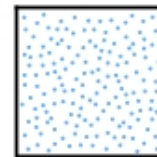


## 14-1 The Ideal Gas Law

Let's say you have a certain number of moles of ideal gas that fills a container that has a known volume. Such a system is shown in Figure 14.1.



**Figure 14.1:** A container of ideal gas.

If you know the absolute temperature of the gas, what is the pressure? The answer can be found from the ideal gas law, which you may well have encountered before.

The ideal gas law connects the pressure  $P$ , the volume  $V$ , and the absolute temperature  $T$ , for an ideal gas of  $n$  moles:

$$PV = nRT, \quad (\text{Equation 14.1: The ideal gas law})$$

where  $R = 8.31 \text{ J/(mol K)}$  is the universal gas constant.

First of all, what is a mole? It is not a cute, furry creature that you might find digging holes in your backyard. In this context, a mole represents an amount, and we use the term mole in the same way we use the word dozen. A dozen represents a particular number, 12. A mole also represents a particular number,  $6.02 \times 10^{23}$ , which we also refer to as Avogadro's number,  $N_A$ . Thus, a mole of something is Avogadro's number of those things. In this chapter, we generally want to know about the number of moles of a particular ideal gas. A toy balloon, for instance, has about 0.1 moles of air molecules inside it. Strangely enough, the number of stars in the observable universe can also be estimated at about 0.1 moles of stars.

In physics, we often find it convenient to state the ideal gas law not in terms of the number of moles but in terms of  $N$ , the number of atoms or molecules, where  $N = nN_A$ . Taking the ideal gas law and multiplying the right-hand side by  $N_A / N_A$  gives:

$$PV = nN_A \frac{R}{N_A} T = N \frac{R}{N_A} T.$$

The constant  $R / N_A$  has the value  $k = 1.38 \times 10^{-23} \text{ J/K}$  and is known as Boltzmann's constant. Using this in the equation above gives:

$$PV = NkT. \quad (\text{Eq. 14.2: Ideal gas law in terms of the number of molecules})$$

Under what conditions is the ideal gas law valid? What is an ideal gas, anyway? For a system to represent an ideal gas it must satisfy the following conditions:

1. The system has a large number of atoms or molecules.
2. The total volume of the atoms or molecules should represent a very small fraction of the volume of the container.
3. The atoms or molecules obey Newton's Laws of motion; and they move about in random motion.
4. All collisions are elastic. The atoms or molecules experience forces only when they collide, and the collisions take a negligible amount of time.

The ideal gas law has a number of interesting implications, including –

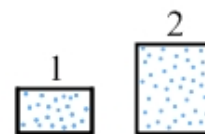
*Boyle's Law*: at constant temperature, pressure and volume are inversely related;

*Charles' Law*: at constant pressure, volume and temperature are directly related;

*Gay-Lussac's Law*: at constant volume, pressure and temperature are directly related.

#### EXAMPLE 14.1 – Two containers of gas

The two sealed containers in Figure 14.2 contain the same type of ideal gas. Container 2 has twice the volume of container 1. Aside from that difference, the containers differ in only one of the following three parameters, pressure, number of moles, and temperature. (a) Could the containers differ only in pressure and volume? If so, explain how. (b) Could the containers differ only in the number of moles and volume? If so, explain how.



**Figure 14.2:** Two containers of ideal gas, one with twice the volume as the other.

#### SOLUTION

(a) Yes, if the number of moles of gas and the temperature are the same in each container, we must have the product of  $PV$  equal in the two containers, according to the ideal gas law. Thus, if container 2 has twice the volume as container 1, it must have half the pressure as container 1.

(b) Yes, if the pressure and the temperature are the same in each container, the number of moles of gas must be twice that in container 2 as it is in container 1. If we double the value of the volume, on the left side of Equation 14.1, we must double the value of  $n$ , the number of moles, on the right side of the equation, if everything else remains constant.

Prove to yourself that the containers could also differ only in volume and temperature.

#### An aside – Thinking about the rms average.

In Section 14.2, we will use the rms (root-mean square) average speed of a set of gas molecules. To gain some insight into the root-mean-square averaging process, let's work out the rms average of the set of numbers  $-1, 1, 3,$  and  $5$ . The average of these numbers is  $2$ . To work out the rms average, square the numbers to give  $1, 1, 9,$  and  $25$ . Then, find the average of these squared values, which is  $9$ . Finally, take the square root of that average to find the rms average,  $3$ .

Clearly, this is a funny way to do an average, because the average is  $2$  while the rms average is  $3$ . There are two reasons why the rms average is larger than the average in this case. The first reason is that squaring the numbers makes everything positive – without this negative values cancel positive values when we add the numbers up. The second reason is that squaring the values weights the larger numbers more heavily (the  $5$  counts five times more than the  $1$  when doing the average, but  $5^2$  counts 25 times more than  $1^2$  when doing the rms average.) Note that we will discuss rms average values again later in the book when we talk about alternating current.

#### Related End-of-Chapter Exercises: 1, 2, 13, 17, 18.

**Essential Question 14.1:** A container of ideal gas is sealed so that it contains a particular number of moles of gas at a constant volume and an initial pressure of  $P_i$ . If the temperature of the system is then raised from  $10^\circ\text{C}$  to  $30^\circ\text{C}$ , by what factor does the pressure increase?

**Answer to Essential Question 14.1:** It is tempting to say that the pressure increases by a factor of 3, but that is incorrect. Because the ideal gas law involves  $T$ , not  $\Delta T$ , we must use temperatures in Kelvin rather than Celsius. In Kelvin, the temperature rises from 283K to 303K. Finding the ratio of the final pressure to the initial pressure shows that pressure increases by a factor of 1.07:

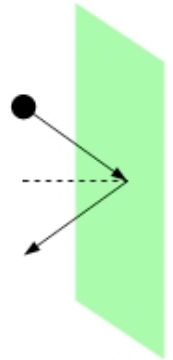
$$\frac{P_f}{P_i} = \frac{nRT_f/V}{nRT_i/V} = \frac{T_f}{T_i} = \frac{303\text{K}}{283\text{K}} = 1.07.$$

## 14-2 Kinetic Theory

We will now apply some principles of physics we learned earlier in the book to help us to come to a fundamental understanding of temperature. Consider a cubical box, measuring  $L$  on each side. The box contains  $N$  identical atoms of a monatomic ideal gas, each of mass  $m$ .

We will assume that all collisions are elastic. This applies to collisions of atoms with one another, and to collisions involving the atoms and the walls of the box. The collisions between the atoms and the walls of the box give rise to the pressure the walls of the box experience because the gas is enclosed within the box, so let's focus on those collisions.

Let's find the pressure associated with one atom because of its collisions with one wall of the box. As shown in Figure 14.3 we will focus on the right-hand wall of the box. Because the atom collides elastically, it has the same speed after hitting the wall that it had before hitting the wall. The direction of its velocity is different, however. The plane of the wall we're interested in is perpendicular to the  $x$ -axis, so collisions with that wall reverse the ball's  $x$ -component of velocity, while having no effect on the ball's  $y$  or  $z$  components of velocity. This is like the situation of the hockey puck bouncing off the boards that we looked at in Chapter 6.



**Figure 14.3:** An atom inside the box bouncing off the right-hand wall of the box.

The collision with the wall changes the  $x$ -component of the ball's velocity from  $+v_x$  to  $-v_x$ , so the ball's change in velocity is  $-2v_x$  and its change in momentum is  $\Delta\vec{p} = -2mv_x$ , where the negative sign tells us that the change in the atom's momentum is in the negative  $x$ -direction.

In Chapter 6, we learned that the change in momentum is equal to the impulse (the product of the force  $\vec{F}$  and the time interval  $\Delta t$  over which the force is applied). Thus:

$$\vec{F}_{\text{wall on molecule}} = \frac{-2mv_x}{\Delta t}. \quad (\text{Equation 14.3: The force the wall exerts on an atom})$$

The atom feels an equal-magnitude force in the opposite direction (Newton's third law):

$$\vec{F}_{\text{molecule on wall}} = \frac{+2mv_x}{\Delta t}. \quad (\text{Equation 14.4: The force the atom exerts on the wall})$$

What is this time interval,  $\Delta t$ ? The atom exerts a force on the wall only during the small intervals it is in contact with the wall while it is changing direction. It spends most of the time not in contact with the wall, not exerting any force on it. We can find the time-averaged force the atom exerts on the wall by setting  $\Delta t$  equal to the time between collisions of the atom with that wall. Because the atom travels a distance  $L$  across the box in the  $x$ -direction at a speed of  $v_x$ , it takes a time of  $L/v_x$  to travel from the right wall of the box to the left wall, and the same amount of time to come back again. Thus:

$$\Delta t = \frac{2L}{v_x}. \quad (\text{Equation 14.5: Time between collisions with the right wall})$$

Substituting this into the force equation, Equation 14.4, tells us that the magnitude of the average force this one atom exerts on the right-hand wall of the box is:

$$\bar{F}_{\text{molecule on wall}} = \frac{2mv_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}. \quad (\text{Eq. 14.6: Average force exerted by one atom})$$

To find the total force exerted on the wall we sum the contributions from all the atoms:

$$\bar{F}_{\text{on wall}} = \sum \frac{mv_x^2}{L} = \frac{m}{L} \sum v_x^2. \quad (\text{Equation 14.7: Average force from all atoms})$$

The Greek letter  $\Sigma$  (sigma) indicates a sum. Here the sum is over all the atoms in the box.

