Chapter 18
Thermal Properties of Matter

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Goals for Chapter 18

• To relate the pressure, volume, and temperature of a gas
• To see how molecular interactions determine the properties of a substance
• To relate temperature and pressure to the kinetic energy of gas molecules
• To learn what the heat capacities of a gas tell us about the motion of its molecules
• To discover what determines if a substance is a gas, liquid, or solid
Introduction

• How does the speed of the molecules in the air above the frying pan compare with that of the ones in the rest of the kitchen?

• How do the atoms of a gas determine its temperature and pressure?

• We’ll see how the microscopic properties of matter determine its macroscopic properties.
Equations of state and the ideal-gas law

- Quantities such as pressure, volume, temperature, and the amount of a substance are *state variables* because they describe the state of the substance.

- The *equation of state* relates the state variables.

- The ideal-gas law, \( pV = nRT \), is an equation of state for an ideal gas.

- The *molar mass* \( M \) (*molecular weight*) is the mass per mole. The total mass of \( n \) moles is \( m_{\text{total}} = nM \).

- Read Problem-Solving Strategy 18.1.

- Follow Example 18.1.
There are relationships among the large-scale or *macroscopic* properties of a substance, such as pressure, volume, temperature, and mass. But we can also describe a substance using a *microscopic* perspective. This means investigating small-scale quantities such as the masses, speeds, kinetic energies, and momenta of the individual molecules that make up a substance.
The macroscopic and microscopic descriptions are intimately related. For example, the (microscopic) forces that occur when air molecules strike a solid surface (such as your skin) cause (macroscopic) atmospheric pressure. To produce standard atmospheric pressure of $1.01 \times 10^5$ Pa, $10^{32}$ molecules strike your skin every day with an average speed of over 1700 km/h (1000 mi/h)!
In this chapter we’ll begin our study of the thermal properties of matter by looking at some macroscopic aspects of matter in general. We’ll pay special attention to the *ideal gas*, one of the simplest types of matter to understand. Using our knowledge of momentum and kinetic energy, we’ll relate the macroscopic properties of an ideal gas to the microscopic behavior of its individual molecules.
The variables like pressure, volume, temperature, and amount of substance describe the state of the material and are called state variables. These variables are not independent. In a few cases the relationship among $p$, $V$, $T$, and $m$ (or $n$) is simple enough that we can express it as an equation called the equation of state. When it’s too complicated for that, we can use graphs or numerical tables. Even then, the relationship among the variables still exists; we call it an equation of state even when we don’t know the actual equation.
Here’s a simple (though approximate) equation of state for a solid material

\[ V = V_0[1 + \beta(T - T_0) - k(p - p_0)] \]

**Measurements** of the behavior of various gases lead to three conclusions:
1. The volume \( V \) is proportional to the number of moles \( n \). If we double the number of moles, keeping pressure and temperature constant, the volume doubles.
2. The volume varies *inversely* with the absolute pressure $p$. If we double the pressure while holding the temperature $T$ and number of moles $n$ constant, the gas compresses to one-half of its initial volume. In other words, $pV = \text{constant}$ when $n$ and $T$ are constant.

3. The pressure is proportional to the *absolute* temperature. If we double the absolute temperature, keeping the volume and number of moles constant, the pressure doubles. In other words, $p = (\text{constant}) T$ when $n$ and $V$ are constant. These three relationships can be combined neatly into a single equation, called the **ideal-gas equation**: 

$$pV = nRT \quad \text{(ideal-gas equation)} \quad (18.3)$$
This is an idealized model; it works best at very low pressures and high temperatures, when the gas molecules are far apart and in rapid motion. Why?

We might expect that the constant $R$ in the ideal-gas equation would have different values for different gases, but it turns out to have the same value for all gases, at least at sufficiently high temperature and low pressure. It is called the gas constant (or ideal-gas constant). The numerical value of $R$ depends on the units of $p$, $V$, and $T$. In SI units, in which the unit of $p$ is Pa ($\text{N/m}^2$) and the unit of $V$ is $\text{m}^3$, the current best numerical value of $R$ is

$$R = 8.314472(15) \text{ J/mol. K}$$
\[ pV = \left( \frac{N}{m^2} \right) (m^3) = N \cdot m = \text{Joule} \]

\[ R = 0.08206 \frac{L \cdot \text{atm}}{\text{mol} \cdot \text{K}} \]

