

## Chapter 17

## GASES, Part 2

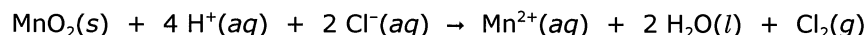
©2004, 2008, 2011 Mark E. Noble

We've completed several mathematical relationships for the gas phase. Now we'll start putting this into stoichiometry.

**17.1 Stoichiometry with gases**

As noted in the prior Chapter, we can use the ideal gas equation in stoichiometry. Remember:  $PVnRT$  provides a link between the number of moles of something and measurable quantities of the sample.

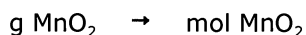
Here's the first stoichiometry problem. Consider the redox reaction given by the following equation.



You react 4.786 g  $\text{MnO}_2$  according to this equation, and you collect all of the chlorine gas in a 458 mL vessel at 19 °C. What is the pressure (in atm) of the chlorine collected under these conditions?

This is still stoichiometry and it's still the same four Steps which we've been doing. Step 1, the balanced equation, is provided. Proceed to the next Steps.

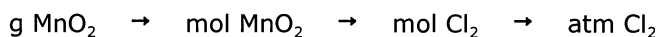
Step 2. Convert g  $\text{MnO}_2$  to mol, using molar mass.



Step 3. Convert mol  $\text{MnO}_2$  to mol  $\text{Cl}_2$ , using rxn ratio.



Step 4. Convert mol  $\text{Cl}_2$  to atm  $\text{Cl}_2$ , using  $PVnRT$ .



Notice that we are able to make this final conversion to  $P$  because we have  $n$  from Step 3 and we have  $V$  and  $T$  in the given information.

Although I have been keeping my calculation strings together as much as possible so far, I am going to break this one at the point of entry into the ideal gas equation. I'm just doing this for a little added clarity for the first example. Let's do Steps 2 and 3 first.

$$\begin{aligned} & \text{g MnO}_2 \rightarrow \text{mol MnO}_2 \rightarrow \text{mol Cl}_2 \\ 4.786 \text{ g MnO}_2 & \times \frac{\text{mol MnO}_2}{86.94 \text{ g MnO}_2} \times \frac{\text{mol Cl}_2}{\text{mol MnO}_2} = 0.05505 \text{ mol Cl}_2 \end{aligned}$$

So far, this tells us that 0.05505 mol  $\text{Cl}_2$  is possible from the reaction. For Step 4, we plug this into  $PVnRT$ , bringing in the given volume and temperature. Notice that you need to convert temperature to K and volume to L.

$$P = \frac{nRT}{V} = \frac{(0.05505 \text{ mol}) \left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (292 \text{ K})}{0.458 \text{ L}} = 2.88 \text{ atm}$$

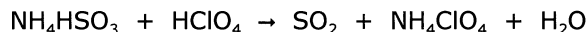
That's it.

That's your first taste of stoichiometry with  $PVnRT$ . Things aren't much different. Let's do another problem, but we'll up the ante.

**Example 1.** Consider the reaction of 25.0 mL of 0.561 M ammonium bisulfite solution with excess perchloric acid. If all the gas is collected at STP, what volume will it occupy?

This is one of those long, multi-step problems like we did in Chapter 15. Break it into parts. This is stoichiometry and we need a balanced equation. For the balanced equation, we need formulas of reactants and products. You were given names of reactants and you can write the formulas for those. You also need the products. What are they? Well, what kind of reaction is this? The reactants include a bisulfite and an acid, so this is a gas-forming reaction: one product is  $\text{SO}_2$  gas, along with a salt and water. Which salt? The anion of the salt comes from the acid, so it's perchlorate. The cation of the salt comes from the other reactant, so it's ammonium. Taken together, the salt is ammonium perchlorate.

Got all that? If so, you can start setting up the equation; if not, go back and review gas-forming reactions in Chapter 12.



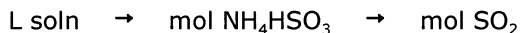
That's your equation and it happens to be balanced as written. Step 1 is done.

Now, we head into the stoichiometry string. Again, I'll cut the calculation string for clarity. By the way, the risk involved when you cut the string in the middle is a round-off error. You can avoid this if you don't round-off at the cut. I'll show that here.

Convert L soln to mol  $\text{NH}_4\text{HSO}_3$  using molarity.



Convert mol  $\text{NH}_4\text{HSO}_3$  to mol  $\text{SO}_2$  by the rxn ratio.



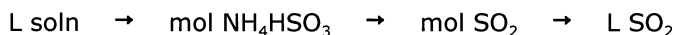
I'll cut the string here. Run it out to this point.

$$\text{L soln} \rightarrow \text{mol NH}_4\text{HSO}_3 \rightarrow \text{mol SO}_2$$

$$0.0250 \text{ L soln} \times \frac{0.561 \text{ mol NH}_4\text{HSO}_3}{\text{L soln}} \times \frac{\text{mol SO}_2}{\text{mol NH}_4\text{HSO}_3} = 0.014025... \text{ mol SO}_2$$

I didn't round-off yet. Leave this full number on your calculator for the next part.

Now do your final conversion: convert mol  $\text{SO}_2$  to L  $\text{SO}_2$ , using  $PVnRT$  and the other information which was provided. That completes the path.



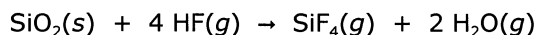
Using the above value of 0.014025... mol, go into  $PVnRT$ ; notice that STP was specified.

$$V = \frac{nRT}{P} = \frac{(0.014025... \text{ mol}) \left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (273.15 \text{ K})}{\text{one atm}} = 0.314 \text{ L}$$

There's your answer: the reaction produces 0.314 L of  $\text{SO}_2$  gas.