If we have  $N$  atoms in the box then we can write this as:

$$\bar{F}_{\text{on wall}} = \frac{Nm}{L} \left( \frac{\sum v_x^2}{N} \right). \quad (\text{Equation 14.8: Average force from all atoms})$$

The term in brackets represents the average of the square of the magnitude of the  $x$ -component of the velocity of each atom. For a given atom if we apply the Pythagorean theorem in three dimensions we have  $v_x^2 + v_y^2 + v_z^2 = v^2$ . Doing this for all the atoms gives:

$$\sum v_x^2 + \sum v_y^2 + \sum v_z^2 = \sum v^2,$$

and there is no reason why the sum over the  $x$ -components would be any different from the sum over the  $y$  or  $z$ -components – there is no preferred direction in the box. We can thus say that  $3 \sum v_x^2 = \sum v^2$  or, equivalently,  $\sum v_x^2 = \frac{1}{3} \sum v^2$ .

Substituting this into the force equation, Equation 14.8, above gives:

$$\bar{F}_{\text{on wall}} = \frac{Nm}{3L} \left( \frac{\sum v^2}{N} \right). \quad (\text{Equation 14.9: Average force on a wall})$$

The term in brackets represents the square of the rms average speed. Thus:

$$\bar{F}_{\text{on wall}} = \frac{Nm}{3L} v_{rms}^2. \quad (\text{Equation 14.10: Average force on a wall})$$

By multiplying by 2 and dividing by 2, we can transform Equation 14.10 to:

$$\bar{F}_{\text{on wall}} = \frac{2N}{3L} \left( \frac{1}{2} m v_{rms}^2 \right) = \frac{2N}{3L} K_{av}, \quad (\text{Eq. 14.11: Force connected to kinetic energy})$$

The term in brackets is a measure of the average kinetic energy,  $K_{av}$ , of the atoms.

### Related End-of-Chapter Exercise: 36.

**Essential Question 14.2:** Why is the rms average speed, and not the average velocity, involved in the equations above? What is the average velocity of the atoms of ideal gas in the box?

**Answer to Essential Question 14.2:** The average velocity of the atoms is zero. This is because the motion of the atoms is random, and with a large number of atoms in the box there are as many, on average, going one way as the opposite way. Because velocity is a vector the individual vectors tend to cancel one another out. The average speed, however, is non-zero, and it makes sense that, the faster the atoms move, the more force they exert on the wall.

### 14-3 Temperature

Let's pick up where we left off at the end of the previous section. Because pressure is force divided by area, we can find the average pressure the atoms exert on the wall by dividing the average force by the wall area,  $L^2$ . This gives:

$$P = \frac{\bar{F}_{\text{on wall}}}{A} = \frac{2N}{3L^3} K_{av}. \quad (\text{Equation 14.12: Pressure in the gas})$$

Now we have a factor of  $L^3$ , which is  $V$ , the volume of the cube. We can thus write Equation 14.12 as:

$$PV = N \left( \frac{2}{3} K_{av} \right). \quad (\text{Equation 14.13: The product } PV)$$

Compare Equation 14.13 to Equation 14.2, the ideal gas law in the form  $PV = NkT$ . These equations must agree with one another, so we must conclude that:

$$\frac{2}{3} K_{av} = kT,$$

or, equivalently,

$$K_{av} = \frac{3}{2} kT. \quad (\text{Equation 14.14: Average kinetic energy is directly related to temperature})$$

This is an amazing result – it tells us what temperature is all about. Temperature is a direct measure of the average kinetic energy of the atoms in a material. It is further amazing that we obtained such a fundamental result by applying basic principles of physics (such as impulse, kinetic energy, and pressure) to an ideal gas. Consider now the following example.

#### EXAMPLE 14.3 – Two containers of ideal gas

Container  $A$  holds  $N$  atoms of ideal gas, while container  $B$  holds  $5N$  atoms of the same ideal gas. The two containers are at the same temperature,  $T$ .

- In which container is the pressure highest?
- In which container do the atoms have the largest average kinetic energy? What is that average kinetic energy in terms of the variables specified above?
- In which container do the atoms have the largest total kinetic energy? What is that total kinetic energy in terms of the variables specified above?

#### SOLUTION

(a) We don't know anything about the volumes of the two containers, so there is not enough information to say how the pressures compare. All we can say is that the product of the pressure multiplied by the volume is five times larger in container  $B$  than in container  $A$ , because  $PV$  is proportional to the product of the number of atoms multiplied by the absolute temperature.

(b) The fact that the temperatures are equal tells us that the average kinetic energy of the atoms is the same in the two containers. Applying Equation 14.14, we get in each case:

$$K_{av} = \frac{3}{2}kT.$$

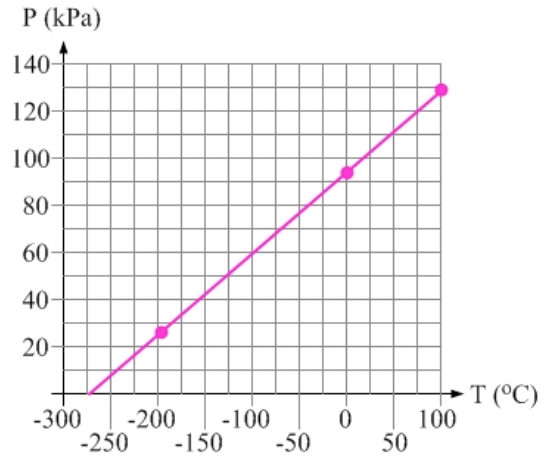
(c) The total kinetic energy is the average energy multiplied by the number of atoms, so container *B* has the larger total kinetic energy. Container *B* has a total kinetic energy of:

$$K_B = 5NK_{av} = 5N\frac{3}{2}kT = \frac{15}{2}NkT.$$

**Related End-of-Chapter Exercises: 8, 10, 37.**

### Absolute zero

Another interesting concept contained in the ideal gas law is the idea of absolute zero. Let's say we seal a sample of ideal gas in a container that has a constant volume. The container has a pressure gauge connected to it that allows us to read the pressure inside. We then measure the pressure as a function of temperature, placing the container into boiling water (100 °C), ice water (0 °C), and liquid nitrogen (−196 °C). The pressures at these temperatures are 129 kPa, 93.9 kPa, and 26.6 kPa, respectively. Plotting pressure as a function of temperature results in the graph shown in Figure 14.4. We find that our three points, and other points we care to measure, fall on a straight line. Extrapolating this line to zero pressure tells us that the pressure equals zero at a temperature of −273 °C (also known as 0 K).



**Figure 14.4:** A graph of pressure as a function of temperature for a constant-volume situation. Extrapolating the graph to zero pressure shows that absolute zero corresponds to a temperature of −273 °C.

Based on the previous section, we would conclude that the pressure drops to zero at absolute zero because the atoms or molecules have no kinetic energy. This is not quite true, although applying ideas of quantum mechanics is necessary to understand why not. If the atoms and molecules stopped completely, we would be able to determine precisely where they are. Heisenberg's uncertainty principle, an idea from quantum mechanics, tells us that this is not possible, that the more accurately we know an object's position the more uncertainty there is in its momentum. The bottom line is that even at absolute zero there is motion, known as zero-point motion. Absolute zero can thus be defined as the temperature that results in the smallest possible average kinetic energy.

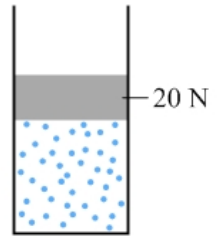
**Essential Question 14.3:** At a particular instant compare the kinetic energy of one particular atom in container *A* to that of one particular atom in container *B*. Which atom has the larger kinetic energy? The two containers are at the same temperature, and there are five times more atoms in container *B* than in container *A*.

**Answer to Essential Question 14.3:** There is no way we can answer this question. The ideal gas law, and kinetic theory, tells us about what the atoms are doing on average, but they tell us nothing about what a particular atom is doing at a particular instant in time. Atoms are continually colliding with one another and these collisions generally change both the magnitude and direction of the atom's velocity, and thus change the atom's kinetic energy. We can find the probability that an atom has a speed larger or smaller than some value, but that's about it.

## 14-4 Example Problems

### EXPLORATION 14.4 – Finding pressure in a cylinder that has a movable piston

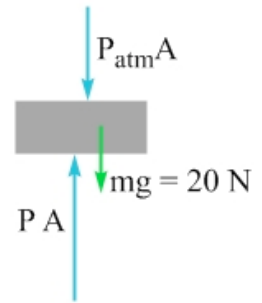
A cylinder filled with ideal gas is sealed by means of a piston. The piston is a disk, with a weight of 20.0 N, that can slide up or down in the cylinder without friction but which is currently at its equilibrium position. The inner radius of the cylinder, and the radius of the piston, is 10.0 cm. The top of the piston is exposed to the atmosphere, and the atmospheric pressure is 101.3 kPa. Our goals for this problem are to determine the pressure inside the cylinder, and then to determine what changes if the temperature is raised from 20°C to 80°C.



**Figure 14.5:** A diagram of the ideal gas sealed inside a cylinder by a piston that is free to move up and down without friction.

**Step 1: Picture the scene.** A diagram of the situation is shown in Figure 14.5.

**Step 2: Organize the data.** The best way to organize what we know in this case is to draw a free-body diagram of the piston, as in Figure 14.6. Three forces act on the piston: the force of gravity; a downward force associated with the top of the piston being exposed to atmospheric pressure; and an upward force from the bottom of the piston being exposed to the pressure in the cylinder.



**Figure 14.6:** The free-body diagram of the piston, showing the forces acting on it.

**Step 3: Solve the problem.** The piston is in equilibrium, so let's apply Newton's second law,  $\sum \vec{F} = m\vec{a} = 0$ , to the piston. Choosing up to be positive gives:

$$+PA - mg - P_{atm}A = 0, \text{ where } A \text{ is the cross-sectional area of the piston.}$$

Solving for  $P$ , the pressure inside the cylinder, gives:

$$P = \frac{mg + P_{atm}A}{A} = \frac{mg}{\pi r^2} + P_{atm} = \frac{20.0 \text{ N}}{\pi (0.100 \text{ m})^2} + 101300 \text{ Pa} = 101900 \text{ Pa} .$$

The pressure inside the cylinder is not much larger than atmospheric pressure.

