linear expansion.
- Calculate the volume expansion of an object given its initial volume, change in temperature, and coefficient of volume expansion.
- Calculate thermal stress on an object given its original volume, temperature change, volume change, and bulk modulus.

13.3. The Ideal Gas Law

- State the ideal gas law in terms of molecules and in terms of moles.
- Use the ideal gas law to calculate pressure change, temperature change, volume change, or the number of molecules or moles in a given volume.
- Use Avogadro's number to convert between number of molecules and number of moles.

13.4. Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature

- Express the ideal gas law in terms of molecular mass and velocity.
- Define thermal energy.
- Calculate the kinetic energy of a gas molecule, given its temperature.
- Describe the relationship between the temperature of a gas and the kinetic energy of atoms and molecules.
- Describe the distribution of speeds of molecules in a gas.

13.5. Phase Changes

- Interpret a phase diagram.
- State Dalton's law.
- Identify and describe the triple point of a gas from its phase diagram.
- Describe the state of equilibrium between a liquid and a gas, a liquid and a solid, and a gas and a solid.

13.6. Humidity, Evaporation, and Boiling

- Explain the relationship between vapor pressure of water and the capacity of air to hold water vapor.
- Explain the relationship between relative humidity and partial pressure of water vapor in the air.
- Calculate vapor density using vapor pressure.
- Calculate humidity and dew point.

Introduction to Temperature, Kinetic Theory, and the Gas Laws

Heat is something familiar to each of us. We feel the warmth of the summer Sun, the chill of a clear summer night, the heat of coffee after a winter stroll, and the cooling effect of our sweat. Heat transfer is maintained by temperature differences. Manifestations of **heat transfer**—the movement of heat energy from one place or material to another—are apparent throughout the universe. Heat from beneath Earth's surface is brought to the surface in flows of incandescent lava. The Sun warms Earth's surface and is the source of much of the energy we find on it. Rising levels of atmospheric carbon dioxide threaten to trap more of the Sun's energy, perhaps fundamentally altering the ecosphere. In space, supernovas explode, briefly radiating more heat than an entire galaxy does.

What is heat? How do we define it? How is it related to temperature? What are heat's effects? How is it related to other forms of energy and to work? We will find that, in spite of the richness of the phenomena, there is a small set of underlying physical principles that unite the subjects and tie them to other fields.



Figure 13.2 In a typical thermometer like this one, the alcohol, with a red dye, expands more rapidly than the glass containing it. When the thermometer's temperature increases, the liquid from the bulb is forced into the narrow tube, producing a large change in the length of the column for a small change in temperature. (credit: Chemical Engineer, Wikimedia Commons)

13.1 Temperature

The concept of temperature has evolved from the common concepts of hot and cold. Human perception of what feels hot or cold is a relative one. For example, if you place one hand in hot water and the other in cold water, and then place both hands in tepid water, the tepid water will feel cool to the hand that was in hot water, and warm to the one that was in cold water. The scientific definition of temperature is less ambiguous than your senses of hot and cold. **Temperature** is operationally defined to be what we measure with a thermometer. (Many physical quantities are defined solely in terms of how they are measured. We shall see later how temperature is related to the kinetic energies of atoms and molecules, a more physical explanation.) Two accurate thermometers, one placed in hot water and the other in cold water, will show the hot water to have a higher temperature. If they are then placed in the tepid water, both will give identical readings (within measurement uncertainties). In this section, we discuss temperature, its measurement by thermometers, and its relationship to thermal equilibrium. Again, temperature is the quantity measured by a thermometer.

Misconception Alert: Human Perception vs. Reality

On a cold winter morning, the wood on a porch feels warmer than the metal of your bike. The wood and bicycle are in thermal equilibrium with the outside air, and are thus the same temperature. They *feel* different because of the difference in the way that they conduct heat away from your skin. The metal conducts heat away from your body faster than the wood does (see more about conductivity in **Conduction**). This is just one example demonstrating that the human sense of hot and cold is not determined by temperature alone.

Another factor that affects our perception of temperature is humidity. Most people feel much hotter on hot, humid days than on hot, dry days. This is because on humid days, sweat does not evaporate from the skin as efficiently as it does on dry days. It is the evaporation of sweat (or water from a sprinkler or pool) that cools us off.

Any physical property that depends on temperature, and whose response to temperature is reproducible, can be used as the basis of a thermometer. Because many physical properties depend on temperature, the variety of thermometers is remarkable. For example, volume increases with temperature for most substances. This property is the basis for the common alcohol thermometer, the old mercury thermometer, and the bimetallic strip (**Figure 13.3**). Other properties used to measure temperature include electrical resistance and color, as shown in **Figure 13.4**, and the emission of infrared radiation, as shown in **Figure 13.5**.

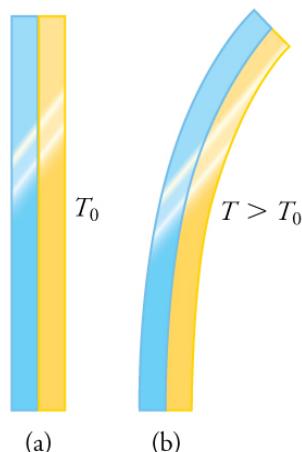


Figure 13.3 The curvature of a bimetallic strip depends on temperature. (a) The strip is straight at the starting temperature, where its two components have the same length. (b) At a higher temperature, this strip bends to the right, because the metal on the left has expanded more than the metal on the right.



Figure 13.4 Each of the six squares on this plastic (liquid crystal) thermometer contains a film of a different heat-sensitive liquid crystal material. Below 95°F , all six squares are black. When the plastic thermometer is exposed to temperature that increases to 95°F , the first liquid crystal square changes color. When the temperature increases above 96.8°F the second liquid crystal square also changes color, and so forth. (credit: Arkrishna, Wikimedia Commons)



Figure 13.5 Fireman Jason Ormand uses a pyrometer to check the temperature of an aircraft carrier's ventilation system. Infrared radiation (whose emission varies with temperature) from the vent is measured and a temperature readout is quickly produced. Infrared measurements are also frequently used as a measure of body temperature. These modern thermometers, placed in the ear canal, are more accurate than alcohol thermometers placed under the tongue or in the armpit. (credit: Lamel J. Hinton/U.S. Navy)

Temperature Scales

Thermometers are used to measure temperature according to well-defined scales of measurement, which use pre-defined reference points to help compare quantities. The three most common temperature scales are the Fahrenheit, Celsius, and Kelvin scales. A temperature scale can be created by identifying two easily reproducible temperatures. The freezing and boiling temperatures of water at standard atmospheric pressure are commonly used.

The **Celsius** scale (which replaced the slightly different *centigrade* scale) has the freezing point of water at 0°C and the boiling point at 100°C . Its unit is the **degree Celsius** ($^{\circ}\text{C}$). On the **Fahrenheit** scale (still the most frequently used in the United States), the freezing point of water is at 32°F and the boiling point is at 212°F . The unit of temperature on this scale is the **degree Fahrenheit** ($^{\circ}\text{F}$). Note that a temperature difference of one degree Celsius is greater than a temperature difference of

one degree Fahrenheit. Only 100 Celsius degrees span the same range as 180 Fahrenheit degrees, thus one degree on the Celsius scale is 1.8 times larger than one degree on the Fahrenheit scale $180/100 = 9/5$.

The **Kelvin** scale is the temperature scale that is commonly used in science. It is an *absolute temperature* scale defined to have 0 K at the lowest possible temperature, called **absolute zero**. The official temperature unit on this scale is the *kelvin*, which is abbreviated K, and is not accompanied by a degree sign. The freezing and boiling points of water are 273.15 K and 373.15 K, respectively. Thus, the magnitude of temperature differences is the same in units of kelvins and degrees Celsius. Unlike other temperature scales, the Kelvin scale is an absolute scale. It is used extensively in scientific work because a number of physical quantities, such as the volume of an ideal gas, are directly related to absolute temperature. The kelvin is the SI unit used in scientific work.

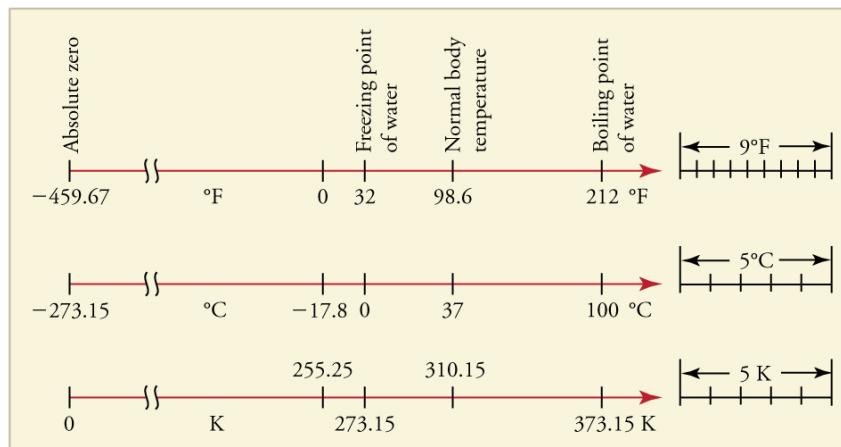


Figure 13.6 Relationships between the Fahrenheit, Celsius, and Kelvin temperature scales, rounded to the nearest degree. The relative sizes of the scales are also shown.

The relationships between the three common temperature scales is shown in **Figure 13.6**. Temperatures on these scales can be converted using the equations in **Table 13.1**.

Table 13.1 Temperature Conversions

To convert from ...	Use this equation ...	Also written as ...
Celsius to Fahrenheit	$T(^{\circ}\text{F}) = \frac{9}{5}T(^{\circ}\text{C}) + 32$	$T_{^{\circ}\text{F}} = \frac{9}{5}T_{^{\circ}\text{C}} + 32$
Fahrenheit to Celsius	$T(^{\circ}\text{C}) = \frac{5}{9}(T(^{\circ}\text{F}) - 32)$	$T_{^{\circ}\text{C}} = \frac{5}{9}(T_{^{\circ}\text{F}} - 32)$
Celsius to Kelvin	$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$	$T_{\text{K}} = T_{^{\circ}\text{C}} + 273.15$
Kelvin to Celsius	$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$	$T_{^{\circ}\text{C}} = T_{\text{K}} - 273.15$
Fahrenheit to Kelvin	$T(\text{K}) = \frac{5}{9}(T(^{\circ}\text{F}) - 32) + 273.15$	$T_{\text{K}} = \frac{5}{9}(T_{^{\circ}\text{F}} - 32) + 273.15$
Kelvin to Fahrenheit	$T(^{\circ}\text{F}) = \frac{9}{5}(T(\text{K}) - 273.15) + 32$	$T_{^{\circ}\text{F}} = \frac{9}{5}(T_{\text{K}} - 273.15) + 32$

Notice that the conversions between Fahrenheit and Kelvin look quite complicated. In fact, they are simple combinations of the conversions between Fahrenheit and Celsius, and the conversions between Celsius and Kelvin.

Example 13.1 Converting between Temperature Scales: Room Temperature

"Room temperature" is generally defined to be 25°C . (a) What is room temperature in $^{\circ}\text{F}$? (b) What is it in K?

Strategy

To answer these questions, all we need to do is choose the correct conversion equations and plug in the known values.

Solution for (a)

1. Choose the right equation. To convert from $^{\circ}\text{C}$ to $^{\circ}\text{F}$, use the equation

$$T_{^{\circ}\text{F}} = \frac{9}{5}T_{^{\circ}\text{C}} + 32. \quad (13.1)$$

2. Plug the known value into the equation and solve:

$$T_{\circ F} = \frac{9}{5}25^{\circ}C + 32 = 77^{\circ}F. \quad (13.2)$$

Solution for (b)

1. Choose the right equation. To convert from $^{\circ}C$ to K, use the equation

$$T_K = T_{\circ C} + 273.15. \quad (13.3)$$

2. Plug the known value into the equation and solve:

$$T_K = 25^{\circ}C + 273.15 = 298 \text{ K.} \quad (13.4)$$

Example 13.2 Converting between Temperature Scales: the Reaumur Scale

The Reaumur scale is a temperature scale that was used widely in Europe in the 18th and 19th centuries. On the Reaumur temperature scale, the freezing point of water is 0°R and the boiling temperature is 80°R . If "room temperature" is 25°C on the Celsius scale, what is it on the Reaumur scale?

Strategy

To answer this question, we must compare the Reaumur scale to the Celsius scale. The difference between the freezing point and boiling point of water on the Reaumur scale is 80°R . On the Celsius scale it is 100°C . Therefore $100^{\circ}\text{C} = 80^{\circ}\text{R}$. Both scales start at 0° for freezing, so we can derive a simple formula to convert between temperatures on the two scales.

Solution

1. Derive a formula to convert from one scale to the other:

$$T_{\circ R} = \frac{0.8^{\circ}\text{R}}{^{\circ}\text{C}} \times T_{\circ C}. \quad (13.5)$$

2. Plug the known value into the equation and solve:

$$T_{\circ R} = \frac{0.8^{\circ}\text{R}}{^{\circ}\text{C}} \times 25^{\circ}\text{C} = 20^{\circ}\text{R}. \quad (13.6)$$

Temperature Ranges in the Universe

Figure 13.8 shows the wide range of temperatures found in the universe. Human beings have been known to survive with body temperatures within a small range, from 24°C to 44°C (75°F to 111°F). The average normal body temperature is usually given as 37.0°C (98.6°F), and variations in this temperature can indicate a medical condition: a fever, an infection, a tumor, or circulatory problems (see **Figure 13.7**).

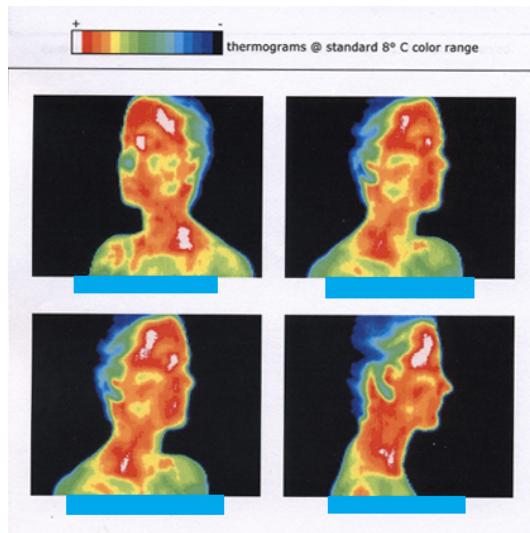


Figure 13.7 This image of radiation from a person's body (an infrared thermograph) shows the location of temperature abnormalities in the upper body. Dark blue corresponds to cold areas and red to white corresponds to hot areas. An elevated temperature might be an indication of malignant tissue (a cancerous tumor in the breast, for example), while a depressed temperature might be due to a decline in blood flow from a clot. In this case, the abnormalities are caused by a condition called hyperhidrosis. (credit: Porcelina81, Wikimedia Commons)

The lowest temperatures ever recorded have been measured during laboratory experiments: 4.5×10^{-10} K at the Massachusetts Institute of Technology (USA), and 1.0×10^{-10} K at Helsinki University of Technology (Finland). In comparison, the coldest recorded place on Earth's surface is Vostok, Antarctica at 183 K (-89°C), and the coldest place (outside the lab) known in the universe is the Boomerang Nebula, with a temperature of 1 K.

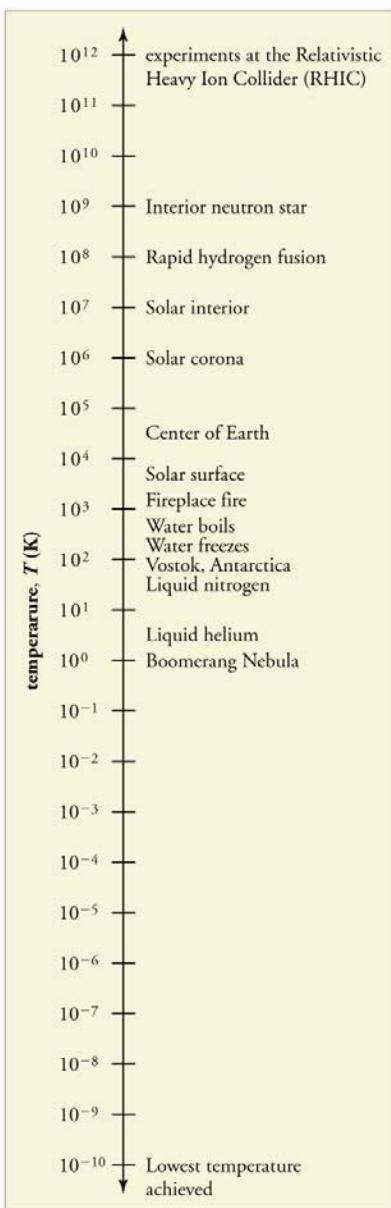


Figure 13.8 Each increment on this logarithmic scale indicates an increase by a factor of ten, and thus illustrates the tremendous range of temperatures in nature. Note that zero on a logarithmic scale would occur off the bottom of the page at infinity.