We can express the ideal-gas equation, Eq. (18.3), in terms of the mass \( m_{\text{total}} \) of gas, using \( m_{\text{total}} = nM \) from Eq. (18.2):

\[ pV = \frac{m_{\text{total}}}{M} RT \]

From this we can get an expression for the density \( \rho = \frac{m_{\text{total}}}{V} \) of the gas:

\[ \rho = \frac{pM}{RT} \]
For a *constant mass* (or constant number of moles) of an ideal gas the product \( nR \) is constant, so the quantity \( pV/T \) is also constant. If the subscripts 1 and 2 refer to any two states of the same mass of a gas, then

\[
p_1 V_1 / T_1 = p_2 V_2 / T_2 \quad \text{(ideal gas, constant mass)} \quad (18.6)
\]

Notice that you don’t need the value of \( R \) to use this equation.
What is the volume of a container that holds exactly 1 mole of an ideal gas at standard temperature and pressure (STP), defined as $T = 0^\circ C = 273.15$ K and $p = 1$ atm $= 1.013 \times 10^5$ Pa?

$$V = \frac{nRT}{p} = \frac{(1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(273.15 \text{ K})}{1.013 \times 10^5 \text{ Pa}}$$

$$= 0.0224 \text{ m}^3 = 22.4 \text{ L}$$
Find the variation of atmospheric pressure with elevation in the earth’s atmosphere. Assume that at all elevation, \( T = 0^\circ C \) and \( g = 9.80 \text{ m/s}^2 \)

\[
\begin{align*}
\frac{\Delta A}{dV} & \quad \Delta p\\
\Delta p & = \frac{F}{A} = -pA dy \cdot g\\
\end{align*}
\]

\[
\therefore \frac{d\Delta p}{dy} = -pg
\]
\[
P = \frac{\beta M}{RT}; \quad \frac{dp}{dy} = -pg = -\frac{\beta M}{RT}g
\]

\[
\int \frac{dp}{p} = -\frac{Mg}{RT} \int_{y_1}^{y_2}
\]

\[
\ln \frac{p_2}{p_1} = -\frac{Mg}{RT} (y_2 - y_1)
\]

\[
\frac{p_2}{p_1} = e^{-\frac{Mg}{RT} (y_2 - y_1)}
\]
Let $y_i = 0$ at sea level.

$p_0 = 1.013 \times 10^5 \text{ Pa}$

$p = p_0 e^{-mg/RT}$
The graph shows the relationship between pressure $p$ and $y$ with the equation $p = p_0 e^{-M_g y/RT}$.
At the summit of Mount Everest, where \( y = 8863 \text{ m} \),

\[
\frac{Mgy}{RT} = \frac{(28.8 \times 10^{-3} \text{ kg/mol})(9.80 \text{ m/s}^2)/(8863 \text{ m})/(8.314 \text{ J/mol.K})(273 \text{ K})}{1.10} = 0.337 \times 10^5 \text{ Pa} = 0.33 \text{ atm}
\]

The assumption of constant temperature isn’t realistic, and \( g \) decreases a little with increasing elevation. Even so, this example shows why mountaineers need to carry oxygen on Mount Everest. It also shows why jet airliners, which typically fly at altitudes of 8000 to 12,000 m, *must* have pressurized cabins for passenger comfort and health.
The van der Waals equation

• The model used for the ideal-gas equation ignores the volumes of molecules and the attractive forces between them. (See Figure 18.5(a) below.)

• The *van der Waals equation* is a more realistic model. (See Figure 18.5(b) below.)

(a) An idealized model of a gas

Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

(b) A more realistic model of a gas

Gas molecules have volume, which reduces the volume in which they can move.

They exert attractive forces on each other, which reduces the pressure ...