**Step 4: The temperature of the gas inside the piston is gradually raised from 20°C to 80°C, bringing the piston to a new equilibrium position. What happens to the pressure of the gas, and what happens to the volume occupied by the gas? Be as quantitative as possible.**

To answer the question about pressure we can once again draw a free-body diagram of the piston. However, the fact that the piston has changed position to a new equilibrium position in the cylinder changes nothing on the free-body diagram. Thus, the pressure in the cylinder is the same as it was before. The fact that the temperature increases, however, means the volume increases by the same factor. Because the pressure is constant, we can re-arrange the ideal gas law to:

$$\frac{P}{nR} = \frac{T}{V} = \text{constant}.$$

This tells us that  $\frac{T_i}{V_i} = \frac{T_f}{V_f}$ .

Re-arranging to find the ratio of the volumes, and using absolute temperatures, gives:

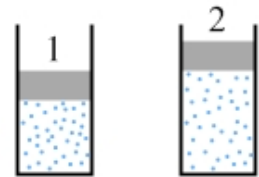
$$\frac{V_f}{V_i} = \frac{T_f}{T_i} = \frac{(273 + 80)\text{K}}{(273 + 20)\text{K}} = 1.20.$$

The volume expands by 20%, increasing by the same factor as the absolute temperature.

**Key Idea for a cylinder sealed by a movable piston:** When ideal gas is sealed inside a cylinder by a piston that is free to move without friction, the pressure of the gas is generally determined by balancing the forces on the piston's free-body diagram rather than from the volume or temperature of the gas. **Related End-of-Chapter Exercises: 5, 26, 27, 30, 35.**

#### EXAMPLE 14.4 – Comparing two pistons

The two cylinders in Figure 14.7 contain an identical number of moles of the same type of ideal gas, and they are sealed at the top by identical pistons that are free to slide up and down without friction. The top of each piston is exposed to the atmosphere. One piston is higher than the other. (a) In which cylinder is the volume of the gas larger? (b) In which piston is the pressure higher? (c) In which piston is the temperature higher?



**Figure 14.7:** The cylinders contain the same number of moles of ideal gas, but the piston in cylinder 2 is at a higher level. The pistons are identical, are free to slide up and down without friction, and the top of each piston is exposed to the atmosphere.

#### SOLUTION

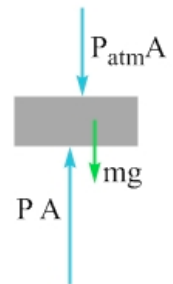
(a) Cylinder 2 has a larger volume. Note that the volume in question is not the volume of the molecules themselves, but the volume of the space the molecules are confined to. In other words, it is the volume inside the cylinder itself, below the piston.

(b) Despite the fact that the piston in cylinder 2 is at a higher level than the piston in cylinder 1, the pressure is the same in both cylinders. This is because the free-body diagrams in Figure 14.8 applies to both pistons. The pressure in both cylinders exceeds atmospheric pressure by an amount that is just enough to balance the pressure associated with the downward force of gravity acting on the piston. The pressure is equal in both cases because the pistons are identical.

(c) Applying the ideal gas law tells us that the temperature is larger in cylinder 2, because  $T = PV/nR$  and the only factor that is different on the right-hand side of that equation is the volume. In this case the absolute temperature is proportional to the volume.

**Related End-of-Chapter Exercises: 6, 7, 20 – 25, 28, 29.**

**Essential Question 14.4:** Piston 2, in Figure 14.7, could be the same piston as piston 1, but just at a later time. What could you do to move the system from the piston 1 state to the piston 2 state?



**Figure 14.8:** The free-body diagram applies equally well to both pistons.



**Answer to Essential Question 14.4:** All we need to do is to increase the temperature of the piston. Based on our analysis in Exploration 14.4, raising the absolute temperature by 20% moves the piston from the state labeled Piston 1 to that labeled Piston 2.

### 14-5 The Maxwell-Boltzmann Distribution; Equipartition

We come now to James Clerk Maxwell, the Scottish physicist who determined that the probability a molecule in a container of ideal gas has a particular speed  $v$  is given by:

$$P(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/(2RT)}, \quad (\text{Equation 14.15: Maxwell-Boltzmann distribution})$$

where  $M$  is the molar mass (mass of 1 mole) of the gas.

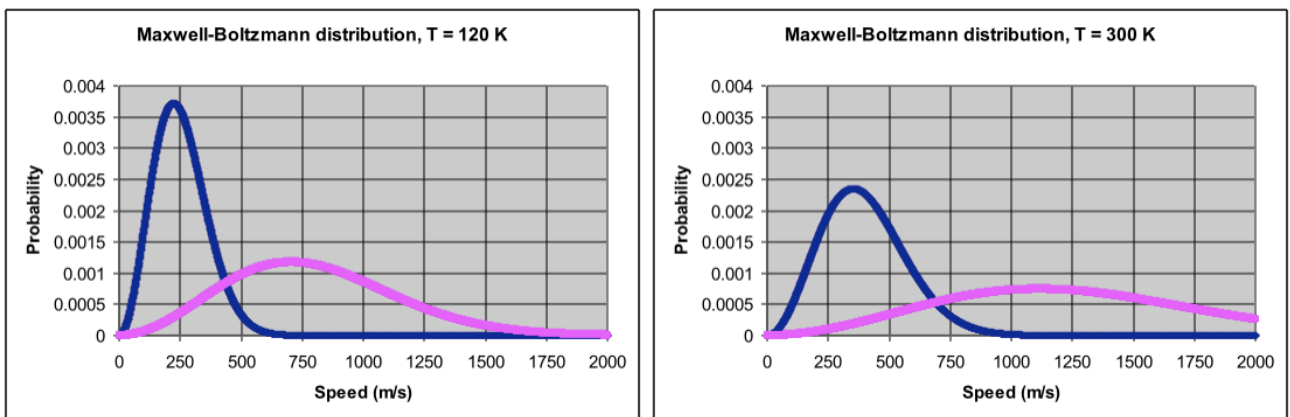
This distribution of speeds is known as the Maxwell-Boltzmann distribution, and it is characterized by three speeds. These are, in decreasing order:

$$v_{rms} = \sqrt{\frac{3RT}{M}}; \quad (\text{Equation 14.16: the rms speed})$$

$$v_{av} = \sqrt{\frac{8RT}{\pi M}}; \quad (\text{Equation 14.17: the average speed})$$

$$v_{prob} = \sqrt{\frac{2RT}{M}}. \quad (\text{Equation 14.18: the most probable speed})$$

Plots of the Maxwell-Boltzmann distribution are shown in Figure 14.9 for two different temperatures and two different monatomic gases, argon and helium. Table 14.1 shows the speeds characterizing the distributions. At low temperatures the molecules do not have much energy, on average, so the distribution clusters around the most probable speed. As temperature increases the distribution stretches out toward higher speeds. The area under the curve stays the same (it is the probability an atom has some velocity, which is 1) so the probability at the peak decreases.



**Figure 14.9:** Maxwell-Boltzmann distributions at two different temperatures, 120 K and 300 K, for monatomic argon gas (the darker and taller curves, for argon with a molar mass of 40 g) and monatomic helium gas (lighter and shorter curves, with a molar mass of 4 g).

**Table 14.1:** The various speeds characterizing the Maxwell-Boltzmann distribution of speeds for monatomic argon gas, and for monatomic helium gas, at temperatures of 120 K and 300 K.

	$v_{rms}$ (m/s)	$v_{av}$ (m/s)	$v_{prob}$ (m/s)
<b>Argon, T = 120 K</b>	273	252	223
<b>Argon, T = 300 K</b>	432	398	353
<b>Helium, T = 120 K</b>	865	797	706
<b>Helium, T = 300 K</b>	1367	1260	1116

### The Equipartition Theorem

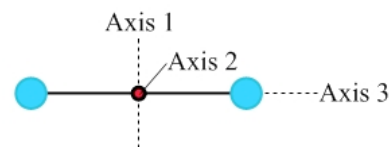
Earlier, we applied basic principles of mechanics to find that  $K_{av} = (3/2)kT$ . If we multiply by a factor of  $N$ , the number of atoms in the ideal gas, the equation becomes:

$$E_{int} = NK_{av} = \frac{3}{2}NkT = \frac{3}{2}nRT. \quad (\text{Eq. 14.19: Internal energy of a monatomic ideal gas})$$

Equation 14.19 gives the total energy associated with the motion of the atoms in the ideal gas. This is known as the **internal energy**. The equipartition theorem states that all contributions to the internal energy contribute equally. For a monatomic ideal gas there are three contributions, coming from motion in the  $x$ ,  $y$ , and  $z$  directions. Each direction thus contributes  $(1/2)NkT$  to the internal energy. Each motion contributing to internal energy is called a **degree of freedom**. Thus:

$$\text{the energy from each degree of freedom} = \frac{1}{2}NkT = \frac{1}{2}nRT. \quad (\text{Eq. 14.20})$$

Consider a diatomic ideal gas, in which each molecule consists of two atoms. At low temperatures, only translational kinetic energy is important, but at intermediate temperatures (the range we will generally be interested in) rotation becomes important. As shown in Figure 14.10, rotational kinetic energy is important for rotation about two axes but can be neglected for the third axis because the rotational inertia is negligible for rotation about that axis. With five degrees of freedom, each counting for  $(1/2)NkT$ , the internal energy of a diatomic ideal gas is:



**Figure 14.10:** A diatomic molecule is modeled as two balls connected by a light rod. In addition to translating in three dimensions the molecule can rotate about axes 1 or 2, for a total of five degrees of freedom. There is no contribution to the internal energy from rotation about axis 3 because the molecule has negligible rotational inertia about that axis.

$$E_{int} = \frac{5}{2}NkT = \frac{5}{2}nRT. \quad (\text{Eq. 14.21: Internal energy of a diatomic ideal gas})$$

At high temperatures, energy associated with the vibration of the atoms becomes important and there are two additional degrees of freedom (one associated with kinetic energy, one with elastic potential energy) to bring the coefficient in front of the  $NkT$  to  $7/2$ .

