

## Chapter 16

## GASES, Part 1

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Having finished our cruise of the water world, we embark on a new journey into the world of gases. This is a fairly different path from what we've been doing. Instead of an emphasis on reactions and stoichiometry, we will actually focus on the characteristics of the phase itself. Yes, we'll still do reactions and we'll still do stoichiometry, but the majority of this and the next Chapter describes what's really going on in the gas phase.

### 16.1 The gas phase

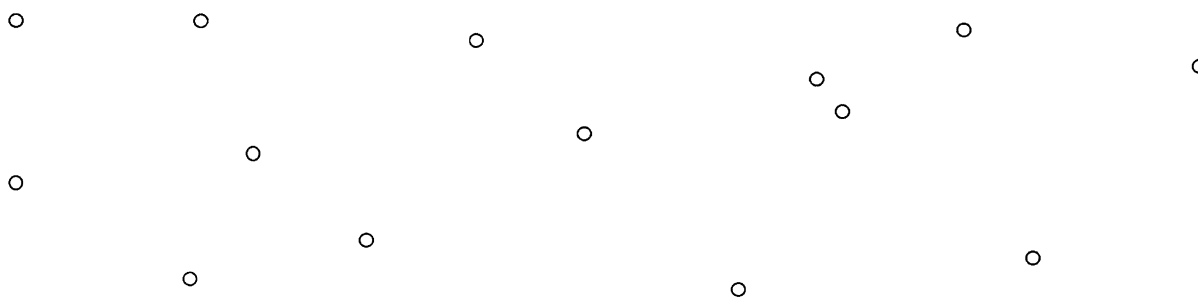
As a whole, the phases are incredibly important. The three common phases, solid, liquid and gas, are very much a part of your life. Why are there three? Notice that I said "common" phases. These three phases are common to the surface of planet Earth, given the conditions that exist here. That's what we're used to. Back in the very beginning of Chapter 10, I briefly mentioned some things about phases.

“ Why is one compound a gas and another compound is a liquid under similar conditions? This is a very interesting question, but we're not ready for the details yet. I'll tell you this much now: there is an inherent drive in all of Nature to favor the gas phase out of all three common phases (gas, liquid, solid). This applies to everything. That drive is part of "entropy" but entropy is bigger than this and I'm not going there right now. ”

Well, I can see you're biting at the bit for entropy, but hold onto your horses because we're not there yet. There's more to entropy than we're ready for here. Besides, we're not covering all phases right now anyway; we're just doing gases here. We will come back to entropy and we will come back to the other phases beginning in Chapter 34.

Why do I start with the gas phase and not with liquids or solids? Why don't we start with something we can usually see? The reason is quite simple: the gas phase is the easiest to describe and the easiest to understand in terms of its characteristics and mathematical relationships.

There's a very good reason why the gas phase is the easiest. Interestingly, the gas phase is mostly about nothing. I mean NOTHING. I mean total, complete zilch. Most of the space of any gas phase sample has no matter in it at all. The reason for this is that the molecules in the gas phase are widely separated from each other. Here's an illustration: at typical Earth surface conditions, the volumes of the actual molecules in the air account for only ~0.06% of the total volume of that air. In other words, 99.94% of the volume of air is empty space, absolute nothing. That's how spread out things are. Most of the volume of air which you breathe is nothing.



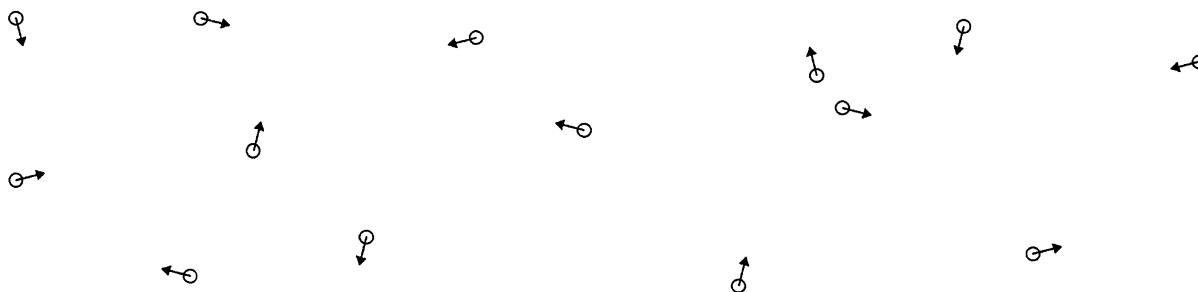
Here's another example of the immense nothingness in the gas phase. At the boiling point of water, 100 °C, one mole of liquid water occupies 19 mL, and that volume involves all the water molecules in fairly loose contact with each other. One mole of gas phase water at 100 °C, however, occupies 31 L. That's 31 L of gas versus 0.019 L of liquid for the same amount of water. Those volumes differ by 1600-fold. In the gas phase, all of those water molecules are spread out over 1600-fold more volume, with nothing in between them.

Gas molecules move randomly and very fast, typically in the range of hundreds or thousands of miles per hour. I'll show you this calculation in Chapter 17. Each molecule moves in a straight line but they will frequently bump into each other; when that happens, they just bounce off and continue in some other direction. They really don't care. They're just going their own way, doing their own thing.

