# Kinetic Molecular Theory, Real Gases 

Kinetic molecular theory<br>Real gases<br>Non-ideal gas behavior

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average speeds determined by their absolute temperatures. The individual molecules of a gas exhibit a range of speeds, the distribution of these speeds being dependent on the temperature of the gas and the mass of its molecules. Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behavior is not necessarily described well by the ideal gas law. Under conditions of low pressure and high temperature, these factors are negligible, the ideal gas equation is an accurate description of gas behavior, and the gas is said to exhibit ideal behavior. However, at lower temperatures and higher pressures, corrections for molecular volume and molecular attractions are required to account for finite molecular size and attractive forces. The van der Waals equation is a modified version of the ideal gas law that can be used to account for the non-ideal behavior of gases under these conditions.

### 26.1 The Kinetic-Molecular Theory

## Learning Objectives

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

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm . Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The kinetic molecular theory (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term
"molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are elastic (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

## The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- Amontons's law. If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure 26.1).
- Charles's law. If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease the both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- Boyle's law. If the gas volume volume of a given amount of gas at a given temperature is decreased (that is, if the gas is compressed), the molecules will be exposed to a decreased container wall area. Collisions with the container wall will therefore occur more frequently and the pressure exerted by the gas will increase (Figure 26.1).
- Avogadro's law. At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure 26.1).
- Dalton's Law. Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.


## Figure 26.1

(a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.


## Molecular Speeds and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at speeds and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the vast number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure 26.2).

## Figure 26.2

The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, $v_{p}$, is a little less than $400 \mathrm{~m} / \mathrm{s}$, while the root mean square speed, $u_{r m s}$, is closer to $500 \mathrm{~m} / \mathrm{s}$.


The kinetic energy (KE) of a particle of mass $(m)$ and speed $(u)$ is given by:

$$
\mathrm{KE}=\frac{1}{2} m u^{2}
$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules $\left(\mathrm{J}=\mathrm{kg} \mathrm{m}^{2} \mathrm{~s}^{-2}\right)$. To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the root mean square speed of a particle, $u_{\text {rms }}$, is defined as the square root of the average of the squares of the speeds with $n=$ the number of particles:

$$
u_{\mathrm{rms}}=\sqrt{\overline{u^{2}}}=\frac{\sqrt{u_{1}^{2}+u_{2}^{2}+u_{3}^{2}+u_{4}^{2}+\ldots}}{n}
$$

The average kinetic energy for a mole of particles, $\mathrm{KE}_{\text {avg }}$, is then equal to:

$$
\mathrm{KE}_{\mathrm{avg}}=\frac{1}{2} M u_{\mathrm{rms}}^{2}
$$

where $M$ is the molar mass expressed in units of $\mathrm{kg} / \mathrm{mol}$. The $\mathrm{KE}_{\text {avg }}$ of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$
\mathrm{KE}_{\mathrm{avg}}=\frac{3}{2} R T
$$

where $R$ is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is $8.314 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}\left(8.314 \mathrm{~kg} \mathrm{~m}^{2} \mathrm{~s}^{-2} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right)$. These two separate equations for $\mathrm{KE}_{\text {avg }}$ may be combined and rearranged to yield a relation between molecular speed and temperature:

$$
\begin{gathered}
\frac{1}{2} M u_{\mathrm{rms}}^{2}=\frac{3}{2} R T \\
u_{\mathrm{rms}}=\frac{\sqrt{3 R T}}{M}
\end{gathered}
$$

## Example 26.1

## Calculation of $u_{\mathrm{rms}}$

Calculate the root-mean-square speed for a nitrogen molecule at $30^{\circ} \mathrm{C}$.