Alright, another Example. We'll combine a gas mixture problem along with stoichiometry.

**Example 2.** The following reaction is conducted at 199 °C in a vessel with a gas volume of 531 L.



Starting with an initial pressure of 1142 Torr of HF and with excess  $\text{SiO}_2$ , what are the pressures (in atm) of  $\text{SiF}_4$  and of  $\text{H}_2\text{O}$  at the end? What is the total pressure (in atm) at the end?

There's a bunch of things here, so you need to break it down. A balanced equation is given, so you don't have to worry about that. You're given an amount for HF. You're told  $\text{SiO}_2$  is in excess, so it won't enter into the stoichiometry issue. You're asked for a pressure of  $\text{SiF}_4$  and that's one stoichiometry part. You're also asked for a pressure of  $\text{H}_2\text{O}$  and that's a second stoichiometry part. (In the past, we worked a lot with liquid phase  $\text{H}_2\text{O}$  but this time you're told it's a gas by the phase designation in the equation.) The third part of the problem is total pressure, which is just adding the two pressures together. By the way, when you're actually running reactions with more than one gas product, it's the total pressure that determines whether your container blows up or not, so total pressure is a useful calculation.

► Part 1. Find the pressure of the  $\text{SiF}_4$  product.

Just follow Steps 2 - 4 for general stoichiometry.

Convert the given units for HF into moles of HF. That needs  $PVnRT$ . I'm plugging 1142/760 straight into the equation for pressure.

$$n(\text{HF}) = \frac{PV}{RT} = \frac{\left(\frac{1142}{760} \text{ atm}\right)(531 \text{ L})}{\left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(472 \text{ K})} = 20.600\dots \text{ mol HF}$$

Convert this to mol  $\text{SiF}_4$  by the rxn ratio.

$$20.600\dots \text{ mol HF} \times \frac{\text{mol SiF}_4}{4 \text{ mol HF}} = 5.1500\dots \text{ mol SiF}_4$$

Notice that I didn't round the 20.600... and the 5.1500... yet. We'll round off at the end.

Now, convert this into  $P(\text{SiF}_4)$  using  $PVnRT$  and the available information.

$$P(\text{SiF}_4) = \frac{nRT}{V} = \frac{(5.1500\dots \text{ mol})\left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(472 \text{ K})}{531 \text{ L}} = 0.376 \text{ atm}$$

✓ The pressure of  $\text{SiF}_4$  is 0.376 atm. That finishes this part.

► Part 2. Find the pressure of the  $\text{H}_2\text{O}$  product.

This starts from moles of HF again, which we already have from Part 1 above: it's 20.600... mol HF.

Relate mol HF to mol  $\text{H}_2\text{O}$  by the rxn ratio.

$$20.600\dots \text{ mol HF} \times \frac{\text{mol H}_2\text{O}}{2 \text{ mol HF}} = 10.300\dots \text{ mol H}_2\text{O}$$

Convert this into  $P(\text{H}_2\text{O})$  using  $PVnRT$  and the available information.

$$P(\text{H}_2\text{O}) = \frac{nRT}{V} = \frac{(10.300\dots \text{ mol})\left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(472 \text{ K})}{531 \text{ L}} = \text{_____ atm}$$

✓ You fill it in. That's the  $\text{H}_2\text{O}$  pressure.

► Part 3. Find total pressure.

This is the bunny part: add the two together.

$$P_{\text{total}} = P(\text{SiF}_4) + P(\text{H}_2\text{O}) = 0.376 \text{ atm} + \text{_____ atm} = 1.127 \text{ atm}$$

✓ The total pressure is 1.127 atm.

We're done.

This is a good opportunity to show another use of the general gas equation.

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

In the prior Chapter, we used this to derive the pressure/mole ratio relationship for mixtures.

“ Since everybody's in the same container,  $V_1 = V_2$  and  $T_1 = T_2$ , so all  $V$ 's and  $T$ 's drop out.

$$\frac{P_1}{n_1} = \frac{P_2}{n_2}$$

Now, rearrange.

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

This says that pressure ratios and mole ratios are equal between the components within any gas mixture. ”

For as long as  $V_1 = V_2$  and  $T_1 = T_2$ , this relationship holds true. We can even use this in stoichiometry when one gas is a reactant and one is a product. I'll show this for Part 1 above in which we had to find the pressure of the  $\text{SiF}_4$  produced from the given amount of HF. Re-arrange the above equation.

$$P_1 = \frac{n_1}{n_2} P_2$$

Set subscript 1 for SiF<sub>4</sub>; set subscript 2 for HF.

$$P(\text{SiF}_4) = \frac{1}{4} P(\text{HF})$$

Notice that the mole ratio is the rxn ratio from the balanced equation. Plug in  $P(\text{HF})$  and solve.

$$P(\text{SiF}_4) = \frac{1}{4} \times \left( \frac{1142}{760} \text{ atm} \right) = 0.3757 \text{ atm}$$

There's your answer. It's the same as above except for the number of sigfigs.

This method is very general and it can be useful in numerous circumstances. Sometimes it may be faster than the full method which I showed above using our standard stoichiometry Steps 2 - 4. Again, you have multiple methods for doing something. This method can also be used when  $T$  changes during the reaction, in which case you have to retain  $T_1$  and  $T_2$  in the equation. There are also other variations, but that's enough for us for right now.

This will end our stoichiometry. It's time to change gears.

To this point, we've pretty much emphasized the "big picture", meaning the bulk properties of the gas phase. The bulk properties are the properties of the sample as a whole. Let's go deeper at this time and look at the gas phase more at the molecular level. I've already mentioned some of this in the last Chapter, but now we're ready to see how the bulk properties are related to the molecular behavior.

