

Lectures on Heat and Thermodynamics

Physics 152

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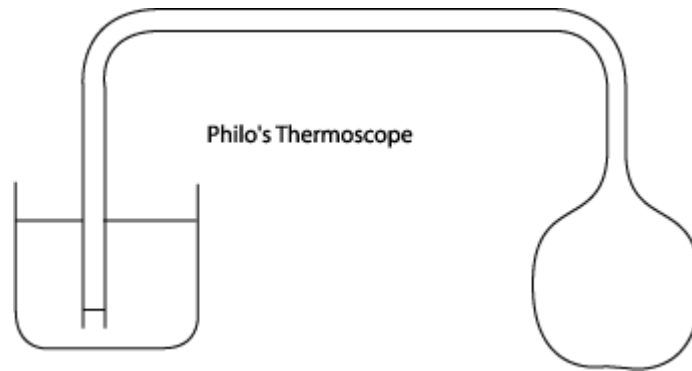
Heat

Feeling and seeing temperature changes

Within some reasonable temperature range, we can get a rough idea how warm something is by touching it. But this can be unreliable—if you put one hand in cold water, one in hot, then plunge both of them into lukewarm water, one hand will tell you it's hot, the other will feel cold. For something too hot to touch, we can often get an impression of how hot it is by approaching and sensing the radiant heat. If the temperature increases enough, it begins to glow and we can *see* it's hot!

The problem with these subjective perceptions of heat is that they may not be the same for everybody. If our two hands can't agree on whether water is warm or cold, how likely is it that a group of people can set a uniform standard? We need to construct a device of some kind that responds to temperature in a simple, measurable way—we need a thermometer.

The first step on the road to a thermometer was taken by one [Philo of Byzantium](#), an engineer, in the second century BC. He took a hollow lead sphere connected with a tight seal to one end of a pipe, the other end of the pipe being under water in another vessel.



To quote Philo: “...if you expose the sphere to the sun, part of the air enclosed in the tube will pass out when the sphere becomes hot. This will be evident because the air will descend from the tube into the water, agitating it and producing a succession of bubbles.

Now if the sphere is put back in the shade, that is, where the sun’s rays do not reach it, the water will rise and pass through the tube ...”

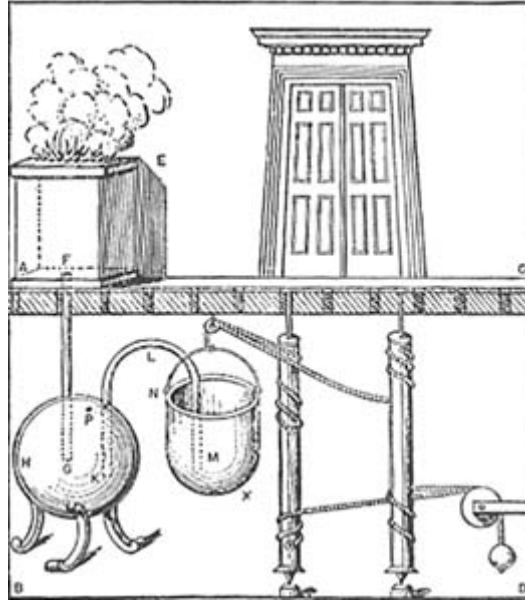
“No matter how many times you repeat the operation, the same thing will happen.

In fact, if you heat the sphere with fire, or even if you pour hot water over it, the result will be the same.”

Notice that Philo did what a real investigative scientist should do—he checked that the experiment was *reproducible*, and he established that the air’s expansion was in response to *heat* being applied to the sphere, and was *independent of the source of the heat*.

Classic Dramatic Uses of Temperature-Dependent Effects

This expansion of air on heating became widely known in classical times, and was used in various dramatic devices. For example, Hero of Alexandria describes a small temple where a fire on the altar causes the doors to open.

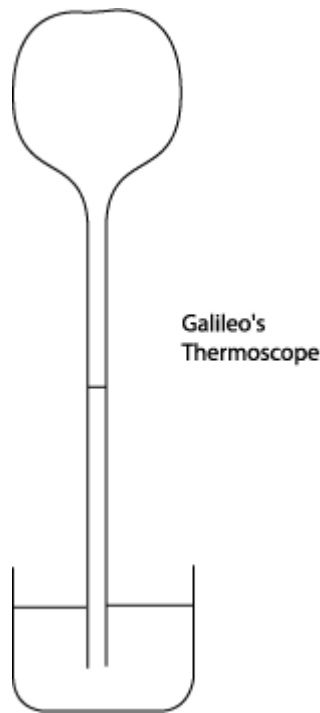


The altar is a large airtight box, with a pipe leading from it to another enclosed container filled with water. When the fire is set on top of the altar, the air in the box heats up and expands into a second container which is filled with water. This water is forced out through an overflow pipe into a bucket hung on a rope attached to the door hinges in such a way that as the bucket fills with water, it drops, turns the hinges, and opens the doors. The pipe into this bucket reaches almost to the bottom, so that when the altar fire goes out, the water is sucked back and the doors close again. (Presumably, once the fire is burning, the god behind the doors is ready to do business and the doors open...)

Still, none of these ingenious devices is a *thermometer*. There was no attempt (at least none recorded) by Philo or his followers to make a *quantitative* measurement of how hot or cold the sphere was. And the “meter” in thermometer means measurement.

The First Thermometer

Galileo claimed to have invented the first thermometer. Well, actually, he called it a [thermoscope](#), but he *did* try to measure “degrees of heat and cold” according to a [colleague](#), and that qualifies it as a thermometer. (Technically, a *thermoscope* is a device making it possible to *see* a temperature change, a *thermometer* can *measure* the temperature change.) Galileo used an inverted narrow-necked bulb with a tubular neck, like a hen’s egg with a long glass tube attached at the tip.



He first heated the bulb with his hands then immediately put it into water. He recorded that the water rose in the bulb the height of “one palm”. Later, either Galileo or his colleague Santorio Santorio put a paper scale next to the tube to read off changes in the water level. This definitely made it a thermometer, but who thought of it first isn’t clear (they argued about it). And, in fact, this thermometer had problems.

Question: what problems? If you occasionally top up the water, why shouldn’t this thermometer be good for recording daily changes in temperature?

Answer: because it’s also a barometer! But—Galileo didn’t know about the atmospheric pressure.

Toricelli, one of Galileo’s pupils, was the first to realize, shortly after Galileo died, that the real driving force in suction was external atmospheric pressure, a satisfying mechanical explanation in contrast to the philosophical “nature abhors a vacuum”. In the 1640’s, Pascal pointed out that the *variability* of atmospheric pressure rendered the air thermometer untrustworthy.

Liquid-in-glass thermometers were used from the 1630’s, and they were of course insensitive to barometric pressure. Meteorological records were kept from this time, but there was no real uniformity of temperature measurement until Fahrenheit, almost a hundred years later.

Newton's Anonymous Table of Temperatures

The first systematic account of a range of different temperatures, “Degrees of Heat”, was written by Newton, but published anonymously, in 1701. Presumably he felt that this project lacked the timeless significance of some of his other achievements.

Taking the freezing point of water as zero, Newton found the temperature of boiling water to be almost three times that of the human body, melting lead eight times as great (actually 327°C , whereas $8 \times 37 = 296$, so this is pretty good!) but for higher temperatures, such as that of a wood fire, he underestimated considerably. He used a linseed oil liquid in glass thermometer up to the melting point of tin (232°C). (Linseed oil doesn't boil until 343°C , but that is also its autoignition temperature!)

Newton tried to estimate the higher temperatures indirectly. He heated up a piece of iron in a fire, then let it cool in a steady breeze. He found that, at least at the lower temperatures where he could cross check with his thermometer, the temperature dropped in a geometric progression, that is, if it took five minutes to drop from 80° above air temperature to 40° above air temperature, it took another five minutes to drop to 20° above air, another five to drop to 10° above, and so on. He then assumed this same pattern of temperature drop was true at the high temperatures beyond the reach of his thermometer, and so estimated the temperature of the fire and of iron glowing red hot. This wasn't very accurate—he (under)estimated the temperature of the fire to be about 600°C .

Fahrenheit's Excellent Thermometer

The first really good thermometer, using mercury expanding from a bulb into a capillary tube, was made by Fahrenheit in the early 1720's. He got the idea of using mercury from a colleague's comment that one should correct a *barometer* reading to allow for the variation of the density of mercury with temperature. The point that has to be borne in mind in constructing thermometers, and defining temperature scales, is that not all liquids expand at uniform rates on heating—water, for example, at first contracts on heating from its freezing point, then begins to expand at around forty degrees Fahrenheit, so a water thermometer wouldn't be very helpful on a cold day. It is also not easy to manufacture a *uniform cross section* capillary tube, but Fahrenheit managed to do it, and demonstrated his success by showing his thermometers agreed with each other over a whole range of temperatures. Fortunately, it turns out that mercury is well behaved in that the temperature scale defined by taking its expansion to be uniform coincides very closely with the true temperature scale, as we shall see later.

Amontons' Air Thermometer: Pressure Increases Linearly with Temperature

A little earlier (1702) Amontons introduced an *air pressure thermometer*. He established that if air at atmospheric pressure (he states 30 inches of mercury) at the freezing point of water is enclosed then heated to the boiling point of water, but meanwhile kept at constant volume by increasing the

pressure on it, the pressure goes up by about 10 inches of mercury. He also discovered that if he compressed the air in the first place, so that it was at a pressure of sixty inches of mercury at the temperature of melting ice, then if he raised its temperature to that of boiling water, at the same time adding mercury to the column to keep the volume of air constant, the pressure increased by 20 inches of mercury. In other words, he found that for a fixed amount of air kept in a container at constant volume, the pressure increased with temperature by about 33% from freezing to boiling, that percentage being *independent of the initial pressure*.

Thermal Equilibrium and the Zeroth Law of Thermodynamics

Once the thermometer came to be widely used, more precise observations of temperature and (as we shall see) *heat flow* became possible. Joseph Black, a professor at the University of Edinburgh in the 1700's, noticed that a collection of objects at different temperatures, if brought together, will all eventually reach the same temperature.

As he wrote, “*By the use of these instruments [thermometers] we have learned, that if we take 1000, or more, different kinds of matter, such as metals, stones, salts, woods, cork, feathers, wool, water and a variety of other fluids, although they be all at first of different heats, let them be placed together in a room without a fire, and into which the sun does not shine, the heat will be communicated from the hotter of these bodies to the colder, during some hours, perhaps, or the course of a day, at the end of which time, if we apply a thermometer to all of them in succession, it will point to precisely the same degree.*”

We say nowadays that bodies in “thermal contact” eventually come into “thermal equilibrium”—which means they finally attain the same temperature, after which no further heat flow takes place. This is equivalent to:

The Zeroth Law of Thermodynamics:

If two objects are in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

The “third body” in a practical situation is just the **thermometer**.

It's perhaps worth pointing out that this trivial sounding statement certainly wasn't obvious before the invention of the thermometer. With only the sense of touch to go on, few people would agree that a piece of wool and a bar of metal, both at 0°C, were at the same temperature.

Measuring Heat Flow: a Unit of Heat

The next obvious question is, can we get more *quantitative* about this “flow of heat” that takes place between bodies as they move towards thermal equilibrium? For example, suppose I reproduce one

of Fahrenheit's experiments, by taking 100 ccs of water at 100°F, and 100ccs at 150°F, and mix them together in an insulated jug so little heat escapes. What is the final temperature of the mix?

Of course, it's close to 125°F—not surprising, but *it does tell us something!* It tells us that the amount of heat required to raise the temperature of 100 cc of water from 100°F to 125°F is *exactly the same* as the amount needed to raise it from 125°F to 150°F. A series of such experiments (done by Fahrenheit, Black and others) established that it *always* took the same amount of heat to raise the temperature of 1 cc of water by one degree.

This makes it possible to define a **unit of heat**. Perhaps unfairly to Fahrenheit,

1 calorie is the heat required to raise the temperature of 1 gram of water by 1 degree Celsius.

(Celsius also lived in the early 1700's. His scale has the freezing point of water as 0°C, the boiling point as 100°C. Fahrenheit's scale is no longer used in science, but lives on in engineering in the US, and in the British Thermal Unit, which is the heat required to raise the temperature of one pound of water by 1°F.)

Specific Heats and Calorimetry

First, let's define **specific heat**:

The *specific heat* of a substance is the heat required in calories to raise the temperature of 1 gram by 1 degree Celsius.

As Fahrenheit continues his measurements of heat flow, it quickly became evident that for different materials, the amount of heat needed to raise the temperature of one gram by one degree could be quite different. For example, it had been widely thought before the measurements were made, that one cc of Mercury, being a lot heavier than one cc of water, would take more heat to raise its temperature by one degree. This proved not to be the case—Fahrenheit himself made the measurement. In an insulating container, called a “calorimeter” he added 100ccs of water at 100°F to 100ccs of mercury at 150°F, and stirred so they quickly reached thermal equilibrium.

Question: what do you think the final temperature was? Approximately?

Answer: The final temperature was, surprisingly, about 120°F. 100 cc of water evidently “contained more heat” than 100 cc of mercury, despite the large difference in weight!

This technique, called **calorimetry**, was widely used to find the specific heats of many different substances, and at first no clear pattern emerged. It was puzzling that the specific heat of mercury was so low compared with water! As more experiments on different substances were done, it gradually became evident that *heavier* substances, paradoxically, had *lower* specific heats.

