

PHYSICS 151 – Notes for Online Lecture #33

Moving From Fluids To Gases

There is a quantity called **compressibility** that helps distinguish between solids, liquids and gases. If you squeeze a solid with your hands, there is generally no effect. You have to squeeze really, really hard to do anything to it. On the other hand, if I put water in a balloon, there is some amount of squeezing I can do before it's too hard to squeeze. If, however, we look at how gases behave, we find that it is much easier to cause a gas to change its volume.

The equation we used for thermal expansion doesn't consider pressure at all. It turns out that the volume of a gas depends on:

- pressure
- temperature (we saw this with the balloon in LN₂)
- mass

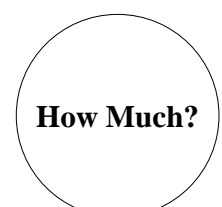
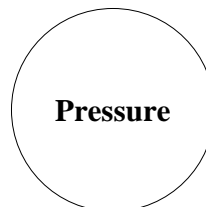
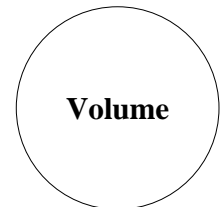
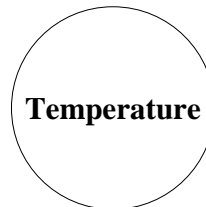
We can express all of these dependencies by something called the **equation of state**. An equation of state is sort of like a master equation, from which you can tell lots of things about a system.

One of the things we have to consider is that if I change the temperature or pressure of a system, it may take some time before the entire system is at the same temperature or pressure. We therefore have to wait for things to settle down before what we're about to derive becomes applicable.

Also, we can't describe gases that are very dense, as there are many interactions between the atoms or molecules and that makes things very difficult. Similarly, if we are close to the temperature at which the gas becomes a liquid, there are correlations between atoms or molecules and again we can't describe that situation.

This theory thus requires:

- a system in thermal equilibrium (all parts of the system are at the same T, P)
- a non-dense gas
- a gas not close to its liquefaction point



Experimentally: someone measured how the volume of a gas depends on the pressure very carefully and found that:

BOYLE'S LAW

$$V \propto \frac{1}{P}$$

at constant temperature and if the amount of gas doesn't change.

This is known as Boyle's Law, after the man who figured this out back in the 1600's. We sometimes write this as:

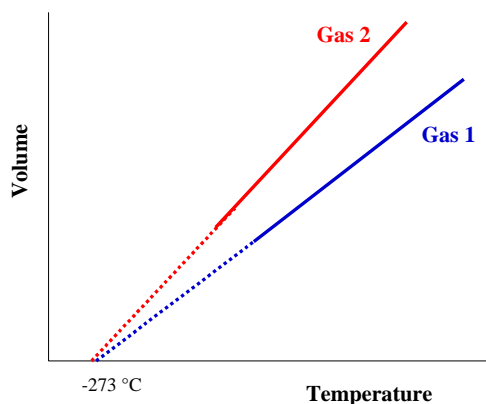
$$PV = \text{constant at constant temperature and constant amount of gas}$$

It took another century before someone (Charles) found that, when the pressure is constant and not too high, the volume varies directly with the temperature:

CHARLES' LAW

$$V \propto T$$

at constant pressure and if the amount of gas doesn't change.

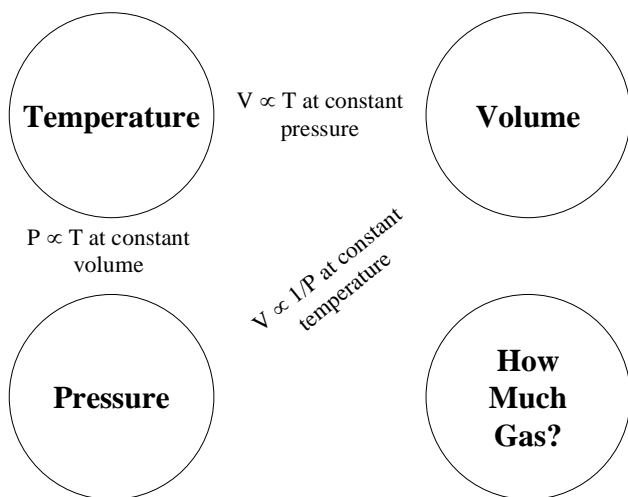


We can experimentally verify Charles' Law by measuring the volume of a gas (say, in a balloon) as a function of the gas's temperature. If we plot the volume as a function of temperature, we find that (until I get near the liquefaction point) we get a straight line. Amazingly, for any gas, at any reasonable pressure, the line has the exact same value for the point at which the volume goes to zero. This temperature is $-273\text{ }^{\circ}\text{C}$ - which you might is 0 K. This is why the Kelvin temperature scale is so special - it is not as arbitrary as the other scales we have studied.

