Chapter 31

31 Heat Transfer and Gas Laws 2.1.6, 2.2.1

Now that we understand heat as a transfer of energy, we should look at how we can move energy around by heat. We will do this in this lecture. We will also develop a relationship between pressure, volume, and temperature for a gas. You probably know this relationship from your high school science classes. But we will look at how we got it and when it is valid.

Fundamental Concepts

- Conduction
- Convection
- Radiation and Stephan's law
- The Ideal Gas Law
- The Van der Waals Gas Law

31.1   Heat Transfer Mechanisms

The change in internal energy is the sum of the energy from each type of energy transfer

$$\Delta E_{int} = Q + W$$

Work we know a lot about, but let's become more familiar with Q. We may talk about different ways to transfer energy, then

$$\Delta E_{int} = \sum_i (\text{Transfer mechanism})_i \tag{31.1}$$

where work is one of those energy transfer mechanisms and there may be many different Q transfer types. In what follows, we will talk about a few.

31.1.1   Thermal Conduction

This is what we have been calling heat up to this point. We define it a little more carefully as the exchange of kinetic energy between microscopic particles (molecules and atoms) through direct contact.

When we add energy by heat to part of a solid, the atoms are locally displaced from their equilibrium locations. These atoms knock into their neighbors, and cause them to be displaced (they increase their kinetic energy). This process continues through the whole solid.

The rate of heat transfer will depend on the properties of the atoms that make up the substance.
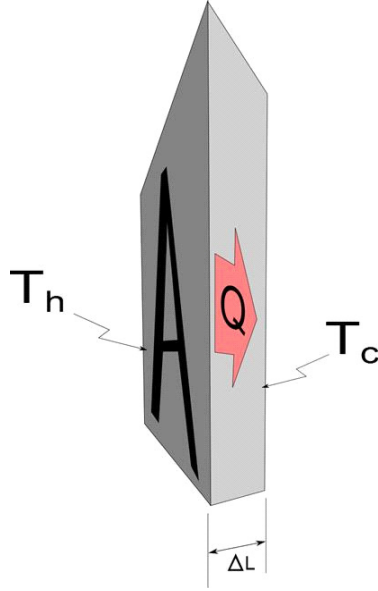
We can envision a piece of solid as in the figure. It has thickness Δx and cross-sectional area A. If one face of the slab is at T_c and the other at T_h. We find that energy Q transfers in a time interval Δt from the hotter face to the colder one. The rate

$$\mathcal{P} = \frac{E}{\Delta t} = \frac{Q}{\Delta t}$$

is proportional to A. and ΔT.

$$\mathcal{P} = \frac{Q}{\Delta t} \propto A \frac{\Delta T}{\Delta L}$$

We can take ΔL very small

$$\mathcal{P} = k_{therm} A \left| \frac{dT}{dL} \right| \tag{31.2}$$

where we now have another constant k! This k_{therm} is the *thermal conductivity* of the material and we define $\left| \frac{dT}{dL} \right|$ as the *temperature gradient.*

A gradient is a rate of change, so this gradient is the rate of change of the temperature with respect to position.

For a one dimensional problem, we take a rod. If we assume that k_{therm} is not temperature dependent and the rod is uniform, then

$$\left| \frac{dT}{dL} \right| = \frac{T_h - T_c}{\Delta L}$$

and

$$\begin{aligned} \mathcal{P}_{rod} &= \frac{Q}{\Delta t} = k_{therm} A \frac{T_h - T_c}{\Delta L} \\ &= \frac{A(T_h - T_c)}{\frac{\Delta L}{k_{therm}}} \end{aligned} \tag{31.3}$$

If we have a complicated multipart rod with n different substances we would have

$$\mathcal{P} = \frac{A\left(T_h - T_c\right)}{\displaystyle\sum_i^n \frac{\Delta L_i}{k_{therm_i}}} \qquad (31.4)$$

The amount of energy transferred by thermal conduction is

$$Q = \mathcal{P}\Delta t = \frac{A\left(T_h - T_c\right)\Delta t}{\displaystyle\sum_i^n \frac{\Delta L_i}{k_{therm_i}}}$$

All this wasn't too bad mathematically. But the building industry does some simplifications to our thermal conduction equation. We define a term

$$R = \frac{\Delta L}{k} \qquad (31.5)$$

as the "R-value" of a material. Then a wall or multipart solid would have

$$\mathcal{P} = \frac{Q}{\Delta t} = \frac{A\left(T_h - T_c\right)}{\displaystyle\sum_i^n R_i} \qquad (31.6)$$

so that

$$Q_{conduction} = \frac{A\left(T_h - T_c\right)\Delta t}{\displaystyle\sum_i^n R_i}$$

These R-values are used in home insulation and heating design and are usually in English units

31.1.2   Convection

This is a fundamentally new type of energy transport in our study of thermodynamics, although we are all familiar with it. IN the last section we used the example of an electric burner that touched our pot of vegetables. But there are other kinds of stoves.