I've just given you the most important characteristics of the gas phase which completely set it apart from liquid and solid phases. The liquid and solid phases have their molecules (or whatever chemical units) in direct contact with little space between. Since they are in contact, they interact with and influence each other strongly. Not so in the gas phase. 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. You must understand this last sentence. It makes the gas phase what it is. It makes the gas phase the easiest to understand. It makes the gas phase the easiest to describe mathematically. Let me say it again.

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.

At least, that's the ideal scenario. The illustration from above doesn't convey the sense of movement very well, so let me show some commotion in that motion.



Here are several consequences so far. Particles of the gas phase are boundless and can travel the entire volume allowed to them. That's not true of solid and liquid phases. Put a rock (or other solid phase) in a jar and close it: the rock sits in the bottom of the jar. The molecules (or other chemical units) of the solid phase are locked in place, bound by whatever interactions apply for that compound. Put water (or other liquid) in a jar and close it: the water sits in the bottom of the jar. The molecules (or other chemical units) of the liquid phase are confined to the volume of that phase, bound by whatever interactions apply for that compound. But when you have just air (or other gas) in a jar, then it fills the entire jar; the molecules fly freely about in all three dimensions: up/down, right/left, backward/forward. The molecules are not bound to other molecules. Yes, the molecules are bound by their container but, if you open the jar, the gas molecules will leave although they will be replaced by others.

Another consequence ties to density. Ever since Chapter 1, we've referred to density for liquids and solids in terms of g/mL, but the density for a gas is usually given as g/L. This is a volume thing again. Since the particles of the gas are so far apart, the density of a gas sample is typically hundreds or thousands of times smaller than the density of liquid or solid samples. We'll see the mathematical relationship for gas density later.

The final consequence to mention for now is that gases are compressible. What this means is that their volume can change readily with pressure. In contrast, liquids and solids are hardly compressible at all. Why? Open space. Remember, the particles in the liquid and solid phase are already in contact; pressurizing them scrunches them together a tad closer, but the effect is very small. On the other hand, gases can be compressed readily since their particles are so far apart. We'll see the mathematical relationship for this later. In the meantime, I want to talk about this pressure business.

## 16.2 Can you feel the pressure?

Humans are somewhat lousy at sensing pressure, at least the normal variations of pressure within their environment. We can easily sense light, temperature, smells, sound, etc.; but pressure, no. Can you tell when the atmospheric pressure is high or low? Most of us need to check the weather report.

Every gas exerts a pressure as a natural consequence of the motion of its own particles banging into things. Since the gas's molecules are moving in all three dimensions, the pressure of the sample is exerted in all three dimensions. This is another difference from solids and liquids. A rock inside a jar exerts a pressure downward on the bottom of the jar, due to gravity. Water in a jar exerts a downward pressure (and a tiny sideways pressure), due to gravity. On the other hand, a gas in a jar exerts a pressure against the jar every which way, including up. The gas's pressure is not due to gravity: if you

closed the jar and took it out into space, it would still have the same pressure inside (assuming it stayed at the same temperature). The pressure of a gas is a result of concentration, as we'll see later.

Molecules in motion. Very fast. Banging into things. That's gas pressure.

Even as you sit there reading this with your eyes open (I presume), massive numbers of air molecules are smacking you in the eyeball every split second, at hundreds and thousands of miles per hour. And all you do is yawn obliviously.

This air pressure that surrounds you is the weather's barometric pressure. I'm sure you've heard the weather reports and such. Today, it might be high pressure and sunny. Maybe the pressure is moderate. Or, maybe you're in the middle of a low pressure disturbance and it's raining like a cow on a flat rock. The weather report might give the pressure as 31.32 inches and rising. Or 29.06 inches and falling. Those inches aren't simply inches; they're "inches of mercury" (abbreviated inHg) as measured by a device called a mercury barometer. Sometimes you'll hear them say the whole thing, like "30.58 inches of mercury". In all of these cases, "inches of mercury" is really a pressure unit which relates to the use of a mercury barometer as one of the oldest ways to measure gas pressure.

Another common gas pressure unit is psi, which is pounds per square inch. This is the typical unit for measuring air pressure in tires and such. Many car tires are in the range of 25 - 35 psi or so, except for the scrawny fifth-wheels which are around 60 psi (if you have one). Bike tires are high also.

Inches of mercury and psi are based on English units. In metric units, millimeters of mercury (mmHg) replaces inHg. These two are related by the usual inch/millimeter conversion factor, so that one inHg = 25.4 mmHg (exact). Another unit is Torr, which is essentially equal to one mmHg. Common atmospheric pressures near sea level are in the range of ~700 - 800 Torr, so one Torr is actually fairly small. Actually, the atmosphere itself has provided the basis for a different pressure unit which is called a "standard atmosphere" unit, atm. One atm is equal to 760 Torr (exact).

These units so far have been very important historically, but none of these is an SI unit. In SI, the unit for pressure is the pascal, Pa. Unfortunately, a pascal is very small, and it takes 101,325 Pa to exactly equal one atm. We can tack on a kilo- prefix, and then one atm is 101.325 kPa. A related unit is the "bar": one bar is defined to be  $10^5$  Pa or  $10^2$  kPa. (Etymologically, "bar" is related to barometer, barocline or other terms dealing with pressure, and not to the type of bar more familiar to some folks.) These relationships place bar on a near-even keel with atm, with one atm equaling exactly 1.01325 bar. A common usage of bar nowadays is found in weather reports: in addition to (or instead of) 31.32 inHg as the barometric pressure, it might be given as 1,061 millibar, mbar (which they abbreviate as mb).