GAY-LUSSAC'S LAW

$$P \propto T$$

at constant volume and if the amount of gas doesn't change.



Your author emphasizes that these three relationships aren't really laws – they hold over a very limited range of the parameters – that is, only under specific conditions. Let's review our chart now.

The problem here is that all we have are proportionalities. So we can find ratios, but we can't actually calculate a number.

There's this fourth variable on the chart because the quantity that we still have to include is the mass of the gas – how many molecules there are.

If I blow up a balloon, I put more molecules and thus more mass into the balloon - this causes it to have a bigger volume. Again, if you carefully measure it, you find that

$$V \propto m \text{ if pressure and temperature are constant}$$

If we put all of these relationships together, we find

$$PV \propto mT$$

But we still can't actually get a number out of this. One of the things we have to introduce in order to make this law work is the idea of a mole. We talked about the balloon and that the pressure and the volume depended on the number of molecules inside, so we know that the number of molecules must somehow be important. m is the mass of the gas, in grams. However, depending on the material, the same weight of a material can have different numbers of molecules.

Molecular mass. The molecular mass of a material is measured in increments of u , the atomic mass unit

$1u = 1.66 \times 10^{-27} \text{ kg}$
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When you're dealing with atoms and molecules, the masses are very small, so we use a different unit to avoid all those very large and very small numbers. This system assigns the mass of carbon to be exactly 12. The molecular mass of any molecule can be calculated by adding up the molecular masses of each atom. The H atom is $1.0079u$ – see the back of the book for the rest. In many cases, the molecular mass is twice the atomic number

So the molecular mass	of $H_2 = 2(1.0079) = 2$	of $CO_2 = 12+2(16) = 44$
	of $O_2 = 2(16) = 32$	of $Ne_2 = 2(20) = 40$

Moles

The number of moles in a certain mass of a material is given by:

$$n(\text{mol}) = \frac{\text{mass(g)}}{\text{molecular mass (u)}}$$

Avogadro's Number: The idea of moles was introduced by Avogadro, who found that, at equal pressures, volumes and temperatures, all gases will contain the same number of molecules. The number of molecules in one mole of gas is the same for all gases. The number of molecules in a mole is

$$N_A = 6.02 \times 10^{23} \text{ molecules/mole.}$$

So the total number of molecules (N) in n moles is

$$N = nN_A$$

$$\text{or } n(\text{mol}) = \frac{\text{mass(g)}}{\text{molecular mass (u)}} = \frac{N}{N_A}$$

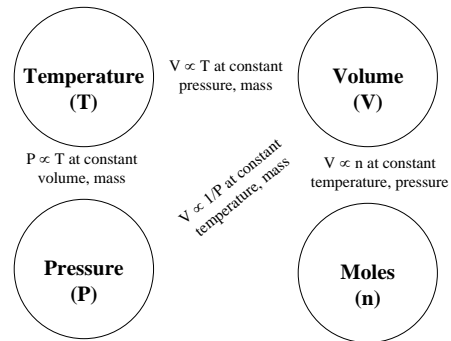
This is how the number of molecules comes into play in our diagram

From $PV \propto mT$, instead of using the mass, let's instead use the number of moles

We had $V \propto m$ so $V \propto n$ at constant P,T and we finally get

$$PV \propto nT$$

It turns out, then, that if you can measure P,V,T and n (which you can), you can determine the proportionality constant. It turns out, nicely enough, that the proportionality constant is the same for all gases!



We call it R, where $R = 8.315 \text{ J/mol-K}$. R is called the **universal gas constant** because it is the same for all different gases. R is sometimes expressed in other units: $R = 0.0821 \text{ L-atm/mol-K}$ for example. Volume is sometimes given in liters and pressure in atmosphere, so this form may be handier.

When you introduce the idea of moles, you can have one law applicable for all gases with only one constant to remember. Note: from looking at the units of R, you see that you have to measure the temperature in K -not °C!