Convection is the transfer of energy by the movement of the atoms or molecules, themselves. Because the group of moving atoms or molecules has internal energy, moving these molecules also moves the energy. So convection is an energy transfer. This is like circulation of air in your home. Your student apartment might have base-board heading. But your parent's home would likely use forced convection where a fan blows the air.

Electric Base-Board Heater
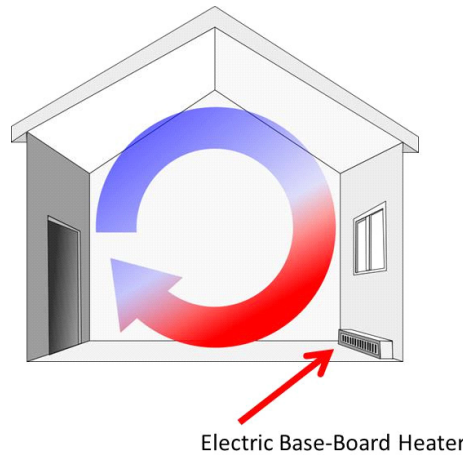
For several decades houses have been made with the idea that you can heat or cool a house with passive convection. Here is an example.
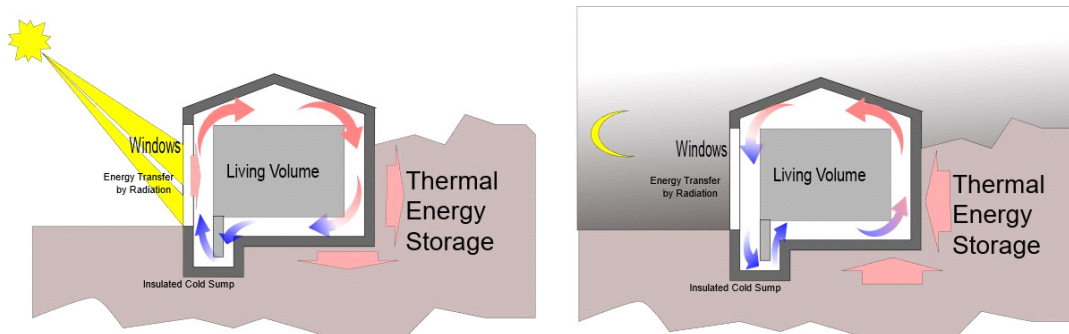
This house tries to control the thermal conduction mechanisms to keep the interior of the house at nearly the same temperature year round.

31.1.3 Radiation

Let's go back to thinking about cooking. Suppose you are cooking over an old wood stove. You open the stove door and see this

And feel a blast of energy transfer by heat. But you don't feel a blast of wind. This isn't convection. And you are not touching the stove.

Light is a form of energy transfer. You will learn more about this in PH220, but we already know that light is a form of wave, and as we know waves carry energy with them. So, light is an energy transfer. We call this energy removal or delivery by light "radiation." This is different than the use of the word "radiation" in nuclear physics.

All objects radiate energy according to Stefan's law

$$\mathcal{P} = \frac{Q}{\Delta t} = \sigma A e T^4 \tag{31.7}$$

The parts of this law are Stephen's constant $\sigma = 5.6696 \times 10^{-8} \frac{\text{W}}{\text{m}^2\,\text{K}}$, the factor, A, is the surface area, e is the emissivity of the material. This e tells us how like a perfect absorber (called a black body) it is, and T is the temperature. Note there are other forms for these! But this is the form we will use.

The emissivity is a value from 0 to 1. If $e = 0$ then the material is a perfect reflector. This would be a perfect mirror. If the emissivity is 1, then it is a perfect absorber. This is more like blacktop in sunlight. The blacktop warms up, even in the winter, because it absorbs the sunlight. Of course, nothing has an emissivity of exactly 0 or exactly 1. Real objects are somewhere in the middle.

It may seem strange that "black" objects glow, but they do. Think again of that blacktop. The ice on the blacktop melts, because the blacktop not only absorbs the radiation from the sun, it also emits radiation.

