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# Molecular Collisions

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O2

N2

Before

Some time after…

Oxygen molecule flies into nitrogen gas

If two spheres both have diameter *d*, they will collide if their centers get within *d* of each other

“Stovepipe” of volume swept out by oxygen molecule

bounce!

bounce!



(We can see from this that the average length of stovepipe sections between elbows is 200 times the pipe radius, so neglecting any volume corrections from the elbows was an excellent approximation, and our diagram has the sections far too short compared with the diameter.)

**Notice that this derivation of the mean free path *in terms of the molecular diameter* depends *only* on knowing the *ratio of the gas density to the liquid density*—*it does not depend on the actual size of the molecules*!**

But it *does* mean that if we can somehow measure the mean free path, by measuring how fast one gas diffuses into another, for example, we can deduce the size of the molecules, and historically this was one of the first ways the size of molecules was determined, and so Avogadro’s number was found.

### But the Pinball Picture is Too Simple: the Target Molecules Are Moving!

There is one further correction we should make. We took the N2 molecules to be at rest, whereas in fact they’re moving as fast as the oxygen molecule, approximately. This means that even if the O2 is temporarily at rest, it can undergo a collision as an N2 comes towards it. Clearly, what really counts in the collision rate is the *relative* velocity of the molecules.

Defining the average velocity as the root mean square velocity, if the O2 has velocity and the N2  , then the square of the relative velocity

,

since  must average to zero, the relative directions being random. So the average *square* of the relative velocity is twice the average square of the velocity, and therefore the average root-mean-square velocity is up by a factor √2, and the collision rate is increased by this factor. Consequently, the mean free path is *decreased* by a factor of √2 when we take into account that *all* the molecules are moving.

Our final result, then, is that the mean free path

.

Finding the mean free path is—literally—the first step in figuring out how rapidly the oxygen atoms will diffuse into the nitrogen gas, and of course vice versa.

### If Gases Intermingle 0.5cm in One Second, How Far in One Hour?

What we really want to know is just how much we can expect the gases to have intermingled after a given period of time. We’ll just follow the one molecule, and estimate how far it gets. To begin with, let’s assume for simplicity that it tales steps all of the same length *l*, but after each collision it bounces off in a random direction. So after *N* steps, it will have moved to a point

,

where each vector  has length *l*, but the vectors all point in random different directions.

If we now imagine many of the oxygen molecules following random paths like this, how far on average can we expect them to have drifted after *N* steps? (Note that they could with equal likelihood be going backwards!) The appropriate measure is the root-mean-square distance,



Since the direction after each collision is completely random, , and the root-mean-square distance

.

If we allow steps of different lengths, the same argument works, but now *l* is the root-mean-square path length. *The important factor here is the* .

This means that the average distance diffused in one second is , say half a centimeter (justified in the next section). The average distance in one *hour* would be *only* 60 times this, or 30 cm., and in a day about a meter and a half—the average distance traveled is only increasing as the *square root* of the time elapsed!

This is a very general result. For example, suppose we have a gas in which the mean free path is *l* and the average speed of the molecules is *v*. Then the average time between collisions. The number of collisions in time *t* will be  so the average distance a molecule moves in time *t* will be .

### Actually Measuring Mean Free Paths

It should be clear from the above that by carefully observing how quickly one gas diffuses into another, the mean free path could be estimated. Obviously, oxygen and nitrogen are not the best candidates: to see what’s going on, a highly visible gas like bromine diffusing into air would be more practical. However, there’s a better way to find the mean free path. As we proved in the [lecture on viscosity](http://galileo.phys.virginia.edu/classes/152.mf1i.spring02/Viscosity.htm), the viscosity coefficient , where *n* is the number density, *m* the molecular mass, *v* the average speed and *l* the mean free path. The viscosity can be measured quite accurately, the mean free path in air was found to be , or 

In 1865, Josef Loschmidt gave the first good estimate of the size of molecules. He used the viscosity data to find the mean free path, assumed as we did above that the molecules were more or less touching each other in the liquid, then used the geometric argument above to nail down the ratio of molecular size to mean free path. He overestimated by a factor of three or so, but this was much closer to the truth than anyone else at the time.

Here are some numbers: for O2, N2, , , the speed of the molecules at room temperature *v* is approximately 500 meters per sec., so the molecule has of order 1010 collisions per second.

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