Polyatomic molecules, at intermediate temperatures, have six degrees of freedom, translational kinetic energy in three dimensions, and rotational kinetic energy about three axes.

$$E_{int} = \frac{6}{2}NkT = 3NkT = 3nRT. \quad (\text{Eq. 14.22: Internal energy of a polyatomic ideal gas})$$

**Related End-of-Chapter Exercises: 38, 47, 48, 53.**

**Essential Question 14.5:** Two containers have identical volumes, temperatures, and the same number of moles of gas. One contains monatomic ideal gas while the other has diatomic ideal gas. Which container has a higher pressure? In which does the gas have more internal energy?

**Answer to Essential Question 14.5:** To find the pressure we can apply the ideal gas law, in the form  $P = nRT/V$ . Because all the factors on the right-hand side are the same for the two containers the pressures must be equal. When applying the ideal gas law we do not have to worry about what the molecules consist of. We do have to account for this in determining which container has the larger internal energy, however. The internal energy for the monatomic gas is  $E_{\text{int}} = (3/2)nRT$ , while for the diatomic gas at room temperature it is  $E_{\text{int}} = (5/2)nRT$ . The monatomic ideal gas has 3/5 of the internal energy of the diatomic ideal gas.

## 14-6 The P-V Diagram

In Chapter 15, one of the tools we will use to analyze thermodynamic systems (systems involving energy in the form of heat and work) is the  $P$ - $V$  diagram, which is a graph showing pressure on the  $y$ -axis and volume on the  $x$ -axis.

### EXPLORATION 14.6 – Working with the $P$ - $V$ diagram

A cylinder of ideal gas is sealed by means of a cylindrical piston that can slide up and down in the cylinder without friction. The piston is above the gas. The entire cylinder is placed in a vacuum chamber, and air is removed from the vacuum chamber very slowly, slowly enough that the gas in the cylinder, and the air in the vacuum chamber, maintains a constant temperature (the temperature of the surroundings).

**Step 1:** *If you multiply pressure in units of kPa by volume in units of liters, what units do you get?*

$$1 \text{ kPa} \times 1 \text{ liter} = (1 \times 10^3 \text{ Pa}) \times (1 \times 10^{-3} \text{ m}^3) = 1 \text{ Pa m}^3 = 1 \text{ N m} = 1 \text{ J}.$$

Thus, the unit is the MKS unit the joule. This will be particularly relevant in the next chapter, when we deal with the area under the curve of the  $P$ - $V$  diagram.

**Step 2:** *Complete Table 14.2, giving the pressure and volume of the ideal gas in the cylinder at various instants as the air is gradually removed from the vacuum chamber in which the cylinder is placed.*

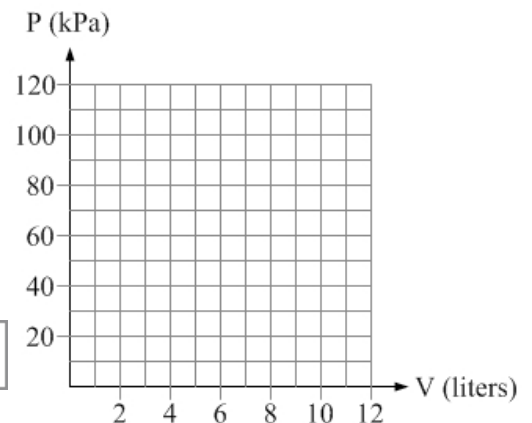
State	Pressure (kPa)	Volume (liters)
1	120	1.0
2	80	
3		2.0
4		3.0
5	30	
6		6.0

Using the ideal gas law, we can say that  $PV = nRT = \text{constant}$ . In state 1, Table 14.2 tells us that the product of pressure and volume is 120 J. Thus the missing values in the table can be found from the equation  $PV = 120 \text{ J}$ . In states 2 and 5, therefore, the gas occupies a volume of 1.5 liters and 4.0 liters, respectively. In states 3, 4, and 6, the pressure is 60 kPa, 40 kPa, and 20 kPa, respectively.

**Table 14.2:** A table giving the pressure and volume for a system of ideal gas with a constant temperature and a constant number of moles of gas.

**Step 3:** *Plot these points on a  $P$ - $V$  diagram similar to that in Figure 14.11, and connect the points with a smooth line. Note that such a line on a  $P$ - $V$  diagram is known as an isotherm, which is a line of constant temperature.*

**Figure 14.11:** A blank  $P$ - $V$  diagram.



The  $P$ - $V$  diagram with the points plotted, and the smooth line drawn through the points representing the isotherm, is shown in Figure 14.12.

**Step 4:** Repeat the process, but this time the absolute temperature of the gas is maintained at a value twice as large as that in the original process. Sketch that isotherm on the same  $P$ - $V$  diagram.

If the absolute temperature is doubled, the constant  $P \times V$  must also double, from 120 J to 240 J. Starting with the original points we plotted, we can find points on the new isotherm by either doubling the pressure or doubling the volume. Several such points are shown on the modified  $P$ - $V$  diagram in Figure 14.13, and we can see that this isotherm, at the higher temperature, is farther from the origin than the original isotherm. This is generally true, that the higher the temperature, the farther from the origin is the isotherm corresponding to that temperature.

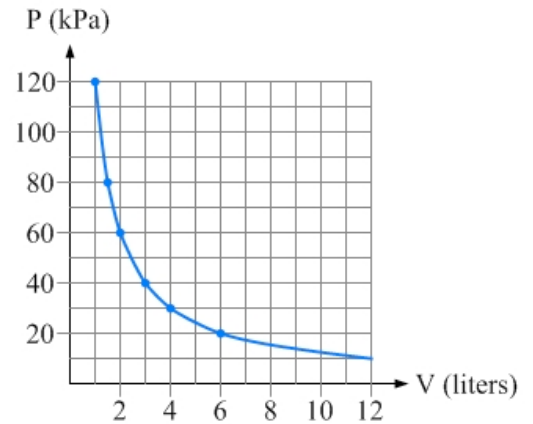
**Key Ideas about P-V diagrams:** The  $P$ - $V$  diagram (the graph of pressure as a function of volume) for a system can convey significant information about the state of the system, including the pressure, volume, and temperature of the system when it is in a particular state. It can be helpful to sketch isotherms on the  $P$ - $V$  diagram to convey temperature information – an isotherm is a line of constant temperature.

**Related End-of-Chapter Exercises:** 11, 12, 49 – 52.

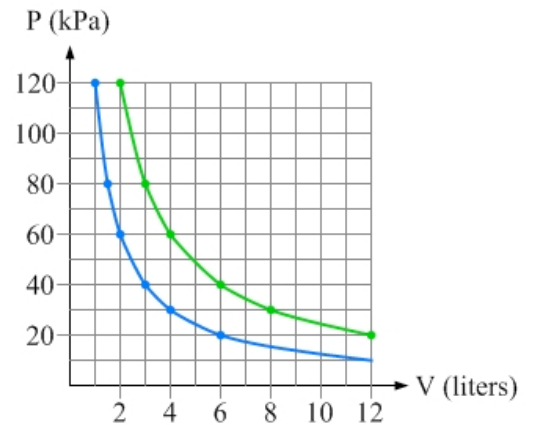
**Essential Question 14.6:** An isotherm on the  $P$ - $V$  diagram has the shape it does because, from the ideal gas law, we are plotting pressure versus volume and the pressure is given by:

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

For a particular isotherm, the value of  $nRT$  is constant, so an isotherm is a line with a shape similar to the plot of  $1/V$  as a function of  $V$ . Let's say we now have two cylinders of ideal gas, sealed by pistons as in the previous Exploration. Cylinder  $A$ , however, has twice the number of moles of gas as cylinder  $B$ . We plot a  $P$ - $V$  diagram for cylinder  $A$ , and plot the isotherm corresponding to a temperature of 300 K. We also draw a separate  $P$ - $V$  diagram for cylinder  $B$ , and we find that the same points we connected to draw the 300 K isotherm on cylinder  $A$ 's  $P$ - $V$  diagram are connected to form an isotherm on cylinder  $B$ 's  $P$ - $V$  diagram. What is the temperature of that isotherm on cylinder  $B$ 's  $P$ - $V$  diagram?



**Figure 14.12:** The  $P$ - $V$  diagram corresponding to the points from Table 14.2. The smooth curve through the points is an isotherm, a line of constant temperature.



**Figure 14.13:** A  $P$ - $V$  diagram showing two different isotherms. The isotherm that is farther from the origin has twice the absolute temperature as the isotherm closer to the origin.

**Answer to Essential Question 14.6:** 600 K. An isotherm is a line connecting all the points satisfying the equation  $PV = nRT =$  a particular constant that depends on  $n$  and  $T$ . Because we're talking about the same line on both  $P$ - $V$  diagrams, we have  $PV = n_A RT_A = n_B RT_B$ . Solving for the temperature in cylinder  $B$  gives:

$$T_B = \frac{n_A R T_A}{n_B R} = \frac{n_A}{n_B} T_A = \frac{2n_B}{n_B} T_A = 2T_A = 2(300\text{K}) = 600\text{K}.$$

In this sense, then, the  $P$ - $V$  diagrams for different ideal gas systems are unique, because the temperature of a particular isotherm depends on the number of moles of gas in the system.

## 14-7 Diffusion and Osmosis

In Chapter 9, we learned a little bit about how surface tension is important in the alveoli of the lungs. Another key process involved is diffusion. Each time we breathe in, oxygen-rich air fills the alveoli of the lungs. Some of this oxygen will then diffuse through the membrane between the alveoli and blood inside the capillaries, infusing the blood with oxygen. Carbon dioxide diffuses in the other direction, from the blood into the lungs, and we then breathe the carbon dioxide out. This can be a highly efficient process in the human body, because the total surface area inside the alveoli can approach  $100 \text{ m}^2$ , and the membrane thickness is extremely thin, generally several hundred nanometers.