An extreme example is the Sun, itself. Light that hits the sun from outside will scatter off the gasses in the sun. It takes a very long time for the light to reemerge, if it ever does. Most likely it will be absorbed by the gasses. So the Sun is considered a "black body!" But it glows, so it does not look black.

We can explain many common experiences using the idea of emissivity. Take this leaf for example. Why is it sinking into the snow?

The leaf has a different emissivity than the snow, so it absorbs more radiation from the sun, the temperature of the leaf rises and it melts the snow around it.

With this understanding, we can see that all objects absorb radiation as well as radiate. If an object is at temperature T and it's surroundings are at temperature T_o. then the net rate of energy gained or lost is

$$\mathcal{P} = \frac{Q}{\Delta t} = \sigma A e \left(T^4 - T_o^4\right) \tag{31.8}$$

and the energy transfer would be

$$Q_{radiation} = \frac{Q}{\Delta t} = \sigma A e \left(T^4 - T_o^4\right) \Delta t$$

31.1.4 Multiple transfer mechanisms

As we said before, we might have many different energy transfer mechanisms. We could have all of these (and more).

$$\Delta E_{int} = Q_{conduction} + Q_{convection} + Q_{radiation} + w$$

Let's think about an example that uses radiation, convection, and insulation to keep something cold. It is called a dewar flask.

This is the same idea as a thermos bottle, only better made (and more expensive). The flask has doubled walls with the space between evacuated to reduce convection and eliminate conduction. The walls are silvered to reduce heat transfer by radiation. The cap has a long piece of insulation attached to it to prevent conduction through the flask opening. New designs use multi-layer films which make their surfaces super Reflective.
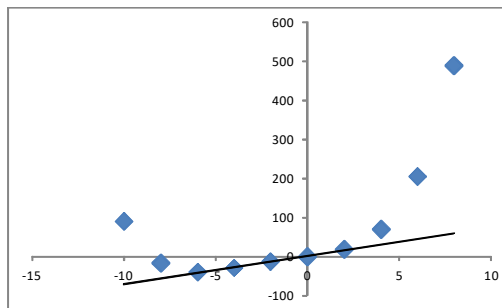
Figure 31.1: You might see our liquid nitrogen dewar in demonstrations. The flask is pictured on the left, and a schematic diagram of how a dewar works is given on the right.

31.2   Gas Laws

Let's consider the following data

The black straight line is a curve fit to the data. What can we say about the curve fit?

It might look useless. But look at the region from about $-6 < x < 5$. In this region, the curve fit is not too bad. Of course, the equation we got for the curve fit is not the right equation, and we know this from the regions $x < -6$ and $x > 4$. If the equation we used for the fit comes from our model for how this physical system works, we know that something is wrong with the model. We do not have an exact theory that explains the behavior of this system well. But could the curve fit be useful? If all you needed was an estimate of the value of the actual function at $x = -1$, then the curve fit might be enough to get your work done! This may not be terribly satisfying, but sometimes it is a useful way to work.

Another way to think about this is that if most of the time, under usual conditions, the phenomena we experience fall within the range $-6 < x < 5$ and

the curve fit equation is much simpler, it might be good enough and convenient to use the curve fit. For example, we know that Newton's laws are not exact. We have to use General Relativity to be accurate. But in calculating our average speed on a trip to Idaho Falls, Newton's laws are plenty good enough, and *much* more convenient than their General Relativistic forms.

We will use the Ideal Gas Law to study the expansion of gasses as temperature changes. The Ideal Gas Law is an approximation very like our curve fit we have been considering. It is an equation that works pretty well under normal conditions, and it is much easier to use than the exact law. It allows us to gain great insight, without the mathematical difficulty of the exact relationship. Given all this, we should realize that there is no such thing as and ideal gas.

In this approximation, the atoms are so weakly bound that there is no equilibrium position between atoms. Thus there is no definite volume defined for an ideal gas. This is generally true at standard pressure and temperature for real gasses. We will let V be a variable for gases. Let's look at where the ideal gas law came from. It is much like our hypothetical experiment. The experimentalists gave us some clues on how to relate V, P, and T.