A Connection With Atomic Theory

Meanwhile, this quantitative approach to scientific observation had spread to chemistry. Towards the end of the 1700's, Lavoisier weighed chemicals involved in reactions before and after the reaction. This involved weighing the gases involved, so had to be carried out in closed containers, so that, for example, the weight of oxygen used and the carbon dioxide, etc., produced would be accounted for in studying combustion. *The big discovery was that mass was neither created nor destroyed.* This had not been realized before because no one had weighed the gases involved. It made the atomic theory suddenly more plausible, with the idea that maybe chemical reactions were just rearrangements of atoms into different combinations.

Lavoisier also clarified the concept of an element, an idea that was taken up in about 1800 by John Dalton, who argues that a given compound consisted of identical molecules, made up of elementary atoms in the same proportion, such as H_2O (although that was thought initially to be HO). This explained why, when substances reacted chemically, such as the burning of hydrogen to form water, it took exactly eight grams of oxygen for each gram of hydrogen. (Well, you could also produce H_2O_2 under the right conditions, with exactly sixteen grams of oxygen to one of hydrogen, but the simple ratios of amounts of oxygen needed for the two reactions were simply explained by different molecular structures, and made the atomic hypothesis even more plausible.)

Much effort was expended carefully weighing the constituents in many chemical reactions, and constructing diagrams of the molecules. The important result of all this work was that it became possible to list the relative weights of the atoms involved. For example, the data on H_2O and H_2O_2 led to the conclusion that an oxygen atom weighed sixteen times the weight of a hydrogen atom.

It must be emphasized, though, that these results gave no clue as to the actual weights of atoms! All that was known was that atoms were too small to see in the best microscopes. Nevertheless, knowing the relative weights of some atoms in 1820 led to an important discovery. Two professors in France, Dulong and Petit, found that for a whole series of elements *the product of atomic weight and specific heat* was the same!

Element	Specific Heat	Relative weights of the atoms	Product of relative atomic weight and specific heat
Lead	0.0293	12.95	0.3794
Tin	0.0514	7.35	0.3779
Zinc	0.0927	4.03	0.3736
Sulphur	0.1880	2.011	0.3780

The significance of this, as they pointed out, was that the “specific heat”, or heat capacity, of each *atom* was the same—a piece of lead and a piece of zinc having the same number of atoms would have the same heat capacity. So heavier atoms absorbed no more heat than lighter atoms for a given rise in temperature. This partially explained why mercury had such a surprisingly low heat capacity. Of course, having no idea how big the atoms might be, they could go no further. And, indeed, many of their colleagues didn’t believe in atoms anyway, so it was hard to convince them of the significance of this discovery.

Latent Heat

One of Black’s experiments was to set a pan of water on a steady fire and observe the temperature as a function of time. He found it steadily increased, reflecting the supply of heat from the fire, until the water began to boil, whereupon the temperature stayed the same for a long time. The steam coming off was at the same (boiling) temperature as the water. So what was happening to the heat being supplied? Black correctly concluded that heat needed to be supplied to change water from its liquid state to its gaseous state, that is, to steam. In fact, a lot of heat had to be supplied: 540 calories per gram, as opposed to the mere 100 calories per gram needed to bring it from the freezing temperature to boiling. He also discovered that it took 80 calories per gram to melt ice into water, with no rise in temperature. This heat is released when the water freezes back to ice, so it is somehow “hidden” in the water. He called it *latent* heat, meaning hidden heat.

Books I used in preparing this lecture:

A Source Book in Greek Science, M. R. Cohen and I. E. Drabkin, Harvard university Press, 1966.

A History of the Thermometer and its Uses in Meteorology, W. E. Knowles Middleton, Johns Hopkins Press, 1966.

A Source Book in Physics, W. F. Magie, McGraw-Hill, New York, 1935.

Thermal Expansion and the Gas Law

Coefficients of Expansion

Almost all materials expand on heating—the most famous exception being water, which contracts as it is warmed from 0 degrees Celsius to 4 degrees. This is actually a good thing, because as freezing weather sets in, the coldest water, which is about to freeze, is less dense than slightly warmer water, so rises to the top of a lake and the ice begins to form there. For almost all other liquids, solidification on cooling begins at the bottom of the container. So, since water behaves in this weird way, ice skating is possible! Also, as a matter of fact, life in lakes is possible—the ice layer that forms insulates the rest of the lake water from very cold air, so fish can make it through the winter.

Linear Expansion

The coefficient of linear expansion α of a given material, for example a bar of copper, at a given temperature is defined as the fractional increase in length that takes place on heating through one degree:

$$L \rightarrow L + \Delta L = (1 + \alpha)L \text{ when } T \rightarrow T + 1^\circ\text{C}$$

Of course, α might vary with temperature (it does for water, as we just mentioned) but in fact for most materials it stays close to constant over wide temperature ranges.

For copper, $\alpha = 17 \times 10^{-6}$.

Volume Expansion

For *liquids and gases*, the natural measure of expansion is the coefficient of volume expansion, β .

$$V \rightarrow V + \Delta V = (1 + \beta)V \text{ when } T \rightarrow T + 1^\circ\text{C}$$

Of course, on heating a bar of copper, clearly the *volume* as well as the *length* increases—the bar expands by an equal fraction in all directions (this could be experimentally verified, or you could just imagine a cube of copper, in which case all directions look the same).

The volume of a cube of copper of side L is $V = L^3$. Suppose we heat it through one degree. Putting together the definitions of α, β above,

$$V \rightarrow (1 + \beta)V, \quad L \rightarrow (1 + \alpha)L, \quad L^3 \rightarrow (1 + \alpha)^3 L^3 \text{ or } V \rightarrow (1 + \alpha)^3 V.$$

So $(1 + \beta) = (1 + \alpha)^3$. But remember α is very, very small—so even though $(1 + \alpha)^3 = 1 + 3\alpha + 3\alpha^2 + \alpha^3$, the last two terms are *completely negligible* (check it out!) so to a fantastically good approximation:

$$\beta = 3\alpha.$$

The coefficient of volume expansion is just three times the coefficient of linear expansion.

Gas Pressure Increase with Temperature

In 1702, Amontons discovered a *linear* increase of P with T for air, and found P to increase about 33% from the freezing point of water to the boiling point of water.

That is to say, he discovered that if a container of air were to be sealed at 0°C, at ordinary atmospheric pressure of 15 pounds per square inch, and then heated to 100°C but kept at the same volume, the air would now exert a pressure of about 20 pounds per square inch on the sides of the container. (Of course, strictly speaking, the container will also have increased in size, that would lower the effect—but it's a tiny correction, about ½% for copper, even less for steel and glass.)

Remarkably, Amontons discovered, if the gas were initially at a pressure of *thirty* pounds per square inch at 0°C, on heating to 100°C the pressure would go to about 40 pounds per square inch—so the *percentage* increase in pressure was the same for *any* initial pressure: on heating through 100°C, the pressure would always increase by about 33%.

Furthermore, the result turned out to be the same for different gases!

Finding a Natural Temperature Scale

In class, we plotted air pressure as a function of temperature for a fixed volume of air, by making several measurements as the air was slowly heated (to give it a chance to all be at the same temperature at each stage). We found a straight line. On the graph, we extended the line backwards, to see how the pressure would presumably drop on cooling the air. We found the remarkable prediction that the pressure should drop to zero at a temperature of about -273°C .

In fact, if we'd done the cooling experiment, we would have found that air doesn't actually follow the line all the way down, but condenses to a liquid at around -200°C . However, helium gas stays a gas almost to -270°C , and follows the line closely.

We shall discuss the physics of gases, and the interpretation of this, much more fully in a couple of lectures. For now, the important point is that this suggests a *much more natural temperature scale* than the Celsius one: we should take -273°C as the zero of temperature! For one thing, if we do that, the pressure/temperature relationship for a gas becomes beautifully simple:

$$P \propto T.$$

This temperature scale, in which the degrees have the same size as in Celsius, is called the Kelvin or absolute scale. Temperatures are written 300K. To get from Celsius to Kelvin, just add 273 (strictly speaking, 273.15).

An Ideal Gas

Physicists at this point introduce the concept of an “Ideal Gas”. This is like the idea of a frictionless surface: it doesn’t exist in nature, but it is a very handy approximation to some real systems, and makes problems much easier to handle mathematically. The ideal gas is one for which $P \propto T$ for all temperatures, so helium is close to ideal over a very wide range, and air is close to ideal at ordinary atmospheric temperatures and above.

The Gas Law

We say earlier in the course that for a gas at constant *temperature* $PV = \text{constant}$ (Boyle’s Law). Now at constant *volume*, $P \propto T$.

We can put these together in one equation to find a relationship between pressure, volume and temperature:

$$PV = CT$$

where C is a constant. Notice, by the way, that we can immediately conclude that at fixed pressure, $V \propto T$, this is called *Charles’ Law*. (*Exercise*: prove from this that the coefficient of volume expansion of a gas varies significantly with temperature.)

But what is C ? Obviously, it depends on how much gas we have—double the amount of gas, keeping the pressure and temperature the same, and the volume will be doubled, so C will be doubled. But notice that C will *not* depend on what gas we are talking about: if we have two separate one-liter containers, one filled with hydrogen, the other with oxygen, both at atmospheric pressure, and both at the same temperature, then C will be the same for both of them.

One might conclude from this that C should be defined for one liter of gas at a specified temperature and pressure, such as 0°C and 1 atmosphere, and that could be a consistent scheme. It might seem more natural, though, to specify a particular *mass* of gas, since then we wouldn't have to specify a particular temperature and pressure in the definition of C .

But that idea brings up a further problem: one gram of oxygen takes up a lot less room than one gram of hydrogen. Since we've just seen that choosing the same *volume* for the two gases gives the same constant C for the two gases, evidently taking the same *mass* of the two gases will give different C 's.

Avogadro's Hypothesis

The resolution to this difficulty is based on a remarkable discovery the chemists made two hundred years or so ago: they found that *one liter* of nitrogen could react with exactly *one liter* of oxygen to produce exactly *two liters* of NO, nitrous oxide, all volume measurements being at the same temperature and pressure. Further, one liter of oxygen combined with *two* liters of hydrogen to produce two liters of steam.

These simple ratios of interacting gases could be understood if one imagined the atoms combining to form molecules, and made the further assumption, known as Avogadro's Hypothesis (1811):

Equal volumes of gases at the same temperature and pressure contain the same number of molecules.

One could then understand the simple volume results by assuming the gases were made of diatomic molecules, H_2 , N_2 , O_2 and the chemical reactions were just molecular recombinations given by the equations $\text{N}_2 + \text{O}_2 = 2\text{NO}$, $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, etc.

Of course, in 1811 Avogadro didn't have the slightest idea what this number of molecules was for, say, one liter, and nobody else did either, for another fifty years. So no-one knew what an atom or molecule weighed, *but* assuming that chemical reactions were atoms combining into molecules, or rearranging from one molecular pairing or grouping to another, they could figure out the *relative* weights of atoms, such as *an oxygen atom had mass 16 times that of a hydrogen atom*—even though they had no idea how big these masses were!

This observation led to defining *the natural mass of a gas* for setting the value of the constant C in the gas law to be a "*mole*" of gas: hydrogen was known to be H_2 molecules, so a mole of hydrogen was 2 grams, oxygen was O_2 , so a mole of oxygen was 32 grams, and so on.

With this definition, a mole of oxygen contains the same number of molecules as a mole of hydrogen: so at the same temperature and pressure, they will occupy the same volume. At 0°C, and atmospheric pressure, the volume is 22.4 liters.

So, for one mole of a gas (for example, two grams of hydrogen), we set the constant C equal to R , known as the **universal gas constant**, and equal to 8.3 J/(mol.K) and $PV = RT$.

For n moles of a gas, such as $2n$ grams of hydrogen, the law is:

$$PV = nRT$$

and this is the standard form of the Gas Law.

(*Footnote*: after the discovery of isotopes, nuclei of the same element having different masses, and in particular of a form of hydrogen called heavy hydrogen present in small quantities in nature, the definition of the mole was refined to be equal to precisely 12 grams of the carbon isotope C^{12} . In practice, this is a tiny correction which doesn't affect anything we've said here.)

Early Attempts to Understand the Nature of Heat

When Heat Flows, What, Exactly is Flowing?

By the late 1700's, the experiments of Fahrenheit, Black and others had established a systematic, quantitative way of measuring temperatures, heat flows and heat capacities—but this didn't really throw any new light on just *what* was flowing. This was a time when the study of electricity was all the rage, led in America by Benjamin Franklin, who had suggested in 1747 that electricity was one (invisible) fluid (it had previously been suggested that there were two fluids, corresponding to the two kinds of electrical charging observed).

Lavoisier's Caloric Fluid Theory

Perhaps heat was another of these invisible fluids? In 1787, Lavoisier, the French founder of modern chemistry, thought so, and called it the *caloric fluid*, from the Greek word for heat. (Lavoisier was the first to attempt to list a table of *elements*, to replace the ancient elements of earth, air, water and fire. His list of thirty-three elements included hydrogen, oxygen, sulphur, charcoal, etc., but he also *included caloric*—and light.)

Lavoisier and wife, by David, from Wikimedia Commons.



