CHAPTER 8.1: KINETIC THEORY OF GASES

A. Learning Objectives: Ideal Gas Laws & Kinetic Theory of Gases

By the end of this section, students will be able to:

- Molecular Model of an Ideal Gas
    - Apply the ideal gas law to situations involving the pressure, volume, temperature, and the number of molecules of a gas
    - Use the unit of moles in relation to numbers of molecules, and molecular and macroscopic masses
    - Explain the ideal gas law in terms of moles rather than numbers of molecules
- Pressure Temperature, and RMS Speed
    - Explain the relations between microscopic and macroscopic quantities in a gas
- Distribution of Molecular Speeds
    - Describe the distribution of molecular speeds in an ideal gas
    - Find the average and most probable molecular speeds in an ideal gas

B. Ideal Gas Law

Molecular Model of an Ideal Gas

In this module, we explore the properties of gases.

In gases, the molecules are much farther apart than those of solids and liquids. Because the typical distances between molecules in gases are large compared to the size of a molecule, the forces between them are considered negligible, except when they come into contact with each other during collisions. Also, at temperatures well above the boiling temperature, the motion of molecules is fast, and the gases expand rapidly to occupy all of the accessible volume. In contrast, in liquids and solids, molecules are closer together, and the behavior of molecules in liquids and solids is highly constrained by the molecules' interactions with one another.

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The Ideal Gas Law

An ideal gas is one in which the molecular distances are so large that we can neglect the forces between molecules.

For ideal gases, it is observed that pressure P is inversely proportional to the volume V of the gas when temperature T and the number of molecules N are constant.

$$P \propto \frac{1}{V} \quad (1)$$

This is known as Boyle's Law, as shown in Figure 1.

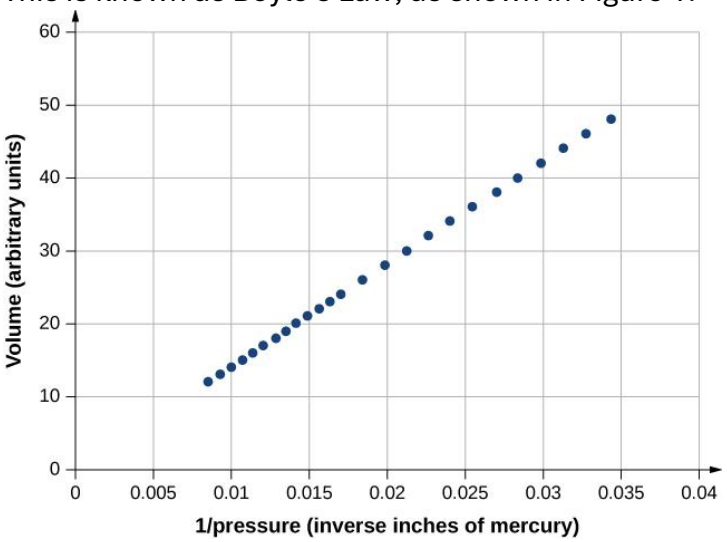


Figure 1: Robert Boyle and his assistant found that volume and pressure are inversely proportional. Here, their data are plotted as V versus 1/p; the linearity of the graph shows the inverse proportionality. The number shown as the volume is actually the height in inches of air in a cylindrical glass tube. The actual volume was that height multiplied by the cross-sectional area of the tube, which Boyle did not publish. The data are from Boyle's book A Defence of the Doctrine Touching the Spring and Weight of the Air..., p. 60.

It is also observed that P is directly proportional to T when V and N are constant,

$$P \propto T \quad (2)$$

This law was first discovered by Jacques Charles (1746–1823) and is known as Charles' Law. (See Figure 2)

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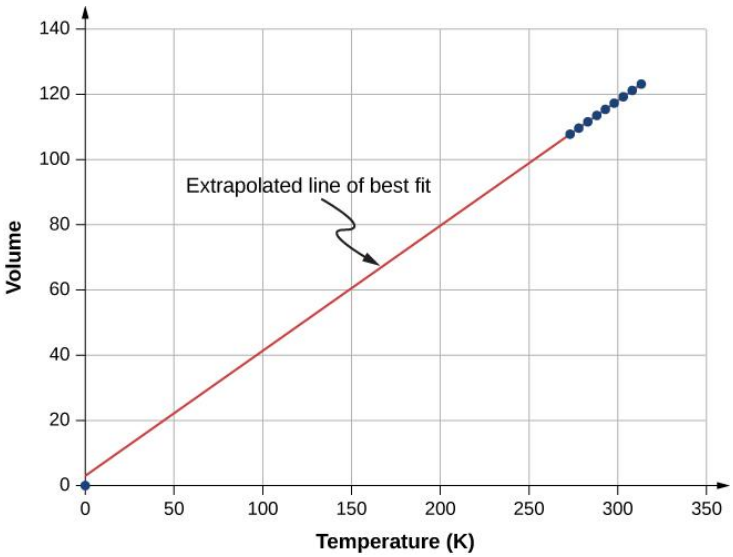


Figure 2: Experimental data showing that at constant pressure, volume is approximately proportional to temperature. The best-fit line passes approximately through the origin.

