Chapter 14 – Thermal Physics: A Microscopic View

The main focus of this chapter is the application of some of the basic principles we learned earlier to thermal physics. This will give us some important insights into what temperature means, and into how systems behave on a microscopic level.

Consider the balloons in the photograph. What is it that keeps the balloons inflated? What would happen to the balloons if we changed the temperature? These questions, and others, will concern us in this chapter. Photo credit: Oleg Prikhodko /iStockPhoto.

14-1 The Ideal Gas Law

Let's say you have a certain number of moles of ideal gas that fills a container. 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,

(Equation 14.1: The ideal gas law)

where R = 8.31 J/(mol K) is the universal gas constant.

First of all, what is a mole? It is a not a cute, furry creature that you might find digging holes in your backyard. In this context it 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, 6.02×10^{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 $N = n N_A$. Taking the ideal gas law and multiplying the right-hand side by N_A / N_A gives:

$$PV = nN_A \frac{R}{N_A}T = N\frac{R}{N_A}T \; . \label{eq:PV}$$

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

PV = NkT. (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.

An aside – Thinking about the rms average.

In the next section we will work with 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, first square the numbers to give 1, 1, 9, and 25. The next step is to find the average of these squared values, which is 9. Finally, we take the square root of that average to find that the rms average is 3.

Clearly this is a funny way to do an average, since 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 is that squaring the numbers makes everything positive – without this negative values cancel positive values when we add the numbers up. The second 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, 6 - 8.

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°C to 30°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 ΔT , we must use temperatures in Kelvin rather than Celsius. In Kelvin the temperature is raised 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:

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

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 14.2 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 14.2: 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 Δt over which the force is applied). Thus:

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

What is this time interval, Δt ? 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 Δt equal to the time between collisions of the atom with that wall. Since the atom travels a distance L across the box in the x-direction at a speed of v_x in the x-direction is 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:



$$\Delta t = \frac{2L}{v_x}.$$
 (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:

$$\overline{F}_{\text{molecule on wall}} = \frac{2mv_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}.$$
 (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:

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

The Greek letter \sum (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:

$$\overline{F}_{\text{on wall}} = \frac{Nm}{L} \left(\frac{\sum v_x^2}{N} \right).$$
 (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:

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

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

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

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

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

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

Related End-of-Chapter Exercises: 1, 2, 6 - 8.

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:

$$P = \frac{F_{\text{on wall}}}{A} = \frac{2N}{3L^3} K_{av}.$$
 (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:

$$PV = N\left(\frac{2}{3}K_{av}\right).$$
 (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,

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

- (a) In which container is the pressure highest?
- (b) 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?
- (c) 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 fives 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: 29, 30, 44, 53.

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 14.7. 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 14.3: 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.

Step 1: Picture the scene. A diagram of the situation is shown in Figure 14.3.

Figure 14.4: A diagram of the ideal gas sealed inside a cylinder by a piston that is free to move up and down without friction.

Step 2: *Organize the data*. The best way to organize what we know in this case is to draw a freebody diagram of the piston, as in Figure 14.4. 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 14.5: 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:

 $+PA - mg - P_{atm}A = 0$, where A 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 $20^{\circ}C$ to $80^{\circ}C$, 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. Since the pressure is constant we can re-arrange the ideal gas law to:

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$$P_{atm}A$$

 $P = 20 N$
 $P A$

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

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: 10-27.**

EXAMPLE 14.4 – Comparing two pistons

The two cylinders in Figure 14.5 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 14.6: 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 is the same. This is because the free-body diagrams in Figure 14.6 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.

Figure 14.7: The free-body diagram applies equally well to both pistons.

(c) Applying the ideal gas law tells us that the temperature is larger in cylinder 2, since 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: 10-27.

Essential Question 14.4: Piston 2 in Figure 14.6 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?





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:

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$
; (Equation 14.16: **the rms speed**)
 $v_{av} = \sqrt{\frac{8RT}{\pi M}}$; (Equation 14.17: **the average speed**)
 $v_{prob} = \sqrt{\frac{2RT}{M}}$. (Equation 14.18: **the most probable speed**)

Plots of the Maxwell-Boltzmann distribution are shown in Figure 14.8 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 14.8: Maxwell-Boltzmann distributions at

two different temperatures, 120 K and 300 K, for monatomic argon gas (in dark blue, with a molar mass of 40 g) and monatomic helium gas (in pink, 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.

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

The Equipartition Theorem

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

$$E_{\text{int}} = NK_{av} = \frac{3}{2}NkT = \frac{3}{2}nRT$$
. (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:

the energy from each degree of freedom $=\frac{1}{2}Nkt = \frac{1}{2}nRt$. (Equation 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 14.9, 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:

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

Figure 14.9: 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.



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.

 $E_{\text{int}} = \frac{6}{2}NkT = 3NkT = 3nRT$. (Eq. 14.21: Internal energy of a polyatomic ideal gas)

Related End-of-Chapter Exercises: 10-27.

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. Since 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 $E_{int} = (3/2)nRT$, while for the diatomic gas at room temperature it is $E_{int} = (5/2)nRT$. 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 kPa × 1 liter = $(1 \times 10^3 \text{ Pa}) \times (1 \times 10^3 \text{ m}^3) = 1 \text{ Pa m}^3 = 1 \text{ Nm} = 1 \text{ J}.$

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.

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

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

Using the ideal gas law we can say that PV = nRT = 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 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.

Step 3: Plot these points on a P-V diagram similar to that in Figure 14.10, 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 14.10: 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 14.11.

Figure 14.11: 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.

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 that $P \times V$ 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 14.12, and we can see that this isotherm, at the higher temperature, is further from the origin than the original isotherm. This is generally true, that the higher the temperature the further from the origin is the isotherm corresponding to that temperature.

Figure 14.12: A *P*-*V* diagram showing two different isotherms. The isotherm in green, farther from the origin, has twice the absolute temperature as the isotherm in blue.





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: 47-52.

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?

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*. Since 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.

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 <i>n</i> , the number of moles of gas, <i>H</i>	PV = nRT, (Equation 14.1)
where $R = 8.31 \text{ J/(mol K)}$ is the universal gas	s constant.

In terms of N, the number of molecules, PV = NkT, (Equation 14.2) where $k = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant.

What Temperature Means

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

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

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.

The energy from each degree of freedom
$$=\frac{1}{2}Nkt = \frac{1}{2}nRt$$
. (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:

$$E_{\text{int}} = NK_{av} = \frac{3}{2}NkT = \frac{3}{2}nRT$$
. (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.

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

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

$$E_{\text{int}} = \frac{6}{2}NkT = 3NkT = 3nRT$$
. (Eq. 14.21: 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 one in blue having half the absolute temperature of the one in green.

