

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

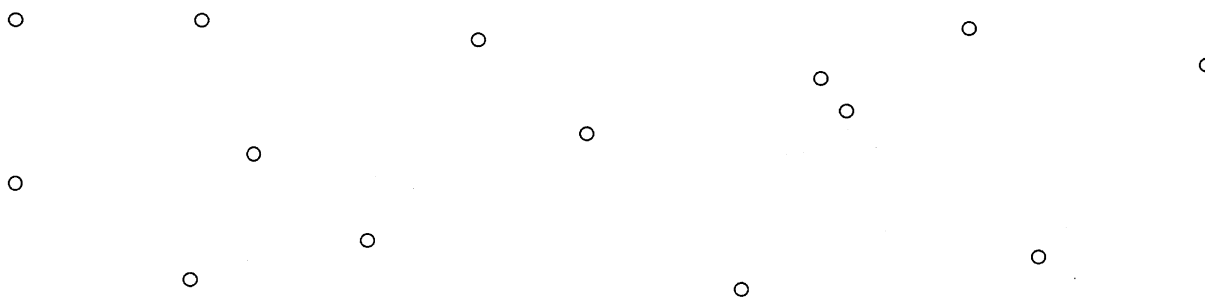
As a whole, the phases are incredibly important. The three common phases, solid, liquid and gas, are very much a part of your life. Why are there three? Notice that I said "common" phases. These three phases are common to the surface of planet Earth, given the conditions that exist here. That's what we're used to. If you change the conditions drastically, you can change the phases. (And, yes, there are other phases.) 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.



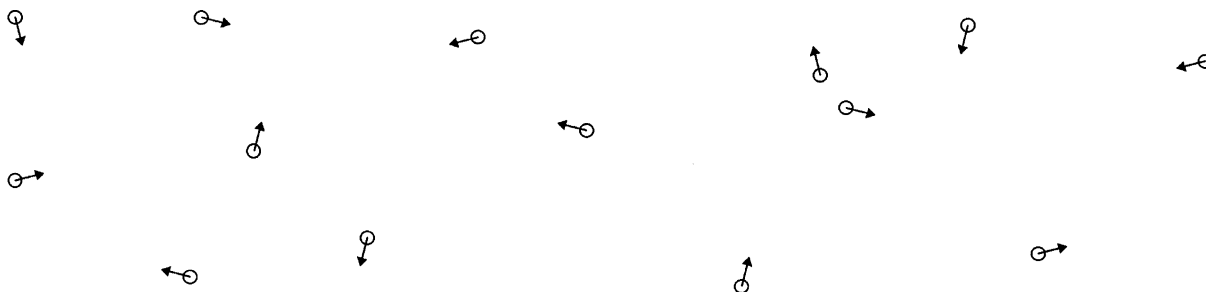
Here's another example of the immensity of nothing in the gas phase. At the boiling point of water, 100 °C, one mole of liquid water occupies 19 mL, and that volume involves all the water molecules in fairly loose contact with each other. One mole of gas phase water at 100 °C, however, occupies 31 L. 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 very 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 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 to find out.

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 to outer 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), zillions of air molecules are smacking you straight in the eyeball at hundreds and thousands of miles per hour. Nature made it that way. 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 real inches, they're "inches of mercury" 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 those scrawny fifth-wheels which are around 60 psi. Bike tires are high also. You're supposed to check your tires periodically, preferably before you start hearing the rim on the road.

Inches of mercury (abbreviated "inHg") and psi are based on English units. In chemistry, we're supposed to use SI units, but pressure is one example of SI units that hasn't really caught on with many chemists. A common unit which we use in chemistry is "mmHg" which is the abbreviation for millimeters of mercury. This is just the metric version for inches of mercury. Another version is "Torr", which is defined to be exactly the same as mmHg. Common atmospheric pressures are in the range of ~700 - 800 Torr, so one Torr is not a lot. Actually, the atmosphere itself has provided the basis for a different pressure unit: this one is called a "standard atmosphere" and it's abbreviated "atm". One atm is defined to be exactly 760 mmHg or 760 Torr. As far as SI is concerned, the official pressure unit is the pascal (Pa). A pascal is so little, however, that kilopascal, kPa, is frequently seen. Here's a bunch of the units we've just covered, set up as one big equality.

$$\underbrace{\text{atm} = 760 \text{ mmHg} = 760 \text{ Torr} = 101,325 \text{ Pa} = 101.325 \text{ kPa} = 29.92 \text{ inHg} = 14.70 \text{ psi}}_{\text{These are all exactly defined.}}$$

These are all exactly defined.

These relationships can be used as conversion factors. Like all conversion factors, any two can be used in right-side-up or upside-down configuration. Also, notice that the first five entries are defined and therefore exact; those conversions will not enter into round-off decisions for sigfigs.

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 .
Although other pressure units can be used, we are going to set this up using atm.
- The volume, V , of the sample.
Although other volume units can be used, we are going to set this up using 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 usual choice 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 are contained within concentration in the form of n/V , with units of mol/L. This brings us to

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

(The unit, mol/L, is like a molarity, but the term molarity is not typically used with gases.) This equation 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 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 . 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.

