

## 9.4: Effusion and Diffusion of Gases

### Learning Objectives

- Define and explain effusion and diffusion
- State Graham's law and use it to compute relevant gas properties

If you have ever been in a room when a piping hot pizza was delivered, you have been made aware of the fact that gaseous molecules can quickly spread throughout a room, as evidenced by the pleasant aroma that soon reaches your nose. Although gaseous molecules travel at tremendous speeds (hundreds of meters per second), they collide with other gaseous molecules and travel in many different directions before reaching the desired target. At room temperature, a gaseous molecule will experience billions of collisions per second. The mean free path is the average distance a molecule travels between collisions. The mean free path increases with decreasing pressure; in general, the mean free path for a gaseous molecule will be hundreds of times the diameter of the molecule

In general, we know that when a sample of gas is introduced to one part of a closed container, its molecules very quickly disperse throughout the container; this process by which molecules disperse in space in response to differences in concentration is called diffusion (shown in Figure 9.4.1). The gaseous atoms or molecules are, of course, unaware of any concentration gradient, they simply move randomly—regions of higher concentration have more particles than regions of lower concentrations, and so a net movement of species from high to low concentration areas takes place. In a closed environment, diffusion will ultimately result in equal concentrations of gas throughout, as depicted in Figure 9.4.1. The gaseous atoms and molecules continue to move, but since their concentrations are the same in both bulbs, the rates of transfer between the bulbs are equal (no *net* transfer of molecules occurs).

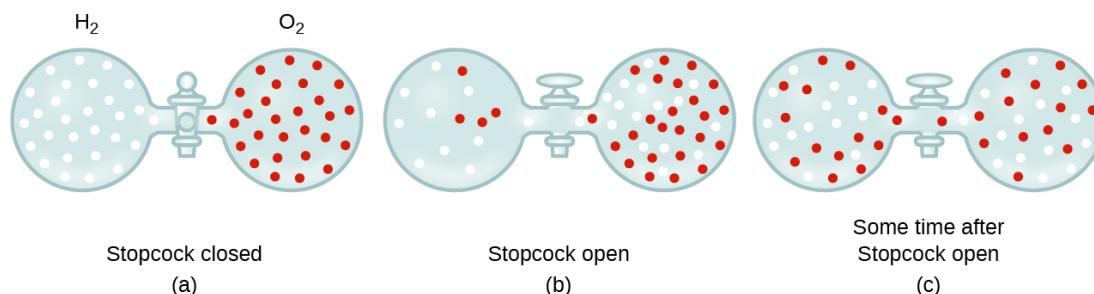


Figure 9.4.1: (a) Two gases,  $\text{H}_2$  and  $\text{O}_2$ , are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas,  $\text{H}_2$ , passes through the opening faster than  $\text{O}_2$ , so just after the stopcock is opened, more  $\text{H}_2$  molecules move to the  $\text{O}_2$  side than  $\text{O}_2$  molecules move to the  $\text{H}_2$  side. (c) After a short time, both the slower-moving  $\text{O}_2$  molecules and the faster-moving  $\text{H}_2$  molecules have distributed themselves evenly on both sides of the vessel.

In this figure, three pairs of gas filled spheres or vessels are shown connected with a stopcock between them. In a, the figure is labeled, "Stopcock closed." Above, the left sphere is labeled, " $\text{H}_2$ ." It contains approximately 30 small, white, evenly distributed circles. The sphere to its right is labeled, " $\text{O}_2$ ." It contains approximately 30 small red evenly distributed circles. In b, the figure is labeled, "Stopcock open." The stopcock valve handle is now parallel to the tube connecting the two spheres. On the left, approximately 9 small, white circles and 4 small, red circles are present, with the red spheres appearing slightly closer to the stopcock. On the right side, approximately 25 small, red spheres and 21 small, white spheres are present, with the concentration of white spheres slightly greater near the stopcock. In c, the figure is labeled "Some time after Stopcock open." In this situation, the red and white spheres appear evenly mixed and uniformly distributed throughout both spheres.