Making Connections: Absolute Zero

What is absolute zero? Absolute zero is the temperature at which all molecular motion has ceased. The concept of absolute zero arises from the behavior of gases. **Figure 13.9** shows how the pressure of gases at a constant volume decreases as temperature decreases. Various scientists have noted that the pressures of gases extrapolate to zero at the same temperature, -273.15°C . This extrapolation implies that there is a lowest temperature. This temperature is called *absolute zero*. Today we know that most gases first liquefy and then freeze, and it is not actually possible to reach absolute zero. The numerical value of absolute zero temperature is -273.15°C or 0 K.

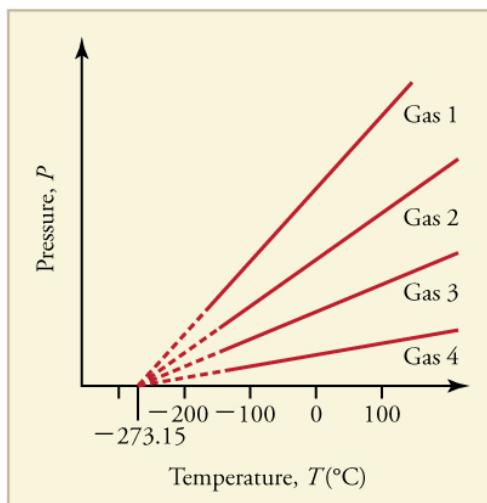


Figure 13.9 Graph of pressure versus temperature for various gases kept at a constant volume. Note that all of the graphs extrapolate to zero pressure at the same temperature.

Thermal Equilibrium and the Zeroth Law of Thermodynamics

Thermometers actually take their own temperature, not the temperature of the object they are measuring. This raises the question of how we can be certain that a thermometer measures the temperature of the object with which it is in contact. It is based on the fact that any two systems placed in *thermal contact* (meaning heat transfer can occur between them) will reach the same temperature. That is, heat will flow from the hotter object to the cooler one until they have exactly the same temperature. The objects are then in **thermal equilibrium**, and no further changes will occur. The systems interact and change because their temperatures differ, and the changes stop once their temperatures are the same. Thus, if enough time is allowed for this transfer of heat to run its course, the temperature a thermometer registers does represent the system with which it is in thermal equilibrium. Thermal equilibrium is established when two bodies are in contact with each other and can freely exchange energy.

Furthermore, experimentation has shown that if two systems, A and B, are in thermal equilibrium with each other, and B is in thermal equilibrium with a third system C, then A is also in thermal equilibrium with C. This conclusion may seem obvious, because all three have the same temperature, but it is basic to thermodynamics. It is called the **zeroth law of thermodynamics**.

The Zeroth Law of Thermodynamics

If two systems, A and B, are in thermal equilibrium with each other, and B is in thermal equilibrium with a third system, C, then A is also in thermal equilibrium with C.

This law was postulated in the 1930s, after the first and second laws of thermodynamics had been developed and named. It is called the *zeroth law* because it comes logically before the first and second laws (discussed in [Thermodynamics](#)). An example of this law in action is seen in babies in incubators: babies in incubators normally have very few clothes on, so to an observer they look as if they may not be warm enough. However, the temperature of the air, the cot, and the baby is the same, because they are in thermal equilibrium, which is accomplished by maintaining air temperature to keep the baby comfortable.

Check Your Understanding

Does the temperature of a body depend on its size?

Solution

No, the system can be divided into smaller parts each of which is at the same temperature. We say that the temperature is an *intensive* quantity. Intensive quantities are independent of size.

13.2 Thermal Expansion of Solids and Liquids



Figure 13.10 Thermal expansion joints like these in the Auckland Harbour Bridge in New Zealand allow bridges to change length without buckling. (credit: Ingolfson, Wikimedia Commons)

The expansion of alcohol in a thermometer is one of many commonly encountered examples of **thermal expansion**, the change in size or volume of a given mass with temperature. Hot air rises because its volume increases, which causes the hot air's density to be smaller than the density of surrounding air, causing a buoyant (upward) force on the hot air. The same happens in all liquids and gases, driving natural heat transfer upwards in homes, oceans, and weather systems. Solids also undergo thermal expansion. Railroad tracks and bridges, for example, have expansion joints to allow them to freely expand and contract with temperature changes.

What are the basic properties of thermal expansion? First, thermal expansion is clearly related to temperature change. The greater the temperature change, the more a bimetallic strip will bend. Second, it depends on the material. In a thermometer, for example, the expansion of alcohol is much greater than the expansion of the glass containing it.

What is the underlying cause of thermal expansion? As is discussed in **Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature**, an increase in temperature implies an increase in the kinetic energy of the individual atoms. In a solid, unlike in a gas, the atoms or molecules are closely packed together, but their kinetic energy (in the form of small, rapid vibrations) pushes neighboring atoms or molecules apart from each other. This neighbor-to-neighbor pushing results in a slightly greater distance, on average, between neighbors, and adds up to a larger size for the whole body. For most substances under ordinary conditions, there is no preferred direction, and an increase in temperature will increase the solid's size by a certain fraction in each dimension.

Linear Thermal Expansion—Thermal Expansion in One Dimension

The change in length ΔL is proportional to length L . The dependence of thermal expansion on temperature, substance, and length is summarized in the equation

$$\Delta L = \alpha L \Delta T, \quad (13.7)$$

where ΔL is the change in length L , ΔT is the change in temperature, and α is the **coefficient of linear expansion**, which varies slightly with temperature.

Table 13.2 lists representative values of the coefficient of linear expansion, which may have units of $1/^\circ\text{C}$ or $1/\text{K}$. Because the size of a kelvin and a degree Celsius are the same, both α and ΔT can be expressed in units of kelvins or degrees Celsius. The equation $\Delta L = \alpha L \Delta T$ is accurate for small changes in temperature and can be used for large changes in temperature if an average value of α is used.

Table 13.2 Thermal Expansion Coefficients at 20°C [1]

Material	Coefficient of linear expansion $\alpha(1/^\circ\text{C})$	Coefficient of volume expansion $\beta(1/^\circ\text{C})$
Solids		
Aluminum	25×10^{-6}	75×10^{-6}
Brass	19×10^{-6}	56×10^{-6}
Copper	17×10^{-6}	51×10^{-6}
Gold	14×10^{-6}	42×10^{-6}
Iron or Steel	12×10^{-6}	35×10^{-6}
Invar (Nickel-iron alloy)	0.9×10^{-6}	2.7×10^{-6}
Lead	29×10^{-6}	87×10^{-6}
Silver	18×10^{-6}	54×10^{-6}
Glass (ordinary)	9×10^{-6}	27×10^{-6}
Glass (Pyrex®)	3×10^{-6}	9×10^{-6}
Quartz	0.4×10^{-6}	1×10^{-6}
Concrete, Brick	$\sim 12 \times 10^{-6}$	$\sim 36 \times 10^{-6}$
Marble (average)	7×10^{-6}	2.1×10^{-5}
Liquids		
Ether		1650×10^{-6}
Ethyl alcohol		1100×10^{-6}
Petrol		950×10^{-6}
Glycerin		500×10^{-6}
Mercury		180×10^{-6}
Water		210×10^{-6}
Gases		
Air and most other gases at atmospheric pressure		3400×10^{-6}

Example 13.3 Calculating Linear Thermal Expansion: The Golden Gate Bridge

The main span of San Francisco's Golden Gate Bridge is 1275 m long at its coldest. The bridge is exposed to temperatures ranging from -15°C to 40°C . What is its change in length between these temperatures? Assume that the bridge is made entirely of steel.

Strategy

Use the equation for linear thermal expansion $\Delta L = \alpha L \Delta T$ to calculate the change in length, ΔL . Use the coefficient of linear expansion, α , for steel from **Table 13.2**, and note that the change in temperature, ΔT , is 55°C .

Solution

Plug all of the known values into the equation to solve for ΔL .

1. Values for liquids and gases are approximate.

$$\Delta L = \alpha L \Delta T = \left(\frac{12 \times 10^{-6}}{^\circ\text{C}} \right) (1275 \text{ m}) (55^\circ\text{C}) = 0.84 \text{ m.} \quad (13.8)$$

Discussion

Although not large compared with the length of the bridge, this change in length is observable. It is generally spread over many expansion joints so that the expansion at each joint is small.

Thermal Expansion in Two and Three Dimensions

Objects expand in all dimensions, as illustrated in **Figure 13.11**. That is, their areas and volumes, as well as their lengths, increase with temperature. Holes also get larger with temperature. If you cut a hole in a metal plate, the remaining material will expand exactly as it would if the plug was still in place. The plug would get bigger, and so the hole must get bigger too. (Think of the ring of neighboring atoms or molecules on the wall of the hole as pushing each other farther apart as temperature increases. Obviously, the ring of neighbors must get slightly larger, so the hole gets slightly larger).

Thermal Expansion in Two Dimensions

For small temperature changes, the change in area ΔA is given by

$$\Delta A = 2\alpha A \Delta T, \quad (13.9)$$

where ΔA is the change in area A , ΔT is the change in temperature, and α is the coefficient of linear expansion, which varies slightly with temperature.

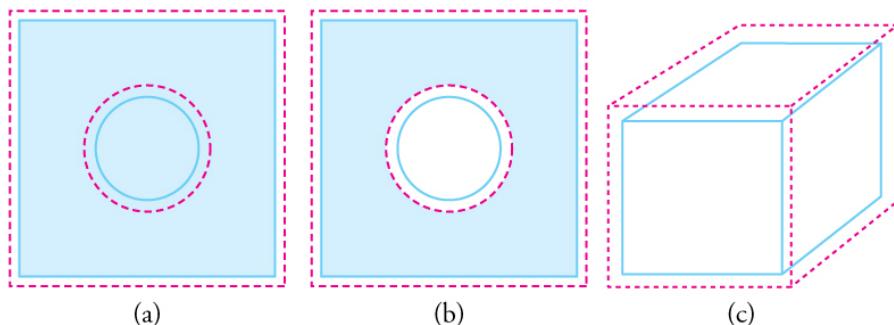


Figure 13.11 In general, objects expand in all directions as temperature increases. In these drawings, the original boundaries of the objects are shown with solid lines, and the expanded boundaries with dashed lines. (a) Area increases because both length and width increase. The area of a circular plug also increases. (b) If the plug is removed, the hole it leaves becomes larger with increasing temperature, just as if the expanding plug were still in place. (c) Volume also increases, because all three dimensions increase.

Thermal Expansion in Three Dimensions

The change in volume ΔV is very nearly $\Delta V = 3\alpha V \Delta T$. This equation is usually written as

$$\Delta V = \beta V \Delta T, \quad (13.10)$$

where β is the **coefficient of volume expansion** and $\beta \approx 3\alpha$. Note that the values of β in **Table 13.2** are almost exactly equal to 3α .

In general, objects will expand with increasing temperature. Water is the most important exception to this rule. Water expands with increasing temperature (its density *decreases*) when it is at temperatures greater than 4°C (40°F). However, it expands with *decreasing* temperature when it is between $+4^\circ\text{C}$ and 0°C (40°F to 32°F). Water is densest at $+4^\circ\text{C}$. (See **Figure 13.12**.) Perhaps the most striking effect of this phenomenon is the freezing of water in a pond. When water near the surface cools down to 4°C it is denser than the remaining water and thus will sink to the bottom. This “turnover” results in a layer of warmer water near the surface, which is then cooled. Eventually the pond has a uniform temperature of 4°C . If the temperature in the surface layer drops below 4°C , the water is less dense than the water below, and thus stays near the top. As a result, the pond surface can completely freeze over. The ice on top of liquid water provides an insulating layer from winter’s harsh exterior air temperatures. Fish and other aquatic life can survive in 4°C water beneath ice, due to this unusual characteristic of water. It also produces circulation of water in the pond that is necessary for a healthy ecosystem of the body of water.

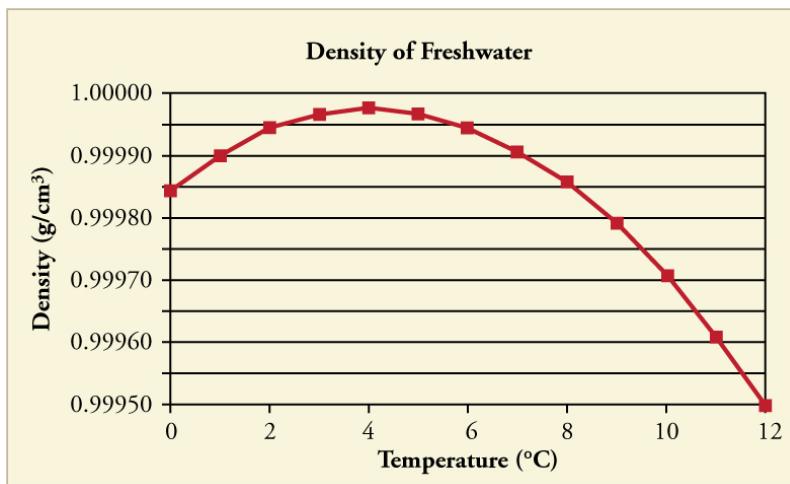


Figure 13.12 The density of water as a function of temperature. Note that the thermal expansion is actually very small. The maximum density at $+4^{\circ}\text{C}$ is only 0.0075% greater than the density at 2°C , and 0.012% greater than that at 0°C .

Making Connections: Real-World Connections—Filling the Tank

Differences in the thermal expansion of materials can lead to interesting effects at the gas station. One example is the dripping of gasoline from a freshly filled tank on a hot day. Gasoline starts out at the temperature of the ground under the gas station, which is cooler than the air temperature above. The gasoline cools the steel tank when it is filled. Both gasoline and steel tank expand as they warm to air temperature, but gasoline expands much more than steel, and so it may overflow.

This difference in expansion can also cause problems when interpreting the gasoline gauge. The actual amount (mass) of gasoline left in the tank when the gauge hits “empty” is a lot less in the summer than in the winter. The gasoline has the same volume as it does in the winter when the “add fuel” light goes on, but because the gasoline has expanded, there is less mass. If you are used to getting another 40 miles on “empty” in the winter, beware—you will probably run out much more quickly in the summer.



Figure 13.13 Because the gas expands more than the gas tank with increasing temperature, you can't drive as many miles on “empty” in the summer as you can in the winter. (credit: Hector Alejandro, Flickr)

Example 13.4 Calculating Thermal Expansion: Gas vs. Gas Tank

Suppose your 60.0-L (15.9-gal) steel gasoline tank is full of gas, so both the tank and the gasoline have a temperature of 15.0°C . How much gasoline has spilled by the time they warm to 35.0°C ?

Strategy

The tank and gasoline increase in volume, but the gasoline increases more, so the amount spilled is the difference in their volume changes. (The gasoline tank can be treated as solid steel.) We can use the equation for volume expansion to calculate the change in volume of the gasoline and of the tank.

Solution

1. Use the equation for volume expansion to calculate the increase in volume of the steel tank:

$$\Delta V_s = \beta_s V_s \Delta T. \quad (13.11)$$

2. The increase in volume of the gasoline is given by this equation:

$$\Delta V_{\text{gas}} = \beta_{\text{gas}} V_{\text{gas}} \Delta T. \quad (13.12)$$

3. Find the difference in volume to determine the amount spilled as

$$V_{\text{spill}} = \Delta V_{\text{gas}} - \Delta V_s. \quad (13.13)$$

Alternatively, we can combine these three equations into a single equation. (Note that the original volumes are equal.)

$$\begin{aligned} V_{\text{spill}} &= (\beta_{\text{gas}} - \beta_s) V \Delta T \\ &= [(950 - 35) \times 10^{-6} / ^\circ\text{C}] (60.0 \text{ L}) (20.0^\circ\text{C}) \\ &= 1.10 \text{ L.} \end{aligned} \quad (13.14)$$

Discussion

This amount is significant, particularly for a 60.0-L tank. The effect is so striking because the gasoline and steel expand quickly. The rate of change in thermal properties is discussed in [Heat and Heat Transfer Methods](#).

If you try to cap the tank tightly to prevent overflow, you will find that it leaks anyway, either around the cap or by bursting the tank. Tightly constricting the expanding gas is equivalent to compressing it, and both liquids and solids resist being compressed with extremely large forces. To avoid rupturing rigid containers, these containers have air gaps, which allow them to expand and contract without stressing them.

Thermal Stress

Thermal stress is created by thermal expansion or contraction (see [Elasticity: Stress and Strain](#) for a discussion of stress and strain). Thermal stress can be destructive, such as when expanding gasoline ruptures a tank. It can also be useful, for example, when two parts are joined together by heating one in manufacturing, then slipping it over the other and allowing the combination to cool. Thermal stress can explain many phenomena, such as the weathering of rocks and pavement by the expansion of ice when it freezes.

Example 13.5 Calculating Thermal Stress: Gas Pressure

What pressure would be created in the gasoline tank considered in [Example 13.4](#), if the gasoline increases in temperature from 15.0°C to 35.0°C without being allowed to expand? Assume that the bulk modulus B for gasoline is

$1.00 \times 10^9 \text{ N/m}^2$. (For more on bulk modulus, see [Elasticity: Stress and Strain](#).)