So finally, we arrive at the **ideal gas law**

$$PV = nRT \text{ where, don't forget, T is measured in Kelvin.}$$

Using $n = N/N_A$, we can also write:

$$PV = nRT$$

$$PV = \frac{N}{N_A} RT = PV = N \frac{R}{N_A} T$$

$$PV = NkT$$

where $k = R/N_A = 1.38 \times 10^{-23} \text{ J/K}$. k is called Boltzmann's constant. As a convention, we frequently use the notation: STP - standard temperature and pressure, meaning

$$T = 0^\circ\text{C} (273 \text{ }^\circ\text{K})$$

$$P = 1.00 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2.$$

At STP, all ideal gases have the same volume. We can show this from writing:

$$PV = nRT$$

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

$$V = \frac{(1\text{mol})\left(8.315 \frac{\text{J}}{\text{mol-K}}\right)273\text{K}}{1.01 \times 10^5 \frac{\text{N}}{\text{m}^2}} = 22.4 \times 10^{-3} \text{ m}^3$$

$1 \text{ L} = 1000 \text{ cm}^3 = 1 \times 10^{-3} \text{ m}^3$, so the volume of one mole of any ideal gas at STP is 22.4 liters.

Applying the Ideal Gas Law

When we use instruments to measure pressure, the changes in pressure are small compared to the value of atmospheric pressure, so we use atmospheric pressure as a reference. The value shown on the instrument is thus the value of the pressure above or below that of the atmosphere.

$$P_{\text{absolute}} = P_{\text{gauge}} + P_{\text{atm}} = P_{\text{gauge}} + 1.01 \times 10^5 \text{ Pa}$$

When using pressures in the ideal gas law, you must use absolute pressure and not gauge pressure!

All temperatures should be in Kelvin!

A common situation in applying the IGL is to be comparing a system at two different times. Your goal is to rewrite the IGL so that all the variables that change are on one side of the equation and those that don't are on the other side. You then write an equation where the variables that change are set equal to each other in the two situations (set the ones that do change equal to each other with subscripts).

EXAMPLE 33-1: A typical region of interstellar space may contain 10^6 atoms per cubic meter (primarily hydrogen) at a temperature of 100 K. What is the pressure exerted by this gas?

$$PV = NkT$$
$$P = \frac{NkT}{V} = \frac{(10^6) \left(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \right) (100\text{K})}{(1\text{m}^3)} = 1 \times 10^{-15} \frac{\text{N}}{\text{m}^2}$$

EXAMPLE 33-2: If the pressure of a gas is quadrupled and the volume expands by a factor of two, how does the temperature change?

Note that pressure, volume, and temperature are changing – the number of moles is not.

$$PV = nRT$$

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

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

$$T_2 = \frac{P_2 V_2}{P_1 V_1} T_1 = \frac{4P_2}{P_1} \frac{2V_2}{V_1} T_1 = 8T_1$$

EXAMPLE 33-3: You check your car's tire pressure in the morning, when the temperature is 10°C and find the gauge pressure to be 180 kPa. After a long drive, the temperature of the air in the tires is 45°C – what will the pressure gauge read?

Convert gauge pressures to absolute pressures: $P_1 = 180 \text{ kPa} + 101 \text{ kPa} = 281 \text{ kPa}$

Convert temperatures to Kelvin: $T_1 = 10^\circ\text{C} = (10+273)\text{K} = 283 \text{ K}$

$T_2 = 45^\circ\text{C} = (45+273)\text{K} = 318 \text{ K}$

n isn't changing, nor is V .

This is a typical IGL problem where you are comparing two different situations. There will be some variables in the IGL that change between the two situations and some that stay the same. You want to move all of those that don't change to one side of the equation, and set the ones that do change equal to each other with subscripts.

$$PV = nRT$$

$$\frac{P}{T} = \frac{nR}{V}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_1 \frac{T_2}{T_1} = P_2$$

$$281 \text{ kPa} \frac{318 \text{ K}}{283 \text{ K}} = P_2$$

$$316 \text{ kPa} = P_2$$

so the gauge pressure will be $316 \text{ kPa} - 101 \text{ kPa} = 215 \text{ kPa}$



A cylindrical flask is fitted with an airtight piston that is free to slide up and down, as shown in the figure below. A mass rests on top of the piston. Contained within the flask is an ideal gas at a constant temperature of 313 K. Initially the pressure applied by the piston and the mass is 137 kPa and the height of the piston above the base of the flask is 23.4 cm. When additional mass is added to the piston, the height of the piston decreases to 20.0 cm. Find the new pressure applied by the piston.

In this problems n and T do not change!

$$\begin{aligned} P_i V_i &= P_f V_f \\ P_i (\pi r^2 h_i) &= P_f (\pi r^2 h_f) \\ P_f &= \frac{P_i h_i}{h_f} \\ &= \frac{(137 \text{ kPa})(23.4 \text{ cm})}{20.0 \text{ cm}} \\ &= \boxed{160 \text{ kPa}} \end{aligned}$$

