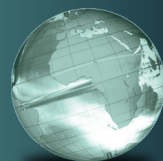


GLOBAL
EDITION



Chemistry

The Central Science

Expanded Edition

Fifteenth Global Edition in SI Units

Brown • LeMay • Bursten
Murphy • Woodward • Stoltzfus
Langford • George



Periodic Table of the Elements

[illegible]

^aThe labels on top (1A, 2A, etc.) are common American usage. The labels below these (1, 2, etc.) are those recommended by the International Union of Pure and Applied Chemistry (IUPAC).

Except for elements 114 and 116, the names and symbols above 113 have not yet been decided.

Atomic weights in brackets are the names of the longest-lived or most important isotope of radioactive elements.

Further information is available at <http://www.webelements.com>

** Discovered in 2010, element 117 is currently under review by IUPAC.

with the container walls, which means the pressure decreases. Thus, kinetic-molecular theory explains Boyle's law.

- 2. A temperature increase at constant volume causes pressure to increase.** An increase in temperature means an increase in the average kinetic energy of the molecules and in u_{rms} . Because there is no change in volume, the temperature increase causes more collisions with the walls per unit time because the molecules are all moving faster. Furthermore, the momentum in each collision increases (the molecules strike the walls more forcefully). A greater number of more forceful collisions means the pressure increases, and the theory explains this increase.

A CLOSER LOOK The Ideal Gas Equation

The ideal gas equation can be derived from the five statements given in the text for the kinetic-molecular theory. Rather than perform the derivation, however, let's consider in qualitative terms how the ideal gas equation might follow from these statements. The total force of the molecular collisions on the walls and hence the pressure (force per unit area, Section 10.2) produced by these collisions depend both on how strongly the molecules strike the walls (impulse imparted per collision) and on the rate at which the collisions occur:

$$P \propto \text{impulse imparted per collision} \times \text{collision rate}$$

For a molecule traveling at the rms speed, the impulse imparted by a collision with a wall depends on the momentum of the molecule; that is, it depends on the product of the molecule's mass and speed: mu_{rms} . The collision rate is proportional to the number of molecules per unit volume, n/V , and to their speed, which is u_{rms}

because we are talking about only molecules traveling at this speed. Thus, we have

$$P \propto mu_{\text{rms}} \times \frac{n}{V} \times u_{\text{rms}} \propto \frac{nm(u_{\text{rms}})^2}{V} \quad [10.17]$$

Because the average kinetic energy, $\frac{1}{2}m(u_{\text{rms}})^2$, is proportional to temperature, we have $m(u_{\text{rms}})^2 \propto T$. Making this substitution in Equation 10.17 gives

$$P \propto \frac{nm(u_{\text{rms}})^2}{V} \propto \frac{nT}{V} \quad [10.18]$$

If we put in a proportionality constant, calling it R , the gas constant, you can see that we obtain the ideal gas equation:

$$P = \frac{nRT}{V} \quad [10.19]$$

Related Exercises: 10.32, 10.91



Sample Exercise 10.12

Applying the Kinetic-Molecular Theory

A sample of O_2 gas initially at STP is compressed to a smaller volume at constant temperature. What effect does this change have on (a) the average kinetic energy of the molecules, (b) their average speed, (c) the number of collisions they make with the container walls per unit time, (d) the number of collisions they make with a unit area of container wall per unit time, (e) the pressure?

SOLUTION

Analyze We need to apply the concepts of the kinetic-molecular theory of gases to a gas compressed at constant temperature.

Plan We will determine how each of the quantities in (a)–(e) is affected by the change in volume at constant temperature.

Solve (a) Because the average kinetic energy of the O_2 molecules is determined only by temperature, this energy is unchanged by the compression. (b) Because the average kinetic energy of the molecules does not change, their average speed remains constant. (c) The number of collisions with the walls per unit time increases because the molecules are moving in a smaller volume but with the same average speed as before. Under these conditions they will strike the walls of the container more frequently. (d) The number of collisions with a unit area of wall per unit time increases because the total number of collisions with the walls per unit time increases and the area of the walls decreases. (e) Although the average force with which the molecules collide with the walls remains constant, the pressure increases because there are more collisions per unit area of wall per unit time.

