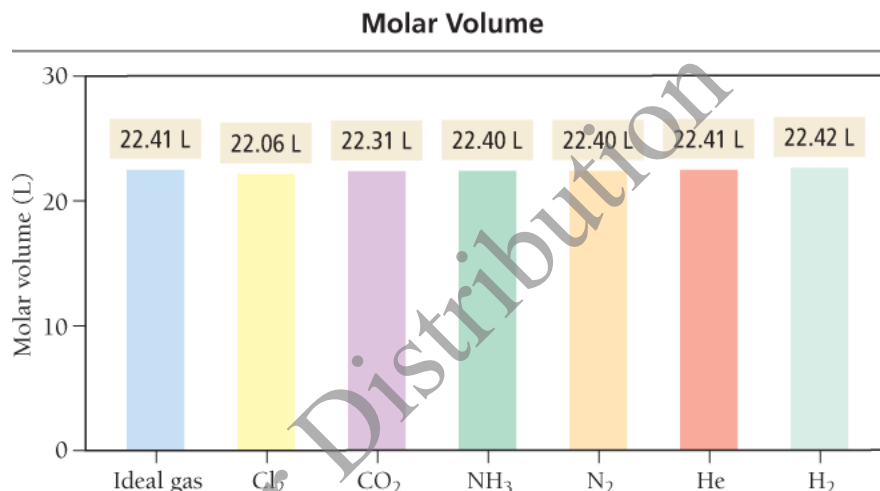


10.11: Real Gases: The Effects of Size and Intermolecular Forces

One mole of an ideal gas has a volume of 22.41 L at STP. [Figure 10.23](#) shows the molar volume of several real gases at STP. As you can see, most of these gases have a volume that is very close to 22.41 L, meaning that they act very nearly as ideal gases. Gases behave ideally when both of the following are true: (a) the volume of the gas particles is small compared to the space between them; and (b) the forces between the gas particles are not significant. At STP, these assumptions are valid for most common gases. However, these assumptions break down at higher pressures or lower temperatures.

Figure 10.23 Molar Volumes of Real Gases

The molar volumes of several gases at STP are close to 22.414 L, indicating that their departures from ideal behavior are small.



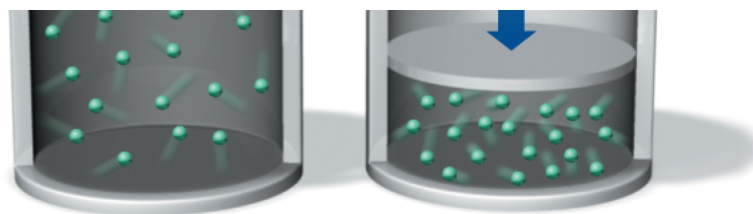
The Effect of the Finite Volume of Gas Particles

The finite volume of gas particles—that is, their actual *size*—becomes important at high pressure because the volume of the particles themselves occupies a significant portion of the total gas volume ([Figure 10.24](#)). We can see the effect of particle volume by comparing the molar volume of argon to the molar volume of an ideal gas as a function of pressure at 500 K, as shown in [Figure 10.25](#). At low pressures, the molar volume of argon is nearly identical to that of an ideal gas. But as the pressure increases, the molar volume of argon becomes *greater than* that of an ideal gas. At the higher pressures, the argon atoms themselves occupy a significant portion of the gas volume, making the actual volume greater than that predicted by the ideal gas law.

Figure 10.24 Particle Volume and Ideal Behavior

As a gas is compressed, the gas particles themselves begin to occupy a significant portion of the total gas volume, leading to deviations from ideal behavior.





As the pressure increases,
particles occupy a larger
portion of volume.

In 1873, Johannes van der Waals (1837–1923) modified the ideal gas equation to fit the behavior of real gases. From the graph for argon in [Figure 10.25](#), we can see that the ideal gas law predicts a volume that is too small. Van der Waals suggested a small correction factor that accounts for the volume of the gas particles themselves:

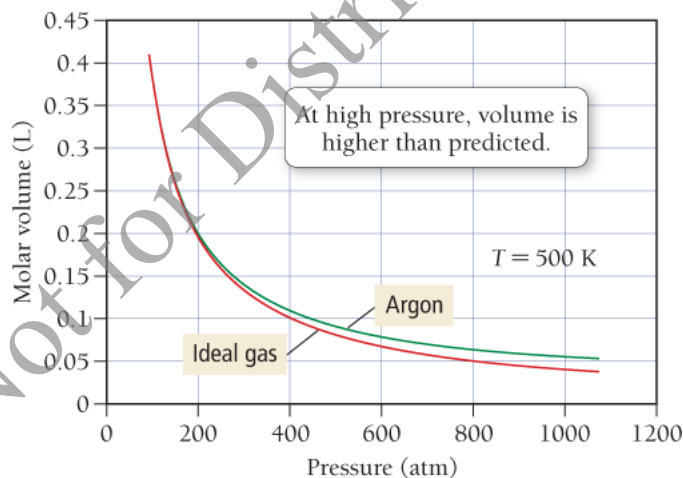
[10.28]

$$\begin{array}{ll} \text{Ideal behavior} & V = \frac{nRT}{P} \\ \text{Corrected for volume of gas particles} & V = \frac{nRT}{P} + nb \end{array}$$