Strategy

To solve this problem, we must use the following equation, which relates a change in volume ΔV to pressure:

$$\Delta V = \frac{F}{BA} V_0, \quad (13.15)$$

where F/A is pressure, V_0 is the original volume, and B is the bulk modulus of the material involved. We will use the amount spilled in [Example 13.4](#) as the change in volume, ΔV .

Solution

1. Rearrange the equation for calculating pressure:

$$P = \frac{F}{A} = \frac{\Delta V}{V_0} B. \quad (13.16)$$

2. Insert the known values. The bulk modulus for gasoline is $B = 1.00 \times 10^9 \text{ N/m}^2$. In the previous example, the change in volume $\Delta V = 1.10 \text{ L}$ is the amount that would spill. Here, $V_0 = 60.0 \text{ L}$ is the original volume of the gasoline.

Substituting these values into the equation, we obtain

$$P = \frac{1.10 \text{ L}}{60.0 \text{ L}} (1.00 \times 10^9 \text{ Pa}) = 1.83 \times 10^7 \text{ Pa.} \quad (13.17)$$

Discussion

This pressure is about 2500 lb/in^2 , much more than a gasoline tank can handle.

Forces and pressures created by thermal stress are typically as great as that in the example above. Railroad tracks and roadways can buckle on hot days if they lack sufficient expansion joints. (See [Figure 13.14](#).) Power lines sag more in the summer than in the winter, and will snap in cold weather if there is insufficient slack. Cracks open and close in plaster walls as a house warms and cools. Glass cooking pans will crack if cooled rapidly or unevenly, because of differential contraction and the

stresses it creates. (Pyrex® is less susceptible because of its small coefficient of thermal expansion.) Nuclear reactor pressure vessels are threatened by overly rapid cooling, and although none have failed, several have been cooled faster than considered desirable. Biological cells are ruptured when foods are frozen, detracting from their taste. Repeated thawing and freezing accentuate the damage. Even the oceans can be affected. A significant portion of the rise in sea level that is resulting from global warming is due to the thermal expansion of sea water.



Figure 13.14 Thermal stress contributes to the formation of potholes. (credit: Editor5807, Wikimedia Commons)

Metal is regularly used in the human body for hip and knee implants. Most implants need to be replaced over time because, among other things, metal does not bond with bone. Researchers are trying to find better metal coatings that would allow metal-to-bone bonding. One challenge is to find a coating that has an expansion coefficient similar to that of metal. If the expansion coefficients are too different, the thermal stresses during the manufacturing process lead to cracks at the coating-metal interface.

Another example of thermal stress is found in the mouth. Dental fillings can expand differently from tooth enamel. It can give pain when eating ice cream or having a hot drink. Cracks might occur in the filling. Metal fillings (gold, silver, etc.) are being replaced by composite fillings (porcelain), which have smaller coefficients of expansion, and are closer to those of teeth.

Check Your Understanding

Two blocks, A and B, are made of the same material. Block A has dimensions $l \times w \times h = L \times 2L \times L$ and Block B has dimensions $2L \times 2L \times 2L$. If the temperature changes, what is (a) the change in the volume of the two blocks, (b) the change in the cross-sectional area $l \times w$, and (c) the change in the height h of the two blocks?

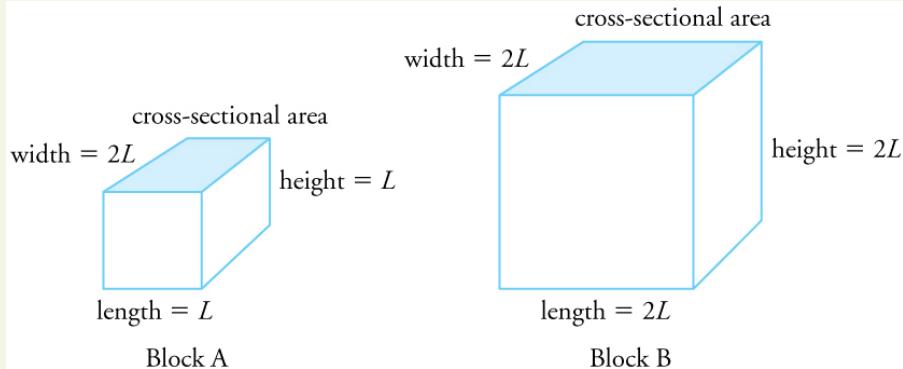


Figure 13.15

Solution

(a) The change in volume is proportional to the original volume. Block A has a volume of $L \times 2L \times L = 2L^3$. Block B has a volume of $2L \times 2L \times 2L = 8L^3$, which is 4 times that of Block A. Thus the change in volume of Block B should be 4 times the change in volume of Block A.

(b) The change in area is proportional to the area. The cross-sectional area of Block A is $L \times 2L = 2L^2$, while that of Block B is $2L \times 2L = 4L^2$. Because cross-sectional area of Block B is twice that of Block A, the change in the cross-sectional area of Block B is twice that of Block A.

(c) The change in height is proportional to the original height. Because the original height of Block B is twice that of A, the change in the height of Block B is twice that of Block A.

13.3 The Ideal Gas Law



Figure 13.16 The air inside this hot air balloon flying over Putrajaya, Malaysia, is hotter than the ambient air. As a result, the balloon experiences a buoyant force pushing it upward. (credit: Kevin Poh, Flickr)

In this section, we continue to explore the thermal behavior of gases. In particular, we examine the characteristics of atoms and molecules that compose gases. (Most gases, for example nitrogen, N_2 , and oxygen, O_2 , are composed of two or more atoms. We will primarily use the term “molecule” in discussing a gas because the term can also be applied to monatomic gases, such as helium.)

Gases are easily compressed. We can see evidence of this in **Table 13.2**, where you will note that gases have the *largest* coefficients of volume expansion. The large coefficients mean that gases expand and contract very rapidly with temperature changes. In addition, you will note that most gases expand at the *same* rate, or have the same β . This raises the question as to why gases should all act in nearly the same way, when liquids and solids have widely varying expansion rates.

The answer lies in the large separation of atoms and molecules in gases, compared to their sizes, as illustrated in **Figure 13.17**. Because atoms and molecules have large separations, forces between them can be ignored, except when they collide with each other during collisions. The motion of atoms and molecules (at temperatures well above the boiling temperature) is fast, such that the gas occupies all of the accessible volume and the expansion of gases is rapid. In contrast, in liquids and solids, atoms and molecules are closer together and are quite sensitive to the forces between them.

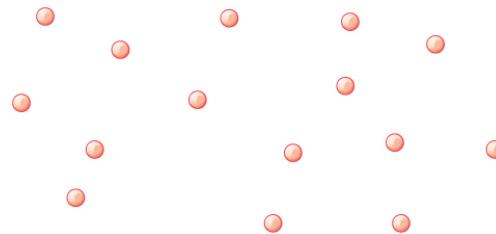


Figure 13.17 Atoms and molecules in a gas are typically widely separated, as shown. Because the forces between them are quite weak at these distances, the properties of a gas depend more on the number of atoms per unit volume and on temperature than on the type of atom.

To get some idea of how pressure, temperature, and volume of a gas are related to one another, consider what happens when you pump air into an initially deflated tire. The tire's volume first increases in direct proportion to the amount of air injected, without much increase in the tire pressure. Once the tire has expanded to nearly its full size, the walls limit volume expansion. If we continue to pump air into it, the pressure increases. The pressure will further increase when the car is driven and the tires move. Most manufacturers specify optimal tire pressure for cold tires. (See **Figure 13.18**.)

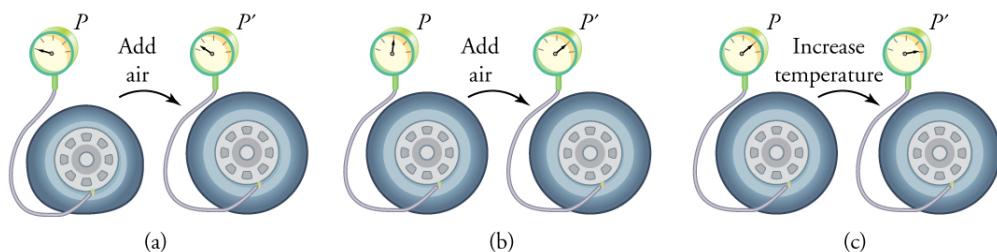


Figure 13.18 (a) When air is pumped into a deflated tire, its volume first increases without much increase in pressure. (b) When the tire is filled to a certain point, the tire walls resist further expansion and the pressure increases with more air. (c) Once the tire is inflated, its pressure increases with temperature.

At room temperatures, collisions between atoms and molecules can be ignored. In this case, the gas is called an ideal gas, in which case the relationship between the pressure, volume, and temperature is given by the equation of state called the ideal gas law.

Ideal Gas Law

The **ideal gas law** states that

$$PV = NkT, \quad (13.18)$$

where P is the absolute pressure of a gas, V is the volume it occupies, N is the number of atoms and molecules in the gas, and T is its absolute temperature. The constant k is called the **Boltzmann constant** in honor of Austrian physicist Ludwig Boltzmann (1844–1906) and has the value

$$k = 1.38 \times 10^{-23} \text{ J/K.} \quad (13.19)$$

The ideal gas law can be derived from basic principles, but was originally deduced from experimental measurements of Charles' law (that volume occupied by a gas is proportional to temperature at a fixed pressure) and from Boyle's law (that for a fixed temperature, the product PV is a constant). In the ideal gas model, the volume occupied by its atoms and molecules is a negligible fraction of V . The ideal gas law describes the behavior of real gases under most conditions. (Note, for example, that N is the total number of atoms and molecules, independent of the type of gas.)

Let us see how the ideal gas law is consistent with the behavior of filling the tire when it is pumped slowly and the temperature is constant. At first, the pressure P is essentially equal to atmospheric pressure, and the volume V increases in direct proportion to the number of atoms and molecules N put into the tire. Once the volume of the tire is constant, the equation $PV = NkT$ predicts that the pressure should increase in proportion to *the number N of atoms and molecules*.

Example 13.6 Calculating Pressure Changes Due to Temperature Changes: Tire Pressure

Suppose your bicycle tire is fully inflated, with an absolute pressure of $7.00 \times 10^5 \text{ Pa}$ (a gauge pressure of just under 90.0 lb/in^2) at a temperature of 18.0°C . What is the pressure after its temperature has risen to 35.0°C ? Assume that there are no appreciable leaks or changes in volume.

Strategy

The pressure in the tire is changing only because of changes in temperature. First we need to identify what we know and what we want to know, and then identify an equation to solve for the unknown.

We know the initial pressure $P_0 = 7.00 \times 10^5 \text{ Pa}$, the initial temperature $T_0 = 18.0^\circ\text{C}$, and the final temperature $T_f = 35.0^\circ\text{C}$. We must find the final pressure P_f . How can we use the equation $PV = NkT$? At first, it may seem that not enough information is given, because the volume V and number of atoms N are not specified. What we can do is use the equation twice: $P_0 V_0 = NkT_0$ and $P_f V_f = NkT_f$. If we divide $P_f V_f$ by $P_0 V_0$ we can come up with an equation that allows us to solve for P_f .

$$\frac{P_f V_f}{P_0 V_0} = \frac{N_f k T_f}{N_0 k T_0} \quad (13.20)$$

Since the volume is constant, V_f and V_0 are the same and they cancel out. The same is true for N_f and N_0 , and k , which is a constant. Therefore,

$$\frac{P_f}{P_0} = \frac{T_f}{T_0}. \quad (13.21)$$

We can then rearrange this to solve for P_f :

$$P_f = P_0 \frac{T_f}{T_0}, \quad (13.22)$$

where the temperature must be in units of kelvins, because T_0 and T_f are absolute temperatures.

Solution

1. Convert temperatures from Celsius to Kelvin.

$$T_0 = (18.0 + 273) \text{ K} = 291 \text{ K} \quad (13.23)$$

$$T_f = (35.0 + 273) \text{ K} = 308 \text{ K}$$

2. Substitute the known values into the equation.

$$P_f = P_0 \frac{T_f}{T_0} = 7.00 \times 10^5 \text{ Pa} \left(\frac{308 \text{ K}}{291 \text{ K}} \right) = 7.41 \times 10^5 \text{ Pa} \quad (13.24)$$

Discussion

The final temperature is about 6% greater than the original temperature, so the final pressure is about 6% greater as well. Note that *absolute* pressure and *absolute* temperature must be used in the ideal gas law.

Making Connections: Take-Home Experiment—Refrigerating a Balloon

Inflate a balloon at room temperature. Leave the inflated balloon in the refrigerator overnight. What happens to the balloon, and why?

Example 13.7 Calculating the Number of Molecules in a Cubic Meter of Gas

How many molecules are in a typical object, such as gas in a tire or water in a drink? We can use the ideal gas law to give us an idea of how large N typically is.

Calculate the number of molecules in a cubic meter of gas at standard temperature and pressure (STP), which is defined to be 0°C and atmospheric pressure.

Strategy

Because pressure, volume, and temperature are all specified, we can use the ideal gas law $PV = NkT$, to find N .

Solution

1. Identify the knowns.

$$T = 0^\circ\text{C} = 273 \text{ K} \quad (13.25)$$

$$P = 1.01 \times 10^5 \text{ Pa}$$

$$V = 1.00 \text{ m}^3$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

2. Identify the unknown: number of molecules, N .

3. Rearrange the ideal gas law to solve for N .

$$PV = NkT \quad (13.26)$$

$$N = \frac{PV}{kT}$$

4. Substitute the known values into the equation and solve for N .

$$N = \frac{PV}{kT} = \frac{(1.01 \times 10^5 \text{ Pa})(1.00 \text{ m}^3)}{(1.38 \times 10^{-23} \text{ J/K})(273 \text{ K})} = 2.68 \times 10^{25} \text{ molecules} \quad (13.27)$$

Discussion

This number is undeniably large, considering that a gas is mostly empty space. N is huge, even in small volumes. For example, 1 cm^3 of a gas at STP has 2.68×10^{19} molecules in it. Once again, note that N is the same for all types or mixtures of gases.

Moles and Avogadro's Number

It is sometimes convenient to work with a unit other than molecules when measuring the amount of substance. A **mole** (abbreviated mol) is defined to be the amount of a substance that contains as many atoms or molecules as there are atoms in exactly 12 grams (0.012 kg) of carbon-12. The actual number of atoms or molecules in one mole is called **Avogadro's number** (N_A), in recognition of Italian scientist Amedeo Avogadro (1776–1856). He developed the concept of the mole, based on the hypothesis that equal volumes of gas, at the same pressure and temperature, contain equal numbers of molecules. That is, the number is independent of the type of gas. This hypothesis has been confirmed, and the value of Avogadro's number is

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}. \quad (13.28)$$

Avogadro's Number

One mole always contains 6.02×10^{23} particles (atoms or molecules), independent of the element or substance. A mole of any substance has a mass in grams equal to its molecular mass, which can be calculated from the atomic masses given in the periodic table of elements.

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad (13.29)$$

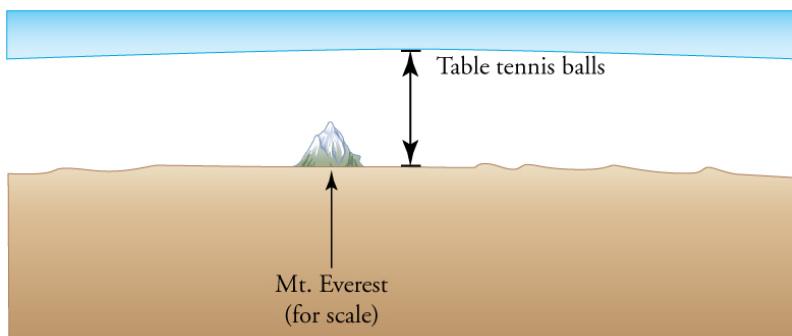


Figure 13.19 How big is a mole? On a macroscopic level, one mole of table tennis balls would cover the Earth to a depth of about 40 km.

Check Your Understanding

The active ingredient in a Tylenol pill is 325 mg of acetaminophen ($\text{C}_8\text{H}_9\text{NO}_2$). Find the number of active molecules of acetaminophen in a single pill.

Solution

We first need to calculate the molar mass (the mass of one mole) of acetaminophen. To do this, we need to multiply the number of atoms of each element by the element's atomic mass.

$$\begin{aligned} & (8 \text{ moles of carbon})(12 \text{ grams/mole}) + (9 \text{ moles hydrogen})(1 \text{ gram/mole}) \\ & + (1 \text{ mole nitrogen})(14 \text{ grams/mole}) + (2 \text{ moles oxygen})(16 \text{ grams/mole}) = 151 \text{ g} \end{aligned} \quad (13.30)$$

Then we need to calculate the number of moles in 325 mg.

$$\left(\frac{325 \text{ mg}}{151 \text{ grams/mole}} \right) \left(\frac{1 \text{ gram}}{1000 \text{ mg}} \right) = 2.15 \times 10^{-3} \text{ moles} \quad (13.31)$$

Then use Avogadro's number to calculate the number of molecules.

$$N = (2.15 \times 10^{-3} \text{ moles}) (6.02 \times 10^{23} \text{ molecules/mole}) = 1.30 \times 10^{21} \text{ molecules} \quad (13.32)$$

Example 13.8 Calculating Moles per Cubic Meter and Liters per Mole

Calculate: (a) the number of moles in 1.00 m^3 of gas at STP, and (b) the number of liters of gas per mole.