Diffusion is a flow of molecules without requiring a net flow of a medium. For instance, in the case of the lungs described above, oxygen molecules diffuse from a region of high concentration of oxygen (in the lungs) to a region of lower concentration (in the blood). The carbon dioxide goes the other way because the high concentration of carbon dioxide is in the blood, and the lower concentration is in the lungs. From a physics perspective, diffusion simply comes from the random motion of molecules, as in an ideal gas.

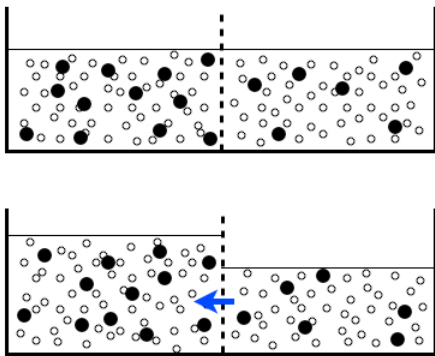
The process of a molecule randomly moving is known as a **random walk**. This was studied by Robert Brown in 1827, hence the term **Brownian motion** for the motion of a small particle immersed in a fluid. Albert Einstein was also a key figure in our understanding of diffusion, as it was he who developed the theory of Brownian motion.

Another example of diffusion is a mylar balloon that is filled with helium. As time passes, helium atoms diffuse through the wall of the balloon, and the balloon gradually deflates.

### Osmosis

The process of osmosis involves the diffusion of molecules of a solute through a membrane that is selectively permeable. Take a container that is divided by a semi-permeable membrane. The membrane allows molecules of the solvent (which might be water, for example) to pass through because these molecules are small. On the other hand, the solute molecules may not pass through because they are too large. If two different concentrations of the solution are placed in the two parts of the container, the solvent molecules will diffuse through the membrane from the low-concentration side to the high-concentration side (thereby diluting the high-concentration side, and increasing the concentration on the low-concentration side). We can refer to an osmotic pressure across the membrane that drives this flow - as shown in Figure 14.14, this osmotic pressure can balance a hydrostatic pressure difference between the two sides, coming from the difference in the height of the fluid columns.

Note that osmotic pressures can be rather large, up to many atmospheres of pressure, even. Because of this, osmosis is a key part of many biological systems.



**Figure 14.14:** In the top diagram, the fluid levels are equal on both sides of a semi-permeable membrane, but the concentration is higher on the left. As shown in the bottom diagram, solvent molecules (small open circles) will then diffuse from right to left until the osmotic pressure balances the hydrostatic pressure. The membrane allows solvent molecules to pass through, but does not allow the larger (dark circles) solute molecules through.

A related phenomenon, which is important in many desalination plants (removing salt from water so that humans can drink it), is reverse osmosis, described below.

### Reverse osmosis and desalination

Let's calculate the osmotic pressure of seawater. This is done by multiplying the molarity ( $M$ ) of the solution, (the concentration in moles / liter), by the universal gas constant ( $R$ ), in units of liter atm / (K moles), and multiplying that by the temperature ( $T$ ) in Kelvin. A typical molarity of seawater is 1.1 moles / L. If we use a temperature of 300 K, the osmotic pressure works out to:

$$P = MR T = (1.1 \text{ moles / L}) [0.082 \text{ L atm / (K moles)}] (300 \text{ K}) = 27 \text{ atm.}$$

Thus, the osmotic pressure of seawater is about 27 atmospheres! This means that if you have a semi-permeable membrane (impermeable to the sodium and chlorine ions) separating fresh water from seawater, there is a very large pressure that drives the pure water through the membrane to the seawater side.

In the reverse-osmosis desalination process, however, we want the flow to go in the other direction, driving pure water from the seawater to the freshwater side. This can be done if the seawater is placed under hydrostatic pressure larger than the 27 atmospheres of osmotic pressure - thus, typical pressures for the seawater in a reverse-osmosis desalination facility are in the range of 40 - 80 atmospheres. A very recent development, in 2013, was the announcement of a new type of membrane, just one atom thick - this is made from graphene (a single sheet of carbon), with holes in it just the right size to pass water molecules but not the salt molecules. Such a very thin sheet offers a lot of promise, as it should be much easier for the water molecules to diffuse through than through the membranes that are currently used, which are many atomic layers thick.

Reverse osmosis is also used in the maple syrup industry, to remove most of the water from the sap before boiling down the rest to make maple syrup and maple sugar.

A related process, **active transport**, is at work in the cells of living things. For instance, the concentration of potassium ions ( $K^+$ ) inside a cell may be 20 times larger than the concentration outside the cell. Just the opposite happens for sodium ions ( $Na^+$ ), for which the outside concentration may be 15 times higher than the concentration inside the cell. Normally, we would expect these ions to diffuse from the high-concentration region to the low-concentration region, but active transport, through the action of a **sodium-potassium pump**, works to maintain the significant imbalance in concentrations. This takes energy, which comes from hydrolyzing ATP. The net result of the sodium-potassium pump is that for every three sodium ions that are pumped out of the cell, two potassium ions are pumped in. This is a key part of why there is generally a potential difference across the cell membrane (positive outside, negative inside).

**Essential Question 14.7:** As fresh water is being removed from seawater in a desalination plant, what happens to the molarity of the seawater? Does this make it harder or easier to remove the pure water? How do you think this issue is addressed in a desalination facility?

**Answer to Essential Question 14.6:** 600 K. An isotherm is a line connecting all the points satisfying the equation  $PV = nRT = \text{a particular constant}$  that depends on  $n$  and  $T$ . Because we're talking about the same line on both  $P$ - $V$  diagrams, we have  $PV = n_A RT_A = n_B RT_B$ . Solving for the temperature in cylinder  $B$  gives:

$$T_B = \frac{n_A RT_A}{n_B R} = \frac{n_A}{n_B} T_A = \frac{2n_B}{n_B} T_A = 2T_A = 2(300\text{K}) = 600\text{K}.$$

In this sense, then, the  $P$ - $V$  diagrams for different ideal gas systems are unique, because the temperature of a particular isotherm depends on the number of moles of gas in the system.

## Chapter Summary

### *Essential Idea regarding looking at thermodynamic systems on a microscopic level*

We can apply basic principles of physics to a system of gas molecules, at the microscopic level, and get important insights into macroscopic properties such as temperature. Temperature is a measure of the average kinetic energy of the atoms or molecules of the gas.

### *The Ideal Gas Law*

The ideal gas law can be written in two equivalent forms.

In terms of  $n$ , the number of moles of gas,  $PV = nRT$ , (Equation 14.1)

where  $R = 8.31 \text{ J}/(\text{mol K})$  is the universal gas constant.

In terms of  $N$ , the number of molecules,  $PV = NkT$ , (Equation 14.2) where

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

### *What Temperature Means*

$$K_{av} = \frac{3}{2} kT. \quad (\text{Equation 14.14: Average kinetic energy is directly related to temperature})$$

As Equation 14.14 shows, temperature is a direct measure of the average kinetic energy of the atoms or molecules in the ideal gas.

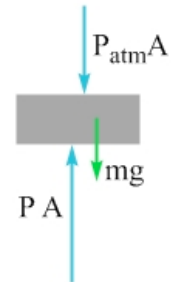
### *The Maxwell-Boltzmann Distribution*

The Maxwell-Boltzmann distribution is the distribution of molecular speeds in a container of ideal gas, which depends on the molar mass  $M$  of the molecules and on the absolute temperature,  $T$ . The distribution is characterized by three speeds. In decreasing order, these are the root-mean-square speed; the average speed; and the most-probable speed. These are given by equations 14.16 – 14.18:

$$v_{rms} = \sqrt{\frac{3RT}{M}}; \quad v_{av} = \sqrt{\frac{8RT}{\pi M}}; \quad v_{prob} = \sqrt{\frac{2RT}{M}}.$$

***A Cylinder Sealed by a Piston that can Move Without Friction***

A common example of an ideal gas system is ideal gas sealed inside a cylinder by means of a piston that is free to move without friction. When the piston is at its equilibrium position the pressure of the gas is generally determined by balancing the forces on the piston's free-body diagram, rather than from the volume or temperature of the gas. The diagram at right illustrates this idea for a cylinder sealed at the top by a piston of area  $A$ . The combined forces directed down, the force and gravity and the force associated with atmospheric pressure acting on the top of the piston, must be balanced by the upward force associated with the gas pressure acting on the bottom of the piston.



***The Equipartition Theorem***

The equipartition theorem is the idea that each contribution to the internal energy (energy associated with the motion of the molecules) of an ideal gas contributes equally. Each contribution is known as a degree of freedom.

$$\text{The energy from each degree of freedom} = \frac{1}{2} Nkt = \frac{1}{2} nRt. \quad (\text{Equation 14.20})$$

A monatomic ideal gas can experience translational motion in three dimensions. With three degrees of freedom the internal energy is given by:

$$E_{\text{int}} = NK_{av} = \frac{3}{2} NkT = \frac{3}{2} nRT. \quad (\text{Eq. 14.19: Internal energy of a monatomic ideal gas})$$

At intermediate temperatures molecules in a diatomic ideal gas have two additional degrees of freedom, associated with rotation about two axes.