Here's a summary of the units we've just covered, set up as one big equality.

$$\text{atm} = 760 \text{ Torr} = 101,325 \text{ Pa} = 101.325 \text{ kPa} = 1.01325 \text{ bar} = 29.92 \text{ inHg} = 14.70 \text{ psi}$$

These are all exactly defined.

You can express any two of these as a ratio to derive a conversion factor between them. As always, exactly defined values do not enter into round-off decisions for sigfig operations.

We will mostly use the traditional units of atm and Torr; other units can be derived from those using the above relationships.

### 16.3 The math of gas

Let's head into the math. Every gas sample can be characterized mathematically using the following four parameters.

- The pressure of the sample, designated  $P$  (or  $p$ ).  
We will set this up using atm.
- The volume,  $V$ , of the sample.  
Although other volume units can come into play, we are going to base this on L.
- The temperature,  $T$ , of the sample.  
No choice here: you must use kelvin. Go back to Chapter 1 if you need to refresh kelvin.
- The amount of molecules,  $n$ , in the sample.  
The mol is the unit here.

All four parameters are inter-related. Under an ideal scenario, if three are known, the fourth can be calculated. I alluded to a part of these relationships earlier when I said pressure is really a concentration

thing. Here's the bottom line: the pressure of a gas sample is proportional to its concentration times its temperature.

$$P \propto \text{concentration} \times T$$

That's not very complicated but it is incredibly important. Note that, when temperature is kept constant, then pressure and concentration are directly related to each other.

OK, let's develop this simple notion further. We'll bring in a proportionality factor, called  $R$ . In that way, we can write the proportionality above as an equality.

$$P = \text{concentration} \times R \times T$$

Glance back a moment and look at the four parameters which I set up for a gas sample:  $P$ ,  $V$ ,  $T$  and  $n$ . We already see the  $P$  and  $T$  connection. The  $V$  and  $n$  connection is contained within concentration in the form of  $n/V$ , with units of mol/L. This brings us to

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

which is commonly presented in the following form

$$PV = nRT$$

and this is called the ideal gas equation. It's a biggie. Vastly and very important. This is the one that ties our four parameters together. Again, if you know three, you can calculate the fourth. That is, if you have  $R$  and, yes, we do have  $R$ .  $R$  is called the gas constant and it will apply 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  $R$ . For now, we're doing units of L, atm, mol and K, so we work with the following version. In the next Chapter, we'll see another version of the very same  $R$ .

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

Ideal. Ideal gas. I keep saying ideal, even if you haven't caught on to it yet. Why ideal? I said from the beginning in Chapter 1 that there's ideality and there's reality and sometimes they're not the same.

“ Models, theories, and such represent the ideal. They say what should happen. These are very useful but many have limitations. Then reality sets in, and what really happens is different from what should happen. We refer to this as ideal versus real, or ideality versus reality. Be ready for reality checks. They happen. ”

We talked about reality checks in Chapter 8 with stoichiometry. We'll be doing reality checks with gases, too, but this will wait until the next Chapter. For now, I'm keeping things simple. For now, we will work with examples which behave according to the ideal. Within this ideal scenario, we say that the sample "behaves ideally" or "follows ideal behavior". Of course, some things follow ideal behavior better than others. For now, we'll behave ideally; we can behave differently later.

Under ideal conditions, the identity of the gas does not matter to this discussion so far. Furthermore, the gas sample can be either a single compound by itself or a mixture of many different gases together. It doesn't matter. Why should it? All those molecules are in there just whizzing around, well separated from each other. Yes, they'll bump into each other but there are no interactions and they don't linger, so who cares? In the air, why should a molecule of  $N_2$  care if it bumps into a molecule of  $O_2$ , a molecule of  $CO_2$  or another molecule of  $N_2$ ? It doesn't. Everybody's treated the same.

There's another version of the ideal gas equation which is frequently useful. I'll show you how we get there. We start with factoring  $R$  out of the ideal gas equation.

$$R = \frac{PV}{nT}$$

Since  $R$  is the same for all gases, this ratio,  $PV/nT$ , is a universal ratio for every gas sample. That means, for some set of conditions "1" and comparing them to a set of conditions "2", the following is true.

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

This form is called the general gas equation. It's frequently handy and it can be more useful than the ideal gas equation in some problems. I will show a couple of applications in this and the next Chapter, but mostly I will stick with using  $PV = nRT$  itself.

Let's show some uses of the ideal gas equation. I won't say "ideal gas equation" every time: I'll usually just say " $PVnRT$ " and that's what I'm referring to. Before going to number-crunching, we'll take a look at some qualitative results which can be obtained by examining the effects of one component in  $PVnRT$  on the other(s). Let's consider the concentration form of  $PVnRT$  from above.

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

Here are some relationships which result.

- ▶ If you increase the concentration of the gas, then this raises the pressure. You can do this by increasing the number of moles present or by reducing the volume. Contrariwise, if you decrease the concentration of the gas, then its pressure decreases.
- ▶ If you heat the gas (increase  $T$ ), then this increases  $P$ . If you cool the gas, this decreases  $P$ .

Notice that both of these relationships were contained in the earlier statement that pressure is proportional to concentration times temperature.

Now, look at things another way.

$$V = \frac{nRT}{P}$$

- ▶ If you increase the amount of gas, then this increases the volume.
- ▶ If you increase the pressure, then the volume decreases. This is the same as compressing a gas sample.
- ▶ If you heat the sample, then volume increases.