Check In a conceptual exercise of this kind, there is no numerical answer to check. All we can check in such cases is our reasoning in the course of solving the problem. The increase in pressure seen in part (e) is consistent with Boyle's law.

Practice Exercise

Consider two gas cylinders of the same volume and temperature, one containing 1.0 mol of propane, C_3H_8 , and the other 2.0 mol of methane, CH_4 . Which of the following statements is true? (a) The C_3H_8 and CH_4 molecules have the same u_{rms} (b) The C_3H_8 and CH_4 molecules have the same average kinetic energy (c) The rate at which the molecules collide with the cylinder walls is the same for both cylinders (d) The gas pressure is the same in both cylinders

Self-Assessment Exercise

10.31 Consider three gases, all at 298 K: Kr, N₂, and NH₃. List the gases in order of increasing average speed of the molecules (or atoms).

- (a) Kr < N₂ < NH₃
 (b) Kr < NH₃ < N₂
 (c) NH₃ < N₂ < Kr
 (d) N₂ < NH₃ < Kr

Exercises

10.32 Indicate which of the following statements regarding the kinetic-molecular theory of gases are correct. (a) The average kinetic energy of a collection of gas molecules at a given temperature is proportional to $m^{1/2}$. (b) The gas molecules are assumed to exert no forces on each other. (c) All the molecules of a gas at a given temperature have the same kinetic energy. (d) The volume of the gas molecules is negligible in comparison to the total volume in which the gas is contained. (e) All gas molecules move with the same speed if they are at the same temperature.

10.33 Radon (Rn) is the heaviest (and only radioactive) member of the noble gases. How much slower is the root-mean-square speed of Rn than He at 300 K?

10.34 (a) Place the following gases in order of increasing average molecular speed at 300 K: CO, SF₆, H₂S, Cl₂, HBr. (b) Calculate the rms speeds of CO and Cl₂ molecules at 300 K. (c) Calculate the most probable speeds of CO and Cl₂ molecules at 300 K.

10.31 (a)

Answers to Self-Assessment Exercises

10.7 | Molecular Effusion and Diffusion



Natural gas is a convenient, efficient fuel source and is transported by pipes, pressurized tankers and in gas bottles. It is colorless and odorless, making the detection of leaks difficult. This is problematic as a buildup of gas in an enclosed space might go undetected and result in an explosion. To guard against this, an additive, usually ethanethiol ($\text{CH}_3\text{CH}_2\text{SH}$), which has an unpleasant smell that can alert people to the possibility of a leak, is used. This compound has the advantages that very small amounts are detected by the human nose (of the order of a few parts per billion), the compound has long term

stability when added to a gas supply and does not interfere with the combustion of the gas. It is sometimes referred to as ‘stench gas’ and in some countries is used to release into the ventilation system of underground mines to alert the miners in the case of an emergency.

By the end of this section, you should be able to

- Distinguish between effusion and diffusion and relate them to the molar mass of the gas.

According to the kinetic-molecular theory of gases, the average kinetic energy of *any* collection of gas molecules, $\frac{1}{2} m(u_{\text{rms}})^2$, has a specific value at a given temperature. Thus, for two gases at the same temperature a gas composed of low-mass particles, such as He, has the same average kinetic energy as one composed of more massive particles, such as Xe. The mass of the particles in the He sample is smaller than that in the Xe sample. Consequently, the He particles must have a higher rms speed than the Xe particles. The equation that expresses this fact quantitatively is

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}} \quad [10.20]$$

where \mathcal{M} is the molar mass of the particles, which can be derived from the kinetic-molecular theory. Because \mathcal{M} appears in the denominator, the less massive the gas particles, the higher their rms speed.

Figure 10.14 shows the distribution of molecular speeds for several gases at 25 °C. Notice how the distributions are shifted toward higher speeds for gases of lower molar masses.