Pressure is also directly proportional to the number of molecules N when T and V are constant,

$$P \propto N \quad (3)$$

Combining equations (1), (2), and (3) by introducing a constant of proportionality, we get

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

Where k is the constant of proportionality, known as the Boltzmann constant ($k = 1.38 \times 10^{-23}\ J/K$).

$PV = kNT$ is known as the **Ideal Gas Law**.

Mole of Gas & Avogadro's Number

One mole of a substance contains as many molecules as the atoms contained by 12 grams of carbon-12.

The actual number of atoms or molecules in one mole is called **Avogadro's number** (N_A), in recognition of Italian scientist Amedeo Avogadro (1776–1856). He developed the concept of the mole, based on the hypothesis that equal volumes of gas, at the same pressure and temperature, contain equal numbers of molecules. That is, the number is

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independent of the type of gas. This hypothesis has been confirmed, and the value of Avogadro's number is

$$N_A = 6.02 \times 10^{23}\ molecules/mole$$

$$\text{The number of moles} = \text{n} = \frac{\text{total number of molecules}}{\text{Avogadro's Number}} = \frac{N}{N_A}$$

Molar Mass, M, of a gas is defined as the mass of one mole of gas. If m is the mass of a single molecule, then the molar mass is $M = mN_A$.

In terms of number of moles, the Ideal Gas Law can be expressed by making the modifications shown below.

$$PV = NkT$$

Multiply & divide the right-hand side by Avogadro's number, N_A.

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

But $n = \frac{N}{N_A}$ is the number of moles.

$$PV = nN_A kT$$

We define a new constant $R = N_A k$, known as the ideal gas constant or simply the gas constant. Therefore, the ideal Gas Law in terms of the number of moles is

$$PV = nRT$$

In SI units,

$$R = N_A k_B = (6.02 \times 10^{23}\ mol^{-1})\left(1.38 \times 10^{-23}\frac{J}{K}\right) = 8.31\ J/mol\ K$$

In other units,

$$R = 1.99\frac{cal}{mol\ K} = 0.0821\frac{L\ atm}{mol\ K}$$

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You can use the appropriate value of R for a particular problem based on the units of the pressure, volume, and temperature of the gas.

Self-Assess

Question: For an ideal gas with N molecules, what is the relationship between the pressure P, temperature T, and the volume V of a gas? Define a mole.
Answer:
For an ideal gas, $PV = kNT$ where $k = 1.38 \times 10^{-23}\ J/K$ is the Boltzmann constant.

One mole of a substance contains as many molecules as the atoms contained by 12 grams of carbon-12. One mole of any gas contains 6.022×10^{23} molecules, which is independent of the type of gas. 6.022×10^{23} is known as Avogadro's number.

C. Simulation: Properties of Ideal Gases

Activity: Boyle's Law

Link to Simulation: https://phet.colorado.edu/en/simulations/gases-intro
This simulation helps you study the properties of ideal gases.

1. Select the "Laws" button.
2. Pump some gas particles into the container.
3. Select "Temperature" in the "Hold Constant" Menu on the right. We are going to study the effects of changing volume on pressure at constant temperature.
4. Assume that the two fixed lengths of the container are 8.8 nm. The width can be changed by pulling on the handle. Change the volume of the container by changing the width and note the pressure at those widths.

Width (nm)	Volume (cubic nm)	P (atm)	1/P (1/atm)
5			
7			
9			
11			
13			
15			

Plot a graph of V vs 1/P, either using a calculator, a graphing software, or graph paper. A link to an online calculator is provided below.