... and they exert forces on the container’s walls.
The ideal-gas equation can be obtained from a simple molecular model that ignores the volumes of the molecules themselves and the attractive forces between them (Fig. 18.5a). Meanwhile, we mention another equation of state, the van der Waals equation, that makes approximate corrections for these two omissions (Fig. 18.5b). This equation was developed by the 19th-century Dutch physicist J. D. van der Waals; the interaction between atoms that we discussed in Section 14.4 was named the van der Waals interaction after him. The van der Waals equation is

\[ \left( p + \frac{an^2}{V^2} \right)(V - nb) = nRT \]  

(18.7)
The constants $a$ and $b$ are empirical constants, different for different gases. Roughly speaking, $b$ represents the volume of a mole of molecules; the total volume of the molecules is then $nb$, and the volume remaining in which the molecules can move is $V-nb$.
The constant $a$ depends on the attractive intermolecular forces, which reduce the pressure of the gas for given values of $n$, $V$, and $T$ by *pulling* the molecules together as they *push* on the walls of the container. The decrease in pressure is proportional to the number of molecules per unit volume in a layer near the wall (which are exerting the pressure on the wall) and is also proportional to the number per unit volume in the next layer beyond the wall (which are doing the attracting). Hence the decrease in pressure due to intermolecular forces is proportional to $n^2/V^2$. 
When \( n/V \) is small (that is, when the gas is *dilute*), the average distance between molecules is large, the corrections in the van der Waals equation become insignificant, and Eq. (18.7) reduces to the ideal-gas equation. As an example, for carbon dioxide gas (\( \text{CO}_2 \)) the constants in the van der Waals equation are \( a = 0.364 \text{ J} \cdot \text{m}^3/\text{mol}^2 \) and \( b = 4.27 \times 10^{-5} \text{ m}^3/\text{mol} \). We found in Example 18.1 that 1 mole of an ideal gas at \( T = 0\,^\circ\text{C} = 273.15 \text{ K} \) and \( p = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} \) occupies a volume \( V = 0.0224 \text{ m}^3 \); according to Eq. (18.7), 1 mole of \( \text{CO}_2 \) occupying this volume at this temperature would be at a pressure 532 Pa less than 1 atm, a difference of only 0.5% from the ideal-gas value.
We could in principle represent the $p$-$V$-$T$ relationship graphically as a *surface* in a three-dimensional space with coordinates $p$, $V$, and $T$. This representation sometimes helps us grasp the overall behavior of the substance, but ordinary two-dimensional graphs are usually more convenient. One of the most useful of these is a set of graphs of pressure as a function of volume, each for a particular constant temperature. Such a diagram is called a *pV-diagram*. Each curve, representing behavior at a specific temperature, is called an *isotherm*, or a *pV-isotherm*. 
A *pV-diagram* is a graph of pressure as a function of volume.

Figure 18.6 at the right is a *pV*-diagram for an ideal gas at various temperatures.

Each curve represents pressure as a function of volume for an ideal gas at a single temperature.

For each curve, *pV* is constant and is directly proportional to *T* (Boyle’s law).

\[ T_4 > T_3 > T_2 > T_1 \]
18.7 A $pV$-diagram for a nonideal gas, showing isotherms for temperatures above and below the critical temperature $T_c$. The liquid–vapor equilibrium region is shown as a green shaded area. At still lower temperatures the material might undergo phase transitions from liquid to solid or from gas to solid; these are not shown in this diagram.

$$T_4 > T_3 > T_c > T_2 > T_1$$

Above the critical temperature $T_c$ there is no liquid–vapor phase transition.

Below $T_c$, the material condenses to liquid as it is compressed.
At temperatures below the isotherms develop flat regions in which we can compress the material (that is, reduce the volume $V$) without increasing the pressure $p$. Observation shows that the gas is condensing from the vapor (gas) to the liquid phase. The flat parts of the isotherms in the shaded area of Fig. 18.7 represent conditions of liquid-vapor phase equilibrium. As the volume decreases, more and more material goes from vapor to liquid, but the pressure does not change. (To keep the temperature constant during condensation, we have to remove the heat of vaporization, discussed in Section 17.6.)
When we compress such a gas at a constant temperature $T_2$ in Fig. 18.7, it is vapor until point $a$ is reached. Then it begins to liquefy; as the volume decreases further, more material liquefies, and both the pressure and the temperature remain constant. At point $b$, all the material is in the liquid state. After this, any further compression requires a very rapid rise of pressure, because liquids are in general much less compressible than gases. At a lower constant temperature $T_1$ similar behavior occurs, but the condensation begins at lower pressure and greater volume than at the constant temperature $T_2$. 
At temperatures greater than $T_c$ no phase transition occurs as the material is compressed; at the highest temperatures, such as $T_4$ the curves resemble the ideal-gas curves of Fig. 18.6. We call $T_c$ the *critical temperature* for this material. In Section 18.6 we’ll discuss what happens to the phase of the gas above the critical temperature.
We will use $pV$-diagrams often in the next two chapters. We will show that the area under a $pV$-curve (whether or not it is an isotherm) represents the work done by the system during a volume change. This work, in turn, is directly related to heat transfer and changes in the internal energy of the system.
Molecules and Intermolecular Forces