## 17.2 Molecules in motion

These three simple words, "molecules in motion", describe a major chunk of the fundamental description of the gas phase. Technically, we refer to the molecular description of the gas phase as the "kinetic molecular theory". "Kinetic" relates to motion anyway, so it's the same thing. But motion isn't the only notion. I'm bringing back the part I said in Chapter 16 for emphasis. It says it more fully.

“ THE MOLECULES OF THE GAS PHASE ARE WIDELY SEPARATED, THEY MOVE RAPIDLY AND RANDOMLY ABOUT, THEIR OWN VOLUME IS VERY LITTLE OF THE ACTUAL VOLUME OF THE SAMPLE, AND THEY DO NOT INTERACT WITH EACH OTHER. ”

These molecules are whizzing through mostly-empty space, banging into each other or anything else that gets in their way. If they hit one another, they bounce off and go on, although now in some other direction. If they hit something else like the wall of the container they're in, then they bounce off that, too, and bolt off in some other direction. This gives rise to that bulk property which we call pressure. The container feels pressure because the gas molecules are constantly colliding with its walls. If you put a pressure gauge in the sample, the molecules will bang into the pressure gauge and that will register some amount of pressure. What we call pressure is the grand product of all these collisions. This grand product has three parts:

- Velocity. That O<sub>2</sub> molecule in the air just hit you in the eyeball at about one thousand miles per hour. Did you forget to duck? Well, it wouldn't matter. You would never notice it. Although we generally regard a collision at that speed as disastrous, velocity is not the only part of this picture.
- Mass. You would never notice an O<sub>2</sub> molecule hitting you at one thousand miles per hour because its mass is so small,  $5.3 \times 10^{-23}$  g. Even at ten thousand miles per hour, you would not notice anything of that little mass. But mass is not the only part of this picture.
- Frequency. By frequency, I mean the frequency of collision within some area of surface, such as your eyeball or the wall of a container. It's not just one molecule of O<sub>2</sub> colliding with that surface, it's zillions of molecules, every fraction of a second, constantly.

Put all three of these together and you get the bulk property we call pressure: zillions and zillions of extremely minute masses striking at very high speeds every split second.

These molecules follow the good, old, classical laws of motion, the stuff going back to Newton. (Isaac, not Fig.) These laws deal with mass, velocity, force, etc. With these laws, you can derive  $PVnRT$ . The derivation ties together the idea of molecules-in-motion with the bulk property of pressure. I won't do the whole thing from scratch right now, but I will derive some of the important results. Our starting point in this discussion is the following equation, using the parameters from above.

$$P = \frac{2}{3} \times \text{mass} \times \text{velocity} \times \text{frequency}$$

Let's look at the terms here. The third in the denominator comes from breaking the motions in three dimensions down to one dimension at a time. The factor of two arises from the physics involved, which relates to the molecule hitting the surface and then bouncing off. The terms mass  $\times$  velocity give momentum,

$$\text{momentum} = \text{mass} \times \text{velocity}$$

which can be viewed as how hard something hits. This relationship says that heavier and/or faster molecules will hit harder. The frequency is related to velocity and concentration.

$$\text{frequency} = \frac{1}{2} \times \text{velocity} \times \text{concentration}$$

The 1/2 factor arises because, on average in any given sample, half the molecules are moving toward the wall and half are moving away. This frequency relationship says that faster particles will hit a surface more often, and, there will be more total hits per time when there are more molecules per volume. Now we return to the starting equation

$$P = \frac{2}{3} \times \text{mass} \times \text{velocity} \times \text{frequency}$$

and we substitute for the frequency.

$$P = \frac{2}{3} \times \text{mass} \times \text{velocity} \times \frac{1}{2} \times \text{velocity} \times \text{concentration}$$

This simplifies to the following.

$$P = \frac{1}{3} \times \text{mass} \times \text{velocity}^2 \times \text{concentration}$$

We can use  $n/V$  for concentration. Let me also abbreviate the other terms:  $m$  is for mass and lower case  $v$  is for velocity. I'll rewrite this as

$$P = \frac{1}{3} \times m \times v^2 \times \frac{n}{V}$$

We need to bring in a couple more equations, this time dealing with kinetic energy,  $KE$ .  $KE$  is just the energy of motion. Laws of motion tell us that, for a single moving object,

$$\text{(for any object)} \quad KE = \frac{1}{2} \times m \times v^2$$

A gas sample has many different molecules moving at many different speeds. For this, we must derive an average kinetic energy by taking the average of the squared speed for all molecules.

$$\text{(avg per molecule)} \quad KE_{\text{avg}} = \frac{1}{2} \times m \times \text{avg}(v^2)$$

Often, an average (or mean) is indicated by an overbar ( $\overline{\quad}$ ). Thus,  $\text{avg}(v^2)$  would be written  $\overline{v^2}$ . Either way, this term is the average (mean) of the squares of the speeds; it is commonly called the "mean-squared" speed.

If we consider one mole of these molecules, then the combined mass is one molar mass ( $M$ ).

$$\text{(for one mole)} \quad KE_{\text{mol}} = \frac{1}{2} \times M \times \overline{v^2}$$

Now, we need one other equation for kinetic energy. This one relates to temperature. It's very important. Although I introduce it last, it is foremost in importance.

$$\text{(for one mole)} \quad KE_{\text{mol}} = \frac{3}{2} \times R \times T$$

This equation is a biggie: the kinetic energy of a gas sample is determined by temperature only. Notice that  $R$  is present. Although  $R$  is called the gas constant, it's actually an energy/temperature constant and it comes into play in other applications. I alluded to this in Chapter 16.