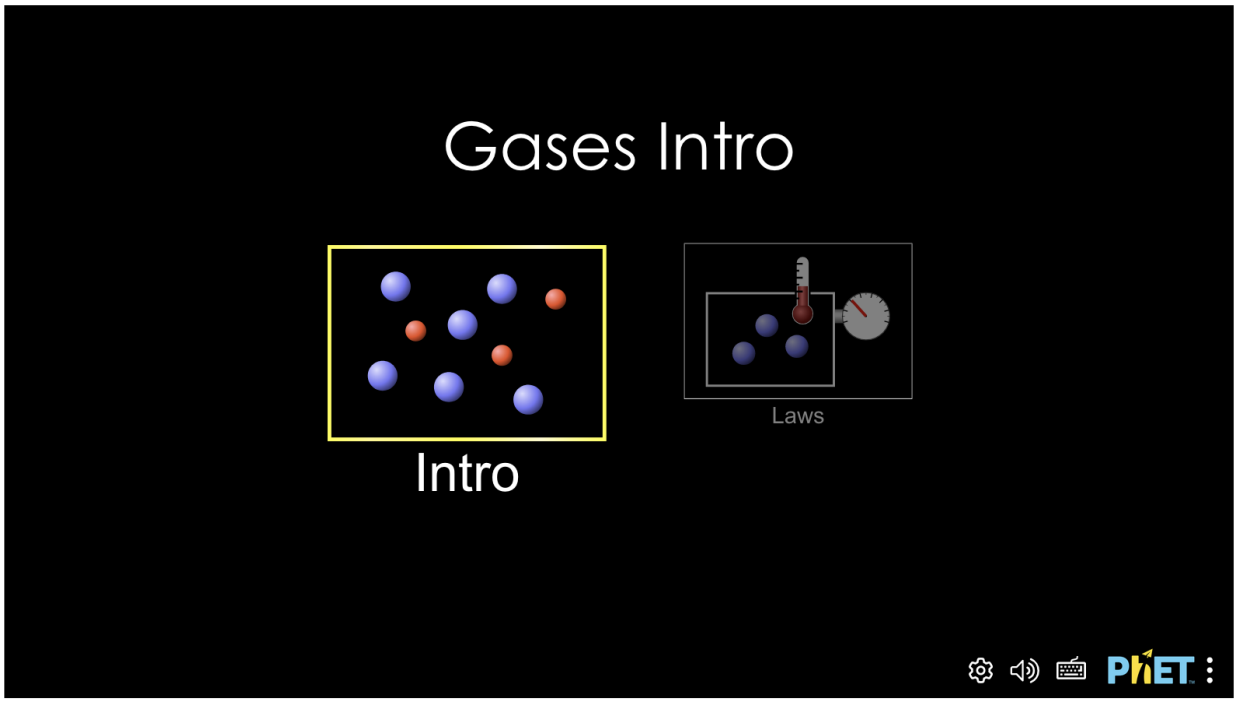
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What does the graph look like? What is the relationship between V & P?

Desmos Graphing Calculator

This is a link to the graphing software Desmos. You can input points to plot on the left side as (x1,y1),(x2,y2), ... To adjust the axes, click on the wrench symbol on the top right corner and change the limits on the axes.



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Activity: Charles' Law

This simulation helps you study the properties of ideal gases.

1. Select the "Laws" button.
2. Pump some gas particles into the container.
3. Select "Pressure" in the "Hold Constant" menu on the right. We are going to study the effects of changing temperature on the volume at constant pressure.

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4. Assume that the two fixed lengths of the container are 8.8 nm. Change the temperature of the gas by adding heat or cooling the gas using the bucket at the bottom of the container. Tabulate your readings as shown.

Width (nm)	Volume (cubic nm)	T (K)
5		
7		
9		
11		
13		
15		

Plot a graph of V vs T, using either a calculator, a graphing software, or graph paper. A link to an online graphing calculator is provided below.

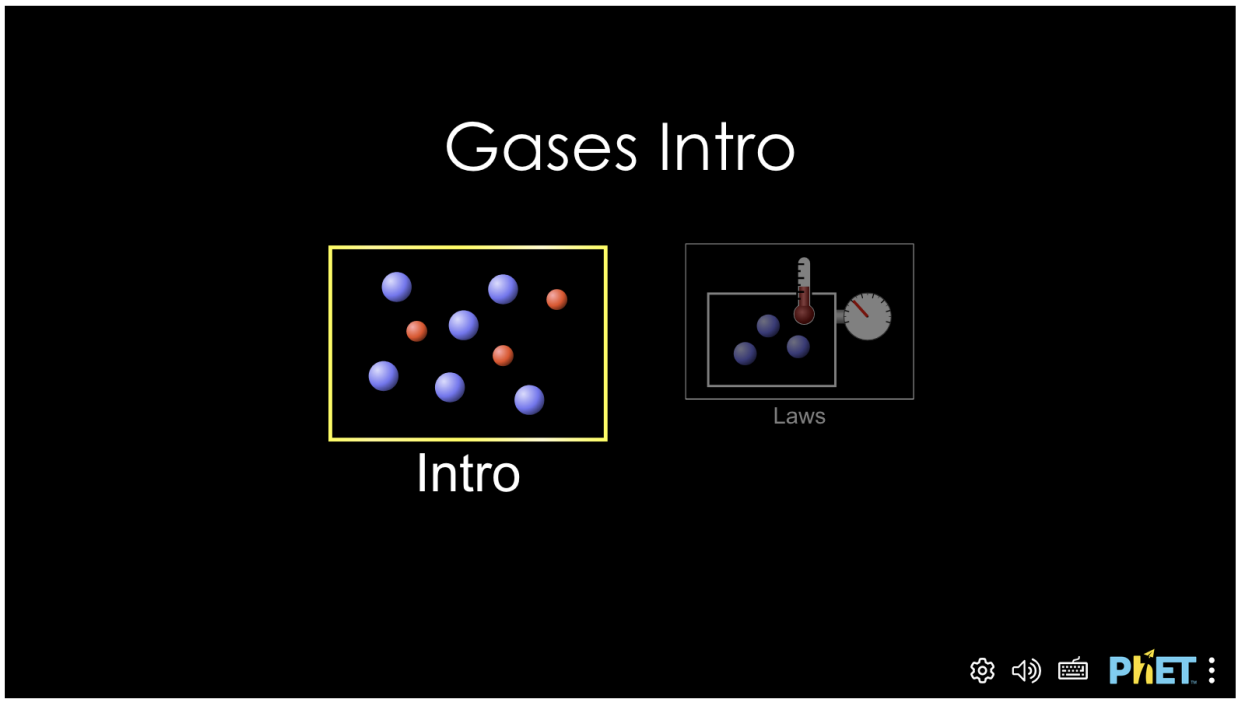
What does the graph look like? What is the relationship between V & T?