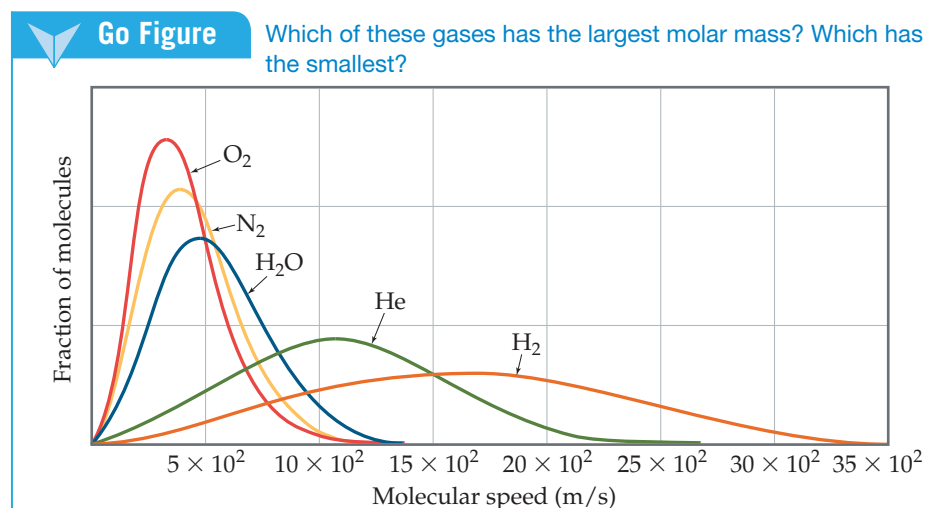
The most probable speed of a gas molecule can also be derived:

$$u_{\text{mp}} = \sqrt{\frac{2RT}{\mathcal{M}}} \quad [10.21]$$

The dependence of molecular speed on mass has two interesting consequences. The first is **effusion**, which is the escape of gas molecules through a tiny hole (**Figure 10.15**). The second is **diffusion**, which is the spread of one substance throughout a space or throughout a second substance. For example, the molecules of a perfume diffuse throughout a room.

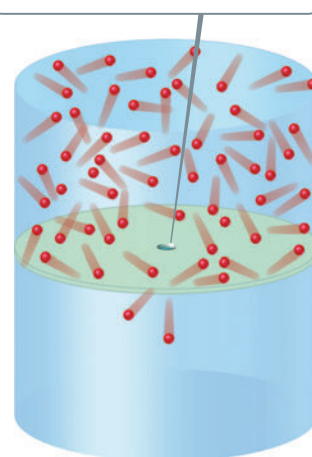
Graham's Law of Effusion

In 1846, Thomas Graham (1805–1869) discovered that the effusion rate of a gas is inversely proportional to the square root of its molar mass. Assume we have two gases at the same temperature and pressure in two containers with identical pinholes. If the rates



▲ **Figure 10.14** The effect of molar mass on molecular speed at 25 °C.

Gas molecules in top half effuse through pinhole only when they happen to hit the pinhole.



▲ **Figure 10.15** Effusion.



Sample Exercise 10.13

Calculating a Root-Mean-Square Speed

Calculate the rms speed of the molecules in a sample of N_2 gas at 25°C .

SOLUTION

Analyze We are given the identity of a gas and the temperature, the two quantities we need to calculate the rms speed.

Plan We calculate the rms speed using Equation 10.20.

Solve We must convert each quantity in our equation to SI units. We will also use R in units of J/mol K (Table 10.2) to make the units cancel correctly.

$$T = 25 + 273 = 298 \text{ K}$$

$$\mathcal{M} = 28.0 \text{ g/mol} = 28.0 \times 10^{-3} \text{ kg/mol}$$

$$R = 8.314 \text{ J/mol K} = 8.314 \text{ kg m}^2/\text{s}^2 \text{ mol K (Since } 1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2\text{)}$$

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{\mathcal{M}}} \\ &= \sqrt{\frac{3(8.314 \text{ kg m}^2/\text{s}^2 \text{ mol K})(298 \text{ K})}{28.0 \times 10^{-3} \text{ kg/mol}}} = 5.15 \times 10^2 \text{ m/s} \end{aligned}$$

Comment This corresponds to a speed of 1854 km/hr. Because the average molecular weight of air molecules is slightly greater than that of N_2 , the rms speed of air molecules is a little smaller than that for N_2 .