There are other variations than these, but this is enough for now. I want to start in on some number problems. Many gas problems involve straight plug-and-chug right into the ideal gas equation, although other problems can get a bit more complicated.

OK, here goes the first Example.

.....  
**Example 1.** A container holds 2.02 L of some gas at 18 °C. How many moles of gas are present in the container if the pressure is 0.601 atm?  
 .....

*PVnRT. PVnRT. PVnRT.* Get used to it. This Example gives three ( $P$ ,  $V$ , and  $T$ ) of the four gas parameters, and you are asked for the fourth ( $n$ ). Now, whenever you do  $PVnRT$ , you need the units L, mol, K and atm. If any parameter is not in the right unit, then you must convert. Here, we need to convert  $T$  from °C into K using 273.15 (as seen in Chapter 1); that means 18 °C is 291 K. Now, let's start.

$$PV = nRT$$

The problem wants mol, so re-arrange for  $n$ .

$$n = \frac{PV}{RT}$$

Throw in your given values.

$$n = \frac{(0.601 \text{ atm})(2.02 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (291 \text{ K})} = 0.0508 \text{ mol}$$

That's it: there are 0.0508 moles of gas in the container. Although the units may appear cumbersome, they do work out. Go ahead and cancel out atm, L and K.

Before going on, I want to point out two things. One is a minor technicality. The other is very important.

The minor technicality has to do with sigfigs. The temperature conversion is +/- and  $PVnRT$  itself is straight  $\times/\div$ . Overall, these constitute mixed operations and they are rounded differently. I mentioned this type of complication in Chapter 1. Here's how I handled the round-off for the above problem. The temperature conversion was its own little addition step, so I first converted to K and then I rounded it off by itself. Then I put it into  $PVnRT$  and executed the multiplication/division part, again rounding afterwards. This is the method which I outlined in Chapter 1 and that is how we will be handling  $T$  conversions for use with  $PVnRT$ .

The second point which I want to note is that  $PVnRT$  now provides a vital link between measurables and number of chemical units. Several chapters ago, we described how important it was to relate something we can measure to knowing how many chemical units were present. We needed this in the very beginning of stoichiometry in Chapter 7:

“ No, we cannot count actual atoms or chemical units directly but, as I told you in the beginning of Chapter 5, we can measure how many. In that Chapter, we used the mass and molar mass to measure how many formula units were in a sample. We will do so again in this Chapter. Later in Chapter 9, we will see how volume also can measure a number of formula units. In Chapter 16 when we talk about gases, we will even see how pressure can be used. ”

As promised, here we are in Chapter 16 talking about pressure. It's not just pressure by itself that tells us moles; it's  $PV/RT$ . This leads to our important result: we can now place the ideal gas equation alongside molar mass and molarity for providing an essential means of knowing how many chemical units are in a sample, based on measurable quantities. Just as we used molar mass and molarity in stoichiometry, we can also do stoichiometry with  $PVnRT$ . We will indeed do stoichiometry in the next Chapter; I want to spend a little more time with other aspects before that.

Let's do one more straight Example with  $PVnRT$  but with more conversions involved.

**Example 2.** You have 0.0217 mol of some gas at a pressure of 152 Torr in some container whose volume is 2,250 mL. What's the temperature of the sample, in °C?

$PVnRT$ .  $PVnRT$ .  $PVnRT$ . Get your units into the required form.

Pressure is given in Torr; that converts readily to atm.

$$152 \text{ Torr} \times \frac{\text{atm}}{760 \text{ Torr}} = 0.200 \text{ atm}$$

Volume needs L, which is a decimal shift from 2,250 mL to 2.25 L.

Mol is the correct unit for  $n$ , so leave it be.

$PVnRT$  will give you K, but the answer requires °C; we'll do that afterwards.

Let's start.

$$PV = nRT$$

You're given  $P$ ,  $V$  and  $n$ ;  $R$  is the usual. You're looking for  $T$ ; re-arrange.

$$T = \frac{PV}{nR}$$

Throw in your values.

$$T = \frac{(0.200 \text{ atm})(2.25 \text{ L})}{(0.0217 \text{ mol}) \left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right)} = 253 \text{ K}$$

There's your  $T$  but you need °C: 253 K converts to -20. °C for your answer.

I'll show you a shortcut for pressure when you're given Torr. Just enter the number of Torr directly into  $PVnRT$  as a fraction over 760, which directly converts Torr into atm. In the above example, you could set this up as the following.

$$T = \frac{\left(\frac{152}{760} \text{ atm}\right)(2.25 \text{ L})}{(0.0217 \text{ mol})\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)}$$

Of course, this is arithmetically the same as above, but this way is a little quicker and it avoids a possible round-off error for pressure.

These are just simple examples of  $PVnRT$ . Let's do one using the general gas equation.

**Example 3.** 1.00 mol ammonia is stored at 15 °C in a 23.6 L tank at 1.00 atm. This gas is then transferred to a 38.9 L tank and stored at 55 °C. What is the pressure (in atm) of the  $\text{NH}_3$  at the final conditions?