Any specific chemical compound is made up of identical **molecules**. The smallest molecules contain one atom each and are of the order of $10^{-10}$ in size; the largest contain many atoms and are at least 10,000 times larger. In gases the molecules move nearly independently; in liquids and solids they are held together by intermolecular forces. These forces arise from interactions among the electrically charged particles that make up the molecules. Gravitational forces between molecules are negligible in comparison with electrical forces.
18.8 How the force between molecules and their potential energy of interaction depend on their separation $r$.

$r =$ separation between molecules

Molecules

$U, F_r$

Force

Potential energy

For $r < r_0$, $F_r > 0$; the force between molecules is repulsive.

For $r > r_0$, $F_r < 0$; the force between molecules is attractive.

At a separation $r = r_0$, the potential energy of the two molecules is minimum and the force between the molecules is zero.
Figure 18.8 also shows the potential energy as a function of $r$. This function has a minimum at $r_0$, where the force is zero. The two curves are related by $F_r(r) = -dU/dr$, as we showed in Section 7.4. Such a potential-energy function is often called a potential well. A molecule at rest at a distance $r_0$ from a second molecule would need an additional energy $|U_0|$, the “depth” of the potential well, to “escape” to an indefinitely large value of $r$. 
Molecules are always in motion; their kinetic energies usually increase with temperature. At very low temperatures the average kinetic energy of a molecule may be much less than the depth of the potential well. The molecules then condense into the liquid or solid phase with average intermolecular spacings of about $r_0$. But at higher temperatures the average kinetic energy becomes larger than the depth $|U_0|$ of the potential well. Molecules can then escape the intermolecular force and become free to move independently, as in the gaseous phase of matter.
In *solids*, molecules vibrate about more or less fixed points. In a crystalline solid these points are arranged in a *crystal lattice*. Figure 18.9 shows the cubic crystal structure of sodium chloride, and Fig. 18.10 shows a scanning tunneling microscope image of individual silicon atoms on the surface of a crystal.
18.9 Schematic representation of the cubic crystal structure of sodium chloride (ordinary salt).
18.10 A scanning tunneling microscope image of the surface of a silicon crystal. The area shown is only 9.0 nm \((9.0 \times 10^{-9} \text{ m})\) across. Each blue “bead” is an individual silicon atom; you can clearly see how these atoms are arranged in a (nearly) perfect array of hexagons.
One mole is the amount of substance that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12.

The number of molecules in a mole is called Avogadro’s number, denoted by $N_A$. The current best numerical value of $N_A$ is

$$N_A = 6.02214179(30) \times 10^{23} \text{ molecules/mol (Avogadro’s number)}$$

The molar mass $M$ of a compound is the mass of 1 mole. It is equal to the mass $m$ of a single molecule multiplied by Avogadro’s number:

$$M = N_A m$$

(18.8) (molar mass, Avogadro’s number, and mass of a molecule)
Moles and Avogadro’s number

• One *mole* of a substance contains as many elementary entities (atoms or molecules) as there are atoms in 0.012 kg of carbon-12.

• One mole of a substance contains *Avogadro’s number* $N_A$ of molecules.

• $N_A = 6.022 \times 10^{23}$ molecules/mol

• The *molar mass* $M$ is the mass of one mole.

• $M = N_A m$, where $m$ is the mass of a single molecule.

• Follow Example 18.5, which illustrates atomic and molecular mass.
Find the mass of a single hydrogen atom and of a single oxygen molecule.

