

2.9: Graham's Laws of Diffusion and Effusion

Learning Objectives

- Understand the difference between effusion and diffusion
- To derive and apply Graham's Law of Effusion

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:

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \quad (2.9.1)$$

Graham Law

The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass.

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 (recall that a result of the Kinetic Theory of Gases is that the temperature, in degrees Kelvin, is directly proportional to the average kinetic energy of the molecules.) . We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE = \frac{1}{2} \frac{M_A}{N_A} v_{\text{rms,A}}^2 = \frac{1}{2} \frac{M_B}{N_A} v_{\text{rms,B}}^2 \quad (2.9.2)$$

Multiplying both sides by 2 and rearranging give

$$\frac{v_{\text{rms,B}}^2}{v_{\text{rms,A}}^2} = \frac{M_A}{M_B} \quad (2.9.3)$$

Taking the square root of both sides gives

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_A}{M_B}} \quad (2.9.4)$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. Equation 2.9.4 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

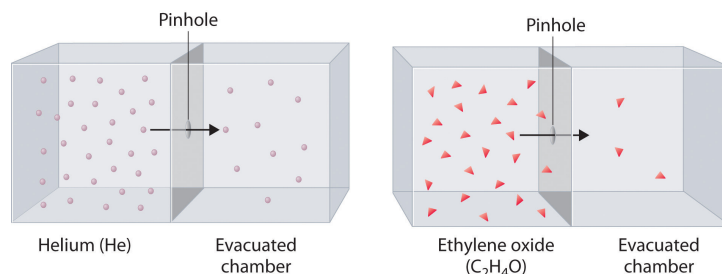


Figure 2.9.1: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms ($M = 4.00$ g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules ($M = 44.0$ g/mol), as predicted by Graham's law.

Heavy molecules effuse through a porous material more slowly than light molecules, as illustrated schematically in Figure 2.9.1 for ethylene oxide C_2H_4O and helium He . 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.

✓ Example 2.9.1

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 = $56^\circ C$).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
2. If n identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the n th power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

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 $^{235}UF_6$

Strategy:

- A. Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.
- B. Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

1. A 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

The molar mass of $^{238}UF_6$ is

$$238.05 + (6)(18.998) = 352.04 \text{ g/mol}$$

The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using Equation 2.9.1:

$$\frac{\text{rate } ^{235}\text{UF}_6}{\text{rate } ^{238}\text{UF}_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043 \quad (2.9.5)$$

2.

Thus passing UF_6 containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is $(0.720\%)(1.0043) = 0.723\% \text{ } ^{235}\text{UF}_6$.

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