

9-7. Additional pressure versus numbers of molecules per unit volume, as measured at the temperature of melting ice.

and so there are 2.70×10^{25} molecules/m³. Consequently, we know how many molecules we have put into V_0 . For example, if V_b , the volume of a bag, is 1 liter (that is, 10^{-3} m³), each bag load is 2.70×10^{25} molecules/m³ $\times 10^{-3}$ m³ = 2.70×10^{22} molecules. We also know the pressure which they exert as measured by the height of the mercury column on the left. At the temperature of melting ice we find that when we have 2.70×10^{25} molecules/m³ the gas pressure holds up a column of mercury 76 cm high. And in general, since the pressure is proportional to the number of molecules per unit volume, the pressure can be expressed by

$$\frac{\text{Pressure in cm height of mercury}}{76 \text{ cm height of mercury}} = \frac{\text{No. of molecules/m}^3}{2.70 \times 10^{25} \text{ molecules/m}^3}$$

In symbols this is

$$\frac{P}{76} = \frac{N/V}{2.70 \times 10^{25}} \quad \text{or} \quad P = 2.81 \times 10^{-24} \frac{N}{V}$$

where N/V is the number N of molecules divided by the volume V they occupy, P has the units of cm height of mercury held up, and the volume V is in m³.

In Chapter 8 we found that the volume occupied by a certain number of molecules at atmospheric pressure is independent of the kind of molecule. Now by using different gases we can see whether the pressure depends on the nature of the gas. With these experiments we find that in general the pressure depends on the number of molecules

per unit volume but not on the nature of the molecules. All gases behave the same way as long as their densities are reasonably low, that is, as long as the average space between molecules is large compared to their dimensions.

We can repeat the whole set of experiments with a different enclosed volume V_1 , in place of the volume V_0 ; we then get the same result in terms of the number of molecules per unit volume. In this way we are further assured that it is N/V , the number of molecules per unit volume, that determines the pressure.

So far we have worked only at the temperature of melting ice. We can repeat these experiments at the temperature of boiling water. Everything comes out the same except the proportionality factor, which is now $3.84 \times 10^{-24} \frac{\text{cm of mercury}}{(\text{molecules/m}^3)}$

instead of $2.81 \times 10^{-24} \frac{\text{cm of mercury}}{(\text{molecules/m}^3)}$ which we found at the ice point. Again at other temperatures the pressure is proportional to the number of molecules per unit volume but the proportionality factor differs, depending on the temperature.

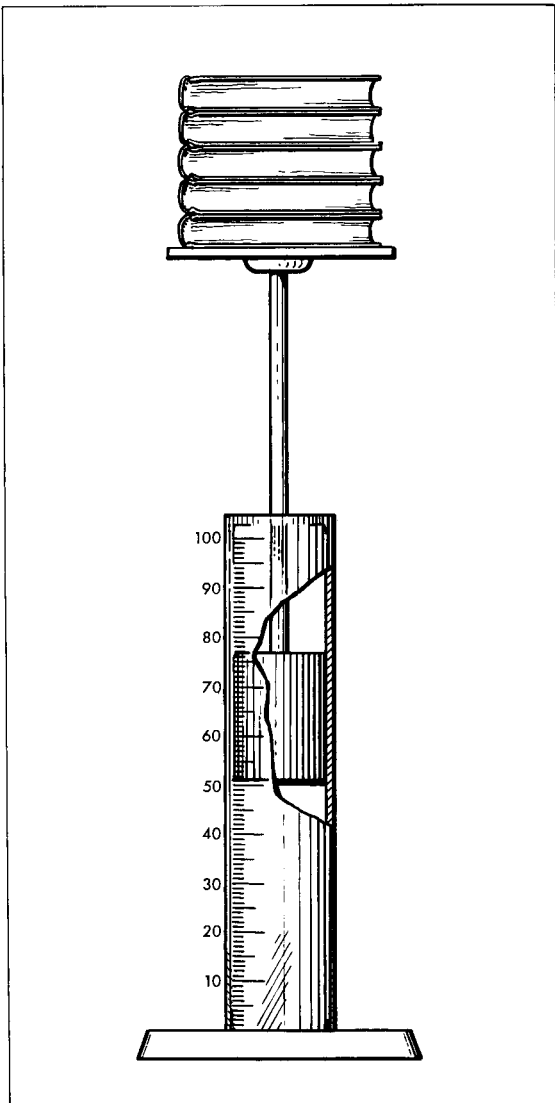
In brief, then, from these experiments, we find that at a given temperature, the pressure exerted by a gas is proportional to the number of molecules divided by the volume they occupy:

$$P = \theta \frac{N}{V}$$

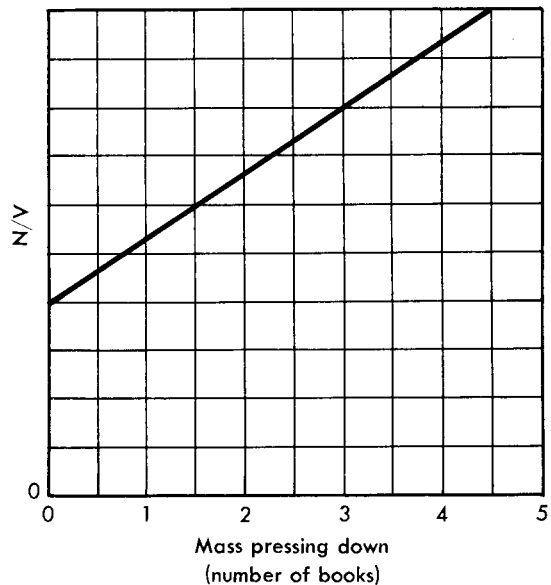
where θ is the proportionality factor. This is just what we should expect as long as the molecules do not get in one another's way too much. As long as they have enough space, the number of molecules bombarding the walls of the container depends on the number that are present in the region next to the wall; and consequently, the pressure should be proportional to N/V as we have found. If there are twice as many molecules per unit volume — twice as many in the region near the wall — then twice as many will hit the same area of wall in a given time, and the pressure will be twice as big. This law of the behavior of gases is known as Boyle's law, after Robert Boyle, brilliant contemporary of Newton, who first showed it experimentally.

You can also demonstrate Boyle's law by experimenting with a particular sample of gas in a container closed by a piston (Fig. 9-8). By placing more and more mass on the piston you can

increase the pressure on the gas and watch the enclosed volume V decrease. If you make all changes slowly, the gas stays at room temperature. Then if you plot N/V versus the mass pressing down, as in Fig. 9-9, you see that the volume is inversely proportional to the pressure. (Remember, the container is closed so that only V , not N , changes.) Here you must remember to include the pressure of the atmosphere. The bombardment of the gas in the atmosphere shoves down on the piston about as hard as a column of mercury 76 cm high.



9-8. Apparatus to demonstrate Boyle's law. As additional books (masses) are placed on the platform, the air in the cylinder is compressed and the height of the air column becomes less. The number of books used serves as a measure of the pressure, and the height of the air column gauges the volume.



9-9. Boyle's-law curve. The data plotted in the above curve we obtain by using the apparatus of Fig. 9-8. Using the apparatus shown in Fig. 9-8, N/V does not become zero when there is no mass on the platform, because the pressure of the atmosphere is still pushing down.

The atmospheric pressure actually varies depending on the amount of air that happens to be above us, but 76 cm of mercury is about the value at sea level, and it is used to define a standard atmospheric pressure.

Boyle's law fits the molecular model of a gas beautifully. It is just what we should expect if a lot of wide-spaced molecules race around hitting the walls of a container. The model looks good. Let us seek its limitations. Suppose we increase the pressure on our sample greatly. We squeeze more and more gas into the same volume. The density goes up. Finally the molecules are no longer flying about freely. They must touch each other a great part of the time, and we are outside the range of our simple model in which it is assumed that the molecules are far apart. The model is therefore no longer valid. When the gas is so compressed, the pressure against the walls will no longer depend upon the collisions of the moving molecules. It has become the pressure required to squeeze the molecules themselves into a smaller volume. This is a property, not of the motion of molecules, but of their internal structure. Long before the molecules are so tightly jammed together, the model fails; and so does Boyle's law.