Gases

The Ideal Gas Theory and Kinetic-Molecular Theory of Gases

The Kinetic-Molecular Theory of Gases

One of the really important ideas in chemistry is that we ought to be able to make a connection between what's going on on the atomic molecular level and what's going on on a macroscopic level. When it comes to ideal gases, what we have on the macroscopic level is the ideal gas law—that there's a relationship between the pressure of the gas, the volume of the container, the number of moles of gas, and the absolute temperature of the gas sample. What we'd like to be able to do now is shrink ourselves down, come up with a model that's operating on the atomic molecular level, and see if, out of that, we can develop the ideal gas law. That connection is known as the kinetic-molecular theory of gases. It begins with a set of assumptions, and from the assumptions, we can build what hopefully is something that looks very much like the ideal gas law.

The assumptions begin with, one, that a pure gas consists of identical molecules separated by distances that are great compared to their size. Why is this important? It's important because what we'd like to imagine is that a given particle has essentially the entire container, the physical volume of the container, in which to move around. The other particles are in the box, but they don't really obstruct that particle, so that particle can move around, particularly because the particles are separated by great distances compared to their size.

A second assumption is that the molecules are in rapid, continuous, and random motion. They're just moving around in the container. Some of them are hardly going to be moving at all, and some of them are going to be moving fast, so there's going to be a distribution of speeds of these gas particles, but we can think of them as all moving at least at some point. They stop, maybe, but then a short time later, because of collisions, that particle is going to be moving again.

The third assumption is that the average kinetic energy of gas molecules is proportional to the temperature—and this is the absolute temperature, regardless of the molecular mass of the gas. This is a relatively non-intuitive assumption, but we're going to see that it fits beautifully with where we're trying to get. What this says is: suppose we have two gas samples, and they're at exactly the same temperature—say, a really big gas, like uranium hexafluoride, and a really tiny gas, like helium. It doesn't say that the particles in the sample, on average, are moving at the same speed, but what it says is that the average kinetic energy of the gas particles is the same. And the average kinetic energy is given by $(1/2) \times$ the mass of a particle times the velocity of the particle squared. This says something about how the kinetic energies are related to the absolute temperature.

The fourth assumption is that the gas molecules collide with one another and with the walls of their container—and colliding with the walls of the container is what we're curious about, times the average momentum of each particle. The idea here would be that if we had a really big particle, a very massive particle, then it's going to somehow contribute more to the pressure than if we had a smaller particle. If we think about getting hit with a bowling ball, that's going to be a lot more painful than getting hit with a ping pong ball, if both of them were traveling at the same speed.
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The average momentum is given by the mass times the average speed. We've just talked about why a bowling ball might carry more momentum than a ping pong ball at the same velocity, or the same speed. Similarly, you'd probably rather get hit with a baseball traveling at 1 mile per hour than a baseball traveling from Randy Johnson at 100 miles per hour. The 100 mph baseball is going to have a much higher momentum. Again, we're talking about collisions with the wall, and if momentum is the important point, then the average momentum is going to depend on both the mass of the particles and the average speed. So that's the average momentum part.

Now let's think about the frequency of collisions part. The frequency of collisions is going to be also proportional to the average speed. Why? If you think about a container, and it has particles, and the particles are moving very slowly, then they're going to encounter a wall relatively less often than if they're moving fast. So it makes sense that the frequency of collisions should depend on the average speed. It's also going to depend on the number of particles. If you imagine there's only one particle in the box, then it's going to run into the wall at a certain frequency of collisions, but if there are Avogadro's number of particles in the box, then the frequency of collisions of any sort is going to be much higher. So it makes sense that the frequency of collisions should be proportional to the number of particles in the box.

Also, the frequency of collisions is inversely proportional to the volume. That is, if the box is small, then the particles are going to run into the wall more often than if the box is gigantic, because if the box is really big, the particles are going to spend a lot more time in the middle of the box somewhere away from the walls, so they're not going to collide with the walls so often.