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

This constant R applies for every gas, so this ratio, PV/nT , is a universal ratio for every gas sample. That means, given any set of conditions "1" and comparing them to any set of conditions "2", the following is true.

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

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. Your instructor may cover further examples with this equation.

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 will raise 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 will increase P . If you cool the gas, this will decrease 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, 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.

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Example 1. A container holds 2.017 L of some gas at 18 °C with a pressure of 0.601 atm. How many moles of gas are present in the container?

$PVnRT$. $PVnRT$. $PVnRT$. Get used to it. Notice that the problem gives three of the four gas parameters and you were asked for the fourth. This one is straightforward, although you have to put temperature into K. I'll tell you right now that, whenever you do $PVnRT$, you need the units L, atm, mol and K. So if somebody is not in the right unit, then you must convert. For T , we convert °C into K using 273.15 (as seen in Chapter 1); that means 18 °C is 291 K. Now do your $PVnRT$.

$$PV = nRT$$

The problem wants moles, so re-arrange for n .

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

Throw in your given values.

$$n = \frac{(0.601 \text{ atm})(2.017 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (291 \text{ K})} = 0.0508 \text{ mol}$$

That's it: you have 0.0508 moles of gas in the container. Although the units may appear confusing, 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 unit conversions involved.

Example 2. You have 0.02186 mol of some gas at a pressure of 152 mmHg in some container whose volume is 2251 mL. What's the temperature of the sample, in °C?

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

Pressure needs atm, but you were given mmHg; you need to convert.

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

Volume needs L, which is a decimal shift from 2251 mL to 2.251 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 need T , so re-arrange.

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

Throw in your values.

$$T = \frac{(0.200 \text{ atm})(2.251 \text{ L})}{(0.02186 \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right)} = 251 \text{ K}$$

There you have it, except you need °C: 251 K converts to -22 °C for your answer.

I'll show you a shortcut for pressure when you're given mmHg or Torr. Just enter the conversion directly into $PVnRT$ as a fraction of 760, since both relate to atm by that number. In the above example, you could set this up as the following.

$$T = \frac{\left(\frac{152}{760} \text{ atm} \right) (2.251 \text{ L})}{(0.02186 \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right)}$$

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 two simple examples of $PVnRT$. There are many uses of this relationship. We will see more below and into the next Chapter.

16.4 STP and d

Many years ago, it was decided to define a certain pressure as a "standard pressure" and a certain temperature as a "standard temperature" for work with gases. The standard pressure was set to exactly one atm. The standard temperature was set to exactly 0 °C. Now, it may seem strange that a so-called "standard temperature" was set to a centigrade value when we have to use kelvins anyway, but that's the way they did it. I wasn't around, so don't blame me. These conditions are called "standard temperature and pressure", which is abbreviated STP. So, if you're talking about gases and you're told that the sample is at STP, then that's exactly one atm and 0 °C.

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

Example 3. How many grams of argon can be contained in a 1.024 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.

$$n = \frac{(\text{one atm})(1.024 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (273.15 \text{ K})}$$

Plug all this in and you get moles. Bring in argon's molar mass (39.95 g) and you get 1.825 g argon. Do the actual number-crunching and make sure you get this answer.

Have you ever breathed argon? You bet! Hundreds of pounds 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 mole of that thing. For liquid water with a density of 1.00 g/mL at 25 °C, the molar volume is 18.0 mL. For solid sodium chloride with a density of 2.16 g/mL, the molar volume is 27.1 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 derive this relationship for STP conditions.

$$PV = nRT$$

Re-arrange for V .

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

Throw in your values. Just enter one mol and the STP conditions of one atm and 0.00 °C (273.15 K).

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

This tells us that an ideal gas of any identity at STP has a molar volume of 22.41 L. Notice that this is ~1200 times the molar volume of water and ~800 times the molar volume of sodium chloride. A gas takes 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 rearrange $PV=nRT$ 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 55.5 mol/L, or to solid sodium chloride which has 37.0 mol/L. This again illustrates that the gas phase has very little of anything in it.

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 $PV=nRT$ 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 relationship 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.

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

Thus, as mentioned above, we see that density does depend on identity because the molar mass depends on identity.

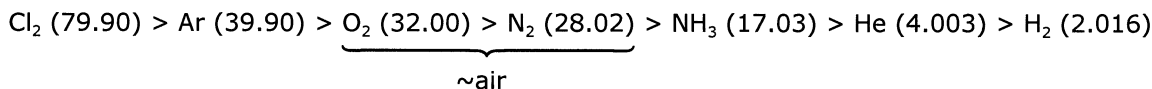
Density is just another plug-in type of calculation. You try it.

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Example 4. Calculate the density of O_2 gas at STP.

Work it out.

You should get 1.428 g/L. If not, find and fix the error. This density is very small compared to the density of a liquid or solid phases: compare this to 1.00 g/mL for liquid water and 2.16 g/mL for sodium chloride. As I keep saying, there's just not much mass in a gas.