Practice Exercise

Fill in the blanks for the following statement: The rms speed of the molecules in a sample of H_2 gas at 300 K will be _____ times larger than the rms speed of O_2 molecules at the same temperature, and the ratio $u_{\text{rms}}(\text{H}_2)/u_{\text{rms}}(\text{O}_2)$ _____ with increasing temperature.

(a) four, will not change (b) four, will increase (c) sixteen, will not change (d) sixteen, will decrease (e) Not enough information is given to answer this question.

of effusion of the two gases are r_1 and r_2 and their molar masses are \mathcal{M}_1 and \mathcal{M}_2 , **Graham's law** states that

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad [10.22]$$

a relationship that indicates that the lighter gas has the higher effusion rate.

The only way for a molecule to escape from its container is for it to “hit” the hole in the partitioning wall of Figure 10.15. The faster the molecules are moving, the more often they hit the partition wall and the greater the likelihood that a molecule will hit the hole and effuse. This implies that the rate of effusion is directly proportional to the rms speed of the molecules. Because R and T are constant, we have, from Equation 10.22

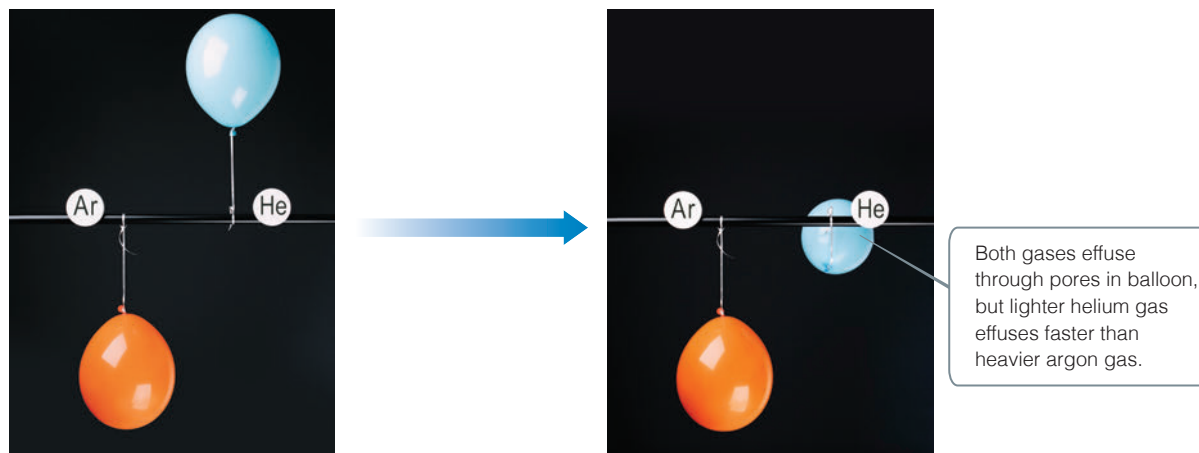
$$\frac{r_1}{r_2} = \frac{u_{\text{rms}1}}{u_{\text{rms}2}} = \sqrt{\frac{3RT/\mathcal{M}_1}{3RT/\mathcal{M}_2}} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad [10.23]$$

As expected from Graham's law, helium escapes from containers through tiny pinhole leaks more rapidly than other gases of higher molecular weight (Figure 10.16).



Go Figure

Because pressure and temperature are constant in this figure but volume changes, which other quantity in the ideal gas equation must also change?



▲ Figure 10.16 An illustration of Graham's law of effusion.

Sample Exercise 10.14

Applying Graham's Law

An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is 0.355 times the rate at which O_2 gas effuses at the same temperature. Calculate the molar mass of the unknown and identify it.