**EXECUTE:** For atomic hydrogen the atomic mass (molar mass) is 
\[ M_H = 1.008 \text{ g/mol}, \] 
so the mass \( m_H \) of a single hydrogen atom is 
\[
m_H = \frac{1.008 \text{ g/mol}}{6.022 \times 10^{23} \text{ atoms/mol}} = 1.674 \times 10^{-24} \text{ g/atom}
\]

For oxygen the atomic mass is 16.0 g/mol, so for the diatomic (two-atom) oxygen molecule the molar mass is 32.0 g/mol. Then the mass of a single oxygen molecule is 
\[
m_{O_2} = \frac{32.0 \text{ g/mol}}{6.022 \times 10^{23} \text{ molecules/mol}} = 53.1 \times 10^{-24} \text{ g/molecule}
\]
Kinetic-molecular model of an ideal gas

• The assumptions of the *kinetic-molecular model* are:

1. A container contains a very large number of identical molecules.

2. The molecules behave like point particles that are small compared to the size of the container and the average distance between molecules.

3. The molecules are in constant motion and undergo perfectly elastic collisions.

4. The container walls are perfectly rigid and do not move.
Collisions and gas pressure

• Pressure is caused by the forces that gas molecules exert on the walls of the container during collisions.

All molecules are assumed to have the same magnitude $|v_x|$ of $x$-velocity.

• Velocity component parallel to the wall ($y$-component) does not change.
• Velocity component perpendicular to the wall ($x$-component) reverses direction.
• Speed $v$ does not change.
Our program is first to determine the *number* of collisions that occur per unit time for a certain area $A$ of wall. Then we find the total momentum change associated with these collisions and the force needed to cause this momentum change. From this we can determine the pressure, which is force per unit area, and compare the result to the ideal-gas equation.
To begin, we will assume that all molecules in the gas have the same magnitude of $x$-velocity, $|v_x|$. This isn’t right, but making this temporary assumption helps to clarify the basic ideas. We will show later that this assumption isn’t really necessary.

As shown in Fig. 18.11, for each collision the $x$-component of velocity changes from $-|v_x|$ to $+|v_x|$. So the $x$-component of momentum changes from $-m|v_x|$ to $+m|v_x|$, and the change in the $x$-component of momentum is $m|v_x| - (-m|v_x|) = 2m|v_x|$. 
If a molecule is going to collide with a given wall area $A$ during a small time interval $dt$, then at the beginning of $dt$ it must be within a distance $|v_x| \, dt$ from the wall (Fig. 18.12) and it must be headed toward the wall. So the number of molecules that collide with $A$ during $dt$ is equal to the number of molecules within a cylinder with base area $A$ and length $|v_x| \, dt$ that have their $x$-velocity aimed toward the wall. The volume of such a cylinder is $A |v_x| \, dt$. Assuming that the number of molecules per unit volume ($N/V$) is uniform, the number of molecules in this cylinder is $(N/V)(A |v_x| \, dt)$. On the average, half of these molecules are moving toward the wall and half are moving away from it. So the number of collisions with $A$ during $dt$ is

$$\frac{1}{2} \left( \frac{N}{V} \right) (A |v_x| \, dt)$$
For the system of all molecules in the gas, the total momentum change \( dP_x \) during \( dt \) is the number of collisions multiplied by \( 2m|v_x| \):

\[
dP_x = \frac{1}{2} \left( \frac{N}{V} \right)(A|v_x| dt)(2m|v_x|) = \frac{NAmv_x^2 dt}{V} \quad (18.9)
\]

(We are using capital \( P \) for total momentum and small \( p \) for pressure. Be careful!) We wrote \( v_x^2 \) rather than \( |v_x|^2 \) in the final expression because the square of the absolute value of a number is equal to the square of that number. The rate of change of momentum component \( P_x \) is

\[
\frac{dP_x}{dt} = \frac{NAmv_x^2}{V} \quad (18.10)
\]
According to Newton’s second law, this rate of change of momentum equals the force exerted by the wall area $A$ on the gas molecules. From Newton’s third law this is equal and opposite to the force exerted on the wall by the molecules. Pressure $p$ is the magnitude of the force exerted on the wall per unit area, and we obtain

$$p = \frac{F}{A} = \frac{Nm v_x^2}{V}$$  \hspace{1cm} (18.11)

The pressure exerted by the gas depends on the number of molecules per volume ($N/V$), the mass $m$ per molecule, and the speed of the molecules.
Pressure and Molecular Kinetic Energies