Strategy and Solution

(a) We are asked to find the number of moles per cubic meter, and we know from [Example 13.7](#) that the number of molecules per cubic meter at STP is 2.68×10^{25} . The number of moles can be found by dividing the number of molecules by Avogadro's number. We let n stand for the number of moles,

$$n \text{ mol/m}^3 = \frac{N \text{ molecules/m}^3}{6.02 \times 10^{23} \text{ molecules/mol}} = \frac{2.68 \times 10^{25} \text{ molecules/m}^3}{6.02 \times 10^{23} \text{ molecules/mol}} = 44.5 \text{ mol/m}^3. \quad (13.33)$$

(b) Using the value obtained for the number of moles in a cubic meter, and converting cubic meters to liters, we obtain

$$\frac{(10^3 \text{ L/m}^3)}{44.5 \text{ mol/m}^3} = 22.5 \text{ L/mol.} \quad (13.34)$$

Discussion

This value is very close to the accepted value of 22.4 L/mol. The slight difference is due to rounding errors caused by using three-digit input. Again this number is the same for all gases. In other words, it is independent of the gas.

The (average) molar weight of air (approximately 80% N_2 and 20% O_2) is $M = 28.8$ g. Thus the mass of one cubic meter of air is 1.28 kg. If a living room has dimensions 5 m \times 5 m \times 3 m, the mass of air inside the room is 96 kg, which is the typical mass of a human.

Check Your Understanding

The density of air at standard conditions ($P = 1$ atm and $T = 20^\circ\text{C}$) is 1.28 kg/m^3 . At what pressure is the density 0.64 kg/m^3 if the temperature and number of molecules are kept constant?

Solution

The best way to approach this question is to think about what is happening. If the density drops to half its original value and no molecules are lost, then the volume must double. If we look at the equation $PV = NkT$, we see that when the temperature is constant, the pressure is inversely proportional to volume. Therefore, if the volume doubles, the pressure must drop to half its original value, and $P_f = 0.50$ atm.

The Ideal Gas Law Restated Using Moles

A very common expression of the ideal gas law uses the number of moles, n , rather than the number of atoms and molecules, N . We start from the ideal gas law,

$$PV = NkT, \quad (13.35)$$

and multiply and divide the equation by Avogadro's number N_A . This gives

$$PV = \frac{N}{N_A} N_A kT. \quad (13.36)$$

Note that $n = N/N_A$ is the number of moles. We define the universal gas constant $R = N_A k$, and obtain the ideal gas law in terms of moles.

Ideal Gas Law (in terms of moles)

The ideal gas law (in terms of moles) is

$$PV = nRT. \quad (13.37)$$

The numerical value of R in SI units is

$$R = N_A k = (6.02 \times 10^{23} \text{ mol}^{-1})(1.38 \times 10^{-23} \text{ J/K}) = 8.31 \text{ J/mol} \cdot \text{K.} \quad (13.38)$$

In other units,

$$\begin{aligned} R &= 1.99 \text{ cal/mol} \cdot \text{K} \\ R &= 0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K.} \end{aligned} \quad (13.39)$$

You can use whichever value of R is most convenient for a particular problem.

Example 13.9 Calculating Number of Moles: Gas in a Bike Tire

How many moles of gas are in a bike tire with a volume of $2.00 \times 10^{-3} \text{ m}^3$ (2.00 L), a pressure of $7.00 \times 10^5 \text{ Pa}$ (a gauge pressure of just under 90.0 lb/in²), and at a temperature of 18.0°C?

Strategy

Identify the knowns and unknowns, and choose an equation to solve for the unknown. In this case, we solve the ideal gas law, $PV = nRT$, for the number of moles n .

Solution

1. Identify the knowns.

$$\begin{aligned} P &= 7.00 \times 10^5 \text{ Pa} \\ V &= 2.00 \times 10^{-3} \text{ m}^3 \\ T &= 18.0^\circ\text{C} = 291 \text{ K} \\ R &= 8.31 \text{ J/mol} \cdot \text{K} \end{aligned} \quad (13.40)$$

2. Rearrange the equation to solve for n and substitute known values.

$$\begin{aligned} n &= \frac{PV}{RT} = \frac{(7.00 \times 10^5 \text{ Pa})(2.00 \times 10^{-3} \text{ m}^3)}{(8.31 \text{ J/mol} \cdot \text{K})(291 \text{ K})} \\ &= 0.579 \text{ mol} \end{aligned} \quad (13.41)$$

Discussion

The most convenient choice for R in this case is 8.31 J/mol · K, because our known quantities are in SI units. The pressure and temperature are obtained from the initial conditions in [Example 13.6](#), but we would get the same answer if we used the final values.

The ideal gas law can be considered to be another manifestation of the law of conservation of energy (see [Conservation of Energy](#)). Work done on a gas results in an increase in its energy, increasing pressure and/or temperature, or decreasing volume. This increased energy can also be viewed as increased internal kinetic energy, given the gas's atoms and molecules.

The Ideal Gas Law and Energy

Let us now examine the role of energy in the behavior of gases. When you inflate a bike tire by hand, you do work by repeatedly exerting a force through a distance. This energy goes into increasing the pressure of air inside the tire and increasing the temperature of the pump and the air.

The ideal gas law is closely related to energy: the units on both sides are joules. The right-hand side of the ideal gas law in $PV = NkT$ is NkT . This term is roughly the amount of translational kinetic energy of N atoms or molecules at an absolute temperature T , as we shall see formally in [Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature](#). The left-hand side of the ideal gas law is PV , which also has the units of joules. We know from our study of fluids that pressure is one type of potential energy per unit volume, so pressure multiplied by volume is energy. The important point is that there is energy in a gas related to both its pressure and its volume. The energy can be changed when the gas is doing work as it expands—something we explore in [Heat and Heat Transfer Methods](#)—similar to what occurs in gasoline or steam engines and turbines.

Problem-Solving Strategy: The Ideal Gas Law

Step 1 Examine the situation to determine that an ideal gas is involved. Most gases are nearly ideal.

Step 2 Make a list of what quantities are given, or can be inferred from the problem as stated (identify the known quantities).

Convert known values into proper SI units (K for temperature, Pa for pressure, m³ for volume, molecules for N , and moles for n).

Step 3 Identify exactly what needs to be determined in the problem (identify the unknown quantities). A written list is useful.

Step 4 Determine whether the number of molecules or the number of moles is known, in order to decide which form of the ideal gas law to use. The first form is $PV = NkT$ and involves N , the number of atoms or molecules. The second form is $PV = nRT$ and involves n , the number of moles.

Step 5 Solve the ideal gas law for the quantity to be determined (the unknown quantity). You may need to take a ratio of final states to initial states to eliminate the unknown quantities that are kept fixed.

Step 6 Substitute the known quantities, along with their units, into the appropriate equation, and obtain numerical solutions complete with units. Be certain to use absolute temperature and absolute pressure.

Step 7 Check the answer to see if it is reasonable: Does it make sense?

Check Your Understanding

Liquids and solids have densities about 1000 times greater than gases. Explain how this implies that the distances between atoms and molecules in gases are about 10 times greater than the size of their atoms and molecules.

Solution

Atoms and molecules are close together in solids and liquids. In gases they are separated by empty space. Thus gases have lower densities than liquids and solids. Density is mass per unit volume, and volume is related to the size of a body (such as a sphere) cubed. So if the distance between atoms and molecules increases by a factor of 10, then the volume occupied increases by a factor of 1000, and the density decreases by a factor of 1000.

13.4 Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature

We have developed macroscopic definitions of pressure and temperature. Pressure is the force divided by the area on which the force is exerted, and temperature is measured with a thermometer. We gain a better understanding of pressure and temperature from the kinetic theory of gases, which assumes that atoms and molecules are in continuous random motion.

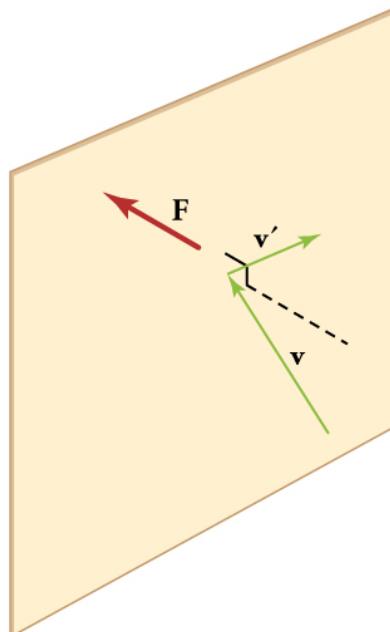


Figure 13.20 When a molecule collides with a rigid wall, the component of its momentum perpendicular to the wall is reversed. A force is thus exerted on the wall, creating pressure.

Figure 13.20 shows an elastic collision of a gas molecule with the wall of a container, so that it exerts a force on the wall (by Newton's third law). Because a huge number of molecules will collide with the wall in a short time, we observe an average force per unit area. These collisions are the source of pressure in a gas. As the number of molecules increases, the number of collisions and thus the pressure increase. Similarly, the gas pressure is higher if the average velocity of molecules is higher. The actual relationship is derived in the **Things Great and Small** feature below. The following relationship is found:

$$PV = \frac{1}{3}Nm\bar{v}^2, \quad (13.42)$$

where P is the pressure (average force per unit area), V is the volume of gas in the container, N is the number of molecules in the container, m is the mass of a molecule, and \bar{v}^2 is the average of the molecular speed squared.

What can we learn from this atomic and molecular version of the ideal gas law? We can derive a relationship between temperature and the average translational kinetic energy of molecules in a gas. Recall the previous expression of the ideal gas law:

$$PV = NkT. \quad (13.43)$$

Equating the right-hand side of this equation with the right-hand side of $PV = \frac{1}{3}Nm\bar{v}^2$ gives

$$\frac{1}{3}Nm\bar{v}^2 = NkT. \quad (13.44)$$

Making Connections: Things Great and Small—Atomic and Molecular Origin of Pressure in a Gas

Figure 13.21 shows a box filled with a gas. We know from our previous discussions that putting more gas into the box produces greater pressure, and that increasing the temperature of the gas also produces a greater pressure. But why should increasing the temperature of the gas increase the pressure in the box? A look at the atomic and molecular scale gives us some answers, and an alternative expression for the ideal gas law.

The figure shows an expanded view of an elastic collision of a gas molecule with the wall of a container. Calculating the average force exerted by such molecules will lead us to the ideal gas law, and to the connection between temperature and molecular kinetic energy. We assume that a molecule is small compared with the separation of molecules in the gas, and that its interaction with other molecules can be ignored. We also assume the wall is rigid and that the molecule's direction changes, but that its speed remains constant (and hence its kinetic energy and the magnitude of its momentum remain constant as well). This assumption is not always valid, but the same result is obtained with a more detailed description of the molecule's exchange of energy and momentum with the wall.

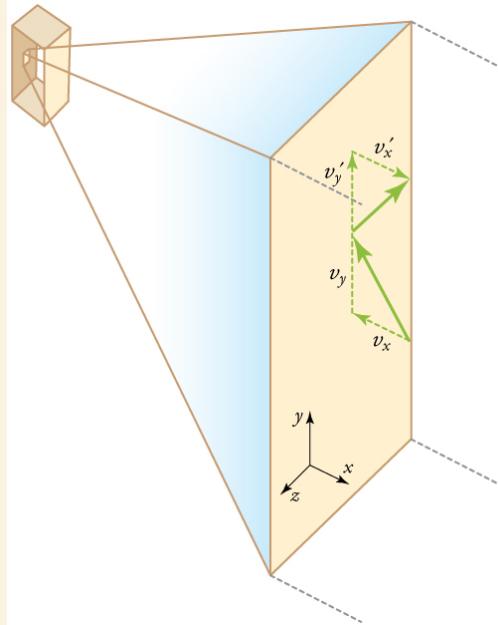


Figure 13.21 Gas in a box exerts an outward pressure on its walls. A molecule colliding with a rigid wall has the direction of its velocity and momentum in the x -direction reversed. This direction is perpendicular to the wall. The components of its velocity and momentum in the y - and z -directions are not changed, which means there is no force parallel to the wall.

If the molecule's velocity changes in the x -direction, its momentum changes from $-mv_x$ to $+mv_x$. Thus, its change in momentum is $\Delta mv = +mv_x - (-mv_x) = 2mv_x$. The force exerted on the molecule is given by

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{\Delta t}. \quad (13.45)$$

There is no force between the wall and the molecule until the molecule hits the wall. During the short time of the collision, the force between the molecule and wall is relatively large. We are looking for an average force; we take Δt to be the average time between collisions of the molecule with this wall. It is the time it would take the molecule to go across the box and back (a distance $2l$) at a speed of v_x . Thus $\Delta t = 2l/v_x$, and the expression for the force becomes

$$F = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}. \quad (13.46)$$

This force is due to *one* molecule. We multiply by the number of molecules N and use their average squared velocity to find the force

$$F = N \frac{mv_x^2}{l}, \quad (13.47)$$

where the bar over a quantity means its average value. We would like to have the force in terms of the speed v , rather than the x -component of the velocity. We note that the total velocity squared is the sum of the squares of its components, so that

$$\bar{v}^2 = v_x^2 + v_y^2 + v_z^2. \quad (13.48)$$

Because the velocities are random, their average components in all directions are the same:

$$\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2. \quad (13.49)$$

Thus,

$$\bar{v}^2 = 3\bar{v}_x^2, \quad (13.50)$$

or

$$\bar{v}_x^2 = \frac{1}{3}\bar{v}^2. \quad (13.51)$$

Substituting $\frac{1}{3}\bar{v}^2$ into the expression for F gives

$$F = N \frac{m\bar{v}^2}{3l}. \quad (13.52)$$

The pressure is F/A , so that we obtain

$$P = \frac{F}{A} = N \frac{m\bar{v}^2}{3Al} = \frac{1}{3} \frac{Nm\bar{v}^2}{V}, \quad (13.53)$$

where we used $V = Al$ for the volume. This gives the important result.

$$PV = \frac{1}{3} Nm\bar{v}^2 \quad (13.54)$$

This equation is another expression of the ideal gas law.

We can get the average kinetic energy of a molecule, $\frac{1}{2}mv^2$, from the left-hand side of the equation by canceling N and multiplying by 3/2. This calculation produces the result that the average kinetic energy of a molecule is directly related to absolute temperature.

$$\bar{KE} = \frac{1}{2}mv^2 = \frac{3}{2}kT \quad (13.55)$$

The average translational kinetic energy of a molecule, \bar{KE} , is called **thermal energy**. The equation $\bar{KE} = \frac{1}{2}mv^2 = \frac{3}{2}kT$ is a molecular interpretation of temperature, and it has been found to be valid for gases and reasonably accurate in liquids and solids. It is another definition of temperature based on an expression of the molecular energy.

It is sometimes useful to rearrange $\bar{KE} = \frac{1}{2}mv^2 = \frac{3}{2}kT$, and solve for the average speed of molecules in a gas in terms of temperature,

$$\sqrt{\bar{v}^2} = v_{rms} = \sqrt{\frac{3kT}{m}}, \quad (13.56)$$

where v_{rms} stands for root-mean-square (rms) speed.

Example 13.10 Calculating Kinetic Energy and Speed of a Gas Molecule

(a) What is the average kinetic energy of a gas molecule at 20.0°C (room temperature)? (b) Find the rms speed of a nitrogen molecule (N_2) at this temperature.

Strategy for (a)

The known in the equation for the average kinetic energy is the temperature.

$$\overline{KE} = \frac{1}{2}mv^2 = \frac{3}{2}kT \quad (13.57)$$

Before substituting values into this equation, we must convert the given temperature to kelvins. This conversion gives $T = (20.0 + 273) \text{ K} = 293 \text{ K}$.