SOLUTION

Analyze We are given the rate of effusion of an unknown gas relative to that of O_2 and asked to find the molar mass and identity of the unknown. Thus, we need to connect relative rates of effusion to relative molar masses.

Plan We use Equation 10.22 to determine the molar mass of the unknown gas. If we let r_x and M_x represent the rate of effusion and molar mass of the gas, we can write

$$\frac{r_x}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_x}}$$

Solve From the information given,

$$r_x = 0.355 \times r_{\text{O}_2}$$

Thus,

$$\begin{aligned}\frac{r_x}{r_{\text{O}_2}} &= 0.355 = \sqrt{\frac{32.0 \text{ g/mol}}{M_x}} \\ \frac{32.0 \text{ g/mol}}{M_x} &= (0.355)^2 = 0.126 \\ M_x &= \frac{32.0 \text{ g/mol}}{0.126} = 254 \text{ g/mol}\end{aligned}$$

Because we are told that the unknown gas is composed of homonuclear diatomic molecules, it must be an element. The molar mass must represent twice the atomic weight of the atoms in the unknown gas. We conclude that the unknown gas must have an atomic weight of 127 g/mol and therefore is I_2 .

► Calculate the ratio of the effusion rates of N_2 gas and O_2 gas.

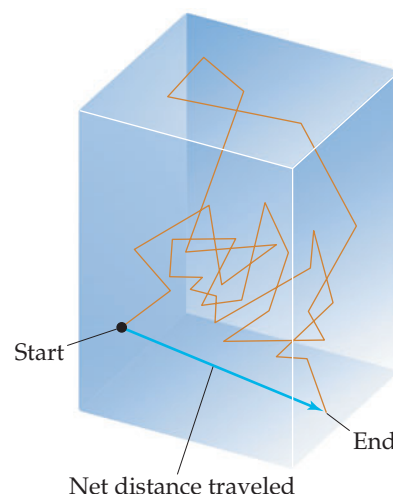
Diffusion and Mean Free Path

Although diffusion, like effusion, is faster for lower-mass molecules than for higher-mass ones, molecular collisions make diffusion more complicated than effusion.

Graham's law, Equation 10.22, approximates the ratio of the diffusion rates of two gases under identical conditions. We can see from the horizontal axis in Figure 10.15 that the speeds of molecules are quite high. For example, the rms speed of molecules of N_2 gas at room temperature is 515 m/s. In spite of this high speed, if someone opens a vial of perfume at one end of a room, some time elapses—perhaps a few minutes—before the scent is detected at the other end of the room. This tells us that the diffusion rate of gases throughout a volume of space is much slower than molecular speeds.* This difference is due to molecular collisions, which occur frequently for a gas at atmospheric pressure—about 10^{10} times per second for each molecule. Collisions occur because real gas molecules have finite volumes.

Because of molecular collisions, the direction of motion of a gas molecule is constantly changing. Therefore, the diffusion of a molecule from one point to another consists of many short, straight-line segments as collisions buffet it around in random directions (Figure 10.17).

The average distance traveled by a molecule between collisions, called the molecule's **mean free path**, varies with pressure as the following analogy illustrates. Imagine



▲ **Figure 10.17** Diffusion of a gas molecule. For clarity, no other gas molecules in the container are shown.

*The rate at which the perfume moves across the room also depends on how well stirred the air is from temperature gradients and the movement of people. Nevertheless, even with the aid of these factors, it still takes much longer for the molecules to traverse the room than one would expect from their rms speed.