The existence of such a fluid was really quite plausible—heat flowed from a hot body to a cold body, and the recent quantitative calorimetric experiments of Black and others seemed to establish that heat was a *conserved quantity*, as one would expect of a fluid. One could also understand some of the well-known effects of heat in terms of a fluid, and establish some of the fluid's properties. For example, since it tended to flow from hot bodies into cold bodies and spread throughout the body, presumably its particles repelled each other, just like those of the electrical fluid. However, in contrast to electricity, which had no noticeable effect on the appearance of a charged object, when heat was added to a solid things changed considerably. First the material expanded, then it changed to a liquid and finally to a gas, if sufficient heat could be delivered. Further heating expanded the gas, or increased its pressure if it was held in a fixed container. To interpret this sequence of events in terms of a caloric fluid being fed into the material, one could imagine the fluid flowing between the atoms of the solid and lessening their attraction for each other, until the solid melted into a liquid, whereupon the caloric continued to accumulate around the atoms until they were pushed apart into a gas. It was thought that in the gas each atom or molecule was surrounded by a ball of caloric, like a springy ball of wool, and these balls were packed in a container like oranges in a crate, except that the caloric balls could expand indefinitely as heat was poured in.

Various other effects could be explained by the caloric theory: when a gas is suddenly compressed, it gets hotter because the same amount of caloric is now occupying a smaller volume. When two solids are rubbed together, some caloric is squeezed out at the surfaces, or perhaps tiny pieces of material are rubbed off, and lose their caloric, so heat appears. Radiant heat was presumed to be caloric particles flying through space. Recall that at that time (just before 1800) it was generally accepted that *light* was a stream of particles.



Painting by Joseph Wright, Wikimedia Commons.

The Industrial Revolution and the Water Wheel

In 1769 a Lancashire wigmaker, [Richard Arkwright](#), patented a successful cotton-spinning machine. Lancashire had been for a long time a center of the textile trade, but before Arkwright the fabrics were woven on hand looms by skilled weavers. The new machines could be operated by less skilled workers, and

in fact were largely operated by children, although, in contrast to some of his competitors, Arkwright refused to employ any child younger than six. The motive power driving the machines was at first horses, but in 1771 Arkwright built a large factory containing many machines all driven by a water wheel. This was the beginning of the modern system of mass production. Prices fell, and the skilled hand weavers became impoverished.

Our interest in this, however, is not the social consequences, but just the water wheel. Previously, water wheels had been used for centuries to grind flour, and for other purposes, but their efficiency had not been a major concern. In the factory, though, the more efficient the wheel, the more children could be spinning the cotton, and the bigger the profits. Twenty years earlier, John Smeaton (the first Englishman to call himself a civil engineer) had investigated different types of water wheels, and found the overshot type (in which the water pours on to the top of the wheel) to perform best.

Measuring Power by Lifting

The power output of a water wheel can be measured by using it to raise a load—in those days, it would be *how many pounds could be raised through one foot per second*, say (we would now just use watts, and it's amusing to note that the first unit of power, the horsepower, was proposed in 1783 by James Watt to be 33,000 foot pounds per minute). The ultimate in efficiency would be a *reversible* water wheel, which could be run backwards, to raise the water back again. This is best visualized by having a wheel with a series of buckets attached. Suppose the wheel is run for some time and its power output is used to lift a weight a given distance. Now reverse it, let the weight fall, running the wheel backwards, making sure the buckets now fill at the bottom and empty at the top. How much water is lifted back up? A truly reversible wheel would put all the water back. We know this isn't going to happen, but if the reversed wheel manages to lift *half* the water back, say, then it's 50% efficient.

In building the first factory, the water wheel was not just placed under a waterfall. The water was channeled to it for maximum efficiency. Smeaton had established that the flow of water into the buckets must be *as smooth as possible*. Turbulence was wasted effort—it didn't help the wheel go round. The water should flow onto the wheel, not fall from some height. Finally, the perfect wheel (not quite realizable in practice) would be reversible—it could be run backwards to put the water back up using the same amount of work it delivered in the first place.

Carnot's Caloric Water Wheel

Arkwright's factory was so successful that within a few years similar factories had been built wherever a water wheel could be operated economically in Northern England. The next step was to use steam power, which had been developed in the previous century to lift water out of mines. As steam engine design improved, the English economy mushroomed far ahead of European

competitors—but in contrast to the present day, these technological advances owed virtually nothing to basic science. It was all inspired tinkering.

The first attempt to analyze the steam engine in a scientific way was by a Frenchman, Sadi Carnot, in 1820—and he relied heavily on an analogy with the water wheel. In the steam engine, heat is delivered to water to boil off steam which is directed through a pipe to a cylinder where it pushes a piston. The piston does work, usually by turning a wheel, the steam cools down, and the relatively cold vapor is expelled, so that the piston will be ready for the next dose of steam.

Where is the analogy to a water wheel? Recall that heat was seen as an invisible fluid, impelled by its nature to flow from *hot* objects to *cold* objects. Water always flows from *high* places to *low* places. Carnot saw these as parallel processes—and, just as a water wheel extracts useful work from falling water, he saw the steam engine extracting work from the “falling” caloric fluid, as it cascaded from a hot object to a cold object.

How Efficient are these Machines?

As we’ve discussed, an ordinary water wheel is most efficient if the water flows in and out very smoothly, so no energy is wasted in turbulence or splashing. If we could make such a wheel with friction-free bearings, etc., then it could be made to drive a twin wheel going backwards, which could lift all the water back up again. This idealized wheel would be 100% efficient.

Carnot’s idealized heat engine had gas in a cylinder which pushed a piston as it expanded, doing work. Heat was fed into the gas, it expanded, then the heat supply was cut off, but the hot gas continued to expand and cool down at the same time. The piston then reversed direction, and the heat generated by the compression was allowed to flow out into a heat sink, until a certain point was reached at which the sink was disconnected, and the further compression heated up the gas to its original temperature, at which point the cycle began again. We’ll be discussing this so-called “Carnot cycle” in much more detail later, all we need to take away from it at this point is that *heat is supplied to the gas at a high temperature, and it flows out to the sink at a lower temperature.*

This “falling” of the “caloric fluid” from hot to cold is the analogy to the water wheel. Carnot argued that if all friction were eliminated, and the heat flow into and out of the gas were smooth—going from one place to another at the same temperature, just like the water moving smoothly on to the water wheel, not dropping on to it, then one could imagine a reversible heat engine: the work output could be used to drive a similar engine in reverse which would take heat from a cold place and expel it in a warmer place (that’s a refrigerator).

Carnot found, not surprisingly, that the amount of work a perfect engine could deliver for a given amount of heat increased as the temperature difference between heat source and heat sink increased. Obviously, water wheels get more energy from the same amount of water if the wheel is bigger so the water has further down to go.

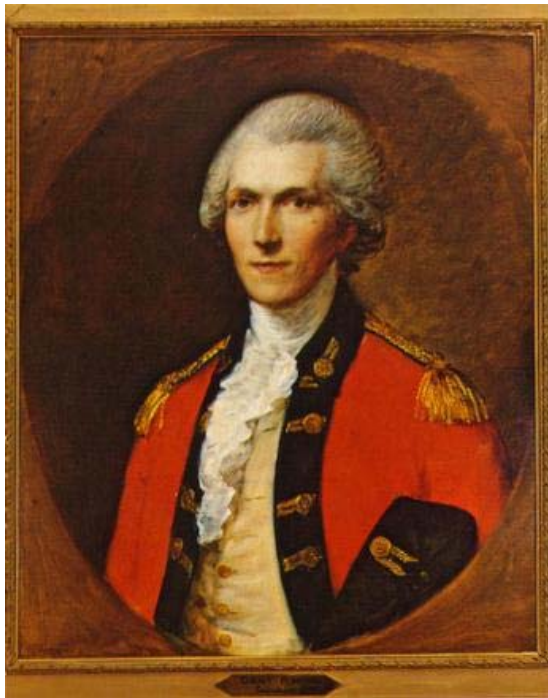
For a given temperature difference, then, a given amount of heat can only deliver so much work. And, this is quite independent of the materials used in constructing the engine, including the gas itself.

As we shall discuss in detail later, he was able to find for such an engine just how much work the engine could perform for a given heat input, and the answer was surprisingly low. Furthermore, no engine could ever be more efficient than a reversible engine, because if it were, it could be used to drive the reversible engine backwards, replacing the heat in the furnace, with energy to spare, and would be a perpetual motion machine.

Carnot's basic assumption that heat is a fluid was flawed, but his reasoning was of sufficient generality that his conclusions about efficiency were correct, and proved to be a crucial step toward understanding engines, as we shall see.

Count Rumford

Picture from <http://www.rumford.com/Rumfordpicture.html>, original Gainsborough painting in Fogg Museum, Harvard.



The first real attack on the caloric theory of heat took place in a cannon factory in Bavaria, under the direction of one Count Rumford of the Holy Roman Empire. This Count was actually born Benjamin Thompson in Woburn, in the English colony of Massachusetts, in 1753, which he left in a hurry after choosing the wrong side in the Revolutionary War. He was a brilliant man, extraordinarily inventive as a scientist and engineer—but it is difficult to form a coherent picture of his character. He seemed genuinely upset by the plight of the poor in Munich (see below) and made great personal efforts for years to ensure they were properly fed and clothed. Throughout his life, he invented practical devices to make daily living better: stoves, fitted kitchens, drip coffeepots, lighting, and many more. Yet, despite this love for humanity and his clear desire to make life

better for everyone, Rumford did not apparently like—or get on with—actual people. The only

exceptions were those with power who might prove useful, and almost any attractive woman he met. Rumford dumped his own family unceremoniously when war broke out and he fled to England. When garrisoned on Long Island in 1782 (fighting for the British) he treated the local people horribly. He always engaged in shameless self-promotion, often with little regard for the truth. But he *did* make important contributions to many fields: food, clothing, work and education for the poor both in Bavaria and (less successfully) later in England, and all manner of engineering improvements, from the domestic devices listed above to state of the art artillery. In fact, his artillery designs were so highly regarded that by 1799 US President Adams tried to persuade him to return to America to found a Military Academy, with assurances that all was forgiven.

His father died when Benjamin was still a child, and although his mother remarried, he felt strongly that he had to take care of himself. He worked hard at school, then at age eighteen began working as a tutor for children of rich families, and after a short time became a teacher in a school in Concord, New Hampshire. At nineteen, he married a rich young widow, who decided to upgrade his appearance to fit in better with her friends. She bought him a scarlet hussar cloak, they used a two-horse chaise called a curricule, the only other curricule in the province belonging to the Royal Governor, John Wentworth. The marriage took place one day after the Governor had reviewed the troops, and the bride and groom were guests at the Governor's table. Thompson assiduously cultivated the Governor. They went together on a surveying expedition exploring the hilly country of the province. Thompson's real ambition was military, and in 1774 Governor Wentworth appointed him a major in the New Hampshire Militia. That year, the people were becoming increasingly rebellious against British rule and British taxes. Order was kept, at least in part, by the British Army. Thompson was part of a scheme to discourage desertion from that army, and when this became known to those plotting revolution, they declared him a "Rebel to the State". He moved rapidly to London, abandoning his wife and two-month-old daughter. In London, he supplied military intelligence, and was rewarded with a salaried position involving no work.

Ever the scientist (with a military bent), he spent a lot of time on gunnery experiments. He used a ballistic pendulum to find how the speed of a bullet was affected by small changes in gun design and in the gunpowder mix. He disproved the widely held view that slightly damp gunpowder was actually more effective.

He made a trip back to America in 1781. He wintered with a few hundred soldiers at Huntington, Long Island, in 1782, setting up camp in the churchyard, and forcing the local people to build fortifications for his camp using the church timbers and their rail fences. He constructed bread ovens using the tombstones. He designed a new gun carriage that could be disassembled, carried by three horses, then put together and fired in a minute and a quarter. But the war was over. He burned all the wood, rather than give it back to the people, and returned to London.

Still enthusiastic for military adventure, he decided to go to Vienna, which seemed a likely trouble spot. He first got himself promoted to full colonel, acquired the splendid uniform, and had his portrait painted by Thomas Gainsborough. When he reached Strasbourg, it happened that a military review was underway. Naturally, Thompson appeared in full regalia, impressing the reviewer, who was a nephew of the Elector of Bavaria. This landed him an important post in Munich, the capital of Bavaria. Among his other duties, he was to organize the feeding and clothing of the army. He took a practical, scientific approach. He had each garrison maintain its own vegetable garden, and gave directions on how to use them most effectively from a nutritional point of view. He ran experiments on the relative thermal conductivity of various fabrics, and found that trapped air in fabrics was the most important measure of heat insulation. He decided that uniforms should be cotton in summer, wool in winter. He invented thermal underwear. In 1792, he became Count Rumford.

It should also be mentioned that he greatly improved the city in many ways: he invented the soup kitchen for the poor, an idea which spread throughout Europe. In Switzerland, the meal tickets had Rumford's picture on them. He built workhouses, to provide work for the unemployed in making uniforms for the military. He helped design and lay out a beautiful park, where a memorial to him still stands. He also worked on many domestic improvements, such as the Rumford stove for more heat and less smoke, coffee makers, and an efficient but soft light, this last at least partly because, to quote him, "that mysterious light which comes from bodies moderately illuminated is certainly most favourable to female beauty" and Rumford was a great connoisseur of female beauty.

Rumford's Theory of Heat

The contribution to physics for which he is most remembered took place in Munich, and he stumbled into it more or less accidentally. But, as he remarks in presenting his findings to the Royal Society in 1798, "a habit of keeping the eyes open to everything that is going on in the ordinary course of the business of life has oftener led, as it were by accident, ... to sensible schemes for investigation ... than all the more intense meditations of philosophers, in the hours expressly set apart for study."

