9.2: The Pressure-Volume Relationship: Boyle's Law

The kinetic molecular theory is useful when we are trying to understand the properties and behaviors of gases. The KMT (and related theories) tell us that:

- There is a tremendous amount of distance between individual particles in the gas phase.
- Gas particles move randomly at various speeds and in every possible direction.
- Attractive forces between individual gas particles are negligible.
- Collisions between gas particles are fully elastic.
- The average kinetic energy of particles in the gas phase is proportional to the temperature of the gas.

In reality, these predictions only apply to "ideal gases". An ideal gas has perfectly elastic collisions and has no interactions with its neighbors or with the container. Real gases deviate from these predictions, but at common temperatures and pressures, the deviations are generally small and in this text we will treat all gases as if they were "ideal".

Because there is so much empty space between gas molecules, it is easy to see why a gas is so compressible. If you have a container filled with a gas, you can *squeeze* it down to a smaller volume by applying pressure. The harder you squeeze (the more pressure you apply) the smaller the resulting volume will be. Imagine a bicycle pump compressing air into a tire. As pressure is applied to the pump, the same number of gas molecules are squeezed into a smaller volume.

The dependence of volume on pressure is not linear. In 1661, Robert Boyle systematically studied the compressibility of gasses in response to increasing pressure. Boyle found that the dependence of volume on pressure was *non-linear* but that a linear plot could be obtained if the volume was plotted against the *reciprocal* of the pressure, $1/P$. This is stated as **Boyle's law**.

Boyle's law

The volume (V) of an ideal gas varies *inversely* with the applied pressure (P) when the temperature (T) and the number of moles (n) of the gas are constant.

Mathematically, Boyle's law can be stated as:

$$V \propto \frac{1}{P} \;\; at\ constant\ T\ and\ n$$

$$V = constant\left(\frac{1}{P}\right) \;\; or \;\; PV = constant$$

We can use Boyle's law to predict what will happen to the volume of a sample of gas as we change the pressure. Because PV is a constant for any given sample of gas (at constant T), we can imagine two states; an initial state with a certain pressure and volume (P_1V_1), and a final state with different values for pressure and volume (P_2V_2). Because PV is always a constant, we can equate the two states and write:

$$P_1V_1 = P_2V_2$$

Example 9.2.1:

Now imagine that we have a container with a piston that we can use to compress the gas inside. You are told that, initially, the pressure in the container is 765 mm Hg and the volume is 1.00 L. The piston is then adjusted so that the volume is now 0.500 L; what is the final pressure?

Solution

We substitute into our Boyle's law equation:

$$P_1V_1 = P_2V_2$$

$$(765\ mm\ Hg)(1.00\ L) = P_2(0.500\ L)$$

$$P_2 = \left(\frac{(765\ mm\ Hg)(1.00\ L)}{(0.500\ L)}\right) = 1530\ mm\ Hg$$

Exercise 9.2.1

1. A container with a piston contains a sample of gas. Initially, the pressure in the container is exactly 1 atm, but the volume is unknown. The piston is adjusted so that the volume is 0.155 L and the pressure is 956 mm Hg; what was the initial volume?
2. The pressure of 12.5 L of a gas is 0.82 atm. If the pressure changes to 1.32 atm, what will the final volume be? A sample of helium gas has a pressure of 860.0 mm Hg. This gas is transferred to a different container having a volume of 25.0 L; in this new container, the pressure is determined to be 770.0 mm Hg. What was the initial volume of the gas?