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D. Pressure, Temperature, and RMS Speed of an Ideal Gas

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

Pressure Exerted by a Gas

Consider a monoatomic gas. The relationship between pressure, the number of molecules, and the average of the square of the speed over all molecules is found to be

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

Where P is the pressure the gas exerts on the container,
V is the volume of gas in the container,

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N is the number of molecules in the container,
m is the mass of a molecule, and
$\overline{v^2} = \frac{v_1^2+v_2^2+\cdots+v_N^2}{N}$ is the average of the square of the molecular speed, denoted by the bar.

Derivation of Pressure Exerted by a Gas

We derive the equation for the pressure of an ideal gas by making these assumptions about molecules in an ideal gas.

- There is a very large number N of molecules, all identical and each having mass m.
- The molecules obey Newton's laws and are in continuous motion, which is random and isotropic, that is, the same in all directions.
- The molecules are much smaller than the average distance between them, so their total volume is much less than that of their container (which has volume V).
- The molecules make perfectly elastic collisions with the walls of the container, assumed to be rigid, and with each other. Other forces on them, including gravity and the attractions, are negligible (Figure 3).

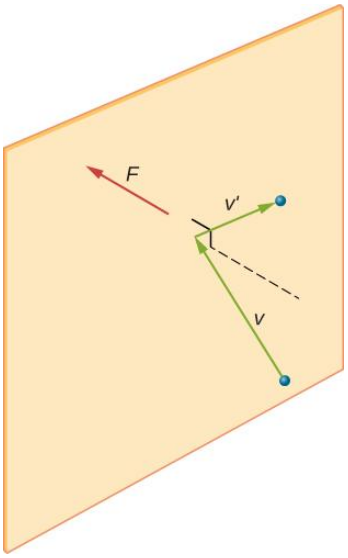


Figure 3: When a molecule collides with a rigid wall, the component of its momentum perpendicular to the wall is reversed. A force is thus exerted on the wall, creating pressure.

Consider a gas enclosed in a volume V. The number density of molecules, $n = \frac{N}{V}$, where N is the number of molecules contained in the volume.

Consider a molecule of mass m traveling in the x-direction with speed v_x and suffering an elastic collision with the wall. The velocity after the collision is $-v_x$.

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The average force exerted by the molecule on the wall in time Δt (Figure 4) is given by the rate of change of its momentum:

$$|F_x| = \frac{|\Delta p|}{\Delta t} = \frac{|-mv_x - mv_x|}{\Delta t} = \frac{2mv_x}{\Delta t}$$

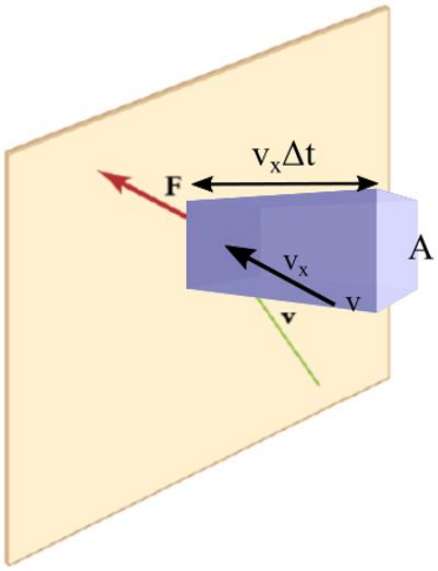


Figure 4: Gas in a box exerts an outward pressure on its walls. A molecule colliding with a rigid wall has its velocity and momentum in the x-direction reversed. This direction is perpendicular to the wall. The components of its velocity and momentum in the y- and z-directions are not changed, which means there is no force parallel to the wall.