CHEMISTRY PUT TO WORK Gas Separations

The fact that lighter molecules move at higher average speeds than more massive ones has many interesting applications. For example, developing the atomic bomb during World War II required scientists to separate the relatively low-abundance uranium isotope ^{235}U (0.7%) from the much more abundant ^{238}U (99.3%). This separation was accomplished by converting the uranium into a volatile compound, UF_6 , that was then allowed to pass through a porous barrier (Figure 10.18). Because of the pore diameters, this process is not simple effusion. Nevertheless, the way in which rate of passing through the pores depends on molar mass is essentially the same as that in effusion. The slight difference in molar mass between $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ caused the molecules to move at slightly different rates:

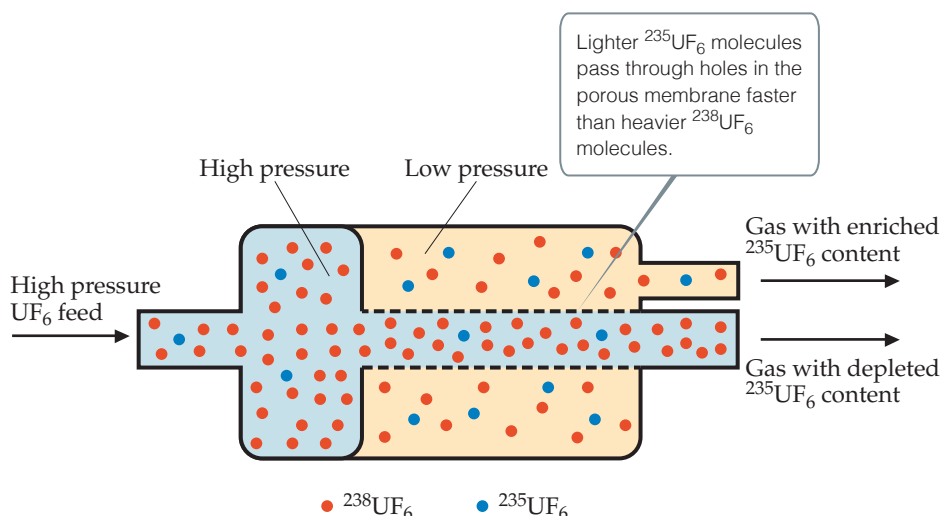
$$\frac{r_{235}}{r_{238}} = \sqrt{\frac{352.04}{349.03}} = 1.0043$$

Thus, the gas initially appearing on the opposite side of the barrier is very slightly enriched in ^{235}U . The process is repeated thousands

of times, leading to a nearly complete separation of the two isotopes. Because of the large number of steps needed to adequately separate the isotopes, gaseous diffusion facilities are large-scale structures.

An increasingly popular method of separating uranium isotopes is by a technique that uses centrifuges. In this procedure, cylindrical rotors containing UF_6 vapor spin at high speed inside an evacuated casing. Molecules of $^{238}\text{UF}_6$ move closer to the spinning walls, whereas molecules of $^{235}\text{UF}_6$ remain in the middle of the cylinders. A stream of gas moves the $^{235}\text{UF}_6$ from the center of one centrifuge into another. Plants that use centrifuges consume less energy than those that use effusion and can be constructed in a more compact, modular fashion.

Related Exercises: 10.37, 10.97



▲ **Figure 10.18** Uranium enrichment by gaseous diffusion. The lighter $^{235}\text{UF}_6$ effuses through a porous barrier at a slightly faster rate than $^{238}\text{UF}_6$. The pressure difference across the membrane drives the effusion. The enrichment shown here for a single step is exaggerated for illustrative purposes.

walking through a shopping mall. When the mall is crowded (high pressure), the average distance you can walk before bumping into someone is short (short mean free path). When the mall is empty (low pressure), you can walk a long way (long mean free path) before bumping into someone. The mean free path for air molecules at sea level is about 60 nm. At about 100 km in altitude, where the air pressure is much lower, the mean free path is about 10 cm, over 1 million times longer than at the Earth's surface.

Self-Assessment Exercise

10.35 One of worst smelling compounds known is thioacetone ($\text{C}_3\text{H}_6\text{S}$). If a sample of thioacetone and ethanethiol ($\text{C}_2\text{H}_6\text{S}$) were released into a laboratory, which compound would travel farther in one minute?

- (a) $\text{C}_2\text{H}_6\text{S}$
(b) $\text{C}_3\text{H}_6\text{S}$