“  $R$  is called the gas constant and the same  $R$  applies for all gases. It's actually a fundamental physical constant which is not just limited to gas things and it pops up in other uses. These other uses can have different units for  $R$  although they are the same  $R$ . ”

This last equation is the origin of  $R$  in  $PVnRT$ . It's an essential part of the kinetic energy connection. Here's something else to notice in the last equation above: there is no dependence on identity. It doesn't matter at all whether the gas is  $N_2$ ,  $O_2$ ,  $CH_4$ ,  $H_2O$  vapor,  $Xe$ , or whatever. I'll say it again: **THE KINETIC ENERGY OF A GAS SAMPLE IS DETERMINED BY ITS TEMPERATURE ONLY.**

Let's continue. Take the last two equations and set them equal.

$$KE_{\text{mol}} = \frac{1}{2} \times M \times \overline{v^2} = \frac{3}{2} \times R \times T$$

Get rid of the halves.

$$\underline{M \times \overline{v^2}} = 3 \times R \times T$$

I underlined a part, but leave the whole thing there for a moment. Bring back pressure from the prior page.

$$P = \frac{1}{3} \times m \times v^2 \times \frac{n}{V}$$

Now convert this equation to mole scale. For one mole, the mass is the molar mass,  $M$ . For  $v^2$ , we use the average,  $\overline{v^2}$ .

$$P = \frac{1}{3} \times \underline{M \times \overline{v^2}} \times \frac{n}{V}$$

Note that the underlined part here is the same as the part underlined above. Substitute  $3 \times R \times T$  for the underlined part.

$$P = \frac{1}{3} \times 3 \times R \times T \times \frac{n}{V}$$

Cancel the 3's and there you have it.

$$P = \frac{n}{V} \times R \times T$$

There's the overall result, just where we started in Chapter 16: the pressure of a gas is proportional to its concentration times its temperature. Here, we see that it all derives from velocity, mass and frequency: zillions and zillions of extremely minute masses striking some surface area at very high speeds every split second. And again, this result does not depend on the identity of the gas.

Identity can become important for some parts of this picture. For example, within the term  $M \times \overline{v^2}$  for kinetic energy, identity is important due to the molar mass. But, as we see above, this term ultimately drops out to get the usual  $PVnRT$ . Whenever the mass and speed terms are retained, however, then identity does matter. This leads us to mass and speed relationships for molecules of different kinds of compounds. This is where we go next.

### 17.3 The need for speed

Fast. Very fast. Let's go into more detail on molecular speed at this time.

Taken together, speed and mass are a function of kinetic energy,

$$KE_{\text{mol}} = \frac{1}{2} \times M \times \overline{v^2}$$

but kinetic energy is determined only by temperature.

$$KE_{\text{mol}} = \frac{3}{2} \times R \times T$$

So really,  $M \times \overline{v^2}$  depends on  $T$ , as derived above.

$$M \times \overline{v^2} = 3 \times R \times T$$

For some specific  $T$ , all gases have the same value of  $M \times \overline{v^2}$ . Different gases will have different molar masses and different speeds, but they will still have the same product,  $M \times \overline{v^2}$ .

The last equation above provides a way to calculate speeds for different gases at different temperatures. Let's re-arrange that equation.

$$\overline{v^2} = \frac{3RT}{M}$$

This provides a calculation for mean-squared speed. What we really want is an average speed, not an average of squared speed. Commonly, we take the square root of the above equation.

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}}$$

The terminology gets a bit weird here, so I want to take a moment and point out the idiosyncrasies of the math. We are going to take the square root of an average (mean) of squared speeds. Many people think that this should come out to be the same as a simple average, but it doesn't. I'll give you an example to illustrate this, using just the two numbers 6 and 8. Find their mean: it's exactly 7. Now take 6 and 8, and square each (36 and 64); take the mean of those (50), and take the square root of that: it's 7.071... . This value differs from the simple mean. This shows you that the simple mean and the square-root-of-the-mean-of-the-squares are not the same thing.

To simplify this terminology, the phrase "square-root-of-the-mean-of-the-squares" gets contracted to "root-mean-squared". To simplify even more, "root-mean-squared" gets abbreviated to "rms". That brings us to the bottom line for what we need right now. The term  $\overline{v^2}$  is the mean-squared speed. When we take its square root, we get the root-mean-squared speed, which gets its own symbol,  $v_{\text{rms}}$ . This is called the "rms speed".

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}}$$

The rms speed is not exactly the average speed, but the derivation for average speed is more involved. For our purposes here, it is sufficient to derive the rms speed and that is what we will use for a representative speed. All the zillions of molecules are moving at a range of different speeds, and  $v_{\text{rms}}$  is our representative value. It's close to the true average, although it's not exactly the average mathematically.

Before doing an actual calculation, let's look at two important qualitative results from that equation. First, compare different gases with different molar masses ( $M$ ), all at the same  $T$ .

➔ As  $M$  increases, then  $v_{\text{rms}}$  decreases.

This means that, as mass increases, then speed decreases. In other words, heavier molecules move slower and lighter molecules move faster. For example, the following is a comparison of increasing molar mass versus decreasing speed.

molar mass:	$\text{H}_2 < \text{He} < \text{N}_2 < \text{CO}_2 < \text{SO}_2 < \text{Cl}_2 < \text{Xe}$
speed:	$\text{H}_2 > \text{He} > \text{N}_2 > \text{CO}_2 > \text{SO}_2 > \text{Cl}_2 > \text{Xe}$

Xe is heavy and slow.  $\text{H}_2$  is light and fast. In fact,  $\text{H}_2$  is the lightest and fastest of all gases.