We are often interested in the rate of diffusion, the amount of gas passing through some area per unit time:

$$\text{rate of diffusion} = \frac{\text{amount of gas passing through an area}}{\text{unit of time}}$$

The diffusion rate depends on several factors: the concentration gradient (the increase or decrease in concentration from one point to another); the amount of surface area available for diffusion; and the distance the gas particles must travel. Note also that the time required for diffusion to occur is inversely proportional to the rate of diffusion, as shown in the rate of diffusion equation.

A process involving movement of gaseous species similar to diffusion is effusion, the escape of gas molecules through a tiny hole such as a pinhole in a balloon into a vacuum (Figure 9.4.1). Although diffusion and effusion rates both depend on the molar mass of the gas involved, their rates are not equal; however, the ratios of their rates are the same.

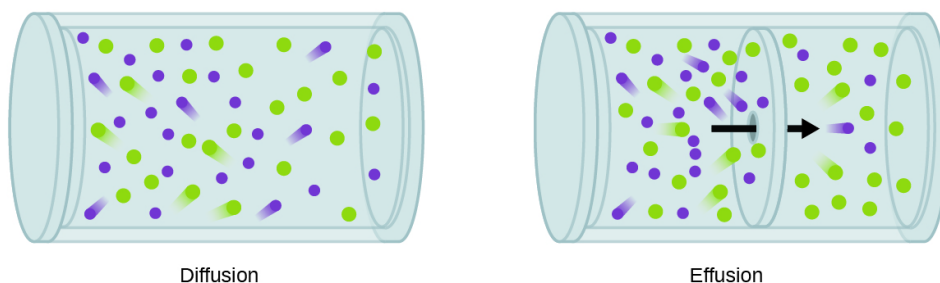


Figure 9.4.2: Diffusion occurs when gas molecules disperse throughout a container. Effusion occurs when a gas passes through an opening that is smaller than the mean free path of the particles, that is, the average distance traveled between collisions. Effectively, this means that only one particle passes through at a time.

This figure contains two cylindrical containers which are oriented horizontally. The first is labeled “Diffusion.” In this container, approximately 25 purple and 25 green circles are shown, evenly distributed throughout the container. “Trails” behind some of the circles indicate motion. In the second container, which is labeled “Effusion,” a boundary layer is evident across the center of the cylindrical container, dividing the cylinder into two halves. A black arrow is drawn pointing through this boundary from left to right. To the left of the boundary, approximately 16 green circles and 20 purple circles are shown again with motion indicated by “trails” behind some of the circles. To the right of the boundary, only 4 purple and 16 green circles are shown.

If a mixture of gases is placed in a container with porous walls, the gases effuse through the small openings in the walls. The lighter gases pass through the small openings more rapidly (at a higher rate) than the heavier ones (Figure 9.4.2). In 1832, Thomas Graham studied the rates of effusion of different gases and formulated Graham’s law of effusion: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles:*

$$\text{rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

This means that if two gases A and B are at the same temperature and pressure, the ratio of their effusion rates is inversely proportional to the ratio of the square roots of the masses of their particles:

$$\frac{\text{rate of effusion of B}}{\text{rate of effusion of A}} = \frac{\sqrt{\mathcal{M}_A}}{\sqrt{\mathcal{M}_B}}$$