During the time interval Δt, consider all molecules that are within a distance $v_x\Delta t$ from the wall. About half of those molecules will travel towards the wall and exert a force.

To calculate the average force exerted on an area A of the wall in time Δt, we need the number of molecules contained in the volume $v_x\Delta tA$ (purple box in Figure 4). The number of molecules that are contained in that volume equals $n \times v_x\Delta tA$.

The total force on the wall of area A in time Δt:

$$F_{x,tot} = \underbrace{\frac{1}{2}n \times v_x\Delta tA}_{see\ note\ 1} \quad \underbrace{\frac{2mv_x}{\Delta t}}_{see\ note\ 2} = nmv_x^2A = \frac{N}{V}mv_x^2A$$

Note 1: Number of molecules hitting the wall in Δt
Note 2: Force exerted by a single molecule

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$$F_{x,tot} = \frac{N}{V} m v_x^2 A$$

$Average\ force\ on\ the\ wall = \bar{F_x} = \frac{N}{V} m\overline{v_x^2} A$ where the bar represents an average over all molecules.

Pressure P on the wall

$$P = \frac{\bar{F_x}}{A} = \frac{N}{V} m\overline{v_x^2}$$

Since the molecules are equally likely to move along the y and the z directions as the x direction, the average of the velocity square in the x-direction is one-third of the average of its total velocity square.

The average of the velocity square in the x direction is

$$\overline{v_x^2} = \frac{1}{3}\overline{v_x^2 + v_y^2 + v_z^2} = \frac{1}{3}\overline{v^2}.$$

Therefore, $PV = \frac{1}{3} N\overline{v^2}$.

The Average Kinetic Energy Per Molecule

Using equation (1), we can calculate the average kinetic energy of a molecule, $\overline{KE} = \overline{\frac{1}{2}mv^2} = \frac{1}{2}m\overline{v^2}$,
where the bar represents an average over all molecules.

From Equation (1), $PV = \frac{1}{3} Nm\overline{v^2}$.

Multiply and divide the right-hand side of equation (1) by 2.

$$PV = \frac{2}{2} \times \frac{1}{3} Nm\overline{v^2} = \frac{2}{3} N \times \overline{KE} \quad (2)$$

From the Ideal Gas Law, $PV = NkT$, where k is the Boltzmann constant.

Substituting for PV in (2), we have

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$$PV = NkT = \frac{2}{3}N \times \overline{KE}$$

Therefore, the average kinetic energy per molecule, $\overline{KE} = \frac{3}{2}kT$.

This calculation produces the result that the average kinetic energy of a molecule is directly related to absolute temperature.

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

The average translational kinetic energy of a molecule, KE, is called **thermal energy**.

The equation $\overline{KE} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ is a molecular interpretation of temperature, and it is valid for gases and reasonably accurate in liquids and solids. It is another definition of temperature based on an expression of the molecular energy.

Note that the equation for the KE **does not** depend on the molecular mass or the pressure, but only on the temperature. If samples of helium and xenon gas, with very different molecular masses, are at the same temperature, the average kinetic energy per molecule is the same.

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Distribution of KE: Maxwell-Boltzmann Distribution

Figure 5 shows the distribution of kinetic energy of molecules at any temperature. The distribution is known as **Maxwell-Boltzmann's distribution**. Note that the average KE is not equal to the most probable KE.