Figure 10.25 The Effect of Particle Volume

At high pressures, 1 mol of argon occupies a larger volume than 1 mol of an ideal gas because of the volume of the argon atoms themselves. (This example was chosen to minimize the effects of intermolecular forces, which are very small in argon at 500 K, thereby isolating the effect of particle volume.)

Nonideal Behavior: The Effect of Particle Volume



The correction adds the quantity nb to the volume, where n is the number of moles and b is a constant that depends on the gas ([Table 10.4](#)). We can rearrange the corrected equation as follows:

[10.29]

$$(V - nb) = \frac{nRT}{P}$$

Table 10.4 Van der Waals Constants for Common Gases

Gas	a ($\text{L}^2 \cdot \text{atm}/\text{mol}^2$)	b (L/mol)
He	0.0342	0.02370

Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
H ₂ O	5.46	0.0305
CH ₄	2.25	0.0428
CO ₂	3.59	0.0427
CCl ₄	20.4	0.1383

The Effect of Intermolecular Forces

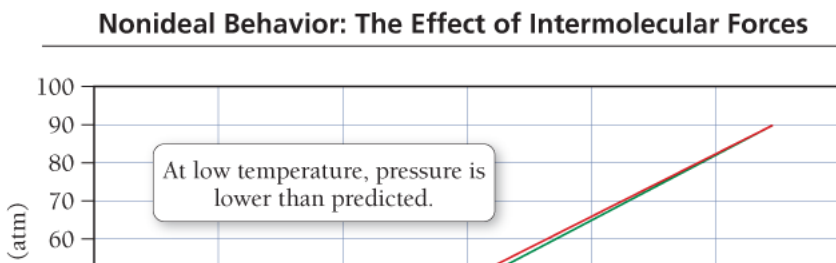
Intermolecular forces, which we will discuss in more detail in [Chapter 11](#), are attractions between the atoms or molecules that compose any substance. These attractions are typically small in gases and therefore do not matter much at low pressure because the molecules are too far apart to “feel” the attractions. They also do not matter much at high temperatures because the molecules have a lot of kinetic energy, and when two particles with high kinetic energies collide, a weak attraction between them does not affect the collision much. At lower temperatures, however, the collisions occur with less kinetic energy, and weak attractions can affect the collisions.

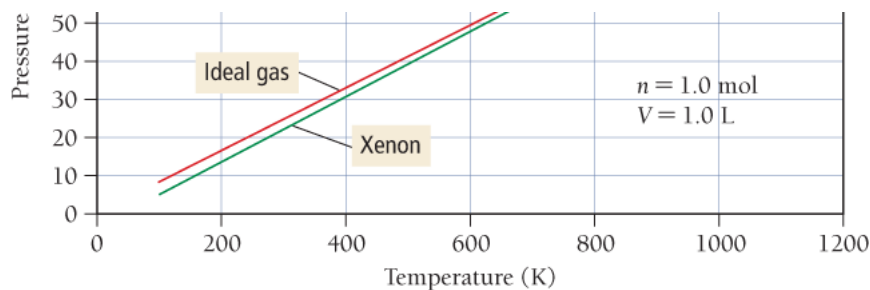
We can understand this difference with an analogy to billiard balls. Imagine two billiard balls that are coated with a substance that makes them slightly sticky. If they collide when moving at high velocities, the stickiness does not have much of an effect—the balls bounce off one another as if the sticky substance is not even there. However, if the two billiard balls collide when moving very slowly (say, barely rolling), the sticky substance has an effect—the billiard balls might even stick together and not bounce off one another.

The effect of these weak attractions between particles is a decrease in the number of collisions with the surfaces of the container, and a corresponding decrease in the pressure compared to that of an ideal gas. We can see the effect of intermolecular forces when we compare the pressure of 1.0 mol of xenon gas to the pressure of 1.0 mol of an ideal gas as a function of temperature and at a fixed volume of 1.0 L, as shown in [Figure 10.26](#). At high temperature, the pressure of the xenon gas is nearly identical to that of an ideal gas. But at lower temperatures, the pressure of xenon is *less than* that of an ideal gas. At the lower temperatures, the xenon atoms spend more time interacting with each other and less time colliding with the walls, making the actual pressure less than that predicted by the ideal gas law.