31.2.1 What lead to the Ideal Gas Law

A researcher named Boyle found that if a system is kept at a constant temperature then

$$P \propto \frac{1}{V} \text{ for constant } T \tag{31.9}$$
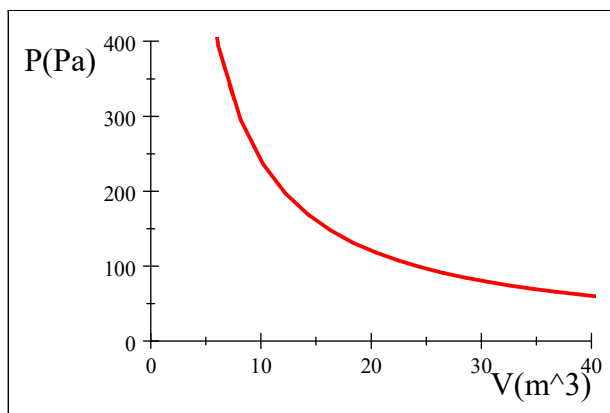

That is, if you don't let the temperature of the gas change, then a change in pressures is inversely related to a change in the volume of the gas. The more pressure, the smaller the volume. We could envision putting our gas in a cylinder, and putting a piston in the cylinder that can be used to compress our gas.
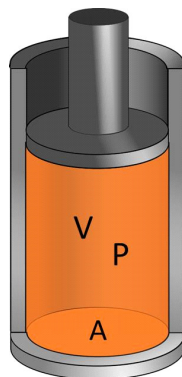
Boyle tells us that as we exert a pressure on the gas using the piston the volume of the gas changes. That seems reasonable.

Two researchers, Charles and Gay-Lussac, found that if a system is kept at constant pressure then

$$V \propto T \text{ for constant } P \tag{31.10}$$
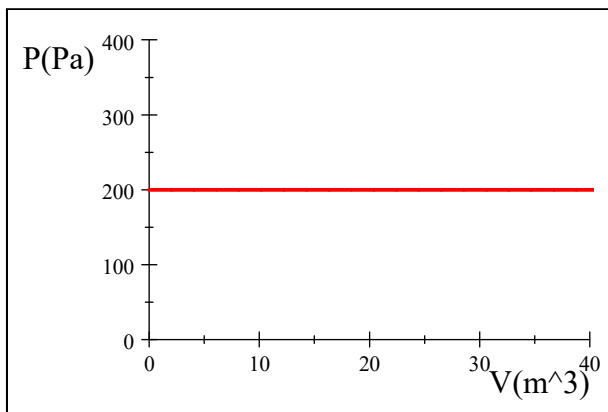
The warmer the gas, the more it will expand. Note that in the graph temperature is not one of the axes! That is a little weird. But you can see the volume of the gas getting larger with the pressure staying the same. Something must be making this happen, and that something is the increase in temperature.

Combining these two findings gives an equation that describes ideal gasses.

$$PV = nRT \tag{31.11}$$

where n is the number of moles, and R is called the *universal gas constant*. This is the *ideal gas law*. The law came from researchers that could not access extreme pressures or temperatures, and so for normal conditions, it works just fine. But it will not work at all for extremely low or height pressures and temperatures.

The variables n, V, P, and T, are state variables for ideal gasses. Depending on the units for V, P, and T, the value for R may be different.

$$R \quad = \quad 8.314 \frac{J}{mol\,K} \tag{31.12}$$

$$= \quad 0.08214 \frac{atm\,l}{mol\,K}$$

31.2.2   Alternate form of the Ideal Gas Law

We know we can describe the number of moles as

$$n = \frac{N}{N_A} \tag{31.13}$$

where N is the number of molecules of gas that we have. Then we can write

$$PV = \frac{N}{N_A} RT \tag{31.14}$$

if we define a new constant

$$k_B = \frac{R}{N_A} \tag{31.15}$$

Then

$$PV = N k_B RT \tag{31.16}$$
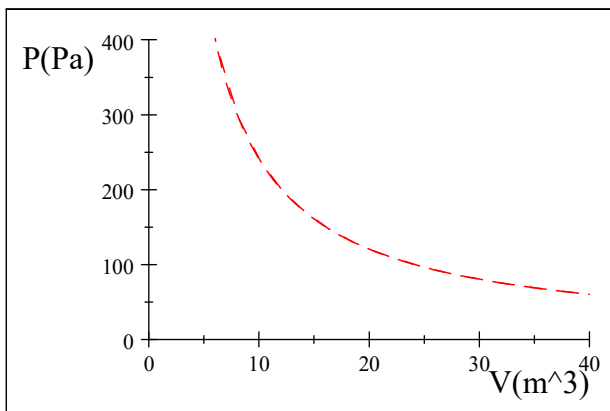
The constant k_B is called *Boltzmann's constant*

$$k_B = 1.38 \times 10^{-23} \frac{J}{K} \tag{31.17}$$

We now have two forms of the ideal gas law!