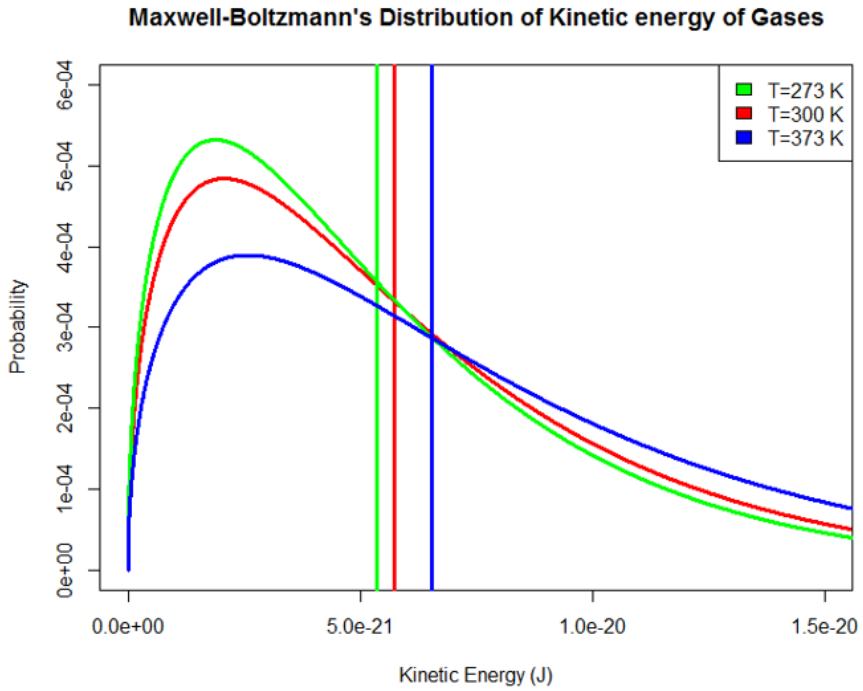


Figure 5: Maxwell-Boltzmann's distribution of kinetic energy of gases

Root Mean Square Speed

The average kinetic energy of gas molecules is given by

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

Rearranging the equation above, we get

$$\overline{v^2} = \frac{3kT}{m}.$$

We define the **root mean square speed** (RMS speed) as

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

The rms speed of a gas molecule is directly proportional to the square root of temperature and inversely proportional to the square root of mass.

$$v_{rms} \propto \sqrt{T} \quad and \quad v_{rms} \propto \frac{1}{\sqrt{m}}$$

IN terms of molar mass M in kg/mol: $M = mN_A \rightarrow m = M/N_A$ where N_A is Avogadro's number.

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3kTN_A}{M}} = \sqrt{\frac{3RT}{M}}$$ using $R = kN_A$ is the ideal gas constant

Mean Square Speed

Average of the square of speed ≠ Square of the average speed

Average of the square of speed for N molecules: $\overline{v^2} = \frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N}$

$\neq$

Square of the average speed: $(\bar{v})^2 = \left(\frac{v_1 + v_2 + \cdots + v_N}{N}\right)^2$

Internal Energy of an Ideal Gas

The internal energy of a thermodynamic system is the sum of the mechanical energies of all of the molecules (N) in it. We can now give an equation for the internal energy of a monatomic ideal gas. In such a gas, the molecules' only energy is their translational kinetic energy. Therefore, denoting the internal energy by E_{int}, we simply have

$$E_{int} = N \times \overline{KE} = N \times \frac{3}{2} k_B T = \frac{3}{2} N k_B T$$

Or often, we would like to use this equation in terms of moles, $n = \frac{N}{N_A}$.

$$E_{int} = \frac{3}{2} n N_A k T = \frac{3}{2} n R T, \quad where\ R = N_A k.$$

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Summary of Pressure, Temperature & RMS Speed of an Ideal Gas

For an ideal gas with a pressure P, volume V, and containing N molecules each with mass m, we have

1. $PV = \frac{1}{3}Nm\overline{v^2}$, where $\overline{v^2}$ is the average of the square of molecular speeds.
2. The average kinetic energy per molecule is $\overline{KE} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$, where k is the Boltzmann constant.
3. Root Mean Square speed $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$
4. Internal energy of an ideal gas: $E_{int} = \frac{3}{2}Nk_BT$. IN terms of the number of moles n, $E_{int} = \frac{3}{2}nRT$, where R is the ideal gas constant.

Self-Assess

Question: What is the dependence of the average kinetic energy per molecule of an ideal gas on the temperature?

Answer:

The average KE per molecule of a gas is directly proportional to the absolute temperature T of the gas.

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

E. Worked Example: Calculating Kinetic Energy and Speed of a Gas Molecule

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

Strategy

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

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$$

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Before substituting values into this equation, we must convert the given temperature into kelvin: $T = (20.0 + 273)K = 293K$.

We can find the rms speed of a nitrogen molecule by using the equation

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$

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

$$m = \frac{M}{N_A} = \frac{2(14.0067) \times 10^{-3}\ kg\ mol^{-1}}{6.022 \times 10^{23}\ mol^{-1}} = 4.65 \times 10^{-26} kg$$

Solution

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

$$\overline{K} = \frac{3}{2} k_B T = \frac{3}{2}(1.38 \times 10^{-23}\ J/K)(293\ K) = 6.07 \times 10^{-21} J$$

b) Substituting this mass and the value for k_B into the equation for v_{rms} yields

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

Significance

Note that the average kinetic energy of the molecule is independent of the type of molecule. The average translational kinetic energy depends only on absolute temperature. The kinetic energy is very small compared to macroscopic energies, so that we do not feel when an air molecule hits our skin. On the other hand, it is much greater than the typical difference in gravitational potential energy when a molecule moves from, say, the top to the bottom of a room, so our neglect of gravitation is justified in typical real-world situations. The rms speed of the nitrogen molecule is surprisingly large. These large molecular velocities do not yield macroscopic movement of air, since the molecules move in all directions with equal likelihood. The *mean free path* (the distance a molecule moves on average between collisions, discussed a bit later in this section) of molecules in air is

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very small, so the molecules move rapidly but do not get very far in a second. The high value for rms speed is reflected in the speed of sound, which is about 340 m/s at room temperature. The higher the rms speed of air molecules, the faster sound vibrations can be transferred through the air. The speed of sound increases with temperature and is greater in gases with small molecular masses, such as helium (see Figure 6).