Solution for (a)

The temperature alone is sufficient to find the average translational kinetic energy. Substituting the temperature into the translational kinetic energy equation gives

$$\overline{KE} = \frac{3}{2}kT = \frac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) = 6.07 \times 10^{-21} \text{ J.} \quad (13.58)$$

Strategy for (b)

Finding the rms speed of a nitrogen molecule involves a straightforward calculation using the equation

$$\sqrt{v^2} = v_{\text{rms}} = \sqrt{\frac{3kT}{m}}, \quad (13.59)$$

but we must first find the mass of a nitrogen molecule. Using the molecular mass of nitrogen N_2 from the periodic table,

$$m = \frac{2(14.0067) \times 10^{-3} \text{ kg/mol}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 4.65 \times 10^{-26} \text{ kg.} \quad (13.60)$$

Solution for (b)

Substituting this mass and the value for k into the equation for v_{rms} yields

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{4.65 \times 10^{-26} \text{ kg}}} = 511 \text{ m/s.} \quad (13.61)$$

Discussion

Note that the average kinetic energy of the molecule is independent of the type of molecule. The average translational kinetic energy depends only on absolute temperature. The kinetic energy is very small compared to macroscopic energies, so that we do not feel when an air molecule is hitting our skin. The rms velocity of the nitrogen molecule is surprisingly large. These large molecular velocities do not yield macroscopic movement of air, since the molecules move in all directions with equal likelihood. The *mean free path* (the distance a molecule can move on average between collisions) of molecules in air is very small, and so the molecules move rapidly but do not get very far in a second. The high value for rms speed is reflected in the speed of sound, however, which is about 340 m/s at room temperature. The faster the rms speed of air molecules, the faster that sound vibrations can be transferred through the air. The speed of sound increases with temperature and is greater in gases with small molecular masses, such as helium. (See [Figure 13.22](#).)

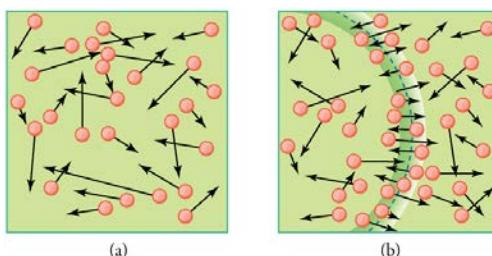


Figure 13.22 (a) There are many molecules moving so fast in an ordinary gas that they collide a billion times every second. (b) Individual molecules do not move very far in a small amount of time, but disturbances like sound waves are transmitted at speeds related to the molecular speeds.

Making Connections: Historical Note—Kinetic Theory of Gases

The kinetic theory of gases was developed by Daniel Bernoulli (1700–1782), who is best known in physics for his work on fluid flow (hydrodynamics). Bernoulli's work predates the atomistic view of matter established by Dalton.

Distribution of Molecular Speeds

The motion of molecules in a gas is random in magnitude and direction for individual molecules, but a gas of many molecules has a predictable distribution of molecular speeds. This distribution is called the *Maxwell-Boltzmann distribution*, after its originators, who calculated it based on kinetic theory, and has since been confirmed experimentally. (See [Figure 13.23](#).) The distribution has a long tail, because a few molecules may go several times the rms speed. The most probable speed v_p is less than the rms speed v_{rms} . [Figure 13.24](#) shows that the curve is shifted to higher speeds at higher temperatures, with a broader range of speeds.

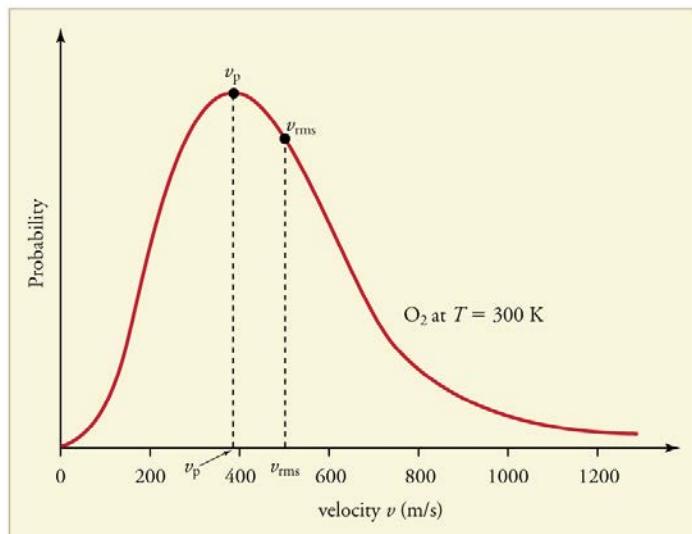


Figure 13.23 The Maxwell-Boltzmann distribution of molecular speeds in an ideal gas. The most likely speed v_p is less than the rms speed v_{rms} . Although very high speeds are possible, only a tiny fraction of the molecules have speeds that are an order of magnitude greater than v_{rms} .

The distribution of thermal speeds depends strongly on temperature. As temperature increases, the speeds are shifted to higher values and the distribution is broadened.

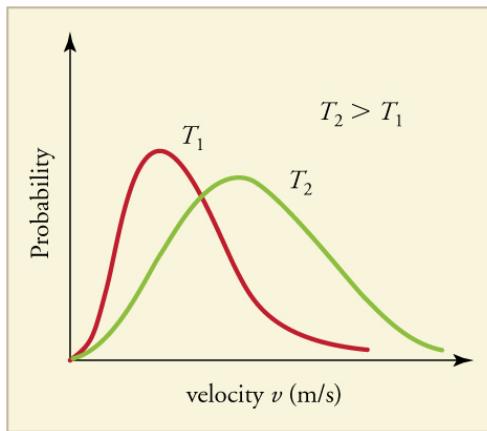


Figure 13.24 The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures.

What is the implication of the change in distribution with temperature shown in [Figure 13.24](#) for humans? All other things being equal, if a person has a fever, he or she is likely to lose more water molecules, particularly from linings along moist cavities such as the lungs and mouth, creating a dry sensation in the mouth.

Example 13.11 Calculating Temperature: Escape Velocity of Helium Atoms

In order to escape Earth's gravity, an object near the top of the atmosphere (at an altitude of 100 km) must travel away from Earth at 11.1 km/s. This speed is called the *escape velocity*. At what temperature would helium atoms have an rms speed equal to the escape velocity?

Strategy

Identify the knowns and unknowns and determine which equations to use to solve the problem.

Solution

1. Identify the knowns: v is the escape velocity, 11.1 km/s.
2. Identify the unknowns: We need to solve for temperature, T . We also need to solve for the mass m of the helium atom.
3. Determine which equations are needed.
 - To solve for mass m of the helium atom, we can use information from the periodic table:

$$m = \frac{\text{molar mass}}{\text{number of atoms per mole}}. \quad (13.62)$$

- To solve for temperature T , we can rearrange either

$$\overline{\text{KE}} = \frac{1}{2}mv^2 = \frac{3}{2}kT \quad (13.63)$$

or

$$\sqrt{\overline{v^2}} = v_{\text{rms}} = \sqrt{\frac{3kT}{m}} \quad (13.64)$$

to yield

$$T = \frac{mv^2}{3k}, \quad (13.65)$$

where k is the Boltzmann constant and m is the mass of a helium atom.

4. Plug the known values into the equations and solve for the unknowns.

$$m = \frac{\text{molar mass}}{\text{number of atoms per mole}} = \frac{4.0026 \times 10^{-3} \text{ kg/mol}}{6.02 \times 10^{23} \text{ mol}} = 6.65 \times 10^{-27} \text{ kg} \quad (13.66)$$

$$T = \frac{(6.65 \times 10^{-27} \text{ kg})(11.1 \times 10^3 \text{ m/s})^2}{3(1.38 \times 10^{-23} \text{ J/K})} = 1.98 \times 10^4 \text{ K} \quad (13.67)$$

Discussion

This temperature is much higher than atmospheric temperature, which is approximately 250 K (-25°C or -10°F) at high altitude. Very few helium atoms are left in the atmosphere, but there were many when the atmosphere was formed. The reason for the loss of helium atoms is that there are a small number of helium atoms with speeds higher than Earth's escape velocity even at normal temperatures. The speed of a helium atom changes from one instant to the next, so that at any instant, there is a small, but nonzero chance that the speed is greater than the escape speed and the molecule escapes from Earth's gravitational pull. Heavier molecules, such as oxygen, nitrogen, and water (very little of which reach a very high altitude), have smaller rms speeds, and so it is much less likely that any of them will have speeds greater than the escape velocity. In fact, so few have speeds above the escape velocity that billions of years are required to lose significant amounts of the atmosphere. **Figure 13.25** shows the impact of a lack of an atmosphere on the Moon. Because the gravitational pull of the Moon is much weaker, it has lost almost its entire atmosphere. The comparison between Earth and the Moon is discussed in this chapter's Problems and Exercises.



Figure 13.25 This photograph of Apollo 17 Commander Eugene Cernan driving the lunar rover on the Moon in 1972 looks as though it was taken at night with a large spotlight. In fact, the light is coming from the Sun. Because the acceleration due to gravity on the Moon is so low (about 1/6 that of Earth), the Moon's escape velocity is much smaller. As a result, gas molecules escape very easily from the Moon, leaving it with virtually no atmosphere. Even during the daytime, the sky is black because there is no gas to scatter sunlight. (credit: Harrison H. Schmitt/NASA)

Check Your Understanding

If you consider a very small object such as a grain of pollen, in a gas, then the number of atoms and molecules striking its surface would also be relatively small. Would the grain of pollen experience any fluctuations in pressure due to statistical fluctuations in the number of gas atoms and molecules striking it in a given amount of time?

Solution

Yes. Such fluctuations actually occur for a body of any size in a gas, but since the numbers of atoms and molecules are immense for macroscopic bodies, the fluctuations are a tiny percentage of the number of collisions, and the averages spoken of in this section vary imperceptibly. Roughly speaking the fluctuations are proportional to the inverse square root of the number of collisions, so for small bodies they can become significant. This was actually observed in the 19th century for pollen grains in water, and is known as the Brownian effect.

PhET Explorations: Gas Properties

Pump gas molecules into a box and see what happens as you change the volume, add or remove heat, change gravity, and more. Measure the temperature and pressure, and discover how the properties of the gas vary in relation to each other.



PhET Interactive Simulation

Figure 13.26 Gas Properties (<http://phet.colorado.edu/en/simulation/gas-properties>)

13.5 Phase Changes

Up to now, we have considered the behavior of ideal gases. Real gases are like ideal gases at high temperatures. At lower temperatures, however, the interactions between the molecules and their volumes cannot be ignored. The molecules are very close (condensation occurs) and there is a dramatic decrease in volume, as seen in **Figure 13.27**. The substance changes from a gas to a liquid. When a liquid is cooled to even lower temperatures, it becomes a solid. The volume never reaches zero because of the finite volume of the molecules.

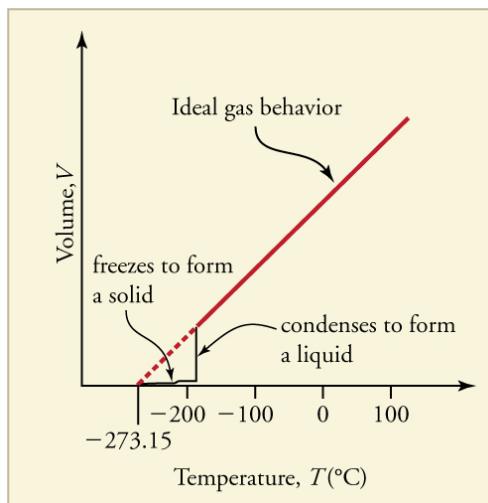


Figure 13.27 A sketch of volume versus temperature for a real gas at constant pressure. The linear (straight line) part of the graph represents ideal gas behavior—volume and temperature are directly and positively related and the line extrapolates to zero volume at -273.15°C , or absolute zero. When the gas becomes a liquid, however, the volume actually decreases precipitously at the liquefaction point. The volume decreases slightly once the substance is solid, but it never becomes zero.

High pressure may also cause a gas to change phase to a liquid. Carbon dioxide, for example, is a gas at room temperature and atmospheric pressure, but becomes a liquid under sufficiently high pressure. If the pressure is reduced, the temperature drops and the liquid carbon dioxide solidifies into a snow-like substance at the temperature -78°C . Solid CO_2 is called “dry ice.”

Another example of a gas that can be in a liquid phase is liquid nitrogen (LN_2). LN_2 is made by liquefaction of atmospheric air (through compression and cooling). It boils at 77 K (-196°C) at atmospheric pressure. LN_2 is useful as a refrigerant and allows for the preservation of blood, sperm, and other biological materials. It is also used to reduce noise in electronic sensors and equipment, and to help cool down their current-carrying wires. In dermatology, LN_2 is used to freeze and painlessly remove warts and other growths from the skin.

PV Diagrams

We can examine aspects of the behavior of a substance by plotting a graph of pressure versus volume, called a **PV diagram**. When the substance behaves like an ideal gas, the ideal gas law describes the relationship between its pressure and volume. That is,

$$PV = NkT \text{ (ideal gas).} \quad (13.68)$$

Now, assuming the number of molecules and the temperature are fixed,

$$PV = \text{constant (ideal gas, constant temperature).} \quad (13.69)$$

For example, the volume of the gas will decrease as the pressure increases. If you plot the relationship $PV = \text{constant}$ on a **PV** diagram, you find a hyperbola. **Figure 13.28** shows a graph of pressure versus volume. The hyperbolas represent ideal-gas behavior at various fixed temperatures, and are called **isotherms**. At lower temperatures, the curves begin to look less like hyperbolas—the gas is not behaving ideally and may even contain liquid. There is a **critical point**—that is, a **critical temperature**—above which liquid cannot exist. At sufficiently high pressure above the critical point, the gas will have the density of a liquid but will not condense. Carbon dioxide, for example, cannot be liquefied at a temperature above 31.0°C . **Critical pressure** is the minimum pressure needed for liquid to exist at the critical temperature. **Table 13.3** lists representative critical temperatures and pressures.

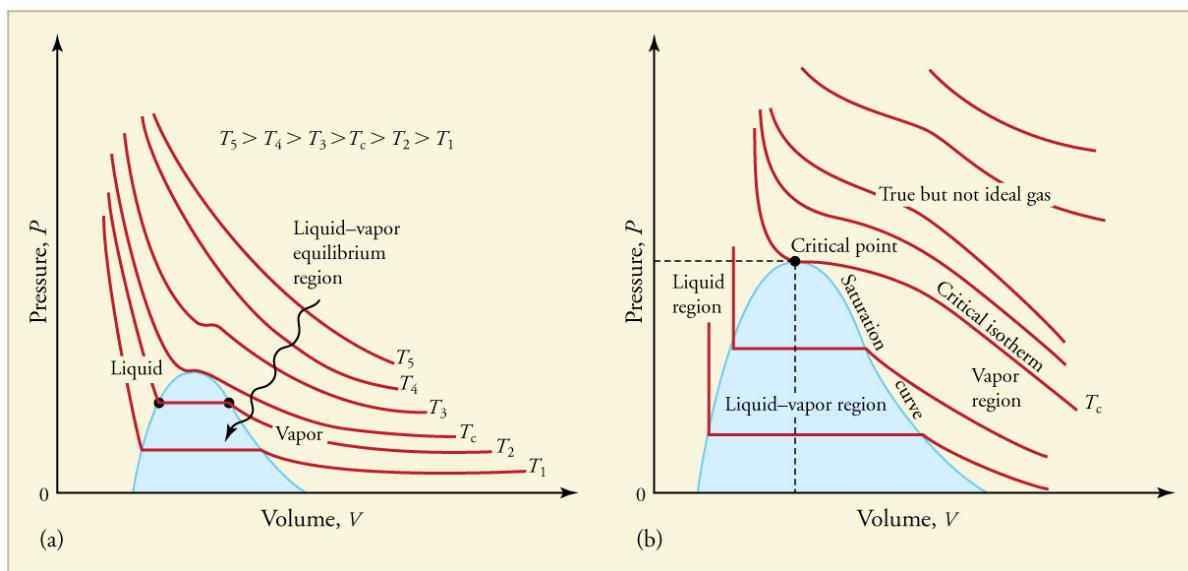


Figure 13.28 PV diagrams. (a) Each curve (isotherm) represents the relationship between P and V at a fixed temperature; the upper curves are at higher temperatures. The lower curves are not hyperbolas, because the gas is no longer an ideal gas. (b) An expanded portion of the PV diagram for low temperatures, where the phase can change from a gas to a liquid. The term “vapor” refers to the gas phase when it exists at a temperature below the boiling temperature.

Table 13.3 Critical Temperatures and Pressures

Substance	Critical temperature		Critical pressure	
	K	°C	Pa	atm
Water	647.4	374.3	22.12×10^6	219.0
Sulfur dioxide	430.7	157.6	7.88×10^6	78.0
Ammonia	405.5	132.4	11.28×10^6	111.7
Carbon dioxide	304.2	31.1	7.39×10^6	73.2
Oxygen	154.8	-118.4	5.08×10^6	50.3
Nitrogen	126.2	-146.9	3.39×10^6	33.6
Hydrogen	33.3	-239.9	1.30×10^6	12.9
Helium	5.3	-267.9	0.229×10^6	2.27

Phase Diagrams

The plots of pressure versus temperatures provide considerable insight into thermal properties of substances. There are well-defined regions on these graphs that correspond to various phases of matter, so PT graphs are called **phase diagrams**.