Note that you are given a complete set of initial conditions ( $n_1, T_1, P_1, V_1$ ) and an incomplete set of final conditions ( $n_2, T_2, V_2$ ); we seek  $P_2$ . Note also that the number of moles of gas is not changing, so  $n_1 = n_2$ . Now go ahead and set this up. As stated previously,  $R$  is the same for any set of conditions,

$$R = \frac{PV}{nT}$$

which means, for two sets of conditions,

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

but  $n_1 = n_2$  in this Example, so we can cancel the  $n$ 's.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Now, re-arrange to find  $P_2$

$$P_2 = \frac{P_1V_1T_2}{T_1V_2}$$

and then plug in, but be sure to change your  $T$ 's to K's.

$$P = \frac{(1.00 \text{ atm})(23.6 \text{ L})(328 \text{ K})}{(288 \text{ K})(38.9 \text{ L})} = 0.691 \text{ atm}$$

Done.

#### 16.4 STP and $d$

Long ago, it was decided to define a specific temperature as a "standard temperature" and a specific pressure as a "standard pressure" for work with gases. These standards have changed over the years and different versions can be found. For our purposes, we adopt traditional values of 0.00 °C (273.15 K) as standard temperature and (exactly) one atm as standard pressure. Together, these constitute "standard temperature and pressure", abbreviated as STP. If you are told STP conditions for a gas sample, then that's 273.15 K and one atm, and those values are considered exact for sigfig purposes.

Let's see how this works. I'll throw in another twist while we're at it.

**Example 4.** How many grams of argon can be contained in a 1.02 L tank at STP?

$PVnRT$ .  $PVnRT$ .  $PVnRT$ . You're told volume, temperature and pressure. That will get you moles. The twist is that the problem asks for grams, but you can get grams from moles using molar mass.

$$PV = nRT$$

Re-arrange for  $n$ .

$$n = \frac{PV}{RT}$$

Throw in your values.

$$n = \frac{(\text{one atm})(1.02 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(273.15 \text{ K})}$$

Punch this out and you get moles. Bring in argon's molar mass (39.95 g/mol) and you get 1.82 g argon. Do the actual number-crunching and make sure you get this answer.

Have you ever breathed argon? You bet! A lot of it!

I want to introduce another term right now, called "molar volume". This term is not limited to gases and it can be applied to any compound in any phase. The molar volume of anything is the volume occupied by one mol of that thing. For liquid water, with a density of 1.00 g/mL (at STP), the molar volume is 18.0 mL. For iron metal with a density of 7.87 g/mL (at STP), the molar volume is 7.10 mL. You can calculate this for any liquid or solid if you know its density. For gases, however, density isn't needed and the molar volume is the same for every gas. This is another consequence of  $PVnRT$ . Let's show this relationship using STP conditions.

$$PV = nRT$$

Re-arrange for  $V$ .

$$V = \frac{nRT}{P}$$

Throw in your values.

$$V = \frac{(\text{one mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(273.15 \text{ K})}{\text{one atm}} = 22.41 \text{ L}$$

This tells us that an ideal gas of any identity at STP has a molar volume of 22.41 L. Notice that this is 1,240 times the molar volume of water and 2,850 times the molar volume of iron. A gas sample occupies more volume because most of the volume of the gas phase is nothing.

Another way to show this empty space is with concentration ( $n/V$ ). For any gas at STP, we can re-arrange  $PVnRT$  for  $n/V$  to get

$$\frac{n}{V} = \frac{P}{RT} = \frac{(\text{one atm})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(273.15 \text{ K})} = 0.04461 \frac{\text{mol}}{\text{L}}$$

This says that any gas at STP has a concentration of 0.04461 mol/L. That's not much. Compare this to liquid water which has a concentration of 55.5 mol/L, or to iron metal which has a concentration of 141 mol/L. This again illustrates that the gas phase has very little of anything in its volume.

Let's go ahead and bring in gas density at this time. We just did concentration as mol/L, and density is g/L; these are related since mol and g are related by molar mass. There will be a catch here: although moles per volume is the same for all gases, mass per volume is different for different gases. Because of this, gas density does depend on identity. We can derive the density of any gas from  $PVnRT$  and molar mass. Let's start with concentration.

$$\frac{n}{V} = \frac{P}{RT}$$

I'll bring in " $m$ " for mass in grams and " $M$ " for molar mass in grams per mole. Thus, our usual molar mass connection can be written as follows for any sample.

$$n = \frac{m}{M}$$

Divide both sides by  $V$  to get concentration,

$$\frac{n}{V} = \frac{m}{VM}$$



and then take this into the concentration expression above with  $n/V = P/RT$ .

$$\frac{m}{VM} = \frac{P}{RT}$$

The mass per volume part,  $m/V$ , is density. Keep it on the left, but take  $M$  to the right.

$$\frac{m}{V} = d = \frac{PM}{RT}$$

That's your density equation. As mentioned above, we see that density does depend on identity because the molar mass depends on identity.

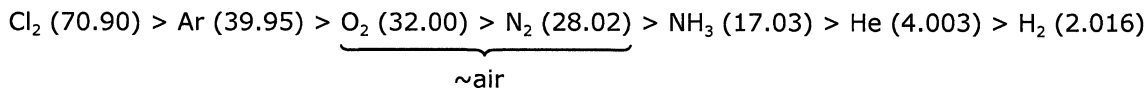
Density is just another plug-in type of calculation. You try it.

.....  
**Example 5.** Calculate the density of O<sub>2</sub> gas at 25 °C and one atm.  
 .....

Work it out.

You should get 1.31 g/L. If not, find and fix the error. This density is very small compared to the density of a liquid or solid phase: compare this to 1.00 g/mL for liquid water and 7.87 g/mL for iron. As I keep saying, there's just not much mass in a gas. (I used the same water and iron densities here at 25 °C as I had given upstairs at 0 °C; to two decimals, the densities are the same at both temperatures.)