What he was looking at was cannon boring, beefing up the Bavarian artillery in case of attack by the French, but what he was thinking about was whether or not Lavoisier's calorific fluid really existed. He was skeptical. Cannon were bored by turning an iron bit inside a brass cylinder, the power being supplied by horses. The friction of the iron bit on the brass generated heat. This was accounted for in the caloric theory by the pressure and movement squeezing out caloric fluid, in particular from the fragments that were sheared off. Rumford carefully collected these fragments and found them to be identical to the ordinary metal in heat capacity, etc., they didn't seem to have lost anything. Then he measured the heat production for an extended period, by having the brass cylinder immersed in water, and insulated. After extended grinding, the water (two gallons) began to boil. This was a startling event! To quote from his account:

“At 2 hours and 20 minutes it was 200°; and at 2 hours 30 minutes it ACTUALLY BOILED!

It would be difficult to describe the surprise and astonishment expressed in the countenances of the by-standers, on seeing so large a quantity of cold water heated, and actually made to boil without any fire.”

Rumford goes on to analyze the whole experiment quantitatively: he gives the weight of the box, and so estimates how much heat it absorbs, as well as other parts of the apparatus which became warm, and measures the rate of cooling with the grinding stopped to estimate how much heat leaked out during the run. Taking all these factors into account, he estimated that heat production was equivalent to nine $\frac{3}{4}$ inch candles burning continuously. Long before the concept was formulated, Rumford had measured the mechanical equivalent of heat, at least approximately. In fact, many years later, Joule went over his Rumford's figures and found he was within 20% or so of the right answer. Rumford realized, of course, this wasn't a good way to produce heat—as he remarked, more heat could have been gained simply by burning the horses' fodder. His real interest here was in demolishing the caloric theory. He concluded:

...we must not forget to consider that most remarkable circumstance, that the source of the Heat generated by Friction, in these Experiments, appeared evidently to be inexhaustible. It is hardly necessary to add, that anything which any insulated body, or system of bodies, can continue to furnish without limitation, cannot possibly be a material substance: and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of any thing, capable of being excited and communicated, in the manner the heat was excited and communicated in these Experiments, except it be MOTION.

Exactly what Rumford meant by MOTION has been debated, but it was some type of internal vibration of material, perhaps only distantly related to our modern, atom based, picture of heat vibrations. Still, by casting real doubt on the caloric theory, it was a step in the right direction. He had also established that if a caloric fluid really existed, it was certainly very light! He took three identical glass bottles containing equal weights of water, mercury and alcohol respectively, made them exactly equal in weight by tying small lengths of wire around the necks, then cooled them until the water froze, and weighed them again. The latent heat of freezing, and the very different heat capacities of the three fluids, should have resulted in quite different amounts of caloric fluid leaving the three bottles, yet their weights remained exactly the same, within one part in a million (the claimed accuracy of the balance).

After he returned to London in 1798, Rumford planned to repeat some of the public welfare successes in Munich. He wanted to build soup kitchens and workhouses for the poor. He also planned to found an institution which would not only facilitate the implementation of new scientific

discoveries in improving living standards, but also train working class men to become mechanics. This became the Royal Institution. Unfortunately, Rumford was difficult to work with, and he did not see eye to eye with the first director, a young Cornishman called Humphry Davy. Sad to report, Rumford's idealistic notions for schooling the poor and improving living standards did not become a priority for the Institution, except for a series of lectures for the public which evolved into entertainments for the wealthy. Nevertheless, the Institution did maintain a first class laboratory in which Davy discovered new elements, including sodium and potassium, and has in fact been an excellent center of scientific research for the last two hundred years. (Check it out [here!](#))

One more remarkable turn of events in Rumford's life is worth mentioning. Lavoisier, founder of the caloric theory, was beheaded by French revolutionaries in 1794, leaving a very attractive widow. Rumford married her in 1805. Perhaps not too surprisingly, the marriage didn't go well.

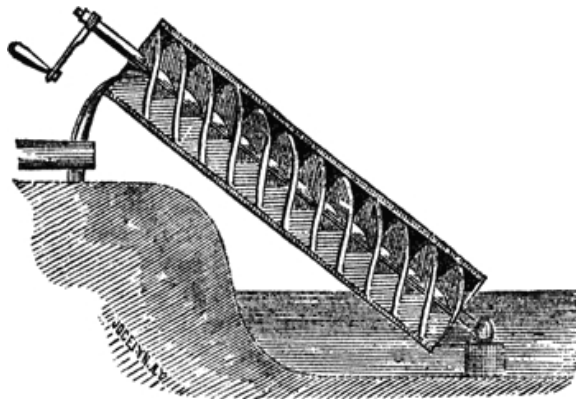
In writing the above section, I used mainly the biography *Benjamin Thompson, Count Rumford*, by Sanford C. Brown, MIT 1979. I have only been able to mention a small number from the extraordinary range of Rumford's inventions (and adventures!) described in this book.

A more recent brief but readable biography: *Count Rumford: The Extraordinary Life of a Scientific Genius*, by G. I. Brown, Sutton (UK) 1999.

The Discovery of Energy Conservation: Mayer and Joule

Robert Mayer and the Color of Blood

Julius Robert Mayer was born in the mill town of Heilbronn, Germany, on the river Neckar, in 1814. The town's whole economy was based on water power. The ten year old Mayer had a great idea: why not use part of a water wheel's output to drive an Archimedean screw which would pump the water back up again? That way you wouldn't have to rely on the river at all!



Archimedes' Screw (Wikimedia Commons)

He decided to build a model. His first try didn't work—some water was pumped back up, but not enough. But surely that could be taken care of by putting in a gear train to make the screw run faster? Disappointingly, he found the water wheel had a tougher time turning the screw faster, and he needed to supply a lot more water over the wheel, so he was back to square one. Increasingly ingenious but unsuccessful fixes finally convinced him that in fact there was no solution: *there was no way to arrange a machine to do work for nothing*. This lesson stayed with Mayer for life.

Mayer studied to become a medical doctor (his studies included one physics course) and in 1840, at age 25, he signed on as a ship's doctor on a ship bound for the tropics. Shortly after reaching the Dutch East Indies, some of the sailors became ill and Mayer's treatment included blood letting. He was amazed to find that the venous blood was a bright red, almost the same as arterial blood. Back in Germany, the venous blood was much darker, and there was a reason: the chemist Lavoisier had explained that the body's use of food, at least in part, amounted to burning it in a controlled way to supply warmth. The darker venous blood in effect contained the ashes, to be delivered to the lungs and expelled as carbon dioxide. Mayer concluded that less burning of food was needed to keep warm in the tropics, hence the less dark blood.

Now, Lavoisier had claimed that the amount of heat generated by burning, or oxygenation, of a certain amount of carbon did not depend on the sequence of chemical reactions involved, so the heat generated by blood chemistry oxygenation would be the same as that from uncontrolled old-fashioned burning in air. This quantitative formulation led Mayer to think about how he would measure the heat generated in the body, to equate it to the food burned. But this soon led to a problem. Anyone can generate extra heat, just by rubbing the hands together, or, for example, by turning a rusty, unoiled wheel: the axle will get hot. Does this 'outside' heat also count as generated by the food? Presumably yes, the food powers the body, and the body generates the heat, even if indirectly. Mayer was convinced from his childhood experience with the water wheel that nothing came from nothing: that outside heat could not just appear from nowhere, it had to have a cause.

But he saw that if the indirectly generated heat must also be included, there is a problem. His analysis ran something like this (I've changed the illustration slightly, but the idea's the same): suppose two people are each steadily turning large wheels at the same rate, and the wheels are equally hard to turn. One of them is our rusty unoiled wheel from the last paragraph, and all that person's efforts are going into generating heat. But the other wheel has a smooth, oiled axle and generates a negligible amount of heat. It is equally hard to turn, though, because it is raising a large bucket of water from a deep well. How do we balance the 'food = heat' budget in this second case?

Mayer was forced to the conclusion that for the ‘food = heat’ equation to make sense, there had to be *another* equivalence: a certain amount of mechanical work, measured for example by raising a known weight through a given distance, had to count the same as a certain amount of heat, measured by raising the temperature of a fixed amount of water, say, a certain number of degrees. In modern terms, a joule has to be equivalent to a fixed number of calories. Mayer was the first to spell out this ‘mechanical equivalent of heat’ and in 1842 he calculated the number using results of experiments done earlier in France on the specific heats of gases. French experimenters had measured the specific heat of the same gas at constant pressure (C_p) and at constant volume (C_v). They always found C_p to be greater than C_v . Mayer interpreted this with the following thought experiment: consider two identical vertical cylinders, closed at the top by moveable pistons, the pistons resting on the gas pressure, each enclosing the same amount of the same gas at the same temperature. Now supply heat to the two gases, for one gas keep the piston fixed, for the other allow it to rise. Measure how much heat is needed to raise the gas temperature by ten degrees, say. It is found that extra heat is needed for the gas at constant pressure, the one where the piston was allowed to rise. Mayer asserted this was because in that case, some of the heat had been expended as work to raise the piston: this followed very naturally from his previous thinking, and the French measurements led to a numerical value for the equivalence. Mayer understood the sequence: a chemical reaction produces heat and work, that work can then produce a definite amount of heat. This amounted to a statement of the conservation of energy. Sad to report, Mayer was not part of the German scientific establishment, and this ground-breaking work was ignored for some years.

James Joule

Meanwhile, in Manchester, England, the center of the industrial revolution, the same problem was being approached from quite a different direction by James Joule, the son of a prosperous brewer. Joule was lucky in that as a teenager, he was tutored at home, along with his brother, by John Dalton, the chemist who founded the atomic theory. Manchester was at the cutting edge of technological progress, and one exciting idea in the 1830’s was that perhaps coal-driven steam engines could be replaced by battery-driven electric motors. Joule, in his twenties, set himself the task of improving the electric motor to the point where it would be competitive with the steam engine. But it was not to be—after years of effort, he concluded that at best it would take five pounds of zinc consumed in a battery to deliver the work from one pound of coal. But he learned a lot. He found an electric current in a wire produced heat at a rate I^2R , now known as Joule heating. The caloric theory interpretation was that caloric fluid originally in the battery was released along with the electric current and settled in the wire. However, Joule discovered the same heating took place with a current generated by moving the wire past a permanent magnet. It was difficult to see how the caloric fluid got into the wire in that situation. Joule decided the caloric theory was suspect. He generated a current by applying a measured force to a dynamo, and established that the heat appearing in the wire was always directly proportional to the work done by the force driving the dynamo.

Finally, it dawned on him that the electrical intermediary was unnecessary: the heat could be produced directly by the force, if instead of turning a dynamo, it turned paddle wheels churning water in an insulated can. The picture below shows his apparatus:



The paddle wheels turn through holes cut in stationary brass sheets, churning up the water. This is all inside an insulated can, of course. In this way, Joule measured the mechanical equivalent of heat, the same number Mayer had deduced from the French gas experiments.

Joule's initial reception by the scientific establishment was not too different from Mayer's. He, too, was a provincial, with a strange accent. But he had a lucky break in 1847, when he reported his work to a meeting of the British Association, and William Thomson was in the audience. Thomson had just spent a year in Paris. He was fully familiar with Carnot's work, and believed the caloric theory to be correct. But he knew that if Joule really had

produced heat by stirring water, the caloric theory must be wrong—he said there were 'insuperable difficulties' in reconciling the two.

But Who Was First: Mayer or Joule?

Mayer and Joule, using entirely different approaches, arrived almost simultaneously at the conclusion that heat and mechanical work were numerically equivalent: a given amount of work could be transformed into a quantitatively predictable amount of heat. Which of the two men deserves more credit (not to mention other contenders!) has been argued for well over a century. Briefly, it is generally conceded that Mayer was the first to spell out the concept of the mechanical equivalent of heat (although closely followed, independently, by Joule) and Joule was the first to put it on a firm experimental basis.

The Emergence of Energy Conservation

In fact, by the 1840's, although many still believed in the caloric theory, it had run into other difficulties. Before the 1820's, almost everyone believed, following Newton, that light was a stream of particles. Around 1800, Herschel discovered that on passing sunlight through a prism, and detecting the heat corresponding to the different colors, in fact there was heat transmitted beyond the red. This suggested that radiant heat was caloric particles streaming through space, and no doubt very similar in character to light. But in the 1820's it was unambiguously

established that light was really a wave. Did this mean heat was a wave too? Perhaps the caloric fluid was oscillations in the ether. Things were now very confused. In 1841, Joule wrote diplomatically: ‘let the space between these compound atoms be supposed to be filled with calorific ether in a state of vibration, or, otherwise, to be occupied with the oscillations of the atoms themselves’ (Joule 1963, p.52).

It transpired, though, that the difficulties in reconciling Carnot’s theory and Joule’s experiments were not as insuperable as Thomson had claimed. In 1850, a German professor, Rudolph Clausius, pointed out that Carnot’s theory was still almost right: the only adjustment needed was that there was a little less heat emerging from the bottom of the ‘caloric water wheel’ than went in at the top—some of the heat became mechanical energy, the work the steam engine was performing. For real steam engines, the efficiency—the fraction of ingoing heat delivered as useful work—was so low that it was easy to understand why Carnot’s picture had been accepted for so long. For the first time, with Clausius’ paper, a coherent theory of heat emerged, and the days of the caloric theory drew to a close.