Figure 13.29 shows the phase diagram for water. Using the graph, if you know the pressure and temperature you can determine the phase of water. The solid lines—boundaries between phases—indicate temperatures and pressures at which the phases coexist (that is, they exist together in ratios, depending on pressure and temperature). For example, the boiling point of water is 100°C at 1.00 atm. As the pressure increases, the boiling temperature rises steadily to 374°C at a pressure of 218 atm. A pressure cooker (or even a covered pot) will cook food faster because the water can exist as a liquid at temperatures greater than 100°C without all boiling away. The curve ends at a point called the *critical point*, because at higher temperatures the liquid phase does not exist at any pressure. The critical point occurs at the critical temperature, as you can see for water from **Table 13.3**. The critical temperature for oxygen is -118°C , so oxygen cannot be liquefied above this temperature.

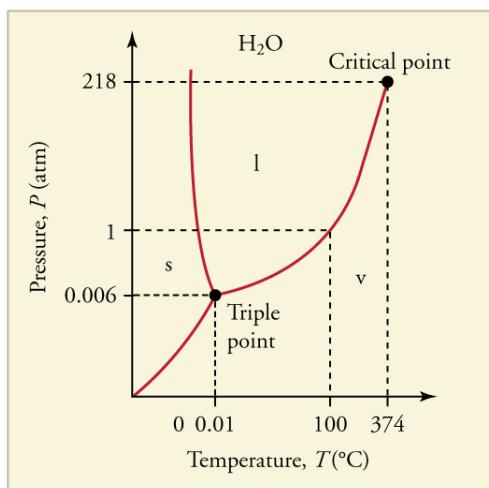


Figure 13.29 The phase diagram (*PT* graph) for water. Note that the axes are nonlinear and the graph is not to scale. This graph is simplified—there are several other exotic phases of ice at higher pressures.

Similarly, the curve between the solid and liquid regions in **Figure 13.29** gives the melting temperature at various pressures. For example, the melting point is 0°C at 1.00 atm, as expected. Note that, at a fixed temperature, you can change the phase from solid (ice) to liquid (water) by increasing the pressure. Ice melts from pressure in the hands of a snowball maker. From the phase diagram, we can also say that the melting temperature of ice rises with increased pressure. When a car is driven over snow, the increased pressure from the tires melts the snowflakes; afterwards the water refreezes and forms an ice layer.

At sufficiently low pressures there is no liquid phase, but the substance can exist as either gas or solid. For water, there is no liquid phase at pressures below 0.00600 atm. The phase change from solid to gas is called **sublimation**. It accounts for large losses of snow pack that never make it into a river, the routine automatic defrosting of a freezer, and the freeze-drying process applied to many foods. Carbon dioxide, on the other hand, sublimates at standard atmospheric pressure of 1 atm. (The solid form of CO_2 is known as dry ice because it does not melt. Instead, it moves directly from the solid to the gas state.)

All three curves on the phase diagram meet at a single point, the **triple point**, where all three phases exist in equilibrium. For water, the triple point occurs at 273.16 K (0.01°C), and is a more accurate calibration temperature than the melting point of water at 1.00 atm, or 273.15 K (0.0°C). See **Table 13.4** for the triple point values of other substances.

Equilibrium

Liquid and gas phases are in equilibrium at the boiling temperature. (See **Figure 13.30**.) If a substance is in a closed container at the boiling point, then the liquid is boiling and the gas is condensing at the same rate without net change in their relative amount. Molecules in the liquid escape as a gas at the same rate at which gas molecules stick to the liquid, or form droplets and become part of the liquid phase. The combination of temperature and pressure has to be “just right”; if the temperature and pressure are increased, equilibrium is maintained by the same increase of boiling and condensation rates.

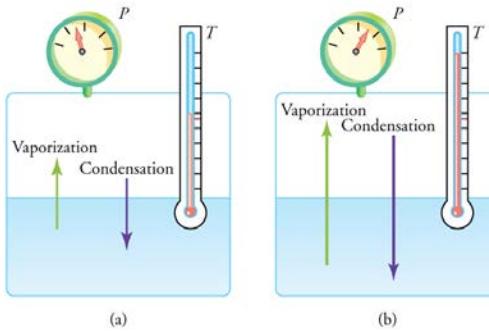


Figure 13.30 Equilibrium between liquid and gas at two different boiling points inside a closed container. (a) The rates of boiling and condensation are equal at this combination of temperature and pressure, so the liquid and gas phases are in equilibrium. (b) At a higher temperature, the boiling rate is faster and the rates at which molecules leave the liquid and enter the gas are also faster. Because there are more molecules in the gas, the gas pressure is higher and the rate at which gas molecules condense and enter the liquid is faster. As a result the gas and liquid are in equilibrium at this higher temperature.

Table 13.4 Triple Point Temperatures and Pressures

Substance	Temperature		Pressure	
	K	°C	Pa	atm
Water	273.16	0.01	6.10×10^2	0.00600
Carbon dioxide	216.55	-56.60	5.16×10^5	5.11
Sulfur dioxide	197.68	-75.47	1.67×10^3	0.0167
Ammonia	195.40	-77.75	6.06×10^3	0.0600
Nitrogen	63.18	-210.0	1.25×10^4	0.124
Oxygen	54.36	-218.8	1.52×10^2	0.00151
Hydrogen	13.84	-259.3	7.04×10^3	0.0697

One example of equilibrium between liquid and gas is that of water and steam at 100°C and 1.00 atm. This temperature is the boiling point at that pressure, so they should exist in equilibrium. Why does an open pot of water at 100°C boil completely away? The gas surrounding an open pot is not pure water: it is mixed with air. If pure water and steam are in a closed container at 100°C and 1.00 atm, they would coexist—but with air over the pot, there are fewer water molecules to condense, and water boils. What about water at 20.0°C and 1.00 atm? This temperature and pressure correspond to the liquid region, yet an open glass of water at this temperature will completely evaporate. Again, the gas around it is air and not pure water vapor, so that the reduced evaporation rate is greater than the condensation rate of water from dry air. If the glass is sealed, then the liquid phase remains. We call the gas phase a **vapor** when it exists, as it does for water at 20.0°C, at a temperature below the boiling temperature.

Check Your Understanding

Explain why a cup of water (or soda) with ice cubes stays at 0°C, even on a hot summer day.

Solution

The ice and liquid water are in thermal equilibrium, so that the temperature stays at the freezing temperature as long as ice remains in the liquid. (Once all of the ice melts, the water temperature will start to rise.)

Vapor Pressure, Partial Pressure, and Dalton's Law

Vapor pressure is defined as the pressure at which a gas coexists with its solid or liquid phase. Vapor pressure is created by faster molecules that break away from the liquid or solid and enter the gas phase. The vapor pressure of a substance depends on both the substance and its temperature—an increase in temperature increases the vapor pressure.

Partial pressure is defined as the pressure a gas would create if it occupied the total volume available. In a mixture of gases, *the total pressure is the sum of partial pressures of the component gases*, assuming ideal gas behavior and no chemical reactions between the components. This law is known as **Dalton's law of partial pressures**, after the English scientist John Dalton (1766–1844), who proposed it. Dalton's law is based on kinetic theory, where each gas creates its pressure by molecular collisions, independent of other gases present. It is consistent with the fact that pressures add according to **Pascal's Principle**. Thus water evaporates and ice sublimates when their vapor pressures exceed the partial pressure of water vapor in the surrounding mixture of gases. If their vapor pressures are less than the partial pressure of water vapor in the surrounding gas, liquid droplets or ice crystals (frost) form.

Check Your Understanding

Is energy transfer involved in a phase change? If so, will energy have to be supplied to change phase from solid to liquid and liquid to gas? What about gas to liquid and liquid to solid? Why do they spray the orange trees with water in Florida when the temperatures are near or just below freezing?

Solution

Yes, energy transfer is involved in a phase change. We know that atoms and molecules in solids and liquids are bound to each other because we know that force is required to separate them. So in a phase change from solid to liquid and liquid to gas, a force must be exerted, perhaps by collision, to separate atoms and molecules. Force exerted through a distance is work, and energy is needed to do work to go from solid to liquid and liquid to gas. This is intuitively consistent with the need for energy to melt ice or boil water. The converse is also true. Going from gas to liquid or liquid to solid involves atoms and molecules pushing together, doing work and releasing energy.

PhET Explorations: States of Matter—Basics

Heat, cool, and compress atoms and molecules and watch as they change between solid, liquid, and gas phases.



PhET Interactive Simulation

Figure 13.31 States of Matter: Basics (<http://phet.colorado.edu/en/simulation/states-of-matter-basics>)

13.6 Humidity, Evaporation, and Boiling

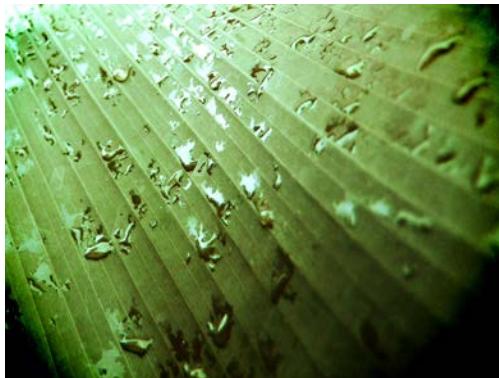


Figure 13.32 Dew drops like these, on a banana leaf photographed just after sunrise, form when the air temperature drops to or below the dew point. At the dew point, the rate at which water molecules join together is greater than the rate at which they separate, and some of the water condenses to form droplets. (credit: Aaron Escobar, Flickr)

The expression “it’s not the heat, it’s the humidity” makes a valid point. We keep cool in hot weather by evaporating sweat from our skin and water from our breathing passages. Because evaporation is inhibited by high humidity, we feel hotter at a given temperature when the humidity is high. Low humidity, on the other hand, can cause discomfort from excessive drying of mucous membranes and can lead to an increased risk of respiratory infections.

When we say humidity, we really mean **relative humidity**. Relative humidity tells us how much water vapor is in the air compared with the maximum possible. At its maximum, denoted as **saturation**, the relative humidity is 100%, and evaporation is inhibited. The amount of water vapor in the air depends on temperature. For example, relative humidity rises in the evening, as air temperature declines, sometimes reaching the **dew point**. At the dew point temperature, relative humidity is 100%, and fog may result from the condensation of water droplets if they are small enough to stay in suspension. Conversely, if you wish to dry something (perhaps your hair), it is more effective to blow hot air over it rather than cold air, because, among other things, the increase in temperature increases the energy of the molecules, so the rate of evaporation increases.

The amount of water vapor in the air depends on the vapor pressure of water. The liquid and solid phases are continuously giving off vapor because some of the molecules have high enough speeds to enter the gas phase; see **Figure 13.33(a)**. If a lid is placed over the container, as in **Figure 13.33(b)**, evaporation continues, increasing the pressure, until sufficient vapor has built up for condensation to balance evaporation. Then equilibrium has been achieved, and the vapor pressure is equal to the partial pressure of water in the container. Vapor pressure increases with temperature because molecular speeds are higher as temperature increases. **Table 13.5** gives representative values of water vapor pressure over a range of temperatures.

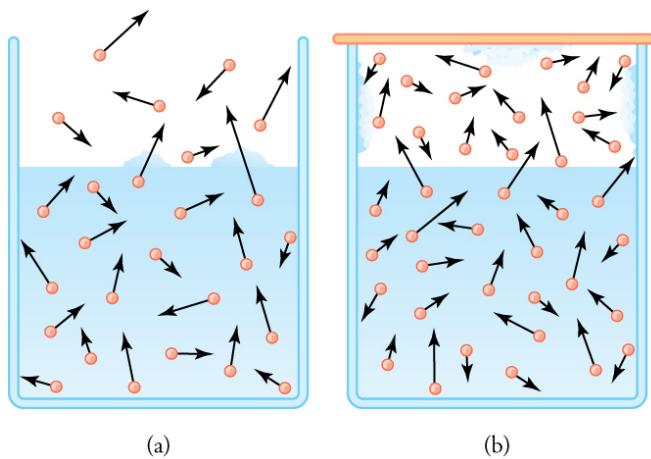


Figure 13.33 (a) Because of the distribution of speeds and kinetic energies, some water molecules can break away to the vapor phase even at temperatures below the ordinary boiling point. (b) If the container is sealed, evaporation will continue until there is enough vapor density for the condensation rate to equal the evaporation rate. This vapor density and the partial pressure it creates are the saturation values. They increase with temperature and are independent of the presence of other gases, such as air. They depend only on the vapor pressure of water.

Relative humidity is related to the partial pressure of water vapor in the air. At 100% humidity, the partial pressure is equal to the vapor pressure, and no more water can enter the vapor phase. If the partial pressure is less than the vapor pressure, then evaporation will take place, as humidity is less than 100%. If the partial pressure is greater than the vapor pressure, condensation takes place. In everyday language, people sometimes refer to the capacity of air to "hold" water vapor, but this is not actually what happens. The water vapor is not held by the air. The amount of water in air is determined by the vapor pressure of water and has nothing to do with the properties of air.

Table 13.5 Saturation Vapor Density of Water

Temperature (°C)	Vapor pressure (Pa)	Saturation vapor density (g/m ³)
-50	4.0	0.039
-20	1.04×10^2	0.89
-10	2.60×10^2	2.36
0	6.10×10^2	4.84
5	8.68×10^2	6.80
10	1.19×10^3	9.40
15	1.69×10^3	12.8
20	2.33×10^3	17.2
25	3.17×10^3	23.0
30	4.24×10^3	30.4
37	6.31×10^3	44.0
40	7.34×10^3	51.1
50	1.23×10^4	82.4
60	1.99×10^4	130
70	3.12×10^4	197
80	4.73×10^4	294
90	7.01×10^4	418
95	8.59×10^4	505
100	1.01×10^5	598
120	1.99×10^5	1095
150	4.76×10^5	2430
200	1.55×10^6	7090
220	2.32×10^6	10,200

Example 13.12 Calculating Density Using Vapor Pressure

Table 13.5 gives the vapor pressure of water at 20.0°C as 2.33×10^3 Pa. Use the ideal gas law to calculate the density of water vapor in g/m³ that would create a partial pressure equal to this vapor pressure. Compare the result with the saturation vapor density given in the table.

Strategy

To solve this problem, we need to break it down into a two steps. The partial pressure follows the ideal gas law,

$$PV = nRT \quad (13.70)$$

where n is the number of moles. If we solve this equation for n/V to calculate the number of moles per cubic meter, we can then convert this quantity to grams per cubic meter as requested. To do this, we need to use the molecular mass of water, which is given in the periodic table.

Solution

1. Identify the knowns and convert them to the proper units:

- temperature $T = 20^\circ\text{C} = 293 \text{ K}$
- vapor pressure P of water at 20°C is $2.33 \times 10^3 \text{ Pa}$
- molecular mass of water is 18.0 g/mol

2. Solve the ideal gas law for n/V .

$$\frac{n}{V} = \frac{P}{RT} \quad (13.71)$$

3. Substitute known values into the equation and solve for n/V .

$$\frac{n}{V} = \frac{P}{RT} = \frac{2.33 \times 10^3 \text{ Pa}}{(8.31 \text{ J/mol} \cdot \text{K})(293 \text{ K})} = 0.957 \text{ mol/m}^3 \quad (13.72)$$

4. Convert the density in moles per cubic meter to grams per cubic meter.

$$\rho = \left(0.957 \frac{\text{mol}}{\text{m}^3}\right) \left(\frac{18.0 \text{ g}}{\text{mol}}\right) = 17.2 \text{ g/m}^3 \quad (13.73)$$

Discussion

The density is obtained by assuming a pressure equal to the vapor pressure of water at 20.0°C . The density found is identical to the value in **Table 13.5**, which means that a vapor density of 17.2 g/m^3 at 20.0°C creates a partial pressure of $2.33 \times 10^3 \text{ Pa}$, equal to the vapor pressure of water at that temperature. If the partial pressure is equal to the vapor pressure, then the liquid and vapor phases are in equilibrium, and the relative humidity is 100%. Thus, there can be no more than 17.2 g of water vapor per m^3 at 20.0°C , so that this value is the saturation vapor density at that temperature. This example illustrates how water vapor behaves like an ideal gas: the pressure and density are consistent with the ideal gas law (assuming the density in the table is correct). The saturation vapor densities listed in **Table 13.5** are the maximum amounts of water vapor that air can hold at various temperatures.

Percent Relative Humidity

We define **percent relative humidity** as the ratio of vapor density to saturation vapor density, or

$$\text{percent relative humidity} = \frac{\text{vapor density}}{\text{saturation vapor density}} \times 100 \quad (13.74)$$

We can use this and the data in **Table 13.5** to do a variety of interesting calculations, keeping in mind that relative humidity is based on the comparison of the partial pressure of water vapor in air and ice.

Example 13.13 Calculating Humidity and Dew Point

(a) Calculate the percent relative humidity on a day when the temperature is 25.0°C and the air contains 9.40 g of water vapor per m^3 . (b) At what temperature will this air reach 100% relative humidity (the saturation density)? This temperature is the dew point. (c) What is the humidity when the air temperature is 25.0°C and the dew point is -10.0°C ?