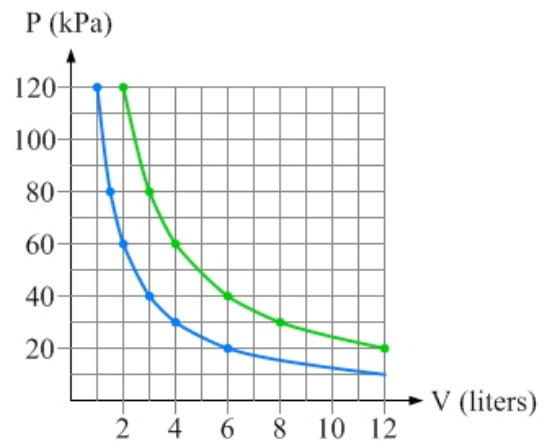
$$E_{\text{int}} = \frac{5}{2} NkT = \frac{5}{2} nRT. \quad (\text{Eq. 14.21: Internal energy of a diatomic ideal gas})$$

Molecules in a polyatomic ideal gas can rotate about three axes.

$$E_{\text{int}} = \frac{6}{2} NkT = 3NkT = 3nRT. \quad (\text{Eq. 14.22: Internal energy of a polyatomic ideal gas})$$

***The P-V Diagram***

A graph of pressure versus volume (a P-V diagram) can be very helpful in understanding an ideal gas system. We will exploit these even more in the next chapter. The ideal gas law tells us that the product of pressure and volume (which has units of energy) is proportional to the temperature of a system. Lines of constant temperature are known as isotherms. The diagram at right shows two isotherms. The isotherm that is farther from the origin has twice the absolute temperature as the isotherm closer to the origin.

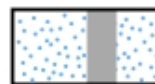




## End of Chapter Exercises

Exercises 1 – 12 are conceptual questions that are designed to see if you have understood the main concepts of the chapter.

1. While on an airplane, you take a drink from your water bottle, and then screw the cap tightly back on the bottle. After landing, you notice that the bottle is a funny shape, as if someone is deforming it by squeezing it. Explain what has happened.
2. A common lecture demonstration involves placing a gob of shaving cream in a bell jar, which is a device that can be sealed off from the atmosphere. Much of the air is then pumped out of the bell jar. What do you expect to happen when this is done? Why?
3. As shown in Figure 14.14, a sealed cylinder of ideal gas is divided into two parts by a piston that can move left and right without friction. There is ideal gas in both parts, but the parts are isolated from one another by the piston. The piston is in its equilibrium position. The volume occupied by the gas on the left side is larger than that occupied by the gas on the right side. On which side is the gas pressure higher? Explain your answer.



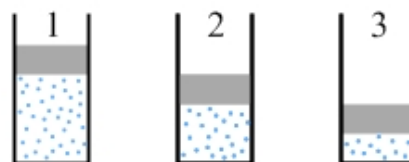
**Figure 14.14:** A sealed cylinder that is divided into two parts by a piston that is free to move left or right without friction. For Exercises 3 and 4.

4. Return to the situation described in Exercise 3 and shown in Figure 14.14. Initially, the temperature of the gas on the right side is larger than that of the gas on the left side. As time goes by, the two sides approach the same equilibrium temperature, as the temperature gradually decreases on the right side and gradually increases on the left side. Describe what happens to the piston as the system progresses toward equilibrium.
5. As shown in Figure 14.15, a sealed cylinder of ideal gas is divided into two parts by a piston that can move up and down without friction. There is ideal gas in both parts, but the gas from one part is isolated from that in the other part by the piston. The piston, which has a weight of 50.0 N, is shown in its equilibrium position. The volume occupied by the gas in the lower part is larger than that occupied by the gas in the upper part. On which side is the gas pressure higher? Explain your answer.



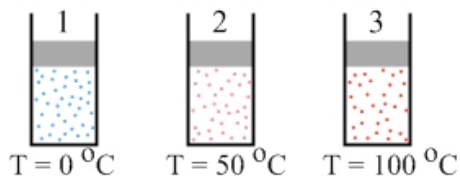
**Figure 14.15:** A sealed cylinder divided into two parts by a piston that is free to slide up and down without friction, for Exercise 5.

6. Three identical cylinders are sealed with identical pistons that are free to slide up and down the cylinder without friction. Each cylinder contains ideal gas, and the temperature is the same in each case, but the volumes occupied by the gases differ. In each cylinder the piston is above the gas, and the top of each piston is exposed to the atmosphere. As shown in Figure 14.16, the volume occupied by the gas is largest in case 1 and smallest in case 3. Rank the cylinders in terms of (a) the pressure of the gas, and (b) the number of moles of gas inside the cylinder.



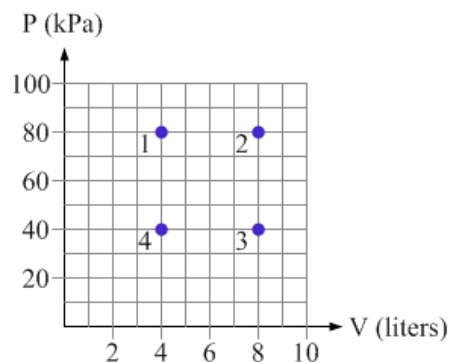
**Figure 14.16:** Three cylinders containing different volumes of gas at the same temperature, for Exercise 6.

7. Three identical cylinders are sealed with identical pistons that are free to slide up and down the cylinder without friction, as shown in Figure 14.17. Each cylinder contains ideal gas, and the gas occupies the same volume in each case, but the temperatures differ. In each cylinder the piston is above the gas, and the top of each piston is exposed to the atmosphere. In cylinders 1, 2, and 3 the temperatures are  $0^{\circ}\text{C}$ ,  $50^{\circ}\text{C}$ , and  $100^{\circ}\text{C}$ , respectively. Rank the cylinders in terms of (a) the pressure of the gas, and (b) the number of moles of gas inside the cylinder.



**Figure 14.17:** Three cylinders containing equal volumes of gas at different temperatures, for Exercise 7.

8. Is it possible for the total kinetic energy of the atoms in one container of ideal gas to be the same as the total kinetic energy of the atoms in a second container of ideal gas, but for their temperatures to be different? If so, describe how you could achieve this.
9. Consider a sealed box of ideal gas that is separated into two parts of equal volume by a partition. All the gas molecules are in one half of the box and there is nothing at all in the other half of the box. The partition consists of two sliding doors, which can be opened quickly and automatically like the doors of an elevator. When the sliding doors open, allowing the molecules to expand into the other half of the box, do you expect either the pressure or the temperature to remain constant? Basing your argument on kinetic theory, state which of these parameters (pressure or temperature) you expect to stay constant, explain why, and explain what happens to the other parameter.
10. Two containers of ideal gas have the same volume, the same pressure, and have the same number of moles of gas, but the type of molecule in each container is different. To be specific, one container contains argon atoms while the other contains xenon atoms, which are both monatomic ideal gases. Which of the following are the same for the two containers and which are different? In cases where there is a difference, state how they differ. (a) Temperature, (b) average kinetic energy of the atoms, (c) total kinetic energy of the atoms, (d) rms speed of the atoms, (e) most probable speed of the atoms.

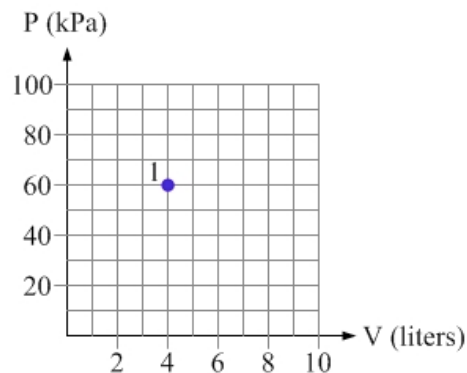


**Figure 14.18:** Four states are shown on the P-V diagram for a particular thermodynamic system. For Exercise 11.

11. Four states, labeled 1 through 4, of a particular thermodynamic system, are shown on the P-V diagram in Figure 14.18. The number of moles of gas in the system is constant. Rank the states based on their temperature, from largest to smallest.

12. Consider the P-V diagram in Figure 14.19. Find three other points on the diagram in which the system would have the same temperature as it has in state 1.

**Figure 14.19:** A P-V diagram for a particular thermodynamic system. For Exercise 12.



**Exercises 13 – 16 deal with the ideal gas law.**

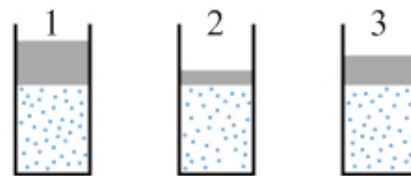
13. A sample of monatomic ideal gas is kept in a container that keeps a constant volume while the temperature of the gas is raised from  $10^{\circ}\text{C}$  to  $20^{\circ}\text{C}$ . If the pressure of the gas is  $P$  at  $10^{\circ}\text{C}$ , what is the pressure at  $20^{\circ}\text{C}$ ?
14. A particular cylindrical bucket has a height of 50 cm, while the radius of its circular cross-section is 15 cm. The bucket is empty, aside from containing air. The bucket is then inverted and, being careful not to lose any of the air trapped inside, lowered 20 m below the surface of a fresh-water lake. (a) If the temperature is the same at both points, what fraction of the bucket's volume is occupied by the air when the bucket is 20 m down? (b) Would the fraction be larger, smaller, or the same if the temperature drops from  $25^{\circ}\text{C}$  at the surface to  $5.0^{\circ}\text{C}$  20 m below the surface? Why? (c) Calculate the fraction of the bucket's volume that is occupied by air when the bucket is 20 m down and the temperature changes as described in (b).
15. An empty metal can is initially open to the atmosphere at  $20^{\circ}\text{C}$ . The can is then sealed tightly, and heated to  $100^{\circ}\text{C}$ . While at  $100^{\circ}\text{C}$ , the lid of the can is loosened, opening the can to the atmosphere, and then the can is sealed tightly again. When the can cools to  $20^{\circ}\text{C}$  again, what is the pressure inside?
16. In 1992, a Danish study concluded that a standard toy balloon, made from latex and filled with helium, could rise to 10000 m (where the pressure is about  $1/3$  of that at sea level) in the atmosphere before bursting. In the study, a number of balloons were filled with helium, and then placed in a chamber maintained at  $-20^{\circ}\text{C}$ . The pressure was gradually reduced until the balloons exploded, and then the researchers determined the height above sea level corresponding to that pressure. Assuming the balloons were filled with helium at  $+20^{\circ}\text{C}$  and about atmospheric pressure, determine the ratio of the balloon's volume when it exploded to its volume when it was filled.