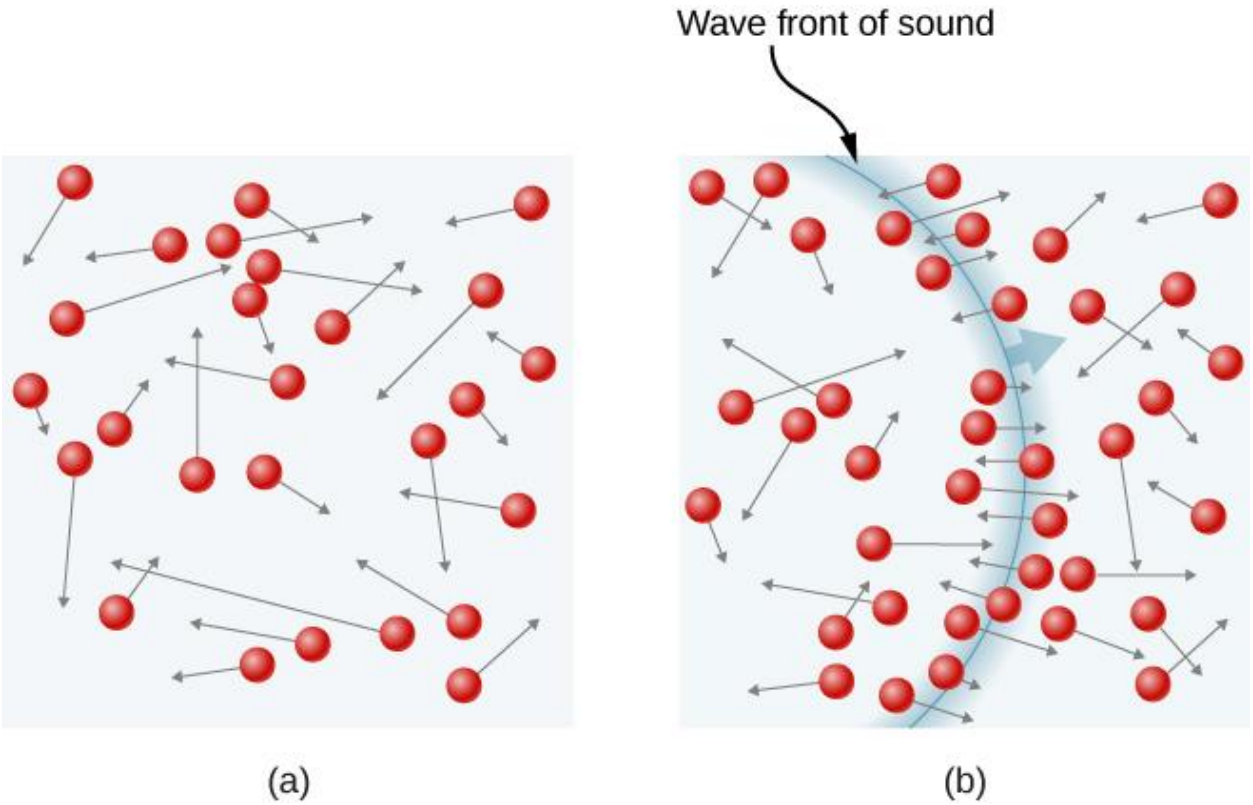


Figure 6: (a) In an ordinary gas, so many molecules move so fast that they collide billions of times every second. (b) Individual molecules do not move very far in a small amount of time, but disturbances like sound waves are transmitted at speeds related to the molecular speeds.

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F. Worked Example: Calculating Temperature: Escape Velocity of Helium Atoms

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

Strategy

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

Solution

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

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

To yield

$$T = \frac{m\overline{v^2}}{2k_B}$$

4. Substitute the known values into the equations and solve for the unknowns,

$$m = \frac{M}{N_A} = \frac{4.0026 \times 10^{-3}\ kg\ mol^{-1}}{6.022 \times 10^{23}\ mol} = 6.65 \times 10^{-27}\ kg$$

and

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

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Significance

This temperature is much higher than atmospheric temperature, which is approximately 250 K (−25°C or −10°F) at high elevation. Very few helium atoms are left in the atmosphere, but many were present when the atmosphere was formed, and more are always being created by radioactive decay (see the chapter on nuclear physics). The reason for the loss of helium atoms is that a small number of helium atoms have speeds higher than Earth's escape velocity, even at normal temperatures. The speed of a helium atom changes from one collision to the next, so that at any instant, there is a small but nonzero chance that the atom's speed is greater than the escape velocity. The chance is high enough that over the lifetime of Earth, almost all the helium atoms that have been in the atmosphere have reached escape velocity at high altitudes and escaped from Earth's gravitational pull. Heavier molecules, such as oxygen, nitrogen, and water, have smaller rms speeds, and so it is much less likely that any of them will have speeds greater than the escape velocity. In fact, the likelihood is so small that billions of years are required to lose significant amounts of heavier molecules from the atmosphere. Figure 7 shows the effect of a lack of an atmosphere on the Moon. Because the gravitational pull of the Moon is much weaker, it has lost almost its entire atmosphere. The atmospheres of Earth and other bodies are compared in this chapter's exercises.