Now let's examine our second qualitative result. Compare the speed and temperature using the above  $v_{\text{rms}}$  equation.

➔ As  $T$  increases, then  $v_{\text{rms}}$  increases.

For any gas, the molecules move faster when the sample is hotter. That carries additional consequences: if the molecules are moving faster, then they are hitting harder and they are hitting more often. That's more pressure!

OK, I said we would do an actual speed calculation. Let's do that now. This is plug-and-chug, using the  $v_{\text{rms}}$  equation.

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Although this is plug-and-chug, there are two catches. Here's the first catch: we derived this equation from laws of motion, and their units are the standard units for those equations. Although  $R$  is still the same old gas constant, it does not enter into this equation with the units of  $\text{L} \cdot \text{atm}/\text{mol} \cdot \text{K}$ . Instead, we use the following SI units and value for  $R$ .

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Here J is the symbol for the SI energy unit called a "joule", homophonous to "jewel". We'll do lots with joules starting next Chapter but, for now, just think of it as an energy unit. This form of  $R$  clearly shows  $R$ 's true nature, which I mentioned upstairs: it's actually an energy/temperature constant and it comes into play in other applications.

This ends the first catch for calculating  $v_{\text{rms}}$ ; the second catch involves the joule itself.

The joule is derived from the SI base units of kilogram, meter and second. The relationship is the following.

$$\text{J} = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

Using these units,  $R$  is the following.

$$R = 8.314 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}}$$

So far, this is just a bunch of units. Here's where the second catch comes in: we need this with g instead of kg. That means we need to use the following version.

$$R = 8,314 \frac{\text{g} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}}$$

OK, there are a lot of equations here so this may seem tedious and confusing. Let's go to the bottom line: here's the final equation which you need to calculate speed, with the necessary version of  $R$  included.

$$v_{\text{rms}} = \sqrt{\frac{3 \left( \frac{8,314 \text{ g} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}} \right) T}{M}}$$

Just plug in  $T$  and  $M$  and chug away.

Let's do a calculation using that pesky  $\text{O}_2$  molecule that keeps bouncing off your face. We'll use a typical temperature of  $25.00^\circ\text{C} = 298.15 \text{ K}$ .  $\text{O}_2$  weighs in at  $32.00 \text{ g/mol}$ . Plug it all in.

$$v_{\text{rms}} = \sqrt{\frac{3 \left( \frac{8,314 \text{ g} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}} \right) 298.15 \text{ K}}{\frac{32.00 \text{ g}}{\text{mol}}}}$$

Although this is just a plug-in, it's a fairly ugly plug-in. If you squint real hard, you can see that all the units under the square root will drop out except  $\text{m}^2/\text{s}^2$ . (Go ahead, scratch out K's, g's and mol's.) Once you take the square root of  $\text{m}^2/\text{s}^2$ , you get  $\text{m/s}$  which is speed. After you plug everything in, punch it out and round it off, you get  $482.1 \text{ m/s}$ .

Does that seem fast? Not everyone is familiar with metric speeds, so let's convert this to miles per hour. First convert meters to miles and then convert seconds to hours.

$$482.1 \frac{\text{m}}{\text{s}} \times \frac{\text{mile}}{1609 \text{ m}} \times \frac{3600 \text{ s}}{\text{h}} = 1,079 \text{ mph}$$

That's 1,079 miles per hour and that's fast. Real fast.



Now remember that  $v_{\text{rms}}$  is a representative speed, but they're not all going that speed. Some of the  $\text{O}_2$  molecules might be only going 200 mph and some might be going 2,000 mph. There's a distribution of speeds involved. Yes, a lot of them are going about 1,000 mph. It just depends on how they hit each other: only through collisions can they change speed (or direction). Unless, of course, you change temperature and start cooking things up, because that makes everybody go faster. What say you do the calculation over again?

**Example 3.** Calculate  $v_{\text{rms}}$  for  $\text{O}_2$  at 250.00 °C.

Set it up and plug it in.

$$v_{\text{rms}} = \sqrt{\frac{3 \left( \frac{8,314 \text{ g} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}} \right) \text{K}}{\frac{32.00 \text{ g}}{\text{mol}}}} = \text{_____ m/s}$$

Compare this speed to the one at 25 °C.

The  $v_{\text{rms}}$  equation provides a useful means to calculate the relative speeds of two different gases as a ratio. For example, let's compare  $\text{H}_2$ , the world's fastest gas, to  $\text{O}_2$ , which we just calculated. How much faster is  $\text{H}_2$  compared to  $\text{O}_2$ ? First, I'll derive the necessary equation for two gases which are just labeled A and B. Start with the  $v_{\text{rms}}$  equation.

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Write this out for A and for B.

$$v_{\text{rms}}(\text{A}) = \sqrt{3RT/M_{\text{A}}} \qquad v_{\text{rms}}(\text{B}) = \sqrt{3RT/M_{\text{B}}}$$

Then set up the ratio of the speeds.

$$\frac{v_{\text{rms}}(\text{A})}{v_{\text{rms}}(\text{B})} = \sqrt{\frac{3RT/M_{\text{A}}}{3RT/M_{\text{B}}}} = \sqrt{\frac{M_{\text{B}}}{M_{\text{A}}}}$$

The  $3RT$  parts drop out. This leaves the molar mass terms but notice that gas speeds are related by the inverse of the square root of their masses. For comparing  $\text{H}_2$  and  $\text{O}_2$ , we get the following.

$$\frac{v_{\text{rms}}(\text{H}_2)}{v_{\text{rms}}(\text{O}_2)} = \sqrt{\frac{M_{\text{B}}}{M_{\text{A}}}} = \sqrt{\frac{32.00 \text{ g/mol}}{2.016 \text{ g/mol}}} = 3.984$$

This means that  $\text{H}_2$  molecules typically move 3.984 times faster than  $\text{O}_2$  molecules at the same temperature. Since  $\text{O}_2$  molecules move ~1,000 miles per hour at 25 °C, then  $\text{H}_2$  molecules are moving ~4,000 miles per hour at 25 °C. Almost takes your breath away, doesn't it?