**Questions 17 – 19 deal with calculating the rms average.**

17. Consider the set of numbers  $-3, -2, -1, 1, 3, 5$ . (a) What is the average of this set of numbers? (b) What is the rms average of this set of numbers?
18. Is it possible for a set of four numbers to have an average of zero but an rms average that is non-zero? If so, come up with a set of four numbers for which this is true.
19. (a) Is it possible for the average of a set of four numbers to be equal to the rms average of those numbers? If so, find a set of four numbers for which this is true. (b) Is it possible for the average of a set of four numbers to be larger than the rms average of those numbers? If so, find a set of four numbers for which this is true.

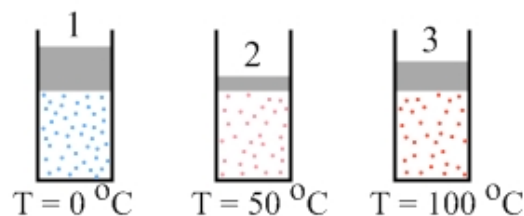
**Questions 20 – 25 are a sequence of ranking tasks that relate to cylinders that are sealed by pistons that are free to slide without friction. In all cases, the piston is at its equilibrium position.**

20. Three identical cylinders are sealed with pistons that are free to slide up and down the cylinder without friction, but the masses of the pistons differ. As shown in Figure 14.20, Piston 1 has the largest mass, while piston 2 has the smallest mass. Each cylinder contains ideal gas at the same temperature and occupying the same volume. In each cylinder, the piston is above the gas, and the top of each piston is exposed to the atmosphere. Rank the cylinders in terms of (a) the pressure of the gas, and (b) the number of moles of gas inside the cylinder.



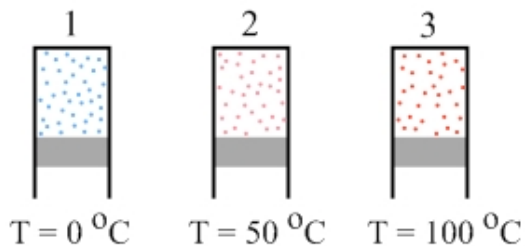
**Figure 14.20:** Three cylinders containing the same volume of gas at the same temperature, but the pistons have different mass. For Exercise 20.

21. As in Exercise 20, three identical cylinders are sealed with pistons that are free to slide up and down the cylinder without friction, but the masses of the pistons differ. As shown in Figure 14.21, piston 1 has the largest mass, while piston 2 has the smallest mass. The gas in each cylinder occupies the same volume, but in cylinders 1, 2, and 3 the temperatures are  $0^{\circ}\text{C}$ ,  $50^{\circ}\text{C}$ , and  $100^{\circ}\text{C}$ , respectively. In each cylinder the piston is above the gas, and the top of each piston is exposed to the atmosphere. Is it possible to rank the cylinders, from largest to smallest, in terms of the pressure of the gas based on the information given here? If so state the ranking, and compare the ranking to that in the previous exercise, explaining either why you expect the rankings to be the same or why you expect the rankings to differ. If it is not possible to rank the cylinders based on their pressures, clearly explain why not.



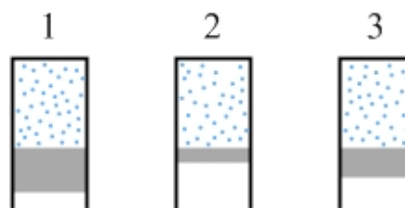
**Figure 14.21:** Three cylinders containing the same volume of gas at different temperatures, and with pistons of different mass. For Exercise 21.

22. Three identical cylinders are sealed with identical pistons that are free to slide up and down the cylinder without friction. Each cylinder contains ideal gas, and the gas occupies the same volume in each case, but the temperatures differ. As shown in Figure 14.22, each cylinder is inverted so the piston is below the gas, and the bottom of each piston is exposed to the atmosphere. In cylinders 1, 2, and 3 the temperatures are  $0^{\circ}\text{C}$ ,  $50^{\circ}\text{C}$ , and  $100^{\circ}\text{C}$ , respectively. Rank the cylinders, from largest to smallest, in terms of (a) the pressure of the gas (b) the number of moles of gas inside the cylinder.



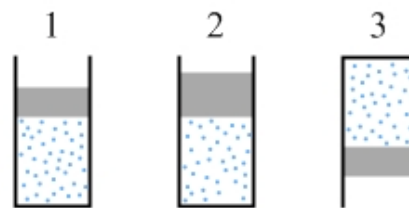
**Figure 14.22:** Three inverted cylinders containing the same volume of gas at different temperatures. For Exercise 22.

23. Three identical cylinders are sealed with pistons that are free to slide up and down the cylinder without friction, but the masses of the pistons differ. Piston 1 has the largest mass, while piston 2 has the smallest mass. Each cylinder contains ideal gas at the same temperature and occupying the same volume. As shown in Figure 14.23, each cylinder is inverted so the piston is below the gas, and the bottom of each piston is exposed to the atmosphere. Rank the cylinders, from largest to smallest, in terms of (a) the pressure of the gas, and (b) the number of moles of gas inside the cylinder.



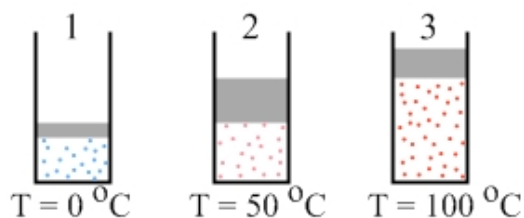
**Figure 14.23:** Three inverted cylinders containing the same volume of gas at equal temperatures, but having pistons of different mass. For Exercise 23.

24. Three identical cylinders are sealed with pistons that are free to slide up and down the cylinder without friction. Each cylinder contains ideal gas, and the gas occupies the same volume in each case and is at the same temperature. As shown in Figure 14.24, the pistons in cylinders 1 and 3 are identical but the piston in cylinder 1 is above the gas while cylinder 3 is inverted so the piston is below the gas. The piston in cylinder 2, which is above the gas, has more mass than the other two pistons. The top surfaces of the pistons in cylinders 1 and 2, and the bottom surface of the piston in cylinder 3, are exposed to the atmosphere. Rank the cylinders, from largest to smallest, in terms of (a) the pressure of the gas, and (b) the number of moles of gas inside the cylinder.



**Figure 14.24:** Three cylinders containing the same volume of gas at equal temperatures, but cylinder 3 is inverted while the piston in cylinder 2 has a larger mass than the other two pistons. For Exercise 24.

25. Three identical cylinders are sealed with pistons that are free to slide up and down the cylinder without friction. Each cylinder contains ideal gas. As shown in Figure 14.25, the volume occupied by the gas is different in each case, and the temperatures are also different. The pistons also have different masses. The piston in cylinder 1 has the smallest mass while the piston in cylinder 2 has the largest mass. In each cylinder the piston is above the gas, and the top of each piston is exposed to the atmosphere. Is it possible to rank the cylinders, from largest to smallest, in terms of the pressure of the gas? If so, provide the ranking. If not, explain why not.

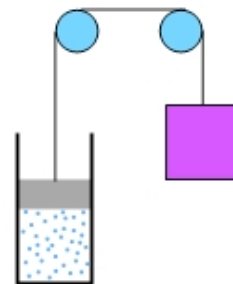


**Figure 14.25:** Three cylinders containing different volumes of gas at different temperatures, and with pistons of different mass. For Exercise 25.

**Exercises 26 – 35 relate to cylinders that are sealed by pistons that are free to slide without friction.**

26. In Exploration 14.4, we analyzed a cylinder filled with ideal gas that is sealed by a piston that is above the gas. The piston is a cylindrical object, with a weight of 20.0 N, that can slide up or down in the cylinder without friction. The inner radius of the cylinder, and the radius of the piston, is 10.0 cm. With the top of the piston exposed to the atmosphere, at a pressure of 101.3 kPa, we determined the pressure inside the cylinder. Now, very slowly, so that the gas inside the cylinder stays constant at the temperature of its surroundings, sand is poured onto the top of the piston. When 30.0 N of sand has been added to the piston, determine: (a) the pressure inside the cylinder, and (b) the ratio of the final volume occupied by the gas after the sand is added to the volume occupied by the gas before the sand is added.
27. A cylinder filled with ideal gas is sealed by a piston that is above the gas. The piston is a cylindrical object, with a weight of 10.0 N, that can slide up or down in the cylinder without friction. The inner radius of the cylinder, and the radius of the piston, is 10.0 cm. (a) If the top of the piston is exposed to the atmosphere, and the atmospheric pressure is 101.3 kPa, what is the pressure inside the cylinder? (b) What happens to the gas pressure, and the volume occupied by the gas, if the cylinder's temperature is gradually increased from 20°C to 60°C? Be as quantitative as possible.