We mentioned that $|v_x|$ is really not the same for all the molecules. But we could have sorted the molecules into groups having the same $|v_x|$ within each group, then added up the resulting contributions to the pressure. The net effect of all this is just to replace $v_x^2$ in Eq. (18.11) by the average value of $v_x^2$, which we denote by $(v_x^2)_{av}$. We can relate $(v_x^2)_{av}$ to the speeds of the molecules. The speed $v$ of a molecule is related to the velocity components $v_x$, $v_y$, and $v_z$ by

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

We can average this relation over all molecules:

$$(v^2)_{av} = (v_x^2)_{av} + (v_y^2)_{av} + (v_z^2)_{av}$$
But there is no real difference in our model between the x-, y-, and z-directions. (Molecular speeds are very fast in a typical gas, so the effects of gravity are negligibly small.) It follows that \((v_x^2)_{av}\), \((v_y^2)_{av}\), and \((v_z^2)_{av}\) must all be equal. Hence \((v^2)_{av}\) is equal to \(3(v_x^2)_{av}\) and

\[
(v_x^2)_{av} = \frac{1}{3} (v^2)_{av}
\]

so Eq. (18.11) becomes

\[
pV = \frac{1}{3} Nm(v^2)_{av} = \frac{2}{3} N \left[ \frac{1}{2} m(v^2)_{av} \right]
\]

(18.12)
We notice that \( \frac{1}{2}m(v^2)_{av} \) is the average translational kinetic energy of a single molecule. The product of this and the total number of molecules \( N \) equals the total random kinetic energy \( K_{tr} \) of translational motion of all the molecules. (The notation \( K_{tr} \) reminds us that this is the energy of translational motion. There may also be energies associated with molecular rotation and vibration.) The product \( pV \) equals two-thirds of the total translational kinetic energy:

\[
pV = \frac{2}{3}K_{tr}
\]  

(18.13)

Now we compare this with the ideal-gas equation,

\[
pV = nRT
\]

which is based on experimental studies of gas behavior. For the two equations to agree, we must have

\[
K_{tr} = \frac{3}{2}nRT
\]

(average translational kinetic energy of \( n \) moles of ideal gas)  

(18.14)
This remarkably simple result shows that $K_{tr}$ is directly proportional to the absolute temperature $T$ (Fig. 18.13).

The average translational kinetic energy of a single molecule is the total translational kinetic energy $K_{tr}$ of all molecules divided by the number of molecules, $N$:

$$\frac{K_{tr}}{N} = \frac{1}{2} m (v^2)_{av} = \frac{3nRT}{2N}$$

Also, the total number of molecules $N$ is the number of moles $n$ multiplied by Avogadro’s number $N_A$, so

$$N = nN_A \quad \frac{n}{N} = \frac{1}{N_A}$$
\[ \frac{K_{tr}}{N} = \frac{1}{2} m(v^2)_{av} = \frac{3}{2} \left( \frac{R}{N_A} \right) T \]  \hspace{1cm} (18.15)

The ratio \( R/N_A \) occurs frequently in molecular theory. It is called the Boltzmann constant, \( k \):

\[ k = \frac{R}{N_A} = \frac{8.314 \text{ J/mol} \cdot \text{K}}{6.022 \times 10^{23} \text{ molecules/mol}} \]

\[ = 1.381 \times 10^{-23} \text{ J/molecule} \cdot \text{K} \]

(The current best numerical value of \( k \) is 1.3806504(24) \( \times 10^{-23} \) J/molecule \( \cdot \) K). In terms of \( k \) we can rewrite Eq. (18.15) as

\[ \frac{1}{2} m(v^2)_{av} = \frac{3}{2} kT \]  \hspace{1cm} (average translational kinetic energy of a gas molecule)  \hspace{1cm} (18.16)
(The current best numerical value of \( k \) is \( 1.3806504(24) \times 10^{-23} \text{ J/molecule} \cdot \text{K} \)).

In terms of \( k \) we can rewrite Eq. (18.15) as

\[
\frac{1}{2} m(v^2)_{av} = \frac{3}{2} kT \quad \text{(average translational kinetic energy of a gas molecule)}
\]

This shows that the average translational kinetic energy \( \textit{per molecule} \) depends only on the temperature, not on the pressure, volume, or kind of molecule. We can obtain the average translational kinetic energy \( \textit{per mole} \) by multiplying Eq. (18.16) by Avogadro’s number and using the relation \( M = N_A m \):

\[
N_A \frac{1}{2} m(v^2)_{av} = \frac{1}{2} M(v^2)_{av} = \frac{3}{2} RT \quad \text{(average translational kinetic energy per mole of gas)}
\]
The translational kinetic energy of a mole of an ideal gas depends only on $T$.