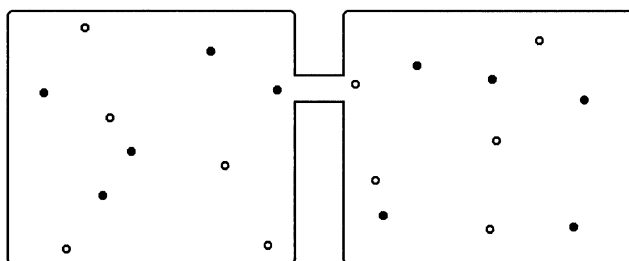
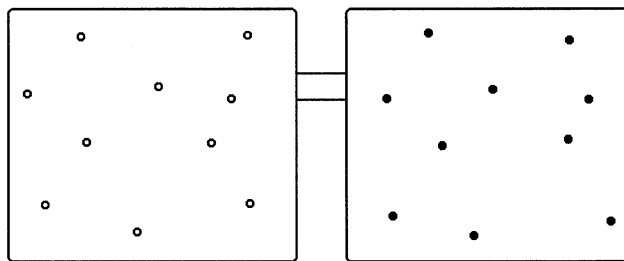
#### 17.4 Diffusion, effusion, deflation and inflation

There are other properties and behaviors of gases which are related to their rapid and random motion. I'll describe a few of these.

First, diffusion. As used with two (or more) gases, diffusion is the natural mixing of one gas into another. By "natural", I mean without fans, pumps, etc. It is entirely due to the natural motions of the molecules by themselves. Let me illustrate this.

We start with a container of He and a container of Ne at equal pressures as shown on the right. The atoms of each are moving about within their given volumes.

We then open the connection between the two containers. Both gases are at the same pressure to start, so there's no initial gush from one container to the other.



Over time (at left), atoms of He will fill the full space allowed to them and atoms of Ne will fill the full space allowed to them. They'll mix together and share the same volume. All of this is a natural consequence of their own independent motions. This is diffusion.

Diffusion is a very common occurrence in your world. You know this by smell. Smells are also gases. They obey the same gas laws as  $N_2$  and  $O_2$ . Let's say you're sitting in a room somewhere and there are no fans, blowers, etc. moving the air around. Only the molecules of the air are moving themselves around. Then let's say that there's a source of a smell in the room such as perfume, pizza, mothballs, a used baby diaper, or whatever. The molecules of that smell will get into the air and then do their gas phase thing: they'll move rapidly and randomly, bump into  $N_2$  molecules, bump into  $O_2$  molecules, bump into an Ar atom now and then, etc. Eventually they will diffuse over to your face and get sucked into your nose. In your nose, they do their olfaction reaction, which sends a signal to your brain proclaiming, "I smell!". All of this diffusion business is just another example of molecules in motion. Most smell molecules are a bit heavy compared to air molecules, so that means they'll be slower on average. Molecules of mothballs, for example, with the formula  $C_{10}H_8$  and molar mass 128.16 g/mol, are a bit hefty compared to  $N_2$  or  $O_2$ , but they'll still get around.

By comparison, liquid solutions can also diffuse but their molecular motions are much more restricted, so the time scale is much longer. If you place food color at the bottom of a jar of water without stirring and leave the jar sit, then eventually all the water will be colored. That can take many days. For gases in a container of that size, it would be done within minutes.

Another phenomenon which applies for gases is effusion. Unlike diffusion, effusion is not a mixing process. It involves one gas by itself, starting in some container which has a small hole. The hole allows the gas molecules to escape in a somewhat controlled fashion. Some laboratory processes use effusion for studying gases, although these are not as common as they were many years ago. One of its important uses was to measure the molar mass of a gas. Compared to diffusion, the mathematics of effusion is a lot easier. The reason for this is simple: effusion involves the motion of one gas by itself and diffusion involves two (or more) gases mixing together.

Since they sound very similar, it's easy to confuse diffusion and effusion. Just remember that diffusion is mixing and effusion is escaping.

Using effusion to measure molar mass is fairly straightforward. The process is based on measuring the effusion rate of your unknown gas and comparing that to the effusion rate of a known gas. Let's say gas A is your unknown and you want to know its molar mass ( $M_A$ ). You conduct the effusion measurement for A and get its effusion rate. You also do the measurement for a gas you know (gas B) and get its effusion rate. Then you take the ratio of the two rates. This effusion ratio equals the ratio of their speeds, and that ratio was derived above.

$$\frac{\text{effusion rate of A}}{\text{effusion rate of B}} = \frac{v_{\text{rms}}(\text{A})}{v_{\text{rms}}(\text{B})} = \sqrt{\frac{M_B}{M_A}}$$

Since you know the identity of gas B, then you know  $M_B$ ; since you measured the effusion ratio, you can use all these things to calculate  $M_A$ .

There's another thing about molecules in motion which I'd like to point out, and it is another kind of diffusion. This is not a strictly gas phase process, but I'll mention it here because there is some tie-in. It's a very common experience: balloons. Balloons deflate with time. Well, some inflate by themselves with time, but I'll get to that later. Given the same kind of balloon, a balloon of helium deflates faster than a balloon of air. Why do balloons deflate and why do helium balloons deflate faster?