Fire   Syringe
Demo

31.3   PV diagrams

You may have noticed that in the diagrams in the previous sections we put pressure and volume on the axes.

This was awkward because our gas laws have three state variables, P, V, and T

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

and there wasn't another axis for T. We commonly do this, so we need to know what happens if we change T. In the next figure, you can see the red dashed line is the same
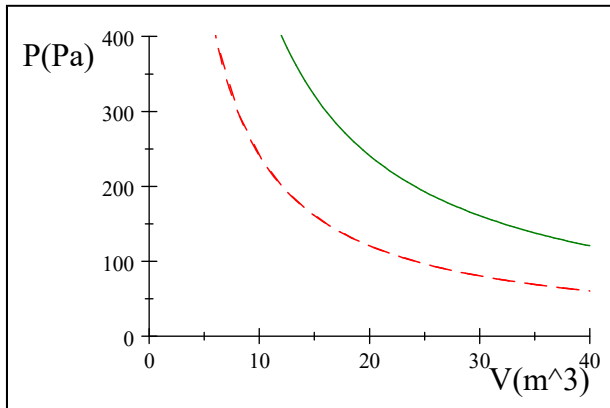
but now there is a green solid line. This is a line for a higher temperature. We expect a $1/V$ line for both, but with a higher temperature the line moves up and a little to the right on the graph. Since the temperature is the same along the whole red dotted line, we call such a line an *isotherm.* The green solid line is a different isotherm with a different temperature.

31.4   Van der Waals Gasses

But of course our ideal gas is missing pieces of the physics of actual gases. For our physics students we have an upper division class in thermodynamics that fills in many of these missing pieces. We also have some quantum mechanics classes that help. Chemists have a thermodynamics class and their physical chemistry class. Mechanical engineers have a thermal class as well. So some of the details will just have to wait. But if you are in one of the disciplines that won't take these fun classes, we should leave you with a slight improvement. We can add in two pieces of physics.

1. As a real gas get's compressed the molecules are more and more attracted to each other. This reduces the pressure in the gas

2. At higher pressures the gas molecules, themselves, constrain where other gas molecules can go. At some point they hit each other!

A researcher named Van der Waals came up with this new approximation, so the result of adding in these two additional bits of physics is called the Van der Waals equitation. Let's see what it looks like.

For the first bit of new physics we can add a term to the pressure that is proportional to the molar density squared.

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

where the constant a depends on the specific gas. It's not obvious why this is the right form for our new gas law equation, but it kind of works. For the second bit of new physics we can subtract a term proportional to the volume of the molecules, themselves b from the volume of the whole gas.

$$V - nb$$

where b is like a molar volume. All together our gas law becomes

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

This gas law equation was formed by a researcher named Van der Waals, and so it is called the Van der Waals gas law.

Although it is an improvement, it still doesn't have all the physics that might be needed to describe a real gas. For example, look at the graph below. You see a plot of isotherms for a Van der Waals gas (CO_2).
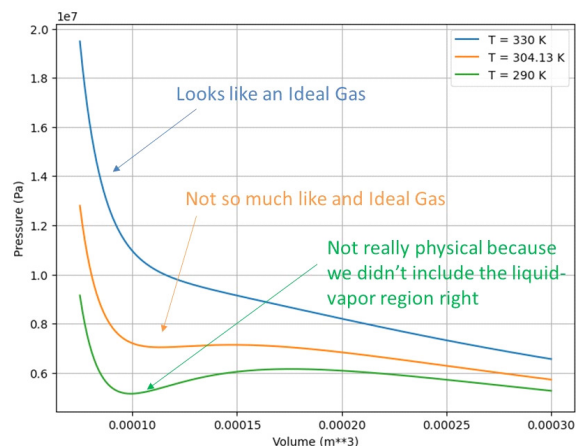
For high temperatures we see something that looks a lot like our ideal gas graph. but at a certain temperature for each gas the graph flattens out (middle orange line). That is really not behavior that we expect from an ideal gas. This temperature is called a *critical temperature, T_c,* and for our CO_2 it is about 304 K. But look at the lower green line) this line dips down and make a valley. This isn't possible. Our "improved" gas law is giving us unphysical predictions. What is missing is that we can have a change from gas to liquid at this pressure and temperature and we didn't include such changes in our Van der Waals gas

law equation. Above T_c our Van der Waals equation isn't too bad. But below T_c it is not as useful. Of course we could improve on our Van der Waals equation, but that is a subject for an upper division class in thermodynamics. For this class, let's concentrate on the ideal gas equation even though we know it has some limitations.