There are several qualitative consequences of the density equation to note. First, for different gases at the same pressure and temperature, their relative densities follow their relative molar masses. Here are some simple density comparisons, with their grams per mole values in parentheses.



Notice that I've shown N<sub>2</sub> and O<sub>2</sub> for the major components of the air. Gases with molar masses less than these will float in air; gases with molar masses greater will sink. You can see why helium balloons are lighter than air: helium's density is less because its molar mass is less. Hydrogen is even lighter than helium, and it floats better than helium. H<sub>2</sub> is the least dense of all gases due to its smallest molar mass. Unfortunately, it likes to blow up. They used to fill large balloons, blimps and dirigibles with hydrogen gas until too many (including the Hindenburg) blew into smithereens. Now, most use helium.

Hot air balloons also float, and that's also density but it's for a different reason. Look at the density equation. Temperature is in the denominator. As  $T$  increases,  $d$  decreases. Thus, hot air rises over cold air. By the way, that's why they tell you to crawl on the floor to get out of a fire. The products of the combustion are very hot and go to the ceiling. That's good: there's a lot of carbon dioxide which can kill you if you breathe a lot of it, but that's not necessarily the biggest threat. What a lot of people don't realize is how very toxic some of those gases are which are produced by house or building fires. There's a lot of deadly carbon monoxide in there. There's also a lot of other killers mixed in. Some plastics, for example, will burn and give off hydrogen cyanide. As long as these gases are hot enough, they will rise. All of these aspects are gas density. All of these things are part of your world.

Also by the way, gas density was historically one way to measure molar masses experimentally. Why is this important? Well, at the end of Chapter 5 we talked about empirical formulas and how you could determine a true chemical formula from an empirical formula if you knew molar mass. Density is one way of measuring molar mass for a gas.

## 16.5 Mixtures

Except for density with its molar mass connection, everything else so far applies regardless of whether the gas sample is one compound or a mixture of different compounds. For example,  $PVnRT$  does not care if it's pure O<sub>2</sub> or if it's air with O<sub>2</sub> in it. Any gas mixture, including air, will follow  $PVnRT$ . Earlier, we showed that the concentration of any gas at STP is 0.04461 mol/L. If you have a sample of O<sub>2</sub> by itself at STP, then there are 0.04461 moles of O<sub>2</sub> molecules per liter. If you have a sample of air at STP, then there is a total of 0.04461 moles of all gas molecules per liter of air.

For mixtures, we can deal with the mixture as a whole or we can break it down into the individual components. It just depends on whichever you want to talk about. I'll show you how this works and introduce some new terminology. Let's say we have a mixture of three gases which we'll just label compound A, compound B and compound C. Molecules of A are flying around, molecules of B are flying around and molecules of C are flying around, all in the same tank. A molecule of A can hit one of B, B can hit C, C can hit A, B can hit another B, etc. All molecules of A together exert some pressure, which we'll call  $P_A$ . Likewise, all molecules of B exert  $P_B$  and all molecules of C exert  $P_C$ . Within the same container, these pressures are additive, so the total pressure in the tank,  $P_{\text{total}}$ , is the sum of the individual pressures.

$$P_A + P_B + P_C = P_{\text{total}}$$

This statement applies for all gases which have the same  $V$  and  $T$ , which is going to be the case if they are in the same tank.

Let's consider a mixture of  $N_2$  and of  $O_2$  since you're used to breathing that anyway, but we'll use different amounts from what you're used to. Let's say we have 0.03569 mol  $N_2$  and 0.03125 mol  $O_2$  in a container of volume 1.767 L and at a temperature of 277 K. What's the total pressure (in atm) inside the container?

Right off the bat, I'm going to tell you that gas mixture problems can frequently be done by different ways. This goes back to multiple methods which I've been harping on since Chapter 1. I'll show you two ways to do this problem.

- **FIRST WAY.** Find the separate, individual pressures of  $N_2$  and of  $O_2$ , and then add these together to get the total pressure.

No big deal: just do  $PVnRT$  for each gas.

For  $N_2$ ,

$$P(N_2) = \frac{(0.03569 \text{ mol}) \left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (277 \text{ K})}{1.767 \text{ L}} = 0.459 \text{ atm } N_2$$

For  $O_2$ ,

$$P(O_2) = \frac{(0.03125 \text{ mol}) \left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (277 \text{ K})}{1.767 \text{ L}} = 0.402 \text{ atm } O_2$$

This tells you the individual pressures for  $N_2$  and for  $O_2$ ; now just add these individual pressures to get the total.

$$0.459 \text{ atm } N_2 + 0.402 \text{ atm } O_2 = 0.861 \text{ atm total}$$

This says that the total pressure in the container is 0.861 atm.

Now we'll solve it the other way.

- **SECOND WAY.** You weren't required to find the individual pressures in this problem (although some problems can ask for that). We could have gone for total moles first,

$$0.03569 \text{ mol } N_2 + 0.03125 \text{ mol } O_2 = 0.06694 \text{ mol total}$$

and then used this to find total pressure.

$$P_{\text{total}} = \frac{(0.06694 \text{ mol}) \left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (277 \text{ K})}{1.767 \text{ L}} = 0.861 \text{ atm total}$$

This method requires only one  $PVnRT$  calculation. Both methods are equal for total pressure.