There are several qualitative consequences to the density equation which I would like 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 in parentheses.



Notice that I've shown N_2 and O_2 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_2 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 is one way of measuring 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_2 or if it's air with O_2 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_2 by itself at STP, then there are 0.04461 moles of O_2 molecules per liter. If you have a sample of air at STP, then there are 0.04461 moles total 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_{total} , is the sum of the individual pressures.

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

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 inside the container?

Right off the bat, I'm going to warn 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 O₂,

$$P(\text{O}_2) = \frac{(0.03125 \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (277 \text{ K})}{1.767 \text{ L}} = 0.402 \text{ atm O}_2$$

This tells you the individual pressures for N₂ and for O₂; 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 $PV=nRT$ 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 O₂ is 0.402 atm or you can say the partial pressure of O₂ 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 . (I don't know why it's an X ; that's just the way it is.) The term applies to one component as present in some solution 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 " $\times 100\%$ " 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 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. This also applies between any one component and the total. We can see this from the following. 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 $\text{N}_2 + \text{O}_2$ mixture from above, we had 0.03569 moles N_2 which came out to 0.459 atm N_2 , and we had 0.03125 moles O_2 which came out 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

$$X(\text{N}_2) = \frac{n(\text{N}_2)}{n_{\text{total}}} = \frac{0.03569 \text{ mol}}{0.06694 \text{ mol}} = 0.5332 \text{ OR } 53.32\%$$

and the mole fraction calculation using pressures is

$$X(\text{N}_2) = \frac{P(\text{N}_2)}{P_{\text{total}}} = \frac{0.459 \text{ atm}}{0.861 \text{ atm}} = 0.533 \text{ OR } 53.3\%$$

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 5. 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.

$$X(\text{O}_2) = \frac{n(\text{O}_2)}{n_{\text{total}}} = \frac{\quad}{0.06694 \text{ mol}} = \quad \text{ OR } \quad \%$$

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

Actually, since there are only two components in this sample, there's another option for doing the 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 N_2 is 53.32% of the mixture, then 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% N_2 , 21% O_2 and 0.9% Ar. You also breathe traces of other things such as CO_2 , Ne, He, 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 N_2 , 21% of the molecules you breathe are 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 N_2 molecules are pressuring you to the extent of 0.78 atm, while the 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 take 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 N₂, 0.21 atm O₂ 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

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

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 pressure of water vapor in the air is limited by temperature, and that limitation is an equilibrium thing as we'll see in Chapter 35. As an illustration, the pressure of water vapor in air at 25 °C can reach 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 N₂ at 28.02 g/mol, O₂ at 32.00 g/mol and Ar at 39.95 g/mol. That means H₂O(*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 H₂O(*g*) is small. Nevertheless, if you want to let the remaining water evaporate out of a narrow-mouth bottle, then aim it upward and not downward. 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 O₂ 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 restrictions on 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 O₂ which are immediately deadly because the pressure is not high enough. (On the other hand, as also mentioned in Chapter 2, the long-term toxic effects of O₂ 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 O₂ and you die. But that's the water world again, and we're trying to stay afloat with gases right now.

Problems

1. True or false.
 - a. Most of the volume of the air you breathe is empty space.
 - b. For a given sample of gas at a fixed temperature, volume decreases as pressure decreases.
 - c. For a given sample of gas at a fixed volume, pressure increases as temperature increases.
 - d. As more moles of gas are added to a container of constant volume and at constant temperature, the pressure increases.
 - e. When a fixed amount of gas is heated at constant pressure, the volume decreases.

- f. Heating a gas sample at constant pressure increases the density of the sample.
- A sample of methane gas is confined in a 2.2 L container at 432 Torr and 87 °C. How many moles of gas are present in the sample?
 - A container contains 4.12 g Kr in a volume of 2.00 L at 17 °C. What is the pressure of the gas sample in atm?
 - A container holds 3.92 g of $\text{CO}_2(g)$ at 146 °C and at a pressure of one standard atmosphere. What is the volume (in L)?
 - A 15.4 L container holds a gas at 38 °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 $\text{CO}_2(g)$ at the same temperature and pressure?
 Cl_2 BF_3 SF_4 Ar HF C_2H_4
 - What is the density (in g/L) of ammonia(g) at STP?
 - Teflon and some related plastics are made from a gas which is 24% carbon and 76% fluorine. The empirical formula is CF_2 . The density at STP is 4.43 g/L. What is the molecular formula of this compound?
 - At 94 °C, a 23.0 L container holds 12.3 g of SO_2 and 18.1 g of CO_2 . What is the total pressure (in atm)?
 - A mixture contains 6.32 g of methane gas and 454 Torr of propane gas in a volume of 13.6 L at 15 °C. What is the mole percent of propane?
 - A mixture of two gases is contained in a 100.0 L vessel at 43 °C. The mixture contains 22.4 g C_2H_6 and 162 Torr C_4H_{10} . What is the density (in g/L) of the gas mixture?