Finally, it is sometimes convenient to rewrite the ideal-gas equation on a molecular basis. We use $N = N_A n$ and $R = N_A k$ to obtain this alternative form:

$$pV = NkT \quad (18.18)$$

This shows that we can think of the Boltzmann constant $k$ as a gas constant on a "per-molecule" basis instead of the usual "per-mole" basis for $R$.

**Molecular Speeds**

From Eqs. (18.16) and (18.17) we can obtain expressions for the square root of $(v^2)_{av}$, called the root-mean-square speed (or rms speed) $v_{rms}$:

$$v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} \quad \text{(root-mean-square speed of a gas molecule)} \quad (18.19)$$
Heat Capacities of Gases

The basis of our analysis is that heat is energy in transit. When we add heat to a substance, we are increasing its molecular energy. In this discussion the volume of the gas will remain constant so that we don’t have to worry about energy transfer through mechanical work.
\[ dK_{tr} = \frac{3}{2} nR \, dT \]  \hspace{1cm} (18.23)

From the definition of molar heat capacity at constant volume, \( C_V \) (see Section 17.5), we also have

\[ dQ = nC_V \, dT \]  \hspace{1cm} (18.24)

where \( dQ \) is the heat input needed for a temperature change \( dT \). Now if \( K_{tr} \) represents the total molecular energy, as we have assumed, then \( dQ \) and \( dK_{tr} \) must be equal (Fig. 18.17). From Eqs. (18.23) and (18.24), this says

\[ nC_V \, dT = \frac{3}{2} nR \, dT \]

\[ C_V = \frac{3}{2} R \quad \text{(ideal gas of point particles)} \]  \hspace{1cm} (18.25)
18.17 (a) A fixed volume $V$ of a monatomic ideal gas. (b) When an amount of heat $dQ$ is added to the gas, the total translational kinetic energy increases by $dK_{tr} = dQ$ and the temperature increases by $dT = dQ/nC_v$. 

![Diagram of a fixed volume gas with a thermometer showing temperature $T$ and translational kinetic energy $K_{tr}$](image1)

![Diagram of a gas with heat added and temperature increased](image2)
Does Eq. (18.25) agree with measured values of molar heat capacities? In SI units, Eq. (18.25) gives

\[ C_V = \frac{3}{2}(8.314 \text{ J/mol} \cdot \text{K}) = 12.47 \text{ J/mol} \cdot \text{K} \]

For comparison, Table 18.1 gives measured values of \( C_V \) for several gases. We see that for monatomic gases our prediction is right on the money, but that it is way off for diatomic and polyatomic gases.
<table>
<thead>
<tr>
<th>Type of Gas</th>
<th>Gas</th>
<th>$C_V$ (J/mol • K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monatomic</td>
<td>He</td>
<td>12.47</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>12.47</td>
</tr>
<tr>
<td>Diatomic</td>
<td>H₂</td>
<td>20.42</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>20.76</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>20.85</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>20.85</td>
</tr>
<tr>
<td>Polyatomic</td>
<td>CO₂</td>
<td>28.46</td>
</tr>
<tr>
<td></td>
<td>SO₂</td>
<td>31.39</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>25.95</td>
</tr>
</tbody>
</table>
Below 50 K, $\text{H}_2$ molecules undergo translation but do not rotate or vibrate.

Appreciable rotational motion begins to occur above 50 K.

Appreciable vibrational motion begins to occur above 600 K.
A transition from one phase to another ordinarily requires phase equilibrium between the two phases, and for a given pressure this occurs at only one specific temperature. We can represent these conditions on a graph with axes $p$ and $T$, called a phase diagram; Fig. 18.24 shows an example. Each point on the diagram represents a pair of values of $p$ and $T$. 
Phases of matter

- Figure 18.24 below shows a typical $pT$ phase diagram, and Table 18.3 gives triple-point data for some substances.