By the way, individual pressures within a mixture are also called partial pressures. In the above example, you can say the pressure of  $O_2$  is 0.402 atm or you can say the partial pressure of  $O_2$  is 0.402 atm. It doesn't matter for our purposes here.

There's another useful relationship to introduce at this time with respect to mixtures. It's called mole fraction and it's abbreviated  $x$ . The term applies to one component which is present in a homogeneous mixture. It's just a ratio of that component's moles to the total moles.

$$x = \text{mole fraction of some component} = \frac{\text{moles of that component}}{\text{sum of moles of all components}}$$

In other words, for some compound A in the sample,

$$\text{mol fraction of A} = x_A = \frac{n_A}{n_{\text{total}}}$$

Mole fraction can be expressed as a decimal or as a percent. For percent, just place "× 100%" after the equations above. The solution can be a gas solution or it can be a liquid solution; it doesn't matter. Right now we are doing gases, so that's what we'll stick with here. We'll do this for liquid solutions later in Chapter 42.

Because all gas components in the same container have the same  $V$ ,  $T$  and  $R$ , then mole fraction relates directly to pressure fraction. This is a useful relationship, and I'll show you how this is derived. For this derivation, I'll use the general gas equation.

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

Since everybody's in the same container,  $V_1 = V_2$  and  $T_1 = T_2$ , so the  $V$ '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. The pressures can be any pressure unit, as long as they are the same unit for both  $P_1$  and  $P_2$ ; as long as the same unit is used, then the units drop out. This pressure and mole ratio business also applies between any one component and the total. We can see this as follows. For any component A in the mixture, we assign the subscripts of 1 to A; we assign the subscripts 2 to the total sample.

$$\frac{P_A}{P_{\text{total}}} = \frac{n_A}{n_{\text{total}}}$$

These are useful relationships when dealing with mixtures. These are further examples of the very important connection between moles and pressures in gas mixtures.

If we return to our  $N_2 + O_2$  mixture from above, we had 0.03569 moles  $N_2$  which came to 0.459 atm  $N_2$ , and we had 0.03125 moles  $O_2$  which came to 0.402 atm  $O_2$ . The mole fractions can be calculated using either the moles or the pressures. For  $N_2$ , the mole fraction calculation using moles is

$$x(N_2) = \frac{n(N_2)}{n_{\text{total}}} = \frac{0.03569 \text{ mol}}{0.06694 \text{ mol}} = 0.5332 \text{ OR } 53.32\%$$

and the mole fraction calculation using pressures is

$$x(N_2) = \frac{P(N_2)}{P_{\text{total}}} = \frac{0.459 \text{ atm}}{0.861 \text{ atm}} = 0.533 \text{ OR } 53.3\%$$

We get our answer either way, although the sigfigs come out differently. That's not unusual. Both ways are correct by the sigfig system which we have adopted.

Here, you do the calculation for  $O_2$  in our sample.

.....  
**Example 6.** Calculate the mole fraction of  $O_2$  in the above mixture of  $N_2$  and  $O_2$ .  
 .....

You can do this also by either mole fraction or pressures.

$$x(O_2) = \frac{n(O_2)}{n_{\text{total}}} = \frac{\quad}{0.06694 \text{ mol}} = \quad \text{ OR } \quad \%$$

$$x(\text{O}_2) = \frac{P(\text{O}_2)}{P_{\text{total}}} = \frac{\quad}{0.861 \text{ atm}} = \quad \text{OR} \quad \quad \%$$

Actually, since there are only two components in this sample, there's another option for doing the  $\text{O}_2$  part. It's based on the simple notion that the sum of all mole fractions in a sample must equal exactly one (or exactly 100%). If we already know that  $\text{N}_2$  is 53.32% of the mixture, then  $\text{O}_2$  must be (100.00% - 53.32%), which is 46.68%.

Let's get back to real air. Your atmosphere. Mine, too. Dry air is mostly a mixture of 78%  $\text{N}_2$ , 21%  $\text{O}_2$  and 0.9% Ar. You also breathe small or even trace amounts of other things such as  $\text{CO}_2$ , Ne,  $\text{CH}_4$ , and who knows what else depending on the pollution levels. Those percents are for mole fractions and pressure fractions. Thus, 78% of the molecules in the air you breathe are  $\text{N}_2$ , 21% of the molecules you breathe are  $\text{O}_2$  and 0.9% of the molecules you breathe aren't molecules: they're monatomic argon atoms. Furthermore, if the pressure of dry air is 1.00 atm, then the  $\text{N}_2$  molecules are pressuring you to the extent of 0.78 atm, while the  $\text{O}_2$  molecules are pressuring you to the extent of 0.21 atm, and those argon atoms are pressuring you to the extent of 0.009 atm. They keep hitting you and hitting you and hitting you at hundreds and thousands of miles per hour. Can you stand the pressure?

I had earlier shown the relationship of densities of various gases and included the comparison for air. The density of a mixture of gases, such as air, can be calculated from the densities of the separate components. Let's see how this relationship is derived.