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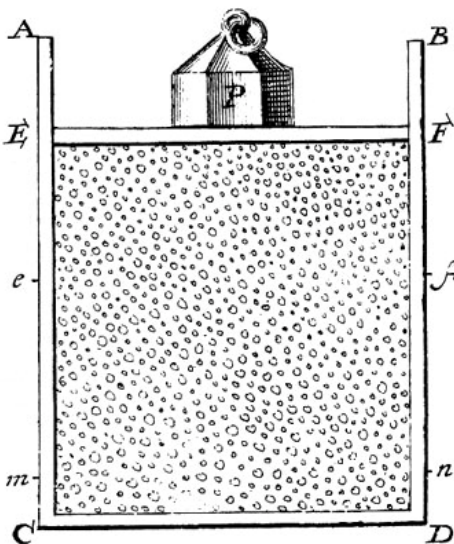
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Kinetic Theory of Gases: A Brief Review

Bernoulli's Picture



Daniel Bernoulli, in 1738, was the first to understand air pressure from a molecular point of view. He drew a picture of a vertical cylinder, closed at the bottom, with a piston at the top, the piston having a weight on it, both piston and weight being supported by the air pressure inside the cylinder. He described what went on inside the cylinder as follows: “let the cavity contain very minute corpuscles, which are driven hither and thither with a very rapid motion; so that these corpuscles, when they strike

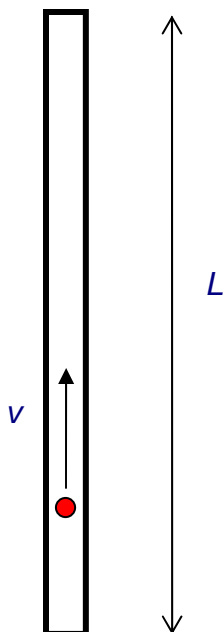
against the piston and sustain it by their repeated impacts, form an elastic fluid which will expand of itself if the weight is removed or diminished...” (An applet is available [here](#).) Sad to report, his insight, although essentially correct, was not widely accepted.

Most scientists believed that the molecules in a gas stayed more or less in place, repelling each other from a distance, held somehow in the ether. Newton had shown that $PV = \text{constant}$ followed if the repulsion were inverse-square. In fact, in the 1820's an Englishman, John Herapath, derived the relationship between pressure and molecular speed given below, and tried to get it published by the Royal Society. It was rejected by the president, Humphry Davy, who pointed out that equating temperature with motion, as Herapath did, implied that there would be an absolute zero of temperature, an idea Davy was reluctant to accept. And it should be added that no-one had the slightest idea how big atoms and molecules were, although Avogadro had conjectured that equal volumes of different gases at the same temperature and pressure contained equal numbers of molecules—his famous number—neither he nor anyone else knew what that number was, only that it was pretty big.

The Link between Molecular Energy and Pressure

It is not difficult to extend Bernoulli's picture to a *quantitative* description, relating the gas pressure to the molecular velocities. As a warm up exercise, let us consider a single perfectly elastic particle, of mass m , bouncing rapidly back and forth at speed v inside a narrow cylinder of length L with a piston at one end, so all motion is along the same line. (For the movie, [click here!](#)) What is the force on the piston?

Obviously, the piston doesn't feel a smooth continuous force, but a series of equally spaced impacts. However, if the piston is much heavier than the particle, this will have the same effect



1-D gas: particle bounces between ends of cylinder

as a smooth force over times long compared with the interval between impacts. So what is the value of the equivalent smooth force?

Using Newton's law in the form *force = rate of change of momentum*, we see that the particle's momentum changes by $2mv$ each time it hits the piston. The time between hits is $2L/v$, so the frequency of hits is $v/2L$ per second. This means that if there were no balancing force, by conservation of momentum the particle would cause the momentum of the piston to change by $2mv \times v/2L$ units in each second. This is the rate of change of momentum, and so must be equal to the balancing force, which is therefore $F = mv^2/L$.

We now generalize to the case of many particles bouncing around inside a rectangular box, of length L in the x -

direction (which is along an edge of the box). The total force on the side of area A perpendicular to the x -direction is just a sum of single particle terms, the relevant velocity being the component of the velocity in the x -direction. The *pressure* is just the force per unit area, $P = F/A$. Of course, we don't know what the velocities of the particles are in an actual gas, but it turns out that we don't need the details. If we sum N contributions, one from each particle in the box, each contribution proportional to v_x^2 for that particle, the sum just gives us N times the *average* value of v_x^2 . That is to say,

$$P = F / A = Nm\overline{v_x^2} / LA = Nm\overline{v_x^2} / V$$

where there are N particles in a box of volume V . Next we note that the particles are equally likely to be moving in any direction, so the average value of v_x^2 must be the same as that of v_y^2 or v_z^2 , and since $v^2 = v_x^2 + v_y^2 + v_z^2$, it follows that

$$P = Nm\overline{v^2} / 3V.$$

This is a surprisingly simple result! *The macroscopic pressure of a gas relates directly to the average kinetic energy per molecule.* Of course, in the above we have not thought about possible complications caused by interactions between particles, but in fact for gases like air at room temperature these interactions are very small. Furthermore, it is well established experimentally that most gases satisfy the Gas Law over a wide temperature range:

$$PV = nRT$$

for n moles of gas, that is, $n = N/N_A$, with N_A Avogadro's number and R the gas constant.

Introducing Boltzmann's constant $k = R/N_A$, it is easy to check from our result for the pressure and the ideal gas law that *the average molecular kinetic energy is proportional to the absolute temperature*,

$$\overline{E_K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT.$$

Boltzmann's constant $k = 1.38 \cdot 10^{-23}$ joules/K.

Maxwell finds the Velocity Distribution

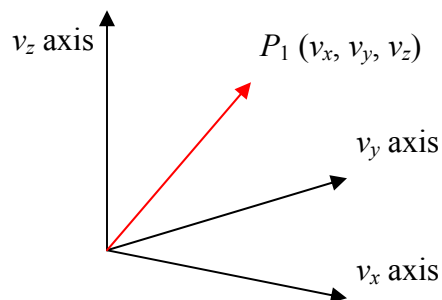
By the 1850's, various difficulties with the existing theories of heat, such as the caloric theory, caused some rethinking, and people took another look at the kinetic theory of Bernoulli, but little real progress was made until Maxwell attacked the problem in 1859. Maxwell worked with Bernoulli's picture, that the atoms or molecules in a gas were perfectly elastic particles, obeying Newton's laws, bouncing off each other (and the sides of the container) with straight-line trajectories in between collisions. (Actually, there is some inelasticity in the collisions with the sides—the bouncing molecule can excite or deexcite vibrations in the wall, this is how the gas

and container come to thermal equilibrium.) Maxwell realized that it was completely hopeless to try to analyze this system using Newton's laws, even though it could be done in principle, there were far too many variables to begin writing down equations. On the other hand, a completely detailed description of how each molecule moved was not really needed anyway. What *was* needed was some understanding of how this microscopic picture connected with the macroscopic properties, which represented averages over huge numbers of molecules.

The *relevant* microscopic information is not knowledge of the position and velocity of every molecule at every instant of time, but just the *distribution function*, that is to say, what percentage of the molecules are in a certain part of the container, and what percentage have velocities within a certain range, at each instant of time. For a gas *in thermal equilibrium*, the distribution function is *independent of time*. Ignoring tiny corrections for gravity, the gas will be distributed uniformly in the container, so the only unknown is the *velocity* distribution function.

Velocity Space

What does a velocity distribution function look like? Suppose at some instant in time one particular molecule has velocity $\vec{v} = (v_x, v_y, v_z)$. We can record this information by constructing a three-dimensional *velocity space*, with axes v_x, v_y, v_z , and putting in a point P_1 representing the molecule's velocity (the red arrow is of course \vec{v}):



Point P_1 represents the location of one molecule in velocity space

Now imagine that at that instant we could measure the velocities of *all* the molecules in a container, and put points $P_2, P_3, P_4, \dots, P_N$ in the velocity space. Since N is of order 10^{21} for 100 ccs of gas, this is not very practical! But we can imagine what the result would be: a cloud of points in velocity space, equally spread in all directions (there's no reason molecules would prefer to be moving in the x -direction, say, rather than the y -direction) and thinning out on going away from the origin towards higher and higher velocities.

Now, if we could keep monitoring the situation as time passes individual points would move around, as molecules bounced off the walls, or each other, so you might think the cloud would shift around a bit. But there's a *vast number* of molecules in any realistic macroscopic situation, and for any reasonably sized container it's safe to assume that the number of molecules in any small region of velocity space remains pretty much constant. Obviously, this cannot be true for a region of velocity space so tiny that it only contains one or two molecules on average. But it can be shown statistically that if there are N molecules in a particular small volume of velocity space, the fluctuation of the number with time is of order \sqrt{N} , so a region containing a million molecules will vary in numbers by about one part in a thousand, a trillion molecule region by one part in a million. Since 100 ccs of air contains of order 10^{21} molecules, we can in practice divide the region of velocity space occupied by the gas into a billion cells, and *still* have variation in each cell of order one part in a million!

The bottom line is that for a macroscopic amount of gas, fluctuations in density, both in ordinary space and in velocity space, are for all practical purposes negligible, and we can take the gas to be *smoothly distributed* in both spaces.

Maxwell's Symmetry Argument

Maxwell found the velocity distribution function for gas molecules in thermal equilibrium by the following elegant argument based on symmetry.

For a gas of N particles, let the number of particles having velocity in the x -direction between v_x and $v_x + dv_x$ be $Nf_1(v_x)dv_x$. In other words, $f_1(v_x)dv_x$ is the fraction of all the particles having x -direction velocity lying in the interval between v_x and $v_x + dv_x$. (I've written f_1 instead of f to help remember this function refers to only one component of the velocity vector.)

If we add the fractions for all possible values of v_x , the result must of course be 1:

$$\int_{-\infty}^{\infty} f_1(v_x) dv_x = 1.$$

But there's nothing special about the x -direction—for gas molecules in a container, at least away from the walls, all directions look the same, so the same function f will give the probability distributions in the other directions too. It follows immediately that the probability for the velocity to lie between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, and v_z and $v_z + dv_z$ must be:

$$Nf_1(v_x)dv_x f_1(v_y)dv_y f_1(v_z)dv_z = Nf_1(v_x)f_1(v_y)f_1(v_z)dv_x dv_y dv_z$$

Note that this distribution function, when integrated over all possible values of the three components of velocity, gives the total number of particles to be N , as it should (since integrating over each $f_1(v)dv$ gives unity).

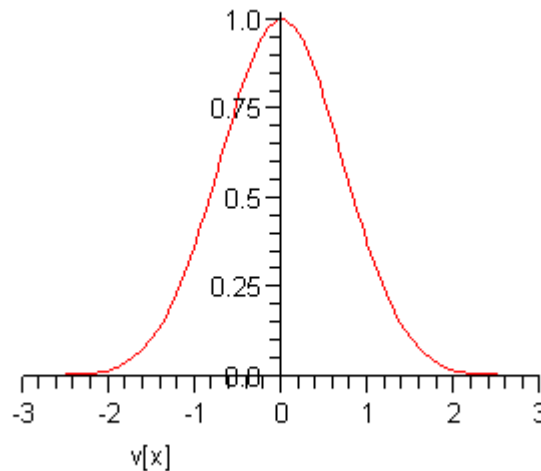
Next comes the clever part—since any direction is as good as any other direction, the distribution function must depend *only* on the total speed of the particle, *not* on the separate velocity components. Therefore, Maxwell argued, it *must* be that:

$$f_1(v_x)f_1(v_y)f_1(v_z) = F(v_x^2 + v_y^2 + v_z^2)$$

where F is another unknown function. However, it is apparent that the *product* of the functions on the left is reflected in the *sum* of variables on the right. It will only come out that way *if the variables appear in an exponent* in the functions on the left. In fact, it is easy to check that this equation is solved by a function of the form:

$$f_1(v_x) = Ae^{-Bv_x^2}.$$

This curve is called a *Gaussian*: it's centered at the origin, and falls off *very* rapidly as v_x increases. Taking $A = B = 1$ just to see the shape, we find:



At this point, A and B are arbitrary constants—we shall eventually find their values for an actual sample of gas at a given temperature. Notice that (following Maxwell) we have put a minus sign in the exponent because there must eventually be fewer and fewer particles on going to higher speeds, certainly not a diverging number.

Multiplying together the probability distributions for the three directions gives the distribution in terms of particle speed v , where $v^2 = v_x^2 + v_y^2 + v_z^2$. Since all velocity directions are equally

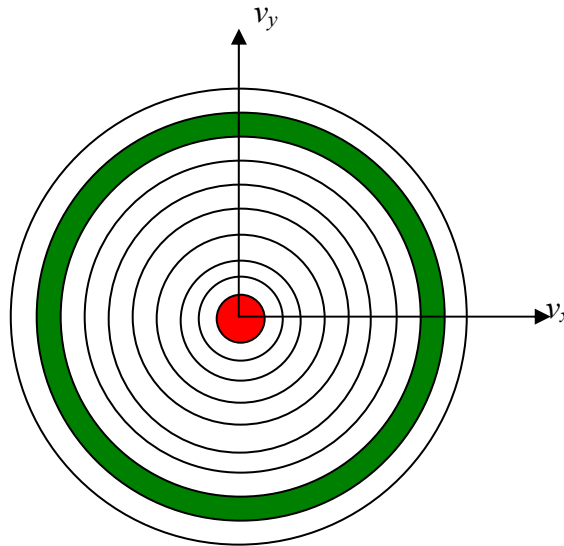
likely, it is clear that the natural distribution function is that giving the number of particles having *speed* between v and $v + dv$.

From the graph above, it is clear that the most likely value of v_x is zero. If the gas molecules were restricted to one dimension, just moving back and forth on a line, then the most likely value of their *speed* would *also* be zero. However, for gas molecules free to move in two or three dimensions, the most likely value of the speed is *not* zero. It's easiest to see this in a two-dimensional example. Suppose we plot the points P representing the velocities of molecules in a region near the origin, so the density of points doesn't vary much over the extent of our plot (we're staying near the top of the peak in the one-dimensional curve shown above).