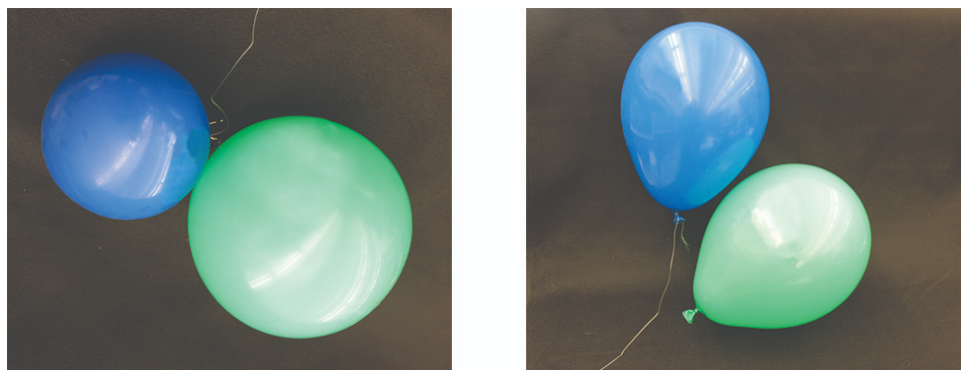


Figure 9.4.3: A balloon filled with air (the blue one) remains full overnight. A balloon filled with helium (the green one) partially deflates because the smaller, light helium atoms effuse through small holes in the rubber much more readily than the heavier molecules of nitrogen and oxygen found in air. (credit: modification of work by Mark Ott)

This figure shows two photos. The first photo shows a blue balloon which floats above a green balloon. The green balloon is resting on a surface. Both balloons are about the same size. The second photo shows the same two balloons, but the blue one is now smaller than the green one. Both are resting on a surface.

#### ✓ Example 9.4.1: Applying Graham's Law to Rates of Effusion

Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen.

##### Solution

From Graham’s law, we have:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{1.43 \text{ g L}^{-1}}}{\sqrt{0.0899 \text{ g L}^{-1}}} = \frac{1.20}{0.300} = \frac{4}{1}$$

Using molar masses:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{32 \text{ g mol}^{-1}}{2 \text{ g mol}^{-1}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Hydrogen effuses four times as rapidly as oxygen.

### ? Exercise 9.4.1

At a particular pressure and temperature, nitrogen gas effuses at the rate of 79 mL/s. Using the same apparatus at the same temperature and pressure, at what rate will sulfur dioxide effuse?

**Answer**

52 mL/s

Here's another example, making the point about how determining times differs from determining rates.

### ✓ Example 9.4.2: Effusion Time Calculations

It takes 243 s for  $4.46 \times 10^{-5}$  mol Xe to effuse through a tiny hole. Under the same conditions, how long will it take  $4.46 \times 10^{-5}$  mol Ne to effuse?

#### Solution

It is important to resist the temptation to use the times directly, and to remember how rate relates to time as well as how it relates to mass. Recall the definition of rate of effusion:

$$\text{rate of effusion} = \frac{\text{amount of gas transferred}}{\text{time}}$$

and combine it with Graham's law:

$$\frac{\text{rate of effusion of gas Xe}}{\text{rate of effusion of gas Ne}} = \frac{\sqrt{M_{\text{Ne}}}}{\sqrt{M_{\text{Xe}}}}$$

To get:

$$\frac{\frac{\text{amount of Xe transferred}}{\text{time for Xe}}}{\frac{\text{amount of Ne transferred}}{\text{time for Ne}}} = \frac{\sqrt{M_{\text{Ne}}}}{\sqrt{M_{\text{Xe}}}}$$

Noting that *amount of A = amount of B*, and solving for *time for Ne*:

$$\frac{\frac{\cancel{\text{amount of Xe}}}{\text{time for Xe}}}{\frac{\cancel{\text{amount of Ne}}}{\text{time for Ne}}} = \frac{\text{time for Ne}}{\text{time for Xe}} = \frac{\sqrt{M_{\text{Ne}}}}{\sqrt{M_{\text{Xe}}}} = \frac{\sqrt{M_{\text{Ne}}}}{\sqrt{M_{\text{Xe}}}}$$

and substitute values:

$$\frac{\text{time for Ne}}{243 \text{ s}} = \sqrt{\frac{20.2 \text{ g mol}^{-1}}{131.3 \text{ g mol}^{-1}}} = 0.392$$

Finally, solve for the desired quantity:

$$\text{time for Ne} = 0.392 \times 243 \text{ s} = 95.3 \text{ s}$$

Note that this answer is reasonable: Since Ne is lighter than Xe, the effusion rate for Ne will be larger than that for Xe, which means the time of effusion for Ne will be smaller than that for Xe.