## Solution

Convert the temperature into Kelvin:

$$
30^{\circ} \mathrm{C}+273=303 \mathrm{~K}
$$

Determine the molar mass of nitrogen in kilograms:

$$
\frac{28.0 \mathrm{~g}}{1 \mathrm{~mol}} \times \frac{1 \mathrm{~kg}}{1000 \mathrm{~g}}=0.028 \mathrm{~kg} / \mathrm{mol}
$$

Replace the variables and constants in the root-mean-square speed equation, replacing Joules with the equivalent $\mathrm{kg} \mathrm{m}^{2} \mathrm{~s}^{-2}$.

$$
\begin{gathered}
u_{\mathrm{rms}}=\frac{\sqrt{3 R T}}{M} \\
u_{\mathrm{rms}}=\frac{\sqrt{3(8.314 \mathrm{~J} / \mathrm{mol} \mathrm{~K})(303 \mathrm{~K})}}{(0.028 \mathrm{~kg} / \mathrm{mol})}=\sqrt{2.70 \times 10^{5} \mathrm{~m}^{2} \mathrm{~s}^{-2}}=519 \mathrm{~m} / \mathrm{s}
\end{gathered}
$$

## Check Your Learning

Calculate the root-mean-square speed for a mole of oxygen molecules at $-23^{\circ} \mathrm{C}$.

## Answer

441 m/s

If the temperature of a gas increases, its $\mathrm{KE}_{\text {avg }}$ increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, $\mathrm{KE}_{\text {avg }}$ decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in Figure 26.3.

## Figure 26.3

The molecular speed distribution for nitrogen gas $\left(N_{2}\right)$ shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.


At a given temperature, all gases have the same $\mathrm{KE}_{\text {avg }}$ for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher $u_{r m s}$, with a speed distribution that peaks at relatively higher speeds. Gases consisting of heavier molecules have more low-speed particles, a lower $u_{r m s}$, and a speed distribution that peaks at relatively lower speeds. This trend is demonstrated by the data for a series of noble gases shown in Figure 26.4.

Figure 26.4
molecular speed is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.


## Link to Learning

This gas simulator may be used to examine the effect of temperature on molecular speeds. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.

## The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$
\text { effusion rate } \propto u_{\mathrm{rms}}
$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$
\begin{gathered}
u_{\mathrm{rms}}=\frac{\sqrt{3 R T}}{M} \\
M=\frac{3 R T}{u_{\mathrm{rms}}^{2}}=\frac{3 R T}{u^{2}}
\end{gathered}
$$

$$
\frac{\text { effusion rate } \mathrm{A}}{\text { effusion rate } \mathrm{B}}=\frac{u_{\mathrm{rms} \mathrm{~A}}}{u_{\mathrm{rms}}}=\frac{\sqrt{\frac{3 R T}{M_{\mathrm{A}}}}}{\sqrt{\frac{3 R T}{M_{\mathrm{B}}}}}=\frac{\sqrt{M_{\mathrm{B}}}}{M_{\mathrm{A}}}
$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

## Link to Supplemental Exercises

Supplemental exercises are available if you would like more practice with these concepts.

### 26.2 Non-Ideal Gas Behavior

## Learning Objectives

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

- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility $(Z)$ and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

Thus far, the ideal gas law, $P V=n R T$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of $P V=n R T$ can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, $V_{m}$ ) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the compressibility factor $(Z)$ with:

$$
\mathrm{Z}=\frac{\text { molar volume of gas at same } T \text { and } P}{\text { molar volume of ideal gas at same } T \text { and } P}=\left(\frac{P V_{m}}{R T}\right)_{\text {measured }}
$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1 , and any deviation from 1 is an indication of nonideal behavior. Figure 26.5 shows plots of $Z$ over a large pressure range for several common gases.

Figure 26.5
A graph of the compressibility factor $(Z)$ vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.


As is apparent from Figure 26.5, the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the
molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas. The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not proportional as predicted by Boyle's law.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (Figure 26.6). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.

Figure 26.6
(a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted at constant volume compared to an ideal gas.