Now divide the two-dimensional space into regions corresponding to equal increments in speed:

$$0 \text{ to } \Delta v, \Delta v \text{ to } 2\Delta v, 2\Delta v \text{ to } 3\Delta v, \dots$$

In the two-dimensional space, $v = \sqrt{v_x^2 + v_y^2} = \text{constant}$ is a circle, so this division of the plane is into annular regions between circles whose successive radii are Δv apart:



Constant speed circles in a two-dimensional example

Each of these annular areas corresponds to the same speed increment Δv . In particular, the green area, between a circle of radius $8\Delta v$ and one of radius $9\Delta v$, corresponds to the same *speed increment* as the small red circle in the middle, which corresponds to speeds between 0 and Δv . Therefore, if the molecular speeds are pretty evenly distributed in this near-the-origin area of the (v_x, v_y) plane, there will be a lot more molecules with speeds between $8\Delta v$ and $9\Delta v$ than between 0 and Δv —so the *most likely speed* will *not* be zero. To find out what it actually is, we

have to put this area argument together with the Gaussian fall off in density on going far from the origin. We'll discuss this shortly.

The same argument works in three dimensions—it's just a little more difficult to visualize. Instead of concentric circles, we have concentric spheres. All points lying on a spherical surface centered at the origin correspond to the same speed.

Let us now figure out the distribution of particles as a function of speed. The distribution in the three-dimensional space (v_x, v_y, v_z) is from Maxwell's analysis

$$\begin{aligned} \# \text{ of particles in small box } dv_x dv_y dv_z &= N f_1(v_x) f_1(v_y) f_1(v_z) dv_x dv_y dv_z \\ &= NA^3 e^{-B(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \\ &= NA^3 e^{-Bv^2} dv_x dv_y dv_z \end{aligned}$$

To translate this to the number of particles having *speed* between v and $v + dv$ we need to figure out how many of those little $dv_x dv_y dv_z$ boxes there are corresponding to speeds between v and $v + dv$. In other words, what is the *volume* of velocity space between the two neighboring spheres, both centered at the origin, the inner one with radius v , the outer one infinitesimally bigger, with radius $v + dv$? Since dv is so tiny, this volume is just the area of the sphere multiplied by dv : that is, $4\pi v^2 dv$.

Finally, then, the probability distribution as a function of speed is:

$$f(v)dv = 4\pi v^2 A^3 e^{-Bv^2} dv.$$

Of course, our job isn't over—we still have these two unknown constants A and B . However, just as for the function $f_1(v_x)$, $f(v)dv$ is the fraction of the molecules corresponding to speeds between v and $v + dv$, and all these fractions taken together must add up to 1.

That is,

$$\int_0^{\infty} f(v)dv = 1.$$

We need the standard result $\int_0^{\infty} x^2 e^{-Bx^2} dx = (1/4B)\sqrt{\pi/B}$ (a derivation can be found in my 152

[Notes](#) on Exponential Integrals), and find:

$$4\pi A^3 \frac{1}{4B} \sqrt{\frac{\pi}{B}} = 1.$$

This means that there is really only one arbitrary variable left: if we can find B , this equation gives us A : that is, $4\pi A^3 = \frac{4}{\sqrt{\pi}} B^{3/2}$, and $4\pi A^3$ is what appears in $f(v)$.

Looking at $f(v)$, we notice that B is a measure of how far the distribution spreads from the origin: if B is small, the distribution drops off more slowly—the average particle is more energetic. Recall now that the average kinetic energy of the particles is related to the temperature by $\overline{\frac{1}{2}mv^2} = \frac{3}{2}kT$. This means that B is related to the inverse temperature.

In fact, since $f(v)dv$ is the fraction of particles in the interval dv at v , and those particles have kinetic energy $\frac{1}{2}mv^2$, we can use the probability distribution to find the average kinetic energy per particle:

$$\overline{\frac{1}{2}mv^2} = \int_0^{\infty} \frac{1}{2}mv^2 f(v)dv.$$

To do this integral we need another standard result: $\int_0^{\infty} x^4 e^{-Bx^2} dx = (3/8B^2)\sqrt{\pi/B}$. We find:

$$\overline{\frac{1}{2}mv^2} = \frac{3m}{4B}.$$

.Substituting the value for the average kinetic energy in terms of the temperature of the gas,

$$\overline{\frac{1}{2}mv^2} = \frac{3}{2}kT$$

gives $B = m/2kT$, so $4\pi A^3 = \frac{4}{\sqrt{\pi}} B^{3/2} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2}$.

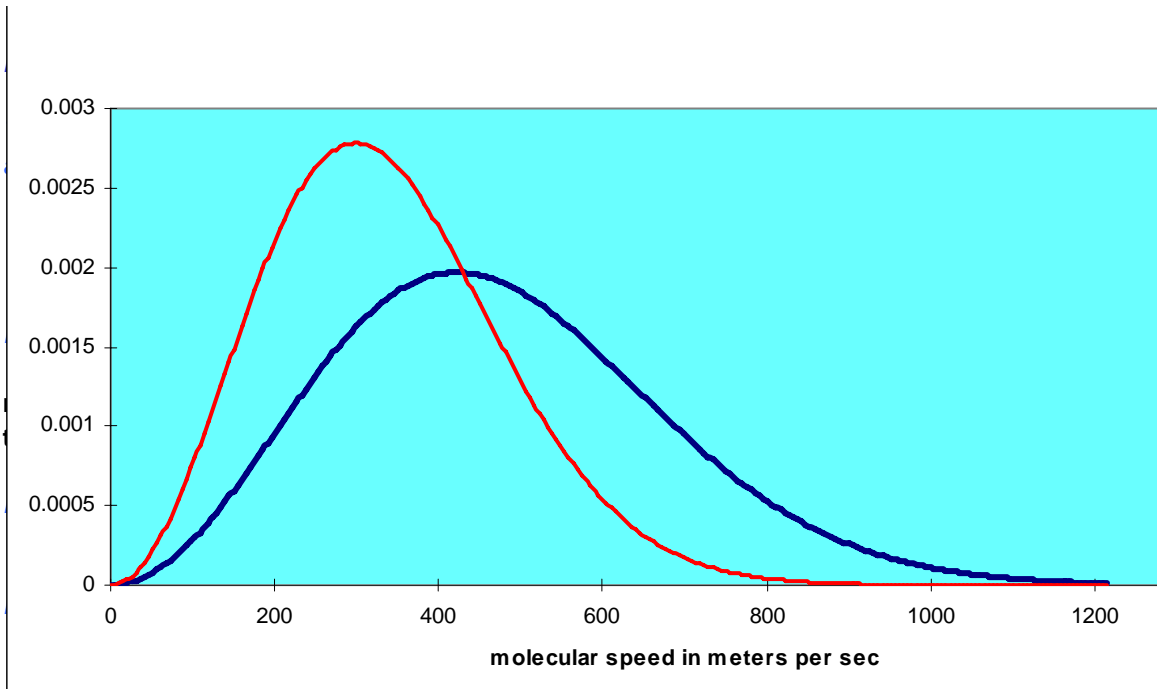
This means the distribution function

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-E/kT}$$

where E is the kinetic energy of the molecule.

Note that this function increases *parabolically* from zero for low speeds, then curves round to reach a maximum and finally decreases exponentially. As the temperature increases, the position of the maximum shifts to the right. *The total area under the curve is always one*, by definition.

For air molecules (say, nitrogen) at room temperature the curve is the blue one below. The red one is for an absolute temperature down by a factor of two:



What about Potential Energy?

Maxwell's analysis solves the problem of finding the statistical velocity distribution of molecules of an ideal gas in a box at a definite temperature T : the relative probability of a molecule having velocity \vec{v} is proportional to $e^{-mv^2/2kT} = e^{-E/kT}$. The *position* distribution is taken to be uniform: the molecules are assumed to be equally likely to be anywhere in the box.

But how is this distribution affected if in fact there is some kind of potential pulling the molecules to one end of the box? In fact, we've already solved this problem, in the discussion earlier on the isothermal atmosphere. Consider a really big box, kilometers high, so air will be significantly denser towards the bottom. Assume the temperature is uniform throughout. We found under these conditions that with Boyle's Law expressed in the form

$$\rho = CP$$

the atmospheric density varied with height as

$$P = P_0 e^{-Cgh}, \text{ or equivalently } \rho = \rho_0 e^{-Cgh}.$$

Now we know that Boyle's Law is just the fixed temperature version of the Gas Law $PV = nRT$, and the density

$$\rho = \text{mass/volume} = Nm/V$$

with N the total number of molecules and m the molecular mass,

$$CP = \rho = Nm/V.$$

Rearranging,

$$PV = Nm/C = nN_A m/C,$$

for n moles of gas, each mole containing Avogadro's number N_A molecules.

Putting this together with the Gas Law,

$$PV = nN_A m/C = nRT,$$

So

$$C = N_A m / RT = m / kT$$

where Boltzmann's constant $k = R / N_A$ as discussed previously.

The dependence of gas density on height can therefore be written

$$\rho = \rho_0 e^{-Cgh} = \rho_0 e^{-mgh/kT}.$$

The important point here is that mgh is the potential energy of the molecule, and the distribution we have found is exactly parallel to Maxwell's velocity distribution, the potential energy now playing the role that kinetic energy played in that case.

We're now ready to put together Maxwell's velocity distribution with this height distribution, to find out how the molecules are distributed in the atmosphere, *both* in velocity space *and* in ordinary space. In other words, in a *six-dimensional* space!

Our result is:

$$f(x, y, z, v_x, v_y, v_z) = f(h, v) \propto e^{-mv^2/2kT} e^{-mgh/kT} = e^{-((1/2)mv^2 + mgh)/kT} = e^{-E/kT}.$$

That is, the probability of a molecule having total energy E is proportional to $e^{-E/kT}$. This is the Boltzmann, or Maxwell-Boltzmann, distribution. It turns out to be correct for any type of potential energy, including that arising from forces between the molecules themselves.

Degrees of Freedom and Equipartition of Energy

By a “degree of freedom” we mean a way in which a molecule is free to move, and thus have energy—in this case, just the x , y , and z directions. Boltzmann reformulated Maxwell’s analysis in terms of degrees of freedom, stating that there was an average energy $\frac{1}{2}kT$ in each degree of freedom, to give total average kinetic energy $3 \cdot \frac{1}{2}kT$, so the specific heat per molecule is presumable $1.5k$, and given that $k = R/N_A$, the specific heat per mole comes out at $1.5R$. In fact, this is experimentally confirmed for monatomic gases. However, it is found that diatomic gases can have specific heats of $2.5R$ and even $3.5R$. This is not difficult to understand—these molecules have more degrees of freedom. A dumbbell molecule can rotate about two directions perpendicular to its axis. A diatomic molecule could also vibrate. Such a simple harmonic oscillator motion has both kinetic and potential energy, and it turns out to have total energy kT in thermal equilibrium. Thus, reasonable explanations for the specific heats of various gases can be concocted by assuming a contribution $\frac{1}{2}k$ from each degree of freedom. But there are problems. Why shouldn’t the dumbbell rotate about its axis? Why do monatomic atoms not rotate at all? Even more ominously, the specific heat of hydrogen, $2.5R$ at room temperature, drops to $1.5R$ at lower temperatures. These problems were not resolved until the advent of quantum mechanics.

Brownian Motion

One of the most convincing demonstrations that gases really *are* made up of fast moving molecules is Brownian motion, the observed constant jiggling around of tiny particles, such as fragments of ash in smoke. This motion was first noticed by a Scottish botanist, who initially assumed he was looking at living creatures, but then found the same motion in what he knew to be particles of inorganic material. Einstein showed how to use Brownian motion to estimate the size of atoms. For the movie, [click here!](#)

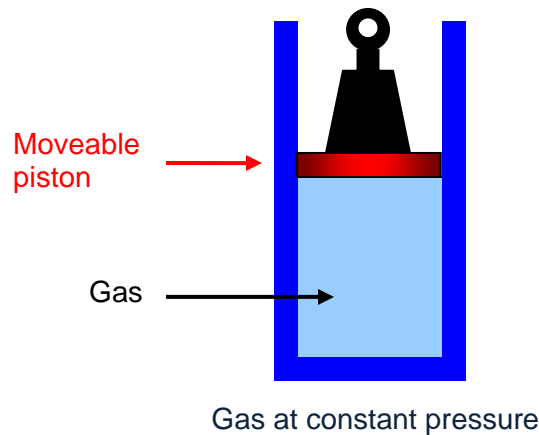
Ideal Gas Thermodynamics: Specific Heats, Isotherms, Adiabats

Introduction: the Ideal Gas Model, Heat, Work and Thermodynamics

The Kinetic Theory picture of a gas (outlined in the previous lecture) is often called the *Ideal Gas Model*. It ignores interactions between molecules, and the finite size of molecules. In fact, though, these only become important when the gas is very close to the temperature at which it become liquid, or under extremely high pressure. In this lecture, we will be analyzing the behavior of gases in the pressure and temperature range corresponding to heat engines, and in this range the Ideal Gas Model is an excellent approximation. Essentially, our program here is to learn how gases absorb heat and turn it into work, and *vice versa*. This heat-work interplay is called *thermodynamics*.

Julius Robert Mayer was the first to appreciate that there *is* an equivalence between heat and mechanical work. The tortuous path that led him to this conclusion is described in an earlier lecture, but once he was there, he realized that in fact the numerical equivalence—how many Joules in one calorie in present day terminology—could be figured out easily from the results of some measurements of gas specific heat by French scientists. The key was that they had measured specific heats both at constant *volume* and at constant *pressure*. Mayer realized that in the latter case, heating the gas necessarily increased its volume, and the gas therefore did work in pushing to expand its container. Having convinced himself that mechanical work and heat were equivalent, evidently the extra heat needed to raise the temperature of the gas at constant pressure was exactly the work the gas did on its container. (*Historical note:* although he did the work in 1842, he didn't publish until 1845, and at first miscalculated—but then gave a figure within 1% of the correct value of 4.2 joules per calorie.)