Molecules in motion. Right through the skin of the balloon. Yes, that's right: gases can pass through many rubber and plastic materials. You can't do that with typical glass or metal containers. Why? It's because of the way the atoms and molecules within the container walls are arranged. In a typical glass or metal, the chemical units are closely arranged and locked in place; nothing can get through. In many rubber and related materials, however, the molecules are extremely long and winding. As such, the molecules do not line up with each other very efficiently. This can leave gaps and channels for something small to sneak through, like a molecule of  $N_2$  or an atom of He. The molecules of a rubber or plastic might also have some wiggle room, and this can open new gaps or even close up some old ones.

The deflation of a balloon is another form of diffusion, but this time it involves the mixing of the gas molecules into the balloon material. This is very different from the diffusion of one gas into another gas as mentioned above. This is also much harder to study, and there are several factors which influence the overall process. Some factors depend on the identity of the gas sneaking through and some factors depend on the material of the rubber or plastic. The size of the gas molecule is a big factor: very small gas molecules can get through more gaps than large gas molecules can. The composition of the balloon material will also have an effect because different balloon materials will have different sizes of gaps. The thickness of the balloon skin is yet another factor: thicker balloon skins will take longer to pass through. As you can see, this can be a bit complicated. Curiously, one factor which does not matter much is the mass of the gas molecules. Although mass affects the speeds of gas molecules in a gas phase by itself, mass effects are small for diffusion through a rubber or plastic; size is a much greater issue because everything is in close quarters.

If you have two balloons of the same material and the same thickness, and if one is full of helium and the other is full of air, then the helium balloon deflates much faster due to size. Monatomic He is the smallest gas particle; air molecules are primarily diatomic  $N_2$  and  $O_2$  and these are significantly larger. To slow things down for He, their balloons are typically made of Mylar or are thicker latex than a common air balloon. Even these deflate with time.

What you may not realize with a helium balloon is that, as it loses helium, it gains air. The passage of gases through a balloon skin can occur in both directions. As helium sneaks out, air sneaks in. Because  $N_2$  and  $O_2$  are much larger than He atoms, however, sneaking in is a lot slower than sneaking out, and the overall effect is still deflation. Nevertheless, some air will still be inside after all He gets out.

Deflation is true in most cases, but not all. I mentioned above that some balloons can inflate by themselves. This is a bit on the weird side since it is not a common experience. Let's talk about a gas with very large molecules, such as sulfur hexafluoride. This is an interesting gas with several interesting applications. For example, it's one of the gases they use in eye operations for repairing some cases of torn retinas: they inject a bubble of it into your eyeball and the bubble helps to hold the retina in place while it heals.

Molecules of  $SF_6$  are very big compared to air molecules. (The molecules also have much more mass compared to molecules of air. Balloons of  $SF_6$  are much heavier than air balloons.) Now think about what I said about helium balloons: the inside gas can sneak out and air molecules can sneak in. In the case of  $SF_6$ , the molecules are big clunkers! Air sneaks in faster than  $SF_6$  can sneak out. That means that the balloon gets bigger by itself and it can burst from the additional air pressure inside. It's slow, but it does happen.

OK, this concludes our molecules in motion discussion. It's time to move on. Remember: so far, we've been behaving ideally. At least I have. I don't know about any of you snoring out there.

### 17.5 Reality check

As promised in Chapter 16, we must do our reality check for gases. Actually, under moderate conditions, the ideal gas properties and all of our equations work fairly well. Under more severe conditions, this won't be the case. Let's see how and why. First, we must return to our basics.

“ THE MOLECULES OF THE GAS PHASE ARE WIDELY SEPARATED, THEY MOVE RAPIDLY AND RANDOMLY ABOUT, THEIR OWN VOLUME IS VERY LITTLE OF THE ACTUAL VOLUME OF THE SAMPLE, AND THEY DO NOT INTERACT WITH EACH OTHER. ”

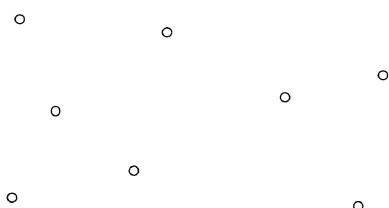
This is the description of an ideal gas. There are two phrases in that statement which are not completely correct and they are the ones which can cause problems. The two phrases are the ones about volume and interactions.

...their own volume is very little of the actual volume of the sample...  
 ...they do not interact with each other.

For this second phrase, I will point out that interactions between molecules can happen and that many of these are attractive. These attractions tend to be weak, especially when the molecules are far apart from each other.

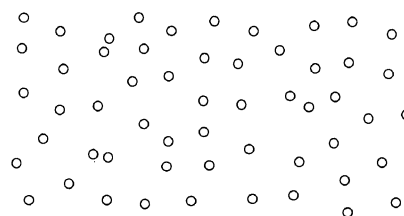
Now, let's see what conditions can lead to deviations from ideal behavior.

Much of the problem deals with concentration: ideality is best obtained at low-to-moderate concentrations, while high concentrations tend to deviate more from ideality. Let's compare.



At low-to-moderate concentrations (on the left), the volumes of the molecules remain small compared to the total volume of the sample, so our volume condition is OK. Since the molecules are well separated (on average), they cannot significantly interact with each other except during random approaches as they fly around. This doesn't amount to much, so the interaction condition is OK. Under such conditions, the sample behaves ideally.

At high concentrations (on the right), you have a lot more molecules crammed closer together. Now, their own volumes are becoming significant to the total volume. The volume condition is no longer OK, and this can cause a deviation from ideality. In addition, the molecules are spending more time closer together (on average), and this allows their total interactions to become more important. This means that the interaction condition is no longer OK and this, too, can cause a deviation from ideality.