Strategy and Solution

(a) Percent relative humidity is defined as the ratio of vapor density to saturation vapor density.

$$\text{percent relative humidity} = \frac{\text{vapor density}}{\text{saturation vapor density}} \times 100 \quad (13.75)$$

The first is given to be 9.40 g/m^3 , and the second is found in **Table 13.5** to be 23.0 g/m^3 . Thus,

$$\text{percent relative humidity} = \frac{9.40 \text{ g/m}^3}{23.0 \text{ g/m}^3} \times 100 = 40.9\% \quad (13.76)$$

(b) The air contains 9.40 g/m^3 of water vapor. The relative humidity will be 100% at a temperature where 9.40 g/m^3 is the saturation density. Inspection of **Table 13.5** reveals this to be the case at 10.0°C , where the relative humidity will be 100%. That temperature is called the dew point for air with this concentration of water vapor.

(c) Here, the dew point temperature is given to be -10.0°C . Using **Table 13.5**, we see that the vapor density is 2.36 g/m^3 , because this value is the saturation vapor density at -10.0°C . The saturation vapor density at 25.0°C is seen to be 23.0 g/m^3 . Thus, the relative humidity at 25.0°C is

$$\text{percent relative humidity} = \frac{2.36 \text{ g/m}^3}{23.0 \text{ g/m}^3} \times 100 = 10.3\%. \quad (13.77)$$

Discussion

The importance of dew point is that air temperature cannot drop below 10.0°C in part (b), or -10.0°C in part (c), without water vapor condensing out of the air. If condensation occurs, considerable transfer of heat occurs (discussed in **Heat and Heat Transfer Methods**), which prevents the temperature from further dropping. When dew points are below 0°C , freezing temperatures are a greater possibility, which explains why farmers keep track of the dew point. Low humidity in deserts means low dew-point temperatures. Thus condensation is unlikely. If the temperature drops, vapor does not condense in liquid drops. Because no heat is released into the air, the air temperature drops more rapidly compared to air with higher humidity. Likewise, at high temperatures, liquid droplets do not evaporate, so that no heat is removed from the gas to the liquid phase. This explains the large range of temperature in arid regions.

Why does water boil at 100°C ? You will note from **Table 13.5** that the vapor pressure of water at 100°C is $1.01 \times 10^5 \text{ Pa}$, or 1.00 atm . Thus, it can evaporate without limit at this temperature and pressure. But why does it form bubbles when it boils? This is because water ordinarily contains significant amounts of dissolved air and other impurities, which are observed as small bubbles of air in a glass of water. If a bubble starts out at the bottom of the container at 20°C , it contains water vapor (about 2.30%). The pressure inside the bubble is fixed at 1.00 atm (we ignore the slight pressure exerted by the water around it). As the temperature rises, the amount of air in the bubble stays the same, but the water vapor increases; the bubble expands to keep the pressure at 1.00 atm . At 100°C , water vapor enters the bubble continuously since the partial pressure of water is equal to 1.00 atm in equilibrium. It cannot reach this pressure, however, since the bubble also contains air and total pressure is 1.00 atm . The bubble grows in size and thereby increases the buoyant force. The bubble breaks away and rises rapidly to the surface—we call this boiling! (See **Figure 13.34**.)

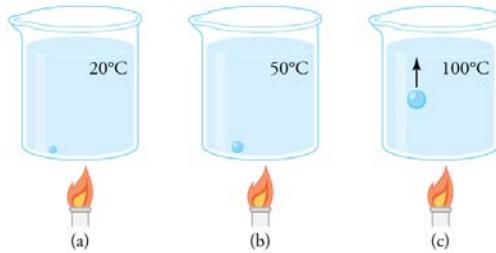


Figure 13.34 (a) An air bubble in water starts out saturated with water vapor at 20°C . (b) As the temperature rises, water vapor enters the bubble because its vapor pressure increases. The bubble expands to keep its pressure at 1.00 atm . (c) At 100°C , water vapor enters the bubble continuously because water's vapor pressure exceeds its partial pressure in the bubble, which must be less than 1.00 atm . The bubble grows and rises to the surface.

Check Your Understanding

Freeze drying is a process in which substances, such as foods, are dried by placing them in a vacuum chamber and lowering the atmospheric pressure around them. How does the lowered atmospheric pressure speed the drying process, and why does it cause the temperature of the food to drop?

Solution

Decreased the atmospheric pressure results in decreased partial pressure of water, hence a lower humidity. So evaporation of water from food, for example, will be enhanced. The molecules of water most likely to break away from the food will be those with the greatest velocities. Those remaining thus have a lower average velocity and a lower temperature. This can (and does) result in the freezing and drying of the food; hence the process is aptly named freeze drying.

PhET Explorations: States of Matter

Watch different types of molecules form a solid, liquid, or gas. Add or remove heat and watch the phase change. Change the temperature or volume of a container and see a pressure-temperature diagram respond in real time. Relate the interaction potential to the forces between molecules.



PhET Interactive Simulation

Figure 13.35 States of Matter: Basics (<http://phet.colorado.edu/en/simulation/states-of-matter>)

Glossary

absolute zero: the lowest possible temperature; the temperature at which all molecular motion ceases

Avogadro's number: N_A , the number of molecules or atoms in one mole of a substance; $N_A = 6.02 \times 10^{23}$ particles/mole

Boltzmann constant: k , a physical constant that relates energy to temperature; $k = 1.38 \times 10^{-23}$ J/K

Celsius scale: temperature scale in which the freezing point of water is 0°C and the boiling point of water is 100°C

coefficient of linear expansion: α , the change in length, per unit length, per 1°C change in temperature; a constant used in the calculation of linear expansion; the coefficient of linear expansion depends on the material and to some degree on the temperature of the material

coefficient of volume expansion: β , the change in volume, per unit volume, per 1°C change in temperature

critical point: the temperature above which a liquid cannot exist

critical pressure: the minimum pressure needed for a liquid to exist at the critical temperature

critical temperature: the temperature above which a liquid cannot exist

Dalton's law of partial pressures: the physical law that states that the total pressure of a gas is the sum of partial pressures of the component gases

degree Celsius: unit on the Celsius temperature scale

degree Fahrenheit: unit on the Fahrenheit temperature scale

dew point: the temperature at which relative humidity is 100%; the temperature at which water starts to condense out of the air

Fahrenheit scale: temperature scale in which the freezing point of water is 32°F and the boiling point of water is 212°F

ideal gas law: the physical law that relates the pressure and volume of a gas to the number of gas molecules or number of moles of gas and the temperature of the gas

Kelvin scale: temperature scale in which 0 K is the lowest possible temperature, representing absolute zero

mole: the quantity of a substance whose mass (in grams) is equal to its molecular mass

partial pressure: the pressure a gas would create if it occupied the total volume of space available

percent relative humidity: the ratio of vapor density to saturation vapor density

phase diagram: a graph of pressure vs. temperature of a particular substance, showing at which pressures and temperatures the three phases of the substance occur

PV diagram: a graph of pressure vs. volume

relative humidity: the amount of water in the air relative to the maximum amount the air can hold

saturation: the condition of 100% relative humidity

sublimation: the phase change from solid to gas

temperature: the quantity measured by a thermometer

thermal energy: \overline{KE} , the average translational kinetic energy of a molecule

thermal equilibrium: the condition in which heat no longer flows between two objects that are in contact; the two objects have the same temperature

thermal expansion: the change in size or volume of an object with change in temperature

thermal stress: stress caused by thermal expansion or contraction

triple point: the pressure and temperature at which a substance exists in equilibrium as a solid, liquid, and gas

vapor: a gas at a temperature below the boiling temperature

vapor pressure: the pressure at which a gas coexists with its solid or liquid phase

zeroth law of thermodynamics: law that states that if two objects are in thermal equilibrium, and a third object is in thermal equilibrium with one of those objects, it is also in thermal equilibrium with the other object

Section Summary

13.1 Temperature

- Temperature is the quantity measured by a thermometer.
- Temperature is related to the average kinetic energy of atoms and molecules in a system.
- Absolute zero is the temperature at which there is no molecular motion.
- There are three main temperature scales: Celsius, Fahrenheit, and Kelvin.
- Temperatures on one scale can be converted to temperatures on another scale using the following equations:

$$T_{\circ F} = \frac{9}{5}T_{\circ C} + 32$$

$$T_{\circ C} = \frac{5}{9}(T_{\circ F} - 32)$$

$$T_K = T_{\circ C} + 273.15$$

$$T_{\circ C} = T_K - 273.15$$

- Systems are in thermal equilibrium when they have the same temperature.
- Thermal equilibrium occurs when two bodies are in contact with each other and can freely exchange energy.
- The zeroth law of thermodynamics states that when two systems, A and B, are in thermal equilibrium with each other, and B is in thermal equilibrium with a third system, C, then A is also in thermal equilibrium with C.

13.2 Thermal Expansion of Solids and Liquids

- Thermal expansion is the increase, or decrease, of the size (length, area, or volume) of a body due to a change in temperature.
- Thermal expansion is large for gases, and relatively small, but not negligible, for liquids and solids.
- Linear thermal expansion is

$$\Delta L = \alpha L \Delta T,$$

where ΔL is the change in length L , ΔT is the change in temperature, and α is the coefficient of linear expansion, which varies slightly with temperature.

- The change in area due to thermal expansion is

$$\Delta A = 2\alpha A \Delta T,$$

where ΔA is the change in area.

- The change in volume due to thermal expansion is

$$\Delta V = \beta V \Delta T,$$

where β is the coefficient of volume expansion and $\beta \approx 3\alpha$. Thermal stress is created when thermal expansion is constrained.

13.3 The Ideal Gas Law

- The ideal gas law relates the pressure and volume of a gas to the number of gas molecules and the temperature of the gas.

- The ideal gas law can be written in terms of the number of molecules of gas:

$$PV = NkT,$$

where P is pressure, V is volume, T is temperature, N is number of molecules, and k is the Boltzmann constant

$$k = 1.38 \times 10^{-23} \text{ J/K}.$$

- A mole is the number of atoms in a 12-g sample of carbon-12.
- The number of molecules in a mole is called Avogadro's number N_A ,

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}.$$

- A mole of any substance has a mass in grams equal to its molecular weight, which can be determined from the periodic table of elements.
- The ideal gas law can also be written and solved in terms of the number of moles of gas:

$$PV = nRT,$$

where n is number of moles and R is the universal gas constant,

$$R = 8.31 \text{ J/mol} \cdot \text{K}.$$

- The ideal gas law is generally valid at temperatures well above the boiling temperature.

13.4 Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature

- Kinetic theory is the atomistic description of gases as well as liquids and solids.
- Kinetic theory models the properties of matter in terms of continuous random motion of atoms and molecules.
- The ideal gas law can also be expressed as

$$PV = \frac{1}{3}Nmv^2,$$

where P is the pressure (average force per unit area), V is the volume of gas in the container, N is the number of molecules in the container, m is the mass of a molecule, and v^2 is the average of the molecular speed squared.

- Thermal energy is defined to be the average translational kinetic energy \overline{KE} of an atom or molecule.
- The temperature of gases is proportional to the average translational kinetic energy of atoms and molecules.

$$\overline{KE} = \frac{1}{2}mv^2 = \frac{3}{2}kT$$

or

$$\sqrt{\overline{v^2}} = v_{\text{rms}} = \sqrt{\frac{3kT}{m}}.$$

- The motion of individual molecules in a gas is random in magnitude and direction. However, a gas of many molecules has a predictable distribution of molecular speeds, known as the *Maxwell-Boltzmann distribution*.

13.5 Phase Changes

- Most substances have three distinct phases: gas, liquid, and solid.
- Phase changes among the various phases of matter depend on temperature and pressure.
- The existence of the three phases with respect to pressure and temperature can be described in a phase diagram.
- Two phases coexist (i.e., they are in thermal equilibrium) at a set of pressures and temperatures. These are described as a line on a phase diagram.
- The three phases coexist at a single pressure and temperature. This is known as the triple point and is described by a single point on a phase diagram.
- A gas at a temperature below its boiling point is called a vapor.
- Vapor pressure is the pressure at which a gas coexists with its solid or liquid phase.
- Partial pressure is the pressure a gas would create if it existed alone.
- Dalton's law states that the total pressure is the sum of the partial pressures of all of the gases present.

13.6 Humidity, Evaporation, and Boiling

- Relative humidity is the fraction of water vapor in a gas compared to the saturation value.
- The saturation vapor density can be determined from the vapor pressure for a given temperature.
- Percent relative humidity is defined to be

$$\text{percent relative humidity} = \frac{\text{vapor density}}{\text{saturation vapor density}} \times 100.$$

- The dew point is the temperature at which air reaches 100% relative humidity.

Conceptual Questions

13.1 Temperature

- What does it mean to say that two systems are in thermal equilibrium?
- Give an example of a physical property that varies with temperature and describe how it is used to measure temperature.
- When a cold alcohol thermometer is placed in a hot liquid, the column of alcohol goes *down* slightly before going up. Explain why.
- If you add boiling water to a cup at room temperature, what would you expect the final equilibrium temperature of the unit to be? You will need to include the surroundings as part of the system. Consider the zeroth law of thermodynamics.

13.2 Thermal Expansion of Solids and Liquids

- Thermal stresses caused by uneven cooling can easily break glass cookware. Explain why Pyrex®, a glass with a small coefficient of linear expansion, is less susceptible.
- Water expands significantly when it freezes: a volume increase of about 9% occurs. As a result of this expansion and because of the formation and growth of crystals as water freezes, anywhere from 10% to 30% of biological cells are burst when animal or plant material is frozen. Discuss the implications of this cell damage for the prospect of preserving human bodies by freezing so that they can be thawed at some future date when it is hoped that all diseases are curable.
- One method of getting a tight fit, say of a metal peg in a hole in a metal block, is to manufacture the peg slightly larger than the hole. The peg is then inserted when at a different temperature than the block. Should the block be hotter or colder than the peg during insertion? Explain your answer.
- Does it really help to run hot water over a tight metal lid on a glass jar before trying to open it? Explain your answer.
- Liquids and solids expand with increasing temperature, because the kinetic energy of a body's atoms and molecules increases. Explain why some materials *shrink* with increasing temperature.

13.3 The Ideal Gas Law

- Find out the human population of Earth. Is there a mole of people inhabiting Earth? If the average mass of a person is 60 kg, calculate the mass of a mole of people. How does the mass of a mole of people compare with the mass of Earth?
- Under what circumstances would you expect a gas to behave significantly differently than predicted by the ideal gas law?
- A constant-volume gas thermometer contains a fixed amount of gas. What property of the gas is measured to indicate its temperature?

13.4 Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature

- How is momentum related to the pressure exerted by a gas? Explain on the atomic and molecular level, considering the behavior of atoms and molecules.

13.5 Phase Changes

- A pressure cooker contains water and steam in equilibrium at a pressure greater than atmospheric pressure. How does this greater pressure increase cooking speed?
- Why does condensation form most rapidly on the coldest object in a room—for example, on a glass of ice water?
- What is the vapor pressure of solid carbon dioxide (dry ice) at -78.5°C ?

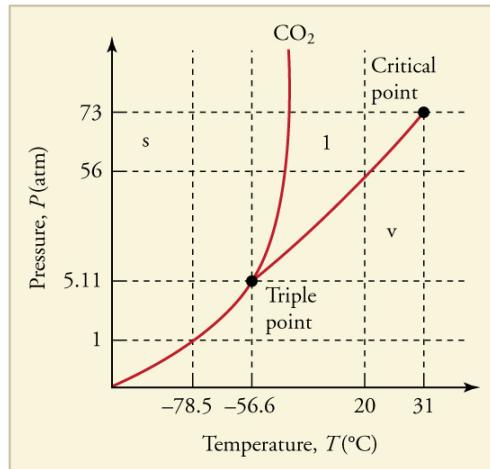


Figure 13.36 The phase diagram for carbon dioxide. The axes are nonlinear, and the graph is not to scale. Dry ice is solid carbon dioxide and has a sublimation temperature of -78.5°C .

17. Can carbon dioxide be liquefied at room temperature (20°C)? If so, how? If not, why not? (See **Figure 13.36**.)
18. Oxygen cannot be liquefied at room temperature by placing it under a large enough pressure to force its molecules together. Explain why this is.
19. What is the distinction between gas and vapor?

13.6 Humidity, Evaporation, and Boiling

20. Because humidity depends only on water's vapor pressure and temperature, are the saturation vapor densities listed in **Table 13.5** valid in an atmosphere of helium at a pressure of $1.01 \times 10^5 \text{ N/m}^2$, rather than air? Are those values affected by altitude on Earth?
21. Why does a beaker of 40.0°C water placed in a vacuum chamber start to boil as the chamber is evacuated (air is pumped out of the chamber)? At what pressure does the boiling begin? Would food cook any faster in such a beaker?
22. Why does rubbing alcohol evaporate much more rapidly than water at STP (standard temperature and pressure)?