The simplest way to see what's going on is to imagine the gas in a cylinder, held in by a piston, carrying a fixed weight, able to move up and down the cylinder smoothly with negligible friction. The pressure on the gas is just the total weight pressing down divided by the area of the piston, and this total weight, of course, will not change as the piston moves slowly up or down: the gas is at *constant pressure*.



The Gas Specific Heats C_V and C_P

Consider now the two specific heats of this same sample of gas, let's say one mole:

Specific heat at constant volume, C_V (piston glued in place),

Specific heat at constant pressure, C_P (piston free to rise, no friction).

In fact, we already worked out C_V in the [Kinetic Theory lecture](#): at temperature T , recall the average kinetic energy per molecule is $\frac{3}{2}kT$, so one mole of gas—Avogadro's number of molecules—will have total kinetic energy, which we'll label *internal energy*,

$$E_{\text{int}} = \frac{3}{2}kT \cdot N_A = \frac{3}{2}RT.$$

(In this simplest case, we are ignoring the possibility of the molecules having their *own* internal energy: they might be spinning or vibrating—we'll include that shortly).

That the internal energy is $\frac{3}{2}RT$ per mole immediately gives us the specific heat of a mole of gas in a fixed volume,

$$C_V = \frac{3}{2}R$$

that being the heat which must be supplied to raise the temperature by one degree.

However, if the gas, instead of being in a fixed box, is held in a cylinder at constant pressure, experiment confirms that *more* heat must be supplied to raise the gas temperature by one degree.

As Mayer realized, the total heat energy that must be supplied to raise the temperature of the gas one degree *at constant pressure* is $\frac{3}{2}k$ per molecule *plus* the energy required to lift the weight.

The work the gas must do to raise the weight is the force the gas exerts on the piston multiplied by the distance the piston moves.

If the area of piston is A , then the gas at pressure P exerts force PA .

If on heating through one degree the piston rises a distance Δh the gas does work

$$PA \cdot \Delta h = P\Delta V.$$

Now, for one mole of gas, $PV = RT$, so at constant P

$$P\Delta V = R\Delta T.$$

Therefore, the work done by the gas in raising the weight is just $R\Delta T$, the specific heat at constant pressure, the total heat energy needed to raise the temperature of one mole by one degree,

$$C_p = C_v + R.$$

In fact, this relationship is true whether or not the molecules have rotational or vibrational internal energy. (It's known as Mayer's relationship.) For example, the specific heat of oxygen at constant volume

$$C_v(\text{O}_2) = \frac{5}{2}R$$

and this is understood as a contribution of $\frac{3}{2}R$ from kinetic energy, and R from the two rotational modes of a dumbbell molecule (just why there is no contribution from rotation about the third axis can only be understood using quantum mechanics). The specific heat of oxygen at constant pressure

$$C_p(\text{O}_2) = \frac{7}{2}R.$$

It's worth having a standard symbol for the *ratio* of the specific heats:

$$\frac{C_p}{C_v} = \gamma.$$

Tracking a Gas in the (P , V) Plane: Isotherms and Adiabats

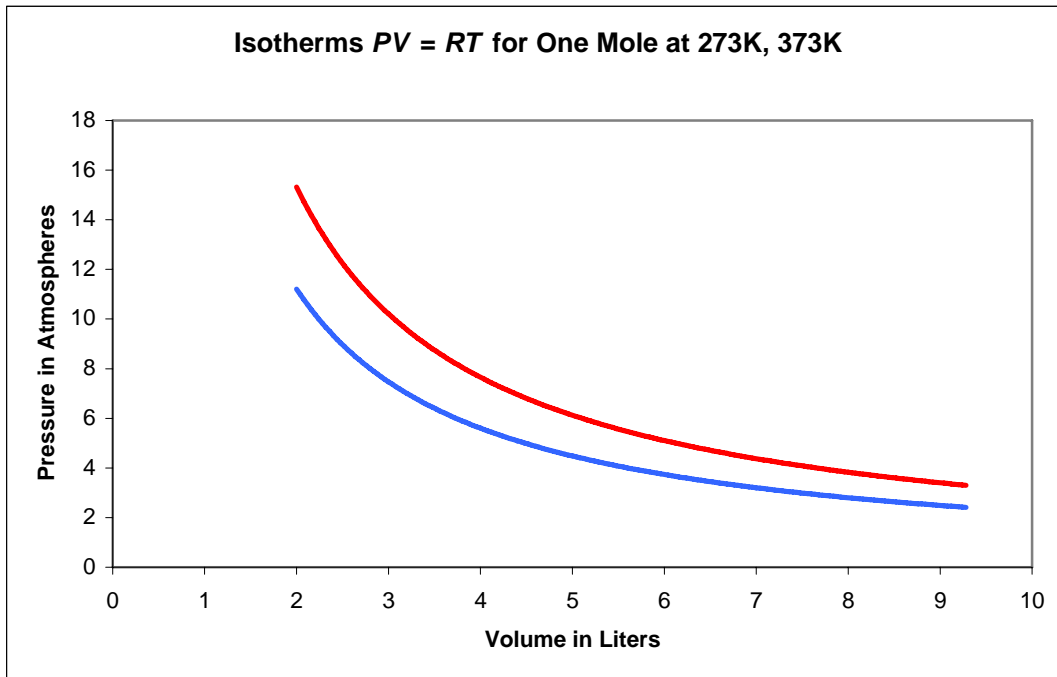
An ideal gas in a box has three thermodynamic variables: P , V , T . But if there is a fixed mass of gas, fixing two of these variables fixes the third from $PV = nRT$ (for n moles). In a heat engine, heat can enter the gas, then leave at a different stage. The gas can expand doing work, or contract as work is done on it. To track what's going on as a gas engine transfers heat to work, say, we must follow the varying state of the gas. We do that by tracing a curve in the (P , V) plane.

Supplying heat to a gas which consequently expands and does mechanical work is the key to the heat engine. But just knowing that a gas is expanding and doing work is not enough information to follow its path in the (P , V) plane. The route it follows will depend on whether or not heat is being supplied (or taken away) at the same time. There are, however, two particular ways a gas can expand reversibly—meaning that a tiny change in the external conditions would be sufficient for the gas to retrace its path in the (P , V) plane backwards. It's important to concentrate on reversible paths, because as Carnot proved and we shall discuss later, they correspond to the most efficient engines. The two sets of reversible paths are the *isotherms* and the *adiabats*.

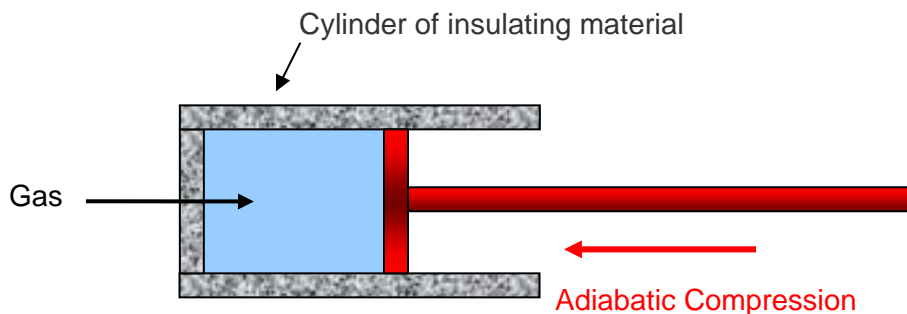
Isothermal behavior: the gas is kept *at constant temperature* by allowing heat flow back and forth with a very large object (a “heat reservoir”) at temperature T . From $PV = nRT$, it is

evident that for a fixed mass of gas, held at constant T but subject to (slowly) varying pressure, the variables P , V will trace a hyperbolic path in the (P, V) plane.

This path, $PV = nRT_1$, say is called the *isotherm* at temperature T_1 . Here are two examples of isotherms:



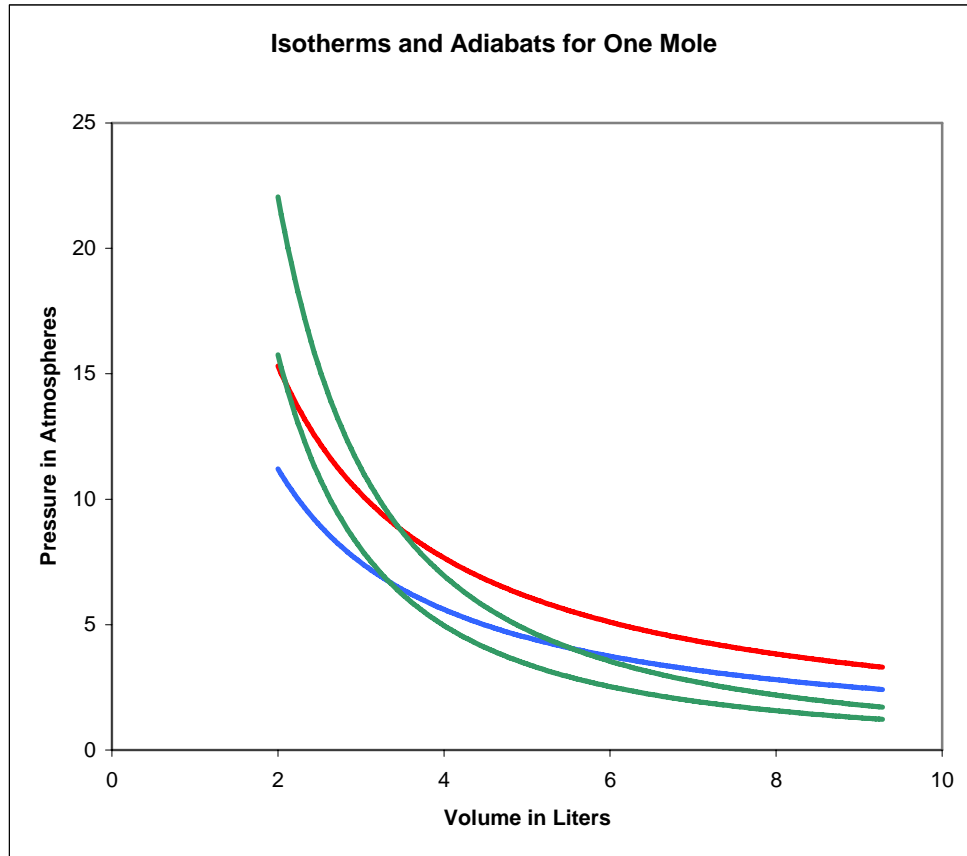
Adiabatic behavior: “adiabatic” means “nothing gets through”, in this case *no heat gets in or out* of the gas through the walls. So all the work done in compressing the gas has to go into the internal energy E_{int} .



As the gas is compressed, it follows a curve in the (P, V) plane called an *adiabat*. To see how an adiabat differs from an isotherm, imagine beginning at some point on the blue 273K isotherm on the above graph, and applying pressure so the gas moves to higher pressure and lower volume. Since the gas’s internal energy is increasing, but the number of molecules is staying the same, its

temperature is necessarily rising, it will move towards the red curve, then above it. This means *the adiabats are always steeper than the isotherms*.

In the diagram below, we've added a couple of **adiabats** to the isotherms:



Equation for an Adiat

What equation for an adiabat corresponds to $PV = nRT_1$ for an isotherm?

On raising the gas temperature by ΔT , the change in the *internal energy*—the sum of molecular kinetic energy, rotational energy and vibrational energy (if any),

$$\Delta E_{\text{int}} = C_V \Delta T.$$

This is always true: whether or not the gas is changing volume is irrelevant, all that counts in E_{int} is the sum of the energies of the individual molecules (assuming as we do here that attractive or repulsive forces between molecules are negligible).

In adiabatic compression, all the work done by the external pressure goes into this internal energy, so

$$-P\Delta V = C_V\Delta T.$$

(Compressing the gas of course gives negative ΔV , positive ΔE_{int} .)

To find the equation of an adiabat, we take the infinitesimal limit

$$-PdV = C_V dT$$

Divide the left-hand side by PV , the right-hand side by nRT (since $PV = nRT$, that's OK) to find

$$-\frac{R}{C_V} \frac{dV}{V} = \frac{dT}{nT}.$$

Recall now that $C_p = C_V + nR$, and $C_p / C_V = \gamma$. It follows that

$$\frac{nR}{C_V} = \frac{C_p - C_V}{C_V} = \gamma - 1.$$

Hence

$$-(\gamma - 1) \int \frac{dV}{V} = \int \frac{dT}{T}$$

and integrating

$$\ln T + (\gamma - 1) \ln V = \text{const.}$$

from which the equation of an adiabat is

$$TV^{\gamma-1} = \text{const.}$$

From $PV = nRT$, the P, V equation for an adiabat can be found by multiplying the left-hand side of this equation by the constant PV/T , giving

$$PV^\gamma = \text{const. for an adiabat,}$$

where $\gamma = 5/3$ for a monatomic gas, $7/5$ for a diatomic gas.

