11.9: Mean Free Path, Diffusion, and Effusion of Gases
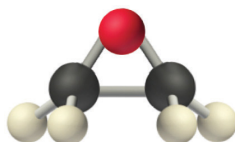
Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant and random motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment.

Diffusion is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. Diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. The related process, effusion, is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship *is referred to as Graham's law*, after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses:

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}}. \tag{11.9.1}$$

Ethylene oxide

Heavy molecules effuse through a porous material more slowly than light molecules, as illustrated schematically in Figure 10.8.1 for ethylene oxide and helium. Helium ($M = 4.00$ g/mol) effuses much more rapidly than ethylene oxide ($M = 44.0$ g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol, whereas air has an average molar mass of about 29 g/mol, pure helium effuses through the microscopic pores in the rubber balloon $\sqrt{\frac{29}{4.00}} = 2.7$ times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Hence, mylar balloons can retain their helium for days.
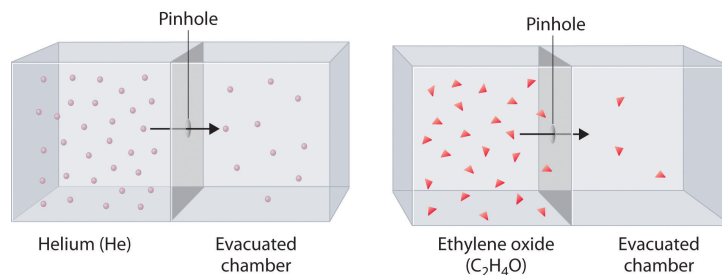

Figure 10.8.1 The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms ($M = 4.00$ g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules ($M = 44.0$ g/mol), as predicted by Graham's law.

Note

At a given temperature, heavier molecules move more slowly than lighter molecules.

Example 10.8.1

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. **Given:** isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

   Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

   A. **Solution:**
      1. The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is 234.04 + (6)(18.998) = 349.03 g/mol 238.05 + (6)(18.998) = 352.04 g/mol
      The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law.

$$\frac{\text{rate }^{235}UF_6}{\text{rate }^{238}UF_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043 \tag{11.9.2}$$

Figure *A Portion of a Plant for Separating Uranium Isotopes by Effusion of UF₆. The large cylindrical objects (note the human for scale) are so-called diffuser (actually effuser) units, in which gaseous UF₆ is pumped through a porous barrier to partially separate the isotopes. The UF₆ must be passed through multiple units to become substantially enriched in ²³⁵U.*

Rates of Diffusion or Effusion

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE = \frac{1}{2}\frac{M_A}{N_A}v^2_{\text{rms,A}} = \frac{1}{2}\frac{M_B}{N_A}v^2_{\text{rms,B}} \tag{10.8.1}$$

Multiplying both sides by 2 and rearranging give