In addition to concentration effects, temperature can also play a role. Temperature has its impact on the interaction part of the story, but this effect is primarily limited to temperatures close to the point where the gas would condense to a liquid. (In fact, liquids form from gases due to these interactions. We'll get into those aspects much more, beginning in Chapter 34.) Near the temperature of condensation, the interaction can cause deviations from ideality. As temperature increases, however, the particles have more energy (on average) and that can override any weak interactions which may be trying to come into play. Thus, as  $T$  increases, interactions become less important and the sample behaves more ideally.

There is no exact equation for real gas behavior which can accurately accommodate these deviations from ideality. Over the many years, quite a few equations have been developed which provide better results for high concentrations and/or low temperatures than the ideal gas equation. These can get quite complicated however, since these must now also take into account the specific identity of the gas. Identity is built into these equations because different gases have different sizes of particles and have different interactions. One of the most common equations is called the van der Waals equation, which is

$$\left( P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

This equation employs adjustments (a.k.a., fudge factors) to the pressure and volume terms.  $a$  and  $b$  are constants and they differ for every different gas. Notice that the adjustment to pressure includes a concentration term which, in fact, is squared. There is also a concentration term in the volume adjustment, which is revealed by factoring.

$$(V - nb) = V \left( 1 - \frac{n}{V} b \right)$$

I won't go into examples for these calculations. Your instructor may provide values of  $a$  and  $b$  for different gases. Calculations using the van der Waals equation are somewhat straightforward if you need to solve for  $P$  or  $T$  but they're much more difficult if you need to solve for  $V$  or  $n$ .

Ironically, this equation does not even include the temperature effects, but it is a decent equation for not-too-severe conditions. At more drastic conditions, this one also deviates more and more from real gases. There are better equations which account for concentration and temperature, and these work better for more drastic conditions, but they just get more and more complicated.

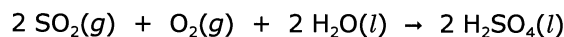
For our purposes right now, this concludes our discussion of the gas phase.

Frequently ideal but always real, these things are part of your world.

### Problems

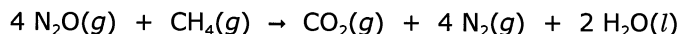
- True or false.
  - Gas pressure is the result of tiny masses striking very fast and very often.
  - Both diffusion and effusion are faster at higher temperatures.
  - In a gas mixture of Ar and Ne, the Ar atoms are generally faster than the Ne atoms.
  - At very high concentrations of gases, the volumes of the gas particles can be significant relative to the total gas volume.
  - At normal concentrations of gases, the interactions between the gas particles are not significant.
- True or false.
  - For a gas sample at constant  $V$  and  $n$ , the pressure increases when the temperature increases because the molecules are hitting harder and more often.
  - At the same temperature, the gases  $\text{CO}_2$  and  $\text{ClO}_2$  have the same kinetic energy.
  - At the same temperature,  $\text{HCl}$  molecules travel faster (on average) than  $\text{NH}_3$  molecules.
  - As temperature increases, gas molecules move faster.
  - Gases deviate more from ideality at lower concentration.

- The following equation is balanced.



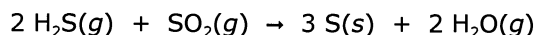
For a reaction to produce 53.2 g  $\text{H}_2\text{SO}_4$ , what volume (in L) of  $\text{O}_2(g)$  at STP is required?

- The following equation is balanced.



The reaction is conducted in a container with a volume of 29.1 L and at 9 °C. The pressure of  $\text{N}_2\text{O}$  is 633 Torr;  $\text{CH}_4$  is in excess. What pressure (in Torr) of  $\text{CO}_2$  can be produced?

- Consider the reaction of excess tin metal with 37.6 g perchloric acid to produce tin(II) perchlorate and hydrogen gas. The hydrogen gas is collected in a volume of 14.6 L at a temperature of 281 K. Circle the pressure (in atm) of the hydrogen gas.
- Consider the following balanced equation.



The reaction uses 23.1 g  $\text{H}_2\text{S}$ .  $\text{SO}_2$  is present in excess; this is supplied from a tank with a fixed volume of 7.00 L and the  $\text{SO}_2$  temperature is held constant at 28 °C. The initial pressure of  $\text{SO}_2$  is 3.19 atm. What is the final pressure (in atm) of the remaining  $\text{SO}_2$  after the reaction is done?

- The following compounds are solely or partly responsible for various common smells. Rank the compounds by how fast (slowest to fastest) their smells will diffuse through a room (at the same temperature).

- |   |   |  |
|---|---|--|
| a. $\text{C}_6\text{H}_{10}\text{S}_2\text{O}$ (garlic) | b. $\text{C}_4\text{H}_8\text{S}$ (skunk)     | c. $\text{C}_{10}\text{H}_8$ (mothballs) |
| d. $\text{C}_{10}\text{H}_{20}\text{O}$ (menthol)       | e. $\text{CH}_3\text{CO}_2\text{H}$ (vinegar) |  |

8. What is the rms speed (in m/s) for  $\text{H}_2\text{O}(g)$  at  $25\text{ }^\circ\text{C}$ ?
9. What is the rms speed (in m/s) for  $\text{H}_2(g)$  molecules at  $24\text{ }^\circ\text{C}$ ?
10. An effusion measurement is done on an unknown gas. Relative to the effusion of  $\text{N}_2$  under the same conditions, the ratio of the effusion rates (unknown/ $\text{N}_2$ ) was 0.565. What is the molar mass of the unknown gas?