9.16: Kinetic Theory of Gases - Graham's Law of Diffusion

Faster-moving molecules can escape more readily through small holes or pores in containers. Such an escape is called **effusion**. They can also mix more rapidly with other gases by **diffusion**. Such processes are usually carried out at constant temperature, and so the relative rates of diffusion or effusion of two gases A and B depend only on the molar masses M_{A} and M_{B}:

$$(u_{\mathrm{A}})_{\mathrm{rms}} = \sqrt{\frac{3RT}{M_{\mathrm{A}}}} \; (u_{\mathrm{B}})_{\mathrm{rms}} = \sqrt{\frac{3RT}{M_{\mathrm{B}}}}$$

The rates of effusion or diffusion are proportional to the *rms* velocities, and so:

$$\frac{\text{Rate of diffusion of A}}{\text{Rate of diffusion of B}} = \frac{(u_{\mathrm{A}})_{\mathrm{rms}}}{(u_{\mathrm{B}})_{\mathrm{rms}}} = \frac{\sqrt{\frac{3RT}{M_{\mathrm{A}}}}}{\sqrt{\frac{3RT}{M_{\mathrm{B}}}}} = \sqrt{\frac{3RT}{M_{\mathrm{A}}} \times \frac{M_{\mathrm{B}}}{3RT}} = \sqrt{\frac{M_{\mathrm{B}}}{M_{\mathrm{A}}}} \tag{9.16.1}$$

This result is known as **Graham's law of diffusion** after Thomas Graham (1805 to 1869), a Scottish chemist, who discovered it by observing effusion of gases through a thin plug of plaster of paris. Graham's law of diffusion states that the ratio of the diffusion rate of two gases is the same as the ratio of the square root of the molar mass of the gases.

Example 9.16.1: Effusion Rates

Calculate the relative rates of effusion of $He(g)$ and $O_2(g)$.

Solution

From Equation 9.16.1

$$\frac{\text{Rate of diffusion of He}}{\text{Rate of diffusion of O}_2} = \frac{\sqrt{M_{\mathrm{O_2}}}}{\sqrt{M_{\mathrm{He}}}} = \sqrt{\frac{32.00 \text{ g mol}^{-1}}{4.003 \text{ g mol}^{-1}}} = 2.83$$

In other words we would expect He to escape from a balloon nearly 3 times as fast as O_2.

The video below demonstrates the difference in effusion rate between air (mostly Nitrogen) and Helium. Both are used to fill a balloon. When the balloon is untied, which do you think will shrink faster, the Helium balloon or the balloon filled with normal air?

The next video is not critical, but can be watched for further demonstrations of Graham's law. Like the last video, it provides examples of Graham's law in action, physically demonstrating the relationship between molar mass and effusion/diffusion rate.