Figure 10.26 The Effect of Intermolecular Forces

At low temperatures, the pressure of xenon is less than an ideal gas exerts because interactions among xenon molecules reduce the number of collisions with the walls of the container.





From the graph for xenon shown in [Figure 10.26](#), we can see that the ideal gas law predicts a pressure that is too large at low temperatures. Van der Waals suggested a small correction factor that accounts for the intermolecular forces between gas particles:

[10.30]

$$\begin{aligned} \text{Ideal behavior} \quad V &= \frac{nRT}{P} \\ \text{Corrected for volume of gas particles} \quad V &= \frac{nRT}{P} - a\left(\frac{n}{V}\right)^2 \end{aligned}$$

The correction subtracts the quantity $a(n/V)^2$ from the pressure, where n is the number of moles, V is the volume, and a is a constant that depends on the gas (see [Table 10.4](#)). Notice that the correction factor increases as n/V (the number of moles of particles per unit volume) increases because a greater concentration of particles makes it more likely that they will interact with one another. We can rearrange the corrected equation as:

[10.31]

$$P + a\left(\frac{n}{V}\right)^2 = \frac{nRT}{V}$$

Van der Waals Equation

We can combine the effects of particle volume ([Equation 10.29](#)) and particle intermolecular forces ([Equation 10.31](#)) into one equation that describes nonideal gas behavior:

$$\left[P + a\left(\frac{n}{V}\right)^2\right] \times [V - nb] = nRT$$

Correction for intermolecular forces
Correction for particle volume

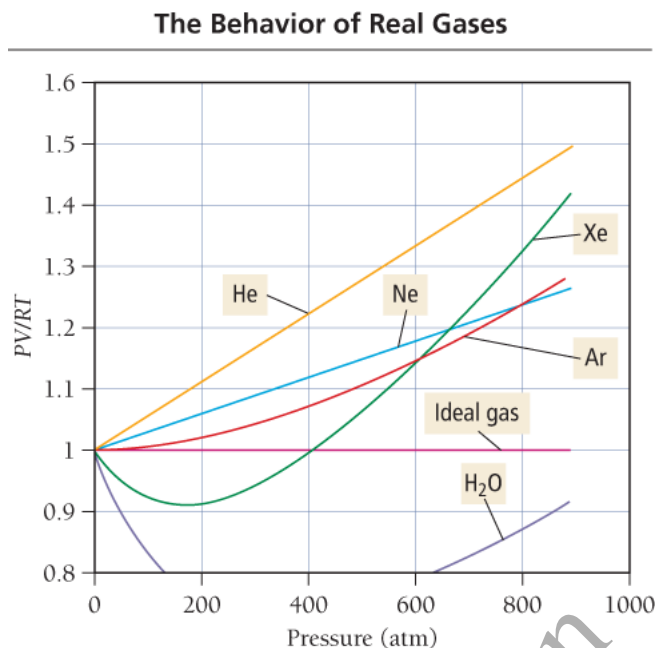
This equation is the van der Waals equation, and we can use it to calculate the properties of a gas under nonideal conditions.

Real Gas Behavior

We can see the combined effects of particle volume and intermolecular forces by examining a plot of PV/RT versus P for 1 mol of a number of real gases ([Figure 10.27](#)). For an ideal gas, $PV/RT = n$, the number of moles of gas. Therefore, for 1 mol of an ideal gas, PV/RT is equal to 1, as shown in the plot. For real gases, PV/RT deviates from 1, but the deviations are not uniform. For example, water displays a large negative deviation from PV/RT because, for water, the effect of intermolecular forces on lowering the pressure (relative to an ideal gas) is far greater than the effect of particle size on increasing the volume. We can see in [Table 10.4](#) that water has a high value of a , the constant that corrects for intermolecular forces, but a moderate value of b , the constant that corrects for particle size. Therefore, PV/RT for water is lower than predicted from the ideal gas law.

Figure 10.27 Real versus Ideal Behavior

For 1 mol of an ideal gas, PV/RT is equal to 1. The combined effects of the volume of gas particles and the interactions among them cause each real gas to deviate from ideal behavior in a slightly different way. These curves were calculated at a temperature of 500 K.



By contrast, consider the behavior of helium, which displays a positive deviation from the ideal behavior. Helium has very weak intermolecular forces, and their effect on lowering the pressure (relative to ideal gas) is small compared to the effect of particle size on increasing the volume. Therefore, PV/RT is greater than predicted from the ideal gas law for helium.

Conceptual Connection 10.8 Real Gases

Interactive

Not for Distribution