Problems & Exercises

13.1 Temperature

- What is the Fahrenheit temperature of a person with a 39.0°C fever?
- Frost damage to most plants occurs at temperatures of 28.0°F or lower. What is this temperature on the Kelvin scale?
- To conserve energy, room temperatures are kept at 68.0°F in the winter and 78.0°F in the summer. What are these temperatures on the Celsius scale?
- A tungsten light bulb filament may operate at 2900 K . What is its Fahrenheit temperature? What is this on the Celsius scale?
- The surface temperature of the Sun is about 5750 K . What is this temperature on the Fahrenheit scale?
- One of the hottest temperatures ever recorded on the surface of Earth was 134°F in Death Valley, CA. What is this temperature in Celsius degrees? What is this temperature in Kelvin?
- (a) Suppose a cold front blows into your locale and drops the temperature by 40.0 Fahrenheit degrees. How many degrees Celsius does the temperature decrease when there is a 40.0°F decrease in temperature? (b) Show that any change in temperature in Fahrenheit degrees is nine-fifths the change in Celsius degrees.
- (a) At what temperature do the Fahrenheit and Celsius scales have the same numerical value? (b) At what temperature do the Fahrenheit and Kelvin scales have the same numerical value?

13.2 Thermal Expansion of Solids and Liquids

- The height of the Washington Monument is measured to be 170 m on a day when the temperature is 35.0°C . What will its height be on a day when the temperature falls to -10.0°C ? Although the monument is made of limestone, assume that its thermal coefficient of expansion is the same as marble's.
- How much taller does the Eiffel Tower become at the end of a day when the temperature has increased by 15°C ? Its original height is 321 m and you can assume it is made of steel.
- What is the change in length of a 3.00-cm-long column of mercury if its temperature changes from 37.0°C to 40.0°C , assuming the mercury is unconstrained?
- How large an expansion gap should be left between steel railroad rails if they may reach a maximum temperature 35.0°C greater than when they were laid? Their original length is 10.0 m .
- You are looking to purchase a small piece of land in Hong Kong. The price is "only" $\$60,000$ per square meter! The land title says the dimensions are $20\text{ m} \times 30\text{ m}$. By how much would the total price change if you measured the parcel with a steel tape measure on a day when the temperature was 20°C above normal?
- Global warming will produce rising sea levels partly due to melting ice caps but also due to the expansion of water as average ocean temperatures rise. To get some idea of the

size of this effect, calculate the change in length of a column of water 1.00 km high for a temperature increase of 1.00°C . Note that this calculation is only approximate because ocean warming is not uniform with depth.

- Show that 60.0 L of gasoline originally at 15.0°C will expand to 61.1 L when it warms to 35.0°C , as claimed in **Example 13.4**.
- (a) Suppose a meter stick made of steel and one made of invar (an alloy of iron and nickel) are the same length at 0°C . What is their difference in length at 22.0°C ? (b) Repeat the calculation for two 30.0-m-long surveyor's tapes.
- (a) If a 500-mL glass beaker is filled to the brim with ethyl alcohol at a temperature of 5.00°C , how much will overflow when its temperature reaches 22.0°C ? (b) How much less water would overflow under the same conditions?
- Most automobiles have a coolant reservoir to catch radiator fluid that may overflow when the engine is hot. A radiator is made of copper and is filled to its 16.0-L capacity when at 10.0°C . What volume of radiator fluid will overflow when the radiator and fluid reach their 95.0°C operating temperature, given that the fluid's volume coefficient of expansion is $\beta = 400 \times 10^{-6}/^{\circ}\text{C}$? Note that this coefficient is approximate, because most car radiators have operating temperatures of greater than 95.0°C .

- A physicist makes a cup of instant coffee and notices that, as the coffee cools, its level drops 3.00 mm in the glass cup. Show that this decrease cannot be due to thermal contraction by calculating the decrease in level if the 350 cm^3 of coffee is in a 7.00-cm-diameter cup and decreases in temperature from 95.0°C to 45.0°C . (Most of the drop in level is actually due to escaping bubbles of air.)

- (a) The density of water at 0°C is very nearly 1000 kg/m^3 (it is actually 999.84 kg/m^3), whereas the density of ice at 0°C is 917 kg/m^3 . Calculate the pressure necessary to keep ice from expanding when it freezes, neglecting the effect such a large pressure would have on the freezing temperature. (This problem gives you only an indication of how large the forces associated with freezing water might be.) (b) What are the implications of this result for biological cells that are frozen?

- Show that $\beta \approx 3\alpha$, by calculating the change in volume ΔV of a cube with sides of length L .

13.3 The Ideal Gas Law

- The gauge pressure in your car tires is $2.50 \times 10^5\text{ N/m}^2$ at a temperature of 35.0°C when you drive it onto a ferry boat to Alaska. What is their gauge pressure later, when their temperature has dropped to -40.0°C ?
- Convert an absolute pressure of $7.00 \times 10^5\text{ N/m}^2$ to gauge pressure in lb/in^2 . (This value was stated to be just less than 90.0 lb/in^2 in **Example 13.9**. Is it?)

24. Suppose a gas-filled incandescent light bulb is manufactured so that the gas inside the bulb is at atmospheric pressure when the bulb has a temperature of 20.0°C . (a) Find the gauge pressure inside such a bulb when it is hot, assuming its average temperature is 60.0°C (an approximation) and neglecting any change in volume due to thermal expansion or gas leaks. (b) The actual final pressure for the light bulb will be less than calculated in part (a) because the glass bulb will expand. What will the actual final pressure be, taking this into account? Is this a negligible difference?

25. Large helium-filled balloons are used to lift scientific equipment to high altitudes. (a) What is the pressure inside such a balloon if it starts out at sea level with a temperature of 10.0°C and rises to an altitude where its volume is twenty times the original volume and its temperature is -50.0°C ? (b) What is the gauge pressure? (Assume atmospheric pressure is constant.)

26. Confirm that the units of nRT are those of energy for each value of R : (a) $8.31 \text{ J/mol} \cdot \text{K}$, (b) $1.99 \text{ cal/mol} \cdot \text{K}$, and (c) $0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$.

27. In the text, it was shown that $N/V = 2.68 \times 10^{25} \text{ m}^{-3}$ for gas at STP. (a) Show that this quantity is equivalent to $N/V = 2.68 \times 10^{19} \text{ cm}^{-3}$, as stated. (b) About how many atoms are there in one μm^3 (a cubic micrometer) at STP? (c) What does your answer to part (b) imply about the separation of atoms and molecules?

28. Calculate the number of moles in the 2.00-L volume of air in the lungs of the average person. Note that the air is at 37.0°C (body temperature).

29. An airplane passenger has 100 cm^3 of air in his stomach just before the plane takes off from a sea-level airport. What volume will the air have at cruising altitude if cabin pressure drops to $7.50 \times 10^4 \text{ N/m}^2$?

30. (a) What is the volume (in km^3) of Avogadro's number of sand grains if each grain is a cube and has sides that are 1.0 mm long? (b) How many kilometers of beaches in length would this cover if the beach averages 100 m in width and 10.0 m in depth? Neglect air spaces between grains.

31. An expensive vacuum system can achieve a pressure as low as $1.00 \times 10^{-7} \text{ N/m}^2$ at 20°C . How many atoms are there in a cubic centimeter at this pressure and temperature?

32. The number density of gas atoms at a certain location in the space above our planet is about $1.00 \times 10^{11} \text{ m}^{-3}$, and the pressure is $2.75 \times 10^{-10} \text{ N/m}^2$ in this space. What is the temperature there?

33. A bicycle tire has a pressure of $7.00 \times 10^5 \text{ N/m}^2$ at a temperature of 18.0°C and contains 2.00 L of gas. What will its pressure be if you let out an amount of air that has a volume of 100 cm^3 at atmospheric pressure? Assume tire temperature and volume remain constant.

34. A high-pressure gas cylinder contains 50.0 L of toxic gas at a pressure of $1.40 \times 10^7 \text{ N/m}^2$ and a temperature of

25.0°C . Its valve leaks after the cylinder is dropped. The cylinder is cooled to dry ice temperature (-78.5°C) to reduce the leak rate and pressure so that it can be safely repaired. (a) What is the final pressure in the tank, assuming a negligible amount of gas leaks while being cooled and that there is no phase change? (b) What is the final pressure if one-tenth of the gas escapes? (c) To what temperature must the tank be cooled to reduce the pressure to 1.00 atm (assuming the gas does not change phase and that there is no leakage during cooling)? (d) Does cooling the tank appear to be a practical solution?

35. Find the number of moles in 2.00 L of gas at 35.0°C and under $7.41 \times 10^7 \text{ N/m}^2$ of pressure.

36. Calculate the depth to which Avogadro's number of table tennis balls would cover Earth. Each ball has a diameter of 3.75 cm. Assume the space between balls adds an extra 25.0% to their volume and assume they are not crushed by their own weight.

37. (a) What is the gauge pressure in a 25.0°C car tire containing 3.60 mol of gas in a 30.0 L volume? (b) What will its gauge pressure be if you add 1.00 L of gas originally at atmospheric pressure and 25.0°C ? Assume the temperature returns to 25.0°C and the volume remains constant.

38. (a) In the deep space between galaxies, the density of atoms is as low as 10^6 atoms/m^3 , and the temperature is a frigid 2.7 K. What is the pressure? (b) What volume (in m^3) is occupied by 1 mol of gas? (c) If this volume is a cube, what is the length of its sides in kilometers?

13.4 Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature

39. Some incandescent light bulbs are filled with argon gas. What is v_{rms} for argon atoms near the filament, assuming their temperature is 2500 K?

40. Average atomic and molecular speeds (v_{rms}) are large, even at low temperatures. What is v_{rms} for helium atoms at 5.00 K, just one degree above helium's liquefaction temperature?

41. (a) What is the average kinetic energy in joules of hydrogen atoms on the 5500°C surface of the Sun? (b) What is the average kinetic energy of helium atoms in a region of the solar corona where the temperature is $6.00 \times 10^5 \text{ K}$?

42. The escape velocity of any object from Earth is 11.2 km/s. (a) Express this speed in m/s and km/h. (b) At what temperature would oxygen molecules (molecular mass is equal to 32.0 g/mol) have an average velocity v_{rms} equal to Earth's escape velocity of 11.1 km/s?

43. The escape velocity from the Moon is much smaller than from Earth and is only 2.38 km/s. At what temperature would hydrogen molecules (molecular mass is equal to 2.016 g/mol) have an average velocity v_{rms} equal to the Moon's escape velocity?

44. Nuclear fusion, the energy source of the Sun, hydrogen bombs, and fusion reactors, occurs much more readily when the average kinetic energy of the atoms is high—that is, at

high temperatures. Suppose you want the atoms in your fusion experiment to have average kinetic energies of 6.40×10^{-14} J. What temperature is needed?

45. Suppose that the average velocity (v_{rms}) of carbon dioxide molecules (molecular mass is equal to 44.0 g/mol) in a flame is found to be 1.05×10^5 m/s. What temperature does this represent?

46. Hydrogen molecules (molecular mass is equal to 2.016 g/mol) have an average velocity v_{rms} equal to 193 m/s. What is the temperature?

47. Much of the gas near the Sun is atomic hydrogen. Its temperature would have to be 1.5×10^7 K for the average velocity v_{rms} to equal the escape velocity from the Sun. What is that velocity?

48. There are two important isotopes of uranium— ^{235}U and ^{238}U ; these isotopes are nearly identical chemically but have different atomic masses. Only ^{235}U is very useful in nuclear reactors. One of the techniques for separating them (gas diffusion) is based on the different average velocities v_{rms} of uranium hexafluoride gas, UF_6 . (a) The molecular masses for ^{235}U UF_6 and ^{238}U UF_6 are 349.0 g/mol and 352.0 g/mol, respectively. What is the ratio of their average velocities? (b) At what temperature would their average velocities differ by 1.00 m/s? (c) Do your answers in this problem imply that this technique may be difficult?

13.6 Humidity, Evaporation, and Boiling

49. Dry air is 78.1% nitrogen. What is the partial pressure of nitrogen when the atmospheric pressure is 1.01×10^5 N/m²?

50. (a) What is the vapor pressure of water at 20.0°C? (b) What percentage of atmospheric pressure does this correspond to? (c) What percent of 20.0°C air is water vapor if it has 100% relative humidity? (The density of dry air at 20.0°C is 1.20 kg/m³.)

51. Pressure cookers increase cooking speed by raising the boiling temperature of water above its value at atmospheric pressure. (a) What pressure is necessary to raise the boiling point to 120.0°C? (b) What gauge pressure does this correspond to?

52. (a) At what temperature does water boil at an altitude of 1500 m (about 5000 ft) on a day when atmospheric pressure is 8.59×10^4 N/m²? (b) What about at an altitude of 3000 m (about 10,000 ft) when atmospheric pressure is 7.00×10^4 N/m²?

53. What is the atmospheric pressure on top of Mt. Everest on a day when water boils there at a temperature of 70.0°C?

54. At a spot in the high Andes, water boils at 80.0°C, greatly reducing the cooking speed of potatoes, for example. What is atmospheric pressure at this location?

55. What is the relative humidity on a 25.0°C day when the air contains 18.0 g/m³ of water vapor?

56. What is the density of water vapor in g/m³ on a hot dry day in the desert when the temperature is 40.0°C and the relative humidity is 6.00%?

57. A deep-sea diver should breathe a gas mixture that has the same oxygen partial pressure as at sea level, where dry air contains 20.9% oxygen and has a total pressure of 1.01×10^5 N/m². (a) What is the partial pressure of oxygen at sea level? (b) If the diver breathes a gas mixture at a pressure of 2.00×10^6 N/m², what percent oxygen should it be to have the same oxygen partial pressure as at sea level?

58. The vapor pressure of water at 40.0°C is 7.34×10^3 N/m². Using the ideal gas law, calculate the density of water vapor in g/m³ that creates a partial pressure equal to this vapor pressure. The result should be the same as the saturation vapor density at that temperature (51.1 g/m³).

59. Air in human lungs has a temperature of 37.0°C and a saturation vapor density of 44.0 g/m³. (a) If 2.00 L of air is exhaled and very dry air inhaled, what is the maximum loss of water vapor by the person? (b) Calculate the partial pressure of water vapor having this density, and compare it with the vapor pressure of 6.31×10^3 N/m².

60. If the relative humidity is 90.0% on a muggy summer morning when the temperature is 20.0°C, what will it be later in the day when the temperature is 30.0°C, assuming the water vapor density remains constant?

61. Late on an autumn day, the relative humidity is 45.0% and the temperature is 20.0°C. What will the relative humidity be that evening when the temperature has dropped to 10.0°C, assuming constant water vapor density?

62. Atmospheric pressure atop Mt. Everest is 3.30×10^4 N/m². (a) What is the partial pressure of oxygen there if it is 20.9% of the air? (b) What percent oxygen should a mountain climber breathe so that its partial pressure is the same as at sea level, where atmospheric pressure is 1.01×10^5 N/m²? (c) One of the most severe problems for those climbing very high mountains is the extreme drying of breathing passages. Why does this drying occur?

63. What is the dew point (the temperature at which 100% relative humidity would occur) on a day when relative humidity is 39.0% at a temperature of 20.0°C?

64. On a certain day, the temperature is 25.0°C and the relative humidity is 90.0%. How many grams of water must condense out of each cubic meter of air if the temperature falls to 15.0°C? Such a drop in temperature can, thus, produce heavy dew or fog.

65. Integrated Concepts

The boiling point of water increases with depth because pressure increases with depth. At what depth will fresh water have a boiling point of 150°C , if the surface of the water is at sea level?

66. Integrated Concepts

(a) At what depth in fresh water is the critical pressure of water reached, given that the surface is at sea level? (b) At what temperature will this water boil? (c) Is a significantly higher temperature needed to boil water at a greater depth?

67. Integrated Concepts

To get an idea of the small effect that temperature has on Archimedes' principle, calculate the fraction of a copper block's weight that is supported by the buoyant force in 0°C water and compare this fraction with the fraction supported in 95.0°C water.

68. Integrated Concepts

If you want to cook in water at 150°C , you need a pressure cooker that can withstand the necessary pressure. (a) What pressure is required for the boiling point of water to be this high? (b) If the lid of the pressure cooker is a disk 25.0 cm in diameter, what force must it be able to withstand at this pressure?

69. Unreasonable Results

(a) How many moles per cubic meter of an ideal gas are there at a pressure of $1.00 \times 10^{14} \text{ N/m}^2$ and at 0°C ? (b) What is unreasonable about this result? (c) Which premise or assumption is responsible?

70. Unreasonable Results

(a) An automobile mechanic claims that an aluminum rod fits loosely into its hole on an aluminum engine block because the engine is hot and the rod is cold. If the hole is 10.0% bigger in diameter than the 22.0°C rod, at what temperature will the rod be the same size as the hole? (b) What is unreasonable about this temperature? (c) Which premise is responsible?

71. Unreasonable Results

The temperature inside a supernova explosion is said to be $2.00 \times 10^{13} \text{ K}$. (a) What would the average velocity v_{rms} of hydrogen atoms be? (b) What is unreasonable about this velocity? (c) Which premise or assumption is responsible?

72. Unreasonable Results

Suppose the relative humidity is 80% on a day when the temperature is 30.0°C . (a) What will the relative humidity be if the air cools to 25.0°C and the vapor density remains constant? (b) What is unreasonable about this result? (c) Which premise is responsible?