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Figure 7: This photograph of Apollo 17 Commander Eugene Cernan driving the lunar rover on the Moon in 1972 looks as though it was taken at night with a large spotlight. In fact, the light is coming from the Sun. Because the acceleration due to gravity on the Moon is so low (about 1/6 that of Earth), the Moon's escape velocity is much smaller. As a result, gas molecules escape very easily from the Moon, leaving it with virtually no atmosphere. Even during the daytime, the sky is black because there is no gas to scatter sunlight. (credit: Harrison H. Schmitt/NASA)

G. Distribution of Molecular Speeds

The motion of molecules in a gas is random in magnitude and direction for individual molecules, but a gas of many molecules has a predictable distribution of molecular speeds. This distribution is called the **Maxwell-Boltzmann distribution**, after its originators, who calculated it based on kinetic theory, and has since been confirmed experimentally, as shown in Figure 8. The distribution has a long tail, because a few molecules may go several times the rms speed. The most probable speed v_p is less than the rms speed v_{rms}.

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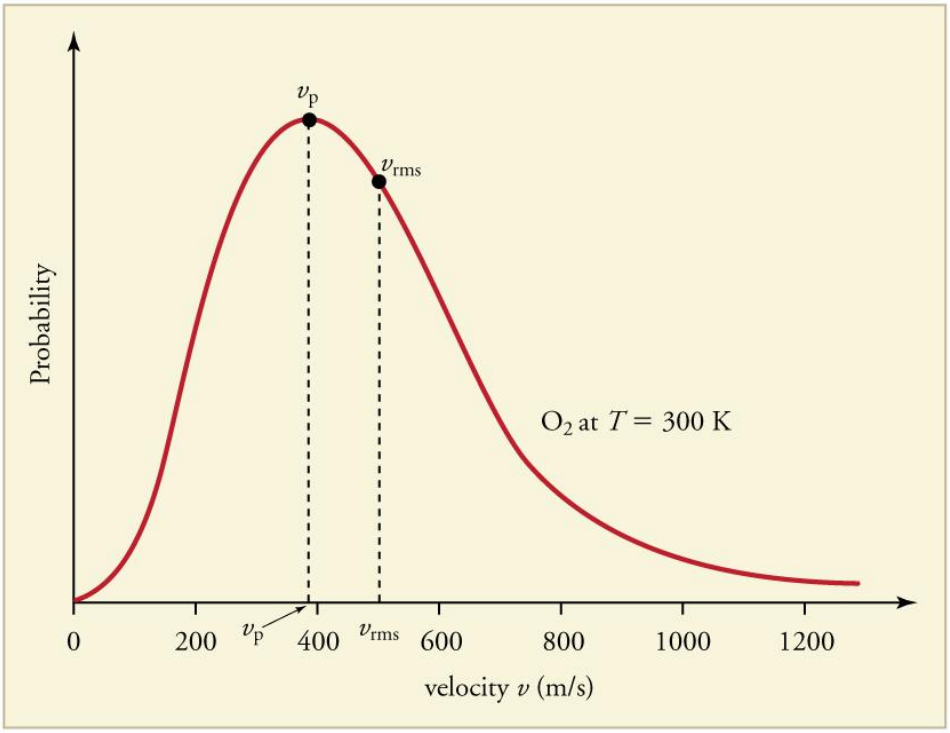


Figure 8: The Maxwell-Boltzmann distribution of molecular speeds in an ideal gas. The most likely speed, v_p, is less than the rms speed, v_{rms}. Although very high speeds are possible, only a tiny fraction of the molecules have speeds that are an order of magnitude greater than v_{rms}.

Self-Assess

Question: What is the relationship between the average KE of a gas molecule and the temperature T? What happens to the average KE of the gas molecule when the temperature increases? What is the relationship between the rms velocity of a gas with its temperature and mass of the molecules?

Answer:

The average kinetic energy of a gas molecule, $KE = \frac{3}{2}kT$ where k is the Boltzmann constant. KE of the gas is directly proportional to the temperature; therefore, KE of the gas increases as the temperature increases.

The rms velocity of a gas molecule is directly proportional to the square root of temperature and inversely proportional to the square root of mass.

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

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