### ? Exercise 9.4.2

A party balloon filled with helium deflates to  $\frac{2}{3}$  of its original volume in 8.0 hours. How long will it take an identical balloon filled with the same number of moles of air ( $\mathcal{M} = 28.2 \text{ g/mol}$ ) to deflate to  $\frac{1}{2}$  of its original volume?

**Answer**

32 h

Finally, here is one more example showing how to calculate molar mass from effusion rate data.

### ✓ Example 9.4.3: Determining Molar Mass Using Graham's Law

An unknown gas effuses 1.66 times more rapidly than  $\text{CO}_2$ . What is the molar mass of the unknown gas? Can you make a reasonable guess as to its identity?

**Solution**

From Graham's law, we have:

$$\frac{\text{rate of effusion of Unknown}}{\text{rate of effusion of CO}_2} = \frac{\sqrt{\mathcal{M}_{\text{CO}_2}}}{\sqrt{\mathcal{M}_{\text{Unknown}}}}$$

Plug in known data:

$$\frac{1.66}{1} = \frac{\sqrt{44.0 \text{ g/mol}}}{\sqrt{\mathcal{M}_{\text{Unknown}}}}$$

Solve:

$$\mathcal{M}_{\text{Unknown}} = \frac{44.0 \text{ g/mol}}{(1.66)^2} = 16.0 \text{ g/mol}$$

The gas could well be  $\text{CH}_4$ , the only gas with this molar mass.

### ? Exercise

Hydrogen gas effuses through a porous container 8.97-times faster than an unknown gas. Estimate the molar mass of the unknown gas.

**Answer**

163 g/mol

### 📌 Application: Use of Diffusion for Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of  $^{235}\text{U}$ , the kind of uranium that is "fissile," that is, capable of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5%  $^{235}\text{U}$ , and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of Graham's law. In a gaseous diffusion enrichment plant,

uranium hexafluoride ( $\text{UF}_6$ , the only uranium compound that is volatile enough to work) is slowly pumped through large cylindrical vessels called diffusers, which contain porous barriers with microscopic openings. The process is one of diffusion because the other side of the barrier is not evacuated. The  $^{235}\text{UF}_6$  molecules have a higher average speed and diffuse through the barrier a little faster than the heavier  $^{238}\text{UF}_6$  molecules. The gas that has passed through the barrier is slightly enriched in  $^{235}\text{UF}_6$  and the residual gas is slightly depleted. The small difference in molecular weights between  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  only about 0.4% enrichment, is achieved in one diffuser (Figure 9.4.4). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.

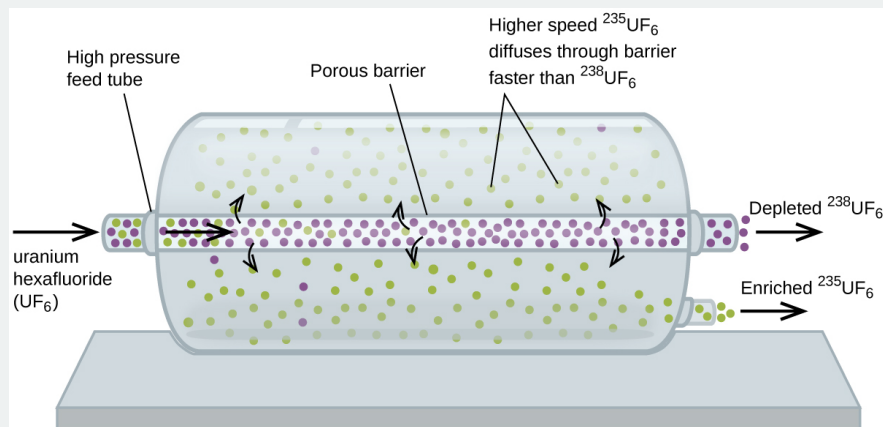


Figure 9.4.4: In a diffuser, gaseous  $\text{UF}_6$  is pumped through a porous barrier, which partially separates  $^{235}\text{UF}_6$  from  $^{238}\text{UF}_6$ . The  $\text{UF}_6$  must pass through many large diffuser units to achieve sufficient enrichment in  $^{235}\text{U}$ .