Now we substitute in. The average speed is still u, the number of particles is N, and the volume is v. We now have algebraic expressions for the frequency of collisions and the average momentum. Those two things are shown here. P is proportional, again, to average momentum and frequency of collisions. We substitute in for our average momentum and substitute in for our frequency of collisions, and we now have that the pressure is proportional to the number of particles times the mass of a given particle times the square of the speed, all divided by the volume of the container. It doesn't seem like we're exactly at the ideal gas law yet, but let's now look at and see if we can find something to substitute for . The N and the v are sort of in place. The ideal gas law says that P is proportional to N, the number of moles, that this is proportional to the number of moles, and inversely proportional to the volume of the container, so that's good. Now we just have to figure out what we're going to do with this part.

What we're going to do with this part is use one of the assumptions of the kinetic-molecular theory, and that is that the kinetic energy is just proportional to the absolute temperature. That would be assumption number three, that the average kinetic energy, which is \( \frac{1}{2}m\bar{v}^2 \), is proportional to the absolute temperature, T. Where does that get us? In addition to making the assumption, or recognizing, that the number of particles is proportional to the number of moles, we now have that the pressure is proportional to the number of moles and the absolute temperature, and inversely proportional to the volume. And this thing, if it's true, is a direct proportionality, and we can say that PV is proportional to nT. That's just multiplying through by V. And if something is proportional to something else, we can turn that into an equality by just inserting a constant. So P times V is equal to the number of moles times the universal gas constant times T, the absolute temperature: PV = nRT. So we've been able to make a connection between what's going on on the atomic molecular level and what's going on that's measurable on the macroscopic level. That's the ideal gas law.

If you believe all of this, or if you understand all of this, then we can consider a problem. Here’s a problem. Consider a sample of helium that behaves as an ideal gas in a container at some pressure and temperature. Based on the kinetic-molecular theory of gases, what is the effect on collisions between helium atoms and the walls of the container, as a result of the following changes? All we're really worried about is what happens to the number of collisions with the walls, of the helium atoms only.

Suppose we have our container, and there's some rate of collisions, some number of collisions with the wall, and we add more helium while keeping the volume and the temperature constant. How is that going to affect what's going on? If we're keeping the volume constant, then particles are going to hit the walls just as often, and if the temperature is constant, then they're still going to have the same kinetic energy. But there are going to be more particles, because we threw a bunch more particles in. We added helium to the container. So there's no effect from the volume, because the volume is constant, and there's no effect from the temperature, but because we just put more particles in, the
pressure should go up. And that’s what we know happens with the ideal gas law. You increase the number of moles, and the pressure goes up. The reason why the pressure goes up in this case is that there are more collisions, because there are more particles.

What about (b) increasing the temperature while keeping the volume and number of helium atoms constant? What happens when we increase the temperature? When we increase the temperature, we increase the average speed. We don’t change anything about the mass, but we increase the temperature, we increase the average kinetic energy, which means we increase the speed. And when we increase the speed of the particles, the average speed, we expect that the particles are going to collide with the walls more frequently and also carry a greater momentum. So the pressure goes up when we increase the temperature.

What about when we increase the volume while keeping the temperature and the number of atoms constant? Now the container is bigger, so the particles spend more time in the middle of the container, not colliding into a wall, so the number of collisions is going to go down, and so we expect the pressure is going to go down. That makes perfect sense in the context of the kinetic-molecular theory.

What about if we add an entirely different gas? Suppose we put some argon in, assuming that the argon is still going to behave like an ideal gas, and suppose that we keep the temperature constant. What effect is this going to have on the helium? We didn’t say anything at all about the effect of heliums running into other heliums. All we said was that if the heliums are running into the wall, that’s going to create pressure. If we have argon atoms in there, it shouldn’t really affect how often helium runs into the wall, particularly because we’ve made the assumption that the particles are so far apart that they’re essentially not interacting. So the helium doesn’t even know the argon is in there, and the partial pressure of helium is going to stay exactly the same. The total pressure is going to go up, and the reason why the total pressure is going to go up is because now we have to think about what’s happening to the argons. The argons are also crashing into walls, so they’re contributing to pressure, but as far as the helium is concerned, the partial pressure of helium is going to be exactly the same. That’s really what Dalton’s law is all about: the helium doesn’t know the argon is there, and the argon doesn’t know that the helium is there.

What we’ve been able to do is make this connection between what’s going on on the atomic molecular level, using your intuition and doing a little bit of hand-waving, but to get an expression that is the ideal gas law. Things have to behave that way. In other words, you have to be able to make a connection between the atomic molecular level and the macroscopic level. Fortunately, using the kinetic-molecular theory of gases, we can do exactly that.