Consider a mixture of three gases, again labeled A, B and C. The total mass is the sum of the individual masses.

$$m_{\text{total}} = m_A + m_B + m_C$$

They are all in the same container of volume  $V$ . Therefore,

$$\frac{m_{\text{total}}}{V} = \frac{m_A}{V} + \frac{m_B}{V} + \frac{m_C}{V}$$

and each of these is a density term.

$$d_{\text{total}} = d_A + d_B + d_C$$

This means that densities are additive for a gas mixture. For dry air at 25 °C with 0.78 atm  $\text{N}_2$ , 0.21 atm  $\text{O}_2$  and 0.009 atm Ar, we have the following.

$$d(\text{air}) = d(\text{N}_2) + d(\text{O}_2) + d(\text{Ar})$$

For each gas,

$$d = \frac{PM}{RT}$$

from which you can calculate

$$d(\text{N}_2) = 0.89 \text{ g/L} \qquad d(\text{O}_2) = 0.27 \text{ g/L} \qquad d(\text{Ar}) = 0.01 \text{ g/L}$$

and their sum gives  $d(\text{air}) = 1.17 \text{ g/L}$ . That's the density for dry air at 25 °C.

Notice that I said dry air. There can also be a significant amount of water vapor in the air. By the way, don't be fooled by that word, "vapor". A vapor is a gas, just like any other gas; vapors obey  $PVnRT$  and all other relationships above. Water vapor in the air is also called humidity. The maximum pressure of water vapor in the air is limited by temperature; that limitation is an equilibrium thing as we'll see in Chapter 35. As an illustration, the maximum pressure of water vapor in air at 25 °C is 0.031 atm, which is not much compared to total air.

Although not much, in hot weather a relatively high humidity is bad news in terms of human comfort. Curiously, a common human perception is that humid air is somehow heavier or denser than dry air. Is it really? Water's molar mass is only 18.02 g/mol, compared to  $\text{N}_2$  at 28.02 g/mol,  $\text{O}_2$  at 32.00 g/mol and Ar at 39.95 g/mol. That means  $\text{H}_2\text{O}(g)$  is lighter than air! (It's less dense for the same  $T$  and  $P$ .) Likewise, humid air is less dense than dry air at the same total pressure, although the difference is small since the amount of  $\text{H}_2\text{O}(g)$  is small. Nevertheless, if you want to dry out a narrow-mouth bottle, then shake out all the liquid water which you can, and then let the bottle stand pointing upward. Upward is the preferred direction to hasten evaporation of residual water. These things are part of your world. Whether you know it or not.

One final point before moving on. I mentioned in Chapter 2 that the O<sub>2</sub> you need to live can be toxic.

“ But this is another great example of Nature's irony: although it is essential to breathe oxygen gas, it is toxic in high concentrations. Fortunately, those toxic concentrations are not readily encountered. Scuba divers can encounter this, however, and there are grave repercussions to diving with pure oxygen. ”

There's a catch in that quote from Chapter 2 and that catch is concentration. On the surface of Earth, you don't naturally encounter concentrations of O<sub>2</sub> which are quickly deadly because the pressure is not high enough. (On the other hand, as also mentioned in Chapter 2, the long-term toxic effects of O<sub>2</sub> do affect you even at normal pressure.) If you dive under water, however, the pressure increases rapidly with descent. If you are breathing pure oxygen beyond a certain depth, you can exceed the safe concentration of O<sub>2</sub> and you die. But that's the water world again, and we're trying to stay afloat with gases right now.

### Problems

- True or false.
  - Most of the volume of the air you breathe is empty space.
  - For a given sample of gas at a fixed temperature, volume decreases as pressure decreases.
  - If a gas mixture contains one mol He and one mol Ar, then the pressure of each gas is the same.
  - For a given sample of gas at a fixed pressure, volume decreases as temperature increases.
  - The total pressure for a mixture of gases is the sum of the pressures of the individual components.
  - At STP, 10.0 L of N<sub>2</sub>(g) has a greater density than 5.0 L of O<sub>2</sub>(g).
- A sample of hydrogen gas is contained in a 2.2 L volume at 432 Torr and -12 °C. How many moles of gas are present in the sample?
- A tank holds 4.12 g Kr in a volume of 2.00 L at 17 °C. What is the pressure of the Kr in atm? What is the pressure of the Kr in bar?
- A container holds 3.92 g CO<sub>2</sub>(g) at 146 °C and at a pressure of 1.000 atm. What is the volume (in L)?
- A 15.4 L container holds a gas at 39 °C and 2.19 atm. The gas is transferred to a new container with a volume of 25.6 L and the new temperature is 87 °C. What is the new pressure (in atm) of the gas?
- Which of the gases below are denser than CO<sub>2</sub>(g) at the same temperature and pressure?
 

Cl <sub>2</sub>	BF <sub>3</sub>	SF <sub>4</sub>	Ar	HF	C <sub>2</sub> H <sub>4</sub>
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- What is the density (in g/L) of ammonia(g) at STP?
- Teflon is made from a gas which is 24% carbon and 76% fluorine. The empirical formula is CF<sub>2</sub>. The density is 3.86 g/L at 20. °C and 0.927 atm. What is the molecular formula of this compound?
- At 94 °C, a 23.0 L container holds 12.3 g of SO<sub>2</sub> and 18.0 g of CO<sub>2</sub>. What is the total pressure (in atm)? What is the mole percent of SO<sub>2</sub>?
- A mixture contains 6.32 g of methane gas and 603 Torr of propane gas in a volume of 13.6 L at 15 °C. What is the mole percent of propane?
- A gas mixture of H<sub>2</sub>S and Ar in a 40.0 L volume at 33 °C has a total pressure of 460. Torr. The mole percent of H<sub>2</sub>S is 60.0%. What is the total density (in g/L) of the mixture?