There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The van der Waals equation improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$
P V=n R T \longrightarrow(P+\underbrace{\left(P V^{2}\right.}_{\substack{\text { Correction for } \\ \text { molecular attraction }}})(V-n b)=n R T
$$

The constant $a$ corresponds to the strength of the attraction between molecules of a particular gas, and the constant $b$ corresponds to the size of the molecules of a particular gas. The "correction" to the pressure term in the ideal gas law is

$$
\frac{n^{2} a}{V^{2}}
$$

and the "correction" to the volume is $n b$. Note that when $V$ is relatively large and $n$ is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, $P V=n R T$. Such a
condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in Table 26.1.

## Table 26.1

Values of van der Waals Constants for Some Common Gases

| Gas | $\boldsymbol{a}\left(\mathrm{L}^{\left.\mathbf{2} \mathbf{a t m} / \mathrm{mol}^{2}\right)}\right.$ | $\boldsymbol{b}(\mathrm{L} / \mathrm{mol})$ |
| :--- | :--- | :--- |
| $\mathrm{N}_{2}$ | 1.39 | 0.0391 |
| $\mathrm{O}_{2}$ | 1.36 | 0.0318 |
| $\mathrm{CO}_{2}$ | 3.59 | 0.0427 |
| $\mathrm{H}_{2} \mathrm{O}$ | 5.46 | 0.0305 |
| He | 0.0342 | 0.0237 |
| $\mathrm{CCl}_{4}$ | 20.4 | 0.1383 |

At low pressures, the correction for intermolecular attraction, $a$, is more important than the one for molecular volume, $b$. At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $P V=n R T$ over a small range of pressures. This behavior is reflected by the "dips" in several of the compressibility curves shown in Figure 26.5. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised ( $Z$ decreases with increasing $P$ ). At very high pressures, the gas becomes less compressible ( $Z$ increases with $P$ ), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of low pressure and high temperature. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded-this is, however, very often not the case.

## Example 26.2

## Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains $3.46 \mathrm{~mol} \mathrm{CO}_{2}$ at $229^{\circ} \mathrm{C}$. Calculate the pressure of this sample of $\mathrm{CO}_{2}$ :
(a) from the ideal gas law
(b) from the van der Waals equation
(c) Explain the reason(s) for the difference.

## Solution

(a) From the ideal gas law:

$$
P=\frac{n R T}{V}=\frac{3.46 \mathrm{~mol} \times 0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~mol}}{}{ }^{-1} \mathrm{~K}^{-1} \times 502 \mathrm{~K} \mathrm{~K}^{2}=33.5 \mathrm{~atm}
$$

(b) From the van der Waals equation:

$$
\begin{gathered}
\left(P+\frac{n^{2} a}{V^{2}}\right) \times(V-n b)=n R T \rightarrow P=\frac{n R T}{(V-n b)}-\frac{n^{2} a}{V^{2}} \\
P=\frac{3.46 \mathrm{~mol} \times 0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \times 502 \mathrm{~K}}{\left(4.25 \mathrm{~L}-3.46 \mathrm{~mol} \times 0.0427 \mathrm{~L} \mathrm{~mol}^{-1}\right)}-\frac{(3.46 \mathrm{~mol})^{2} \times 3.59 \mathrm{~L}^{2} \mathrm{~atm} \mathrm{~mol}^{2}}{(4.25 \mathrm{~L})^{2}}
\end{gathered}
$$

This finally yields $P=32.4$ atm.
(c) This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because $\mathrm{CO}_{2}$ molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

## Check your Learning

A $560-\mathrm{mL}$ flask contains $21.3 \mathrm{~g} \mathrm{~N} \mathrm{~N}_{2}$ at $145^{\circ} \mathrm{C}$. Calculate the pressure of $\mathrm{N}_{2}$ :
(a) from the ideal gas law
(b) from the van der Waals equation
(c) Explain the reason(s) for the difference.

## Answer

(a) 46.562 atm ; (b) 46.594 atm ; (c) The van der Waals equation takes into account the volume of

## Link to Supplemental Exercises

Supplemental exercises are available if you would like more practice with these concepts.

## Files

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