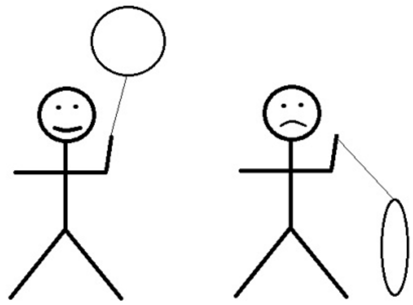
2.5: Graham’s Law of Effusion

An important consequence of the kinetic molecular theory is what it predicts in terms of *effusion* and *diffusion* effects. Effusion is defined as a loss of material across a boundary. A common example of effusion is the loss of gas inside of a balloon over time.



The rate at which gases will effuse from a balloon is affected by a number of factors. But one of the most important is the frequency with which molecules collide with the interior surface of the balloon. Since this is a function of the average molecular speed, it has an inverse dependence on the square root of the molecular weight.

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{MW}}$$

This can be used to compare the relative rates of effusion for gases of different molar masses.

The Knudsen Cell Experiment

A Knudsen cell is a chamber in which a thermalized sample of gas is kept, but allowed to effuse through a small orifice in the wall. The gas sample can be modeled using the Kinetic Molecular Theory model as a collection of particles traveling throughout the cell, colliding with one another and also with the wall. If a small orifice is present, any molecules that would collide with that portion of the wall will be lost through the orifice.

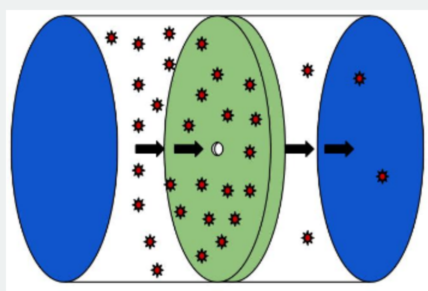


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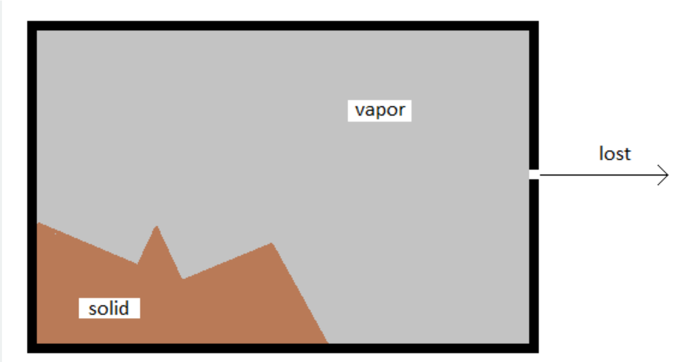
Figure 2.5.1: Effusion of gas particles through an orifice. (CC BY-SA 3.0; Astrang13).

This makes a convenient arrangement to measure the vapor pressure of the material inside the cell, as the total mass lost by effusion through the orifice will be proportional to the vapor pressure of the substance. The vapor pressure can be related to the mass lost by the expression

$$p = \frac{g}{A\Delta t}\sqrt{\frac{2\pi RT}{MW}}$$

where g is the mass lost, A is the area of the orifice, Δt is the time the effusion is allowed to proceed, T is the temperature and MW is the molar mass of the compound in the vapor phase. The pressure is then given by p. A schematic of what a Knudsen cell might look like is given below.


vapor
lost
solid