![Phase diagram](image)

At the **triple point**, solid, liquid, and vapor coexist.

At $T$ and $p$ values above the **critical point**, the material properties change smoothly with changing $p$ or $T$, rather than undergoing a phase change.

**Table 18.3** Triple-Point Data

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature (K)</th>
<th>Pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>13.80</td>
<td>$0.0704 \times 10^5$</td>
</tr>
<tr>
<td>Deuterium</td>
<td>18.63</td>
<td>$0.171 \times 10^5$</td>
</tr>
<tr>
<td>Neon</td>
<td>24.56</td>
<td>$0.432 \times 10^5$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>63.18</td>
<td>$0.125 \times 10^5$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>54.36</td>
<td>$0.00152 \times 10^5$</td>
</tr>
<tr>
<td>Ammonia</td>
<td>195.40</td>
<td>$0.0607 \times 10^5$</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>216.55</td>
<td>$5.17 \times 10^5$</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>197.68</td>
<td>$0.00167 \times 10^5$</td>
</tr>
<tr>
<td>Water</td>
<td>273.16</td>
<td>$0.00610 \times 10^5$</td>
</tr>
</tbody>
</table>
Only a single phase can exist at each point in Fig. 18.24, except for points on the solid lines, where two phases can coexist in phase equilibrium. The fusion curve separates the solid and liquid areas and represents possible conditions of solid-liquid phase equilibrium. The vaporization curve separates the liquid and vapor areas, and the sublimation curve separates the solid and vapor areas. All three curves meet at the triple point, the only condition under which all three phases can coexist (Fig. 18.25). In Section 17.3 we used the triple-point temperature of water to define the Kelvin temperature scale. Table 18.3 gives triple-point data for several substances.
A liquid-vapor phase transition occurs only when the temperature and pressure are less than those at the point lying at the top of the green shaded area labeled “Liquid-vapor phase equilibrium region.” This point corresponds to the endpoint at the top of the vaporization curve in Fig. 18.24. It is called the critical point, and the corresponding values of $p$ and $T$ are called the critical pressure and temperature. A gas at a pressure above the critical pressure does not separate into two phases when it is cooled at constant pressure (along a horizontal line above the critical point in Fig. 18.24). Instead, its properties change gradually and continuously from those we ordinarily associate with a gas (low density, large compressibility) to those of a liquid (high density, small compressibility) without a phase transition.
A $pVT$-surface graphically represents the equation of state. Projections onto the $pT$- and $pV$-planes are shown.
The $pVT$-surface for an ideal gas is much simpler than the $pVT$-surface for a real substance, as seen in the previous slide.
Collisions between molecules

• We model molecules as rigid spheres of radius $r$ as shown at the right.

• The *mean free path* of a molecule is the average distance it travels between collisions.

• The average time between collisions is the *mean free time*.

• Follow the derivation of the mean free path.

• Follow Example 18.8.
Heat capacities of gases

- The **degrees of freedom** are the number of velocity components needed to describe a molecule completely. A monatomic gas has three degrees of freedom and a diatomic gas has five. Figure 18.18 at the right illustrates the motions of a diatomic molecule.

- The **equipartition of energy** principle states that each degree of freedom has $1/2 kT$ of kinetic energy associated with it.

- Follow the derivation of the molar heat capacity at constant volume, $C_V$, for monatomic and diatomic gases and for solids. The results are $C_V = 3/2 \, R$ for an ideal monatomic gas, $C_V = 5/2 \, R$ for a diatomic gas, and $C_V = 3R$ for an ideal monatomic solid.
Table 18.1 shows that the calculated values for $C_V$ for monatomic gases and diatomic gases agree quite well with the measured values.
Molecular speeds

• The *Maxwell-Boltzmann distribution* $f(v)$ gives the distribution of molecular speeds.

• Figure 18.23 at the right helps to interpret $f(v)$. Part (a) shows how the shape of the curve depends on temperature. Part (b) shows the fraction of molecules within certain speed ranges. The most probable speed for a given temperature is at the peak of the curve.

As temperature increases:
- the curve flattens.
- the maximum shifts to higher speeds.
Phases of matter

- Figure 18.24 below shows a typical $pT$ phase diagram, and Table 18.3 gives triple-point data for some substances.

Table 18.3  Triple-Point Data

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