28. Consider the cylinder in Exercise 27. If the cylinder is inverted, so the piston lies below the gas, what will happen to the piston? Will it remain in the cylinder, or will it fall out? Explain qualitatively what will happen, and explain why. Assume the piston is initially located about halfway down the cylinder.
29. Return to Exercise 28, but now analyze it quantitatively. (a) Assuming the piston is in equilibrium below the gas, determine (a) the gas pressure, and (b) the ratio of the volume occupied by the gas when the piston is below the gas to the volume occupied by the gas when the piston is above the gas.
30. A cylinder filled with ideal gas is sealed by a piston that is above the gas. The piston is a cylindrical object, with a weight of 50.0 N, that can slide up or down in the cylinder without friction. The inner radius of the cylinder, and the radius of the piston, is 5.00 cm. The top of the piston is exposed to the atmosphere, and the atmospheric pressure is 101.3 kPa. The cylinder has a height of 30.0 cm, and, when the temperature of the gas is 20°C, the bottom of the piston is 15.0 cm above the bottom of the cylinder. Find the number of moles of ideal gas in the cylinder.
31. Return to the cylinder described in Exercise 30. When the temperature of the gas is raised from 20°C to 200°C, find the distance between the bottom of the cylinder and the bottom of the piston when the piston comes to its new equilibrium position.
32. Consider again the cylinder described in Exercise 30. What is the maximum temperature the ideal gas can have for the cylinder to remain sealed?
33. Consider again the cylinder described in Exercise 30. Now, the entire cylinder is sealed in a vacuum chamber and air is gradually pumped out of the chamber. Assume the temperature of the gas remains the same. (a) Describe qualitatively what, if anything, happens to the cylinder as the air is removed from the chamber. (b) What is the lowest pressure the chamber can have for the cylinder to remain sealed?
34. Consider again the cylinder described in Exercise 30. As the temperature of the gas is gradually raised from 20°C to 220°C you, wearing insulating gloves to prevent a nasty burn, push down on the top of the piston so that the piston remains in the same position at all times. How much downward force do you have to exert on the piston when the gas temperature is (a) 120°C? (b) 220°C?
35. Consider again the cylinder described in Exercise 30, except this time the piston is tied to a string that passes over a pulley system and is tied to a block that has a weight of 90.0 N, as shown in Figure 14.26. Both the block and the piston are in equilibrium. What is the pressure in the cylinder?



**Figure 14.26:** The 50.0 N piston is tied to a 90.0 N block by a string passing over a pulley system. The system is in static equilibrium. For Exercise 35.

### General exercises and conceptual questions

36. Kids love to bounce around inside a moonwalk, which consists of a floor inflated with air and four walls made of elastic mesh. In a particular moonwalk, there are 8 children, each with a mass of 15 kg. Each wall of the moonwalk measures 3.0 m by 3.0 m and, on average, each child bounces off a wall once every 5.0 s. Assume that each child has a speed of 2.0 m/s when he or she hits a wall; that the child's velocity is directed perpendicular to the plane of the wall; and that the collision with the wall simply reverses the direction of the child's velocity. What is the average pressure experienced by a wall because of the children in the moonwalk?

37. A box of ideal gas contains two kinds of atoms, which have different masses. The atoms are in thermal equilibrium. You observe that the average speed of one of the kinds of atoms is 50% larger than the average speed of the other. What is the ratio of the masses of the atoms?
38. Equation 14.16 gives an expression for the root-mean-square speed of the Maxwell-Boltzmann distribution. Derive this equation by starting from Equation 14.14,

$$K_{av} = \frac{3}{2} kT.$$

39. You have two identical cylinders that are sealed with identical pistons that are free to slide up and down the cylinder without friction. Each cylinder contains ideal gas, and the gas occupies the same volume and is at the same temperature in each case. In each cylinder the piston is above the gas. Cylinder A contains argon gas (atomic mass = 40 g), while cylinder B contains xenon (atomic mass = 131 g). (a) In which cylinder is the pressure larger? Explain your answer. (b) In which cylinder is the number of moles of gas larger? Explain your answer.
40. You have two identical cylinders that are sealed with identical pistons that are free to slide up and down the cylinder without friction. Each cylinder contains the same number of moles of a diatomic ideal gas, and the gas is at the same temperature in each case. In each cylinder the piston is above the gas. Cylinder A contains oxygen gas (molecular mass = 32 g), while cylinder B contains nitrogen (molecular mass = 28 g). (a) In which cylinder is the pressure larger? Explain your answer. (b) In which cylinder is the volume occupied by the gas larger? Explain your answer.

41. As shown in Figure 14.27, a sealed cylinder of ideal gas is divided into two parts by a piston that can move up and down without friction. There is ideal gas in both parts, but the gas from one part is isolated from that in the other part by the piston. The volume occupied by the gas in the lower part is twice that occupied by the gas in the upper part, while the temperature is the same in both parts. The pressure in the lower part is 2000 Pa, and the weight of the piston is 50.0 N. The piston is in its equilibrium position. The cross-sectional area of the cylinder is 100 cm<sup>2</sup>. Determine (a) the pressure in the upper part, and (b) the ratio of the number of moles of gas in the lower part to the number of moles in the upper part.



**Figure 14.27:** A sealed cylinder divided into two parts by a piston that is free to slide up and down without friction, for Exercise 41.

42. A cylinder sealed by a movable piston contains a certain number of molecules of air, which we can treat as an ideal gas. The pressure is initially  $1 \times 10^5$  Pa in the cylinder, and the temperature is 20°C. Very slowly, so the temperature of the gas remains constant, you push on the piston so that the volume occupied by the gas changes from  $V$ , its original value, to  $V/4$ . Plot a graph of the pressure in the cylinder as a function of the volume occupied by the gas.
43. Return to the situation described in Exercise 42. If you carry out the compression very quickly, instead of slowly, the temperature of the gas can change significantly. (a) Would you expect the temperature in the cylinder to increase or decrease? (b) Thinking about the interaction between the piston and the individual gas molecules, come up with an explanation regarding why and how the average kinetic energy of the gas molecules changes.

44. On a hot summer day, you are sitting at a café drinking a carbonated beverage from a tall glass. As you watch bubbles rise from the bottom to the top of the glass you start thinking that they should be changing in volume as they rise. (a) Why, and in what way, would you expect the bubbles to change in volume as they rise? (b) Assuming the beverage has the same density as water,  $1000 \text{ kg/m}^3$ , estimate the ratio of the volume of a bubble at the surface to its volume at the bottom of the glass, 30 cm below the surface.
45. A spherical copper container with a radius of 8.0 cm is sealed when the air inside is at atmospheric pressure, 101.3 kPa, and the temperature is  $20^\circ\text{C}$ . (a) How many moles of gas does the sphere contain? (b) Neglecting any change in volume in the copper sphere itself, plot a graph of the pressure in the container as a function of temperature over the range of  $-150^\circ\text{C}$  to  $+150^\circ\text{C}$ . (c) What is the slope of the graph equal to? State your answer in terms of variables as well as giving a numerical value.

46. Consider the set of pressures, volumes, and temperatures for a sealed container of ideal gas shown in Table 14.3. Complete the table, and then rank the four states, from largest to smallest, based on their (a) pressure, (b) volume, and (c) temperature.

State	Pressure	Volume	Temperature
A	$P_i$	$V_i$	$T_i$
B	$3P_i$	$2V_i$	
C	$\frac{1}{2}P_i$		$2T_i$
D		$3V_i$	$\frac{1}{2}T_i$

**Table 14.3:** A table showing the pressure, volume, and temperature of a sealed ideal gas in four different states, for Exercise 46.

47. You have a cubical box measuring 30 cm on each side. Sealed in this box is monatomic argon gas at a temperature of  $20^\circ\text{C}$  and at a pressure of 100 kPa. (a) Determine the number of moles of argon in the box. (b) Determine the number of atoms of argon in the box. For these argon atoms, determine the (c) most probable speed (d) average speed (e) rms speed.
48. Return to the box of argon gas described in Exercise 47. Let's make some simple calculations to work out approximately how many collisions each side of the box experiences every second, and to determine the average force exerted on one side of the box by a single colliding atom. (a) Using the given pressure and the area of one side of the box, determine the average force applied by the atoms to one side of the box. (b) Use the value of  $v_{rms}$  and the relationship  $v_{rms}^2 = 3v_x^2$  to find the value of  $v_x$ . (c) Use Equation 14.5 to determine the time interval between successive collisions of one atom with one side of the box. (d) Determine how many collisions one atom makes with one side of the box every second. (e) Multiply by the number of atoms to determine the total number of collisions that one side of the box experiences every second. (f) Divide your answer from part (a) by your answer from part (e) to determine the average force associated with one collision.



49. A particular ideal gas system contains a fixed number of moles of ideal gas. The number of moles of gas is such that the product  $nR = 0.300 \text{ J/K}$ . Values of the volume and temperature for particular states of the system are shown in Table 14.4. (a) Find the pressure for each of the states shown in the table. (b) Plot these points on a P-V diagram. (c) Describe a system that these states could correspond to, and explain how you could move the system from state 1 through the other states listed to state 5.

State	P (kPa)	V (liters)	T (K)
1		1.0	150
2		2.0	300
3		3.0	450
4		4.0	600
5		5.0	750

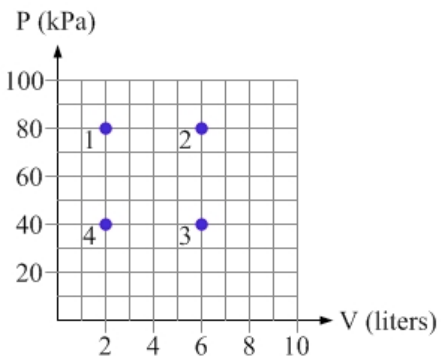
**Table 14.4:** Volume and temperature readings in five states of an ideal gas system, for Exercise 49.

50. A particular ideal gas system contains a fixed number of moles of ideal gas. The number of moles of gas is such that the product  $nR = 0.100 \text{ J/K}$ . Values of the pressure and temperature for particular states of the system are shown in Table 14.5. (a) Find the volume for each of the states shown in the table. (b) Plot these points on a P-V diagram. (c) Describe a system that these states could correspond to, and explain how you could move the system from state 1 through the other states listed to state 5.

State	P (kPa)	V (liters)	T (K)
1	40		80
2	80		160
3	120		240
4	160		320
5	200		400

**Table 14.5:** Pressure and temperature readings in five states of an ideal gas system, for Exercise 50.

51. Four states, labeled 1 through 4, of a particular thermodynamic system, are shown on the P-V diagram in Figure 14.28. The number of moles of gas in the system is constant. (a) Rank the states based on their temperature, from largest to smallest. (b) If the number of moles of gas is chosen such that the product  $nR = 10.0 \text{ J/K}$ , find the absolute temperature of the system in the various states.



**Figure 14.28:** Four states are shown on the P-V diagram for a particular thermodynamic system. For Exercise 51.

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# Chapter 14: Additional Resources

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