This figure shows a large cylindrical container oriented horizontally. A narrow tube or pipe which is labeled “porous barrier” runs horizontally through the center of the tube and extends a short distance out from the left and right ends of the cylinder. At the far left, an arrow points right into the tube. This arrow is labeled, “Uranium hexafluoride (  $\text{U F}$  subscript 6 ).” A line segment connects the label, “High pressure feed tube,” to the tube where it enters the cylinder. In the short region of tube outside the cylinder, 5 small, purple circles and 4 small, green circles are present. Inside the cylinder, an arrow points right through the tube which contains many evenly distributed, purple circles and a handful of green circles which decrease in quantity moving left to right through the cylinder. Curved arrows extend from the inner area of the tube into the outer region of the cylinder. Three of these arrows point into the area above the tube and three point into the area below. Two line segments extend from the label, “Higher speed superscript 235 U F subscript 6 diffuses through barrier faster than superscript 238 U F subscript 6,” to two green circles in the space above the tube. In the short section of tubing just outside the cylinder, 8 small, purple circles are present. An arrow labeled, “Depleted superscript 238 U F subscript 6,” points right extending from the end of this tube. The larger space outside the tube contains approximately 100 evenly distributed small green circles and only 5 purple circles. Eight of the purple circles appear at the left end of the cylinder. A tube exits the lower right end of the cylinder. It has 5 green circles followed by a right pointing arrow and the label, “Enriched superscript 235 U F subscript 6.”

The large scale separation of gaseous  $^{235}\text{UF}_6$  from  $^{238}\text{UF}_6$  was first done during the World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about  $10^{-6}$  cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive  $\text{UF}_6$ .

Because gaseous diffusion plants require very large amounts of energy (to compress the gas to the high pressures required and drive it through the diffuser cascade, to remove the heat produced during compression, and so on), it is now being replaced by gas centrifuge technology, which requires far less energy. A current hot political issue is how to deny this technology to Iran, to prevent it from producing enough enriched uranium for them to use to make nuclear weapons.

## Summary

Gaseous atoms and molecules move freely and randomly through space. Diffusion is the process whereby gaseous atoms and molecules are transferred from regions of relatively high concentration to regions of relatively low concentration. Effusion is a similar process in which gaseous species pass from a container to a vacuum through very small orifices. The rates of effusion of gases are inversely proportional to the square roots of their densities or to the square roots of their atoms/molecules’ masses (Graham’s law).

#### 9.4.0.0.1: Key Equations

- rate of diffusion =  $\frac{\text{amount of gas passing through an area}}{\text{unit of time}}$
- $\frac{\text{rate of effusion of gas A}}{\text{rate of effusion of gas B}} = \frac{\sqrt{m_B}}{\sqrt{m_A}} = \frac{\sqrt{\mathcal{M}_B}}{\sqrt{\mathcal{M}_A}}$

### Summary

#### diffusion

movement of an atom or molecule from a region of relatively high concentration to one of relatively low concentration (discussed in this chapter with regard to gaseous species, but applicable to species in any phase)

#### effusion

transfer of gaseous atoms or molecules from a container to a vacuum through very small openings

#### Graham's law of effusion

rates of diffusion and effusion of gases are inversely proportional to the square roots of their molecular masses

#### mean free path

average distance a molecule travels between collisions

#### rate of diffusion

amount of gas diffusing through a given area over a given time

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