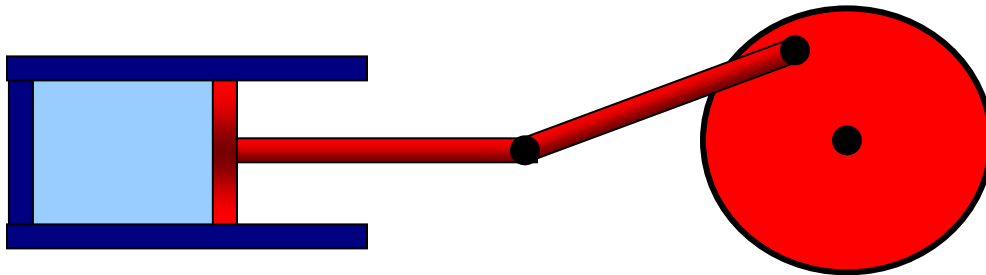
Heat Engines: the Carnot Cycle

Flashlet [here!](#)

The Ultimate in Fuel Efficiency

All standard heat engines (steam, gasoline, diesel) work by supplying heat to a gas, the gas then expands in a cylinder and pushes a piston to do its work. The catch is that the heat and/or the gas must somehow then be dumped out of the cylinder to get ready for the next cycle.

Our aim in this lecture is to figure out just how efficient such a heat engine *can* be: what's the most work we can possibly get for a given amount of fuel? We'll examine here the simplest cyclical model: an ideal gas enclosed in a cylinder, with external connections to supply and take away heat, and a frictionless piston for the gas to perform (and to absorb) mechanical work:



Carnot Engine

The efficiency question was first posed—and solved—by Sadi Carnot in 1820, not long after steam engines had become efficient enough to begin replacing water wheels, at that time the main power sources for industry. Not surprisingly, perhaps, Carnot visualized the heat engine as a kind of water wheel in which heat (the “fluid”) dropped from a high temperature to a low temperature, losing “potential energy” which the engine turned into work done, just like a water wheel.

(*Historical Note*: actually, Carnot thought at the time that heat *was* a fluid—he believed in the *Caloric Theory*. Remarkably, the naïve “potential energy of a caloric fluid” approach gives *exactly the right answer* for the efficiency of an ideal engine! Carnot accepted that there was an absolute zero of temperature, from which he figured out that on being cooled to absolute zero, the caloric fluid would give up *all* its heat energy. Therefore, if it falls only half way to absolute zero from its beginning temperature, it will give up half its heat, and an engine taking in heat at T and shedding it at $\frac{1}{2}T$ will be utilizing half the possible heat, and be 50% efficient. Picture a water wheel that takes in water at the top of a waterfall, but lets it out halfway down. So, the efficiency of an ideal engine operating between two temperatures will be equal to the fraction of the temperature drop towards absolute zero that the heat undergoes. This turns out to be exactly correct, even though the reasoning is based on a false model.)

The water wheel analogy proved to be useful in another way: Carnot knew that the most efficient water wheels were those that operated smoothly, the water went into the buckets at the top from the same level, it didn't fall into them through any height, and didn't splash around. In the idealized limit of a frictionless water wheel, with gentle flow on and off the wheel, such a machine would be *reversible*—if the wheel is run backwards by power supplied from the outside, so it raises water back up, it will take the *same* power that the wheel was itself delivering in normal operation. This idealized water wheel is clearly perfectly efficient, so the analogs of *zero friction* and *gentle flow* are what we need in the perfect heat engine.

Getting friction as low as possible is obviously necessary, but what, exactly, is “gentle flow” in the heat engine? For the water wheel, it meant having water at the top flow smoothly into buckets at the same height, no wasteful drop that would lose potential energy with no gain. For the heat engine, the analog is to have heat flow from the heat supply into the engine with no drop in temperature. In a real engine, there must of course be a slight drop in temperature for the heat to flow at all (just as there is for a real water wheel), but this has to be minimized.

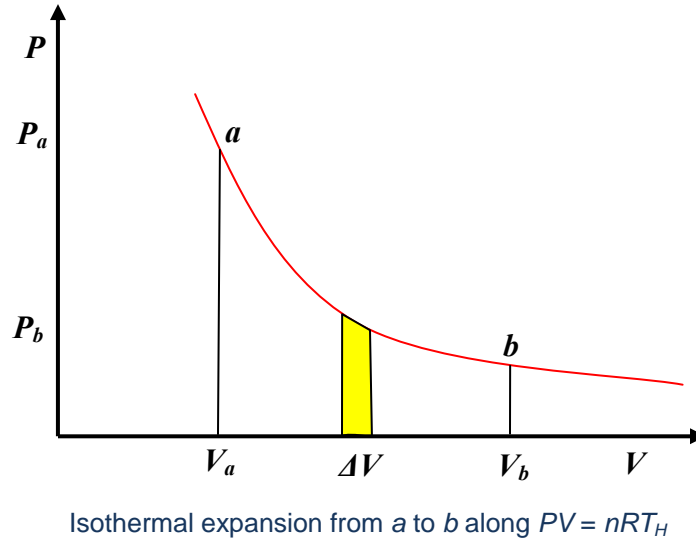
So, as the heat is supplied and the gas expands, the temperature of the gas must stay the same as that of the heat supply (the “heat reservoir”): the gas is expanding *isothermally*. Similarly, it must contract isothermally later in the cycle as it sheds heat.

To figure out the efficiency, we need to track the engine through a complete cycle, finding out how much work it does, how much heat is taken in from the fuel, and how much heat is dumped in getting ready for the next cycle. You might want to look at the [flashlet](#) to get the picture at this point: the cycle has four steps, an isothermal expansion as heat is absorbed, followed by an adiabatic expansion, then an isothermal contraction as heat is shed, finally an adiabatic contraction to the original configuration. We'll take it one step at a time.

Step 1: Isothermal Expansion

So the first question is: *How much heat is supplied, and how much work is done, as the gas expands isothermally?*

Taking the temperature of the heat reservoir to be T_H (H for hot), the expanding gas follows the isothermal path $PV = nRT_H$ in the (P, V) plane.



The work done by the gas in a small volume expansion ΔV is just $P\Delta V$, the area under the curve (as we proved in the last lecture).

Hence the work done in expanding isothermally from volume V_a to V_b is the total area under the curve between those values,

$$\text{work done isothermally} = \int_{V_a}^{V_b} P dV = \int_{V_a}^{V_b} \frac{nRT_H}{V} dV = nRT_H \ln \frac{V_b}{V_a}.$$

Since the gas is at constant temperature T_H , there is no change in its internal energy during this expansion, so the total heat supplied must be $nRT_H \ln \frac{V_b}{V_a}$, the same as the external work the gas has done.

In fact, this isothermal expansion is only the first step: the gas is at the temperature of the heat reservoir, hotter than its other surroundings, and will be able to continue expanding even if the heat supply is cut off. To ensure that this further expansion is also reversible, the gas must not be losing heat to the surroundings. That is, after the heat supply is cut off, there must be no further heat exchange with the surroundings, the expansion must be *adiabatic*.

Step 2: Adiabatic Expansion

By definition, no heat is supplied in adiabatic expansion, but work is done.

The work the gas does in adiabatic expansion is like that of a compressed spring expanding against a force—equal to the work needed to compress it in the first place, for an ideal (and perfectly insulated) gas. So adiabatic expansion is *reversible*.

To find the work the gas does expanding adiabatically from V_b to V_c , say, the Step 1 analysis above is repeated for the **adiabat** $PV^\gamma = P_bV_b^\gamma$,

$$\text{work done adiabatically } W_{\text{adiabat}} = \int_{V_b}^{V_c} PdV = P_bV_b^\gamma \int_{V_b}^{V_c} \frac{dV}{V^\gamma} = P_bV_b^\gamma \frac{V_c^{1-\gamma} - V_b^{1-\gamma}}{1-\gamma}.$$

Again, this work equals the *area under the curve* from b to c in the (P, V) plane.

Now $P_cV_c^\gamma = P_bV_b^\gamma$, so the expression can be written more neatly:

$$W_{\text{adiabat}} = \frac{P_cV_c - P_bV_b}{1-\gamma}.$$

This is a useful expression for the work done since we are plotting in the (P, V) plane, but note that from the gas law $PV = nRT$ the numerator is just $nR(T_c - T_b)$, and from this

$W_{\text{adiabat}} = nC_V(T_c - T_b)$, as of course it must be—this is the loss of internal energy by the gas on expanding against the external pressure.

Steps 3 and 4: Completing the Cycle

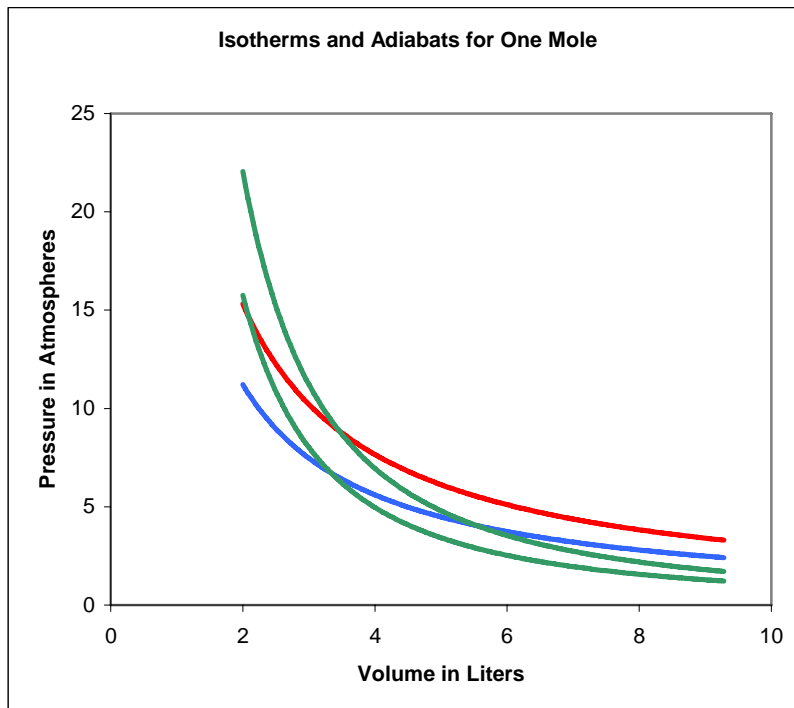
We've looked in detail at the work a gas does in expanding as heat is supplied (isothermally) and when there is no heat exchange (adiabatically). These are the two initial steps in a heat engine, but it is necessary for the engine to get back to where it began, for the next cycle. The general idea is that the piston drives a wheel (as in the diagram at the beginning of this lecture), which continues to turn and pushes the gas back to the original volume.

But it is also essential for the gas to be as cold as possible on this return leg, because the *wheel* is now having to expend work on the *gas*, and we want that to be as little work as possible—it's costing us. The colder the gas, the less pressure the wheel is pushing against.

To ensure that the engine is as efficient as possible, this return path to the starting point (P_a, V_a) must also be reversible. We can't just retrace the path taken in the first two legs, that would take all the work the engine did along those legs, and leave us with no net output. Now the gas cooled during the adiabatic expansion from b to c , from T_H to T_C , say, so we can go some

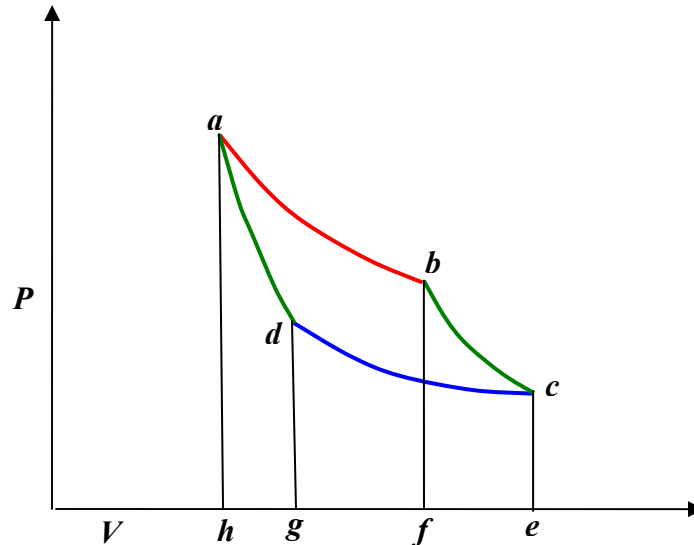
distance back along the reversible colder isotherm T_C . But this won't get us back to (P_a, V_a) , because that's on the T_H isotherm. The simplest option—the one chosen by Carnot—is to proceed back along the cold isotherm to the point where it intersects the adiabat through a , then follow that adiabat back to a . That route keeps the gas as cold as possible for as long as possible, minimizing the external work needed to get it back to the original state.

To picture the Carnot cycle in the (P, V) plane, recall from the previous lecture the graph showing two isotherms and two adiabats:



Carnot's cycle is around that curved quadrilateral having these four curves as its sides.

Let us redraw this, slightly less realistically but more conveniently:



Efficiency of the Carnot Engine

In a complete cycle of Carnot's heat engine, the gas traces the path $abcd$. The important question is: what fraction of the heat supplied from the hot reservoir (along the red top isotherm) is turned into mechanical work? This fraction is called the *efficiency* of the engine.

The work output along any curve in the (P, V) plane is just $\int PdV$, the area under the curve, but it will be *negative* if the volume is decreasing! So the work done by the engine during the hot isothermal segment is the area $abfh$, then the adiabatic expansion adds the area $bcef$, but as the gas is compressed back, the wheel has to do work on the gas equal to the area $cdge$ as heat is dumped into the cold reservoir, then $dahg$ as the gas is recompressed to the starting point.

The bottom line is that:

the total work done by the gas is the area of the circuit $abcd$

that is, the area of the curved "parallelogram" in the (P, V) graph above.

We could compute this area by finding $\int PdV$ for each segment, but that is unnecessary—on completing the cycle, the gas is back to its initial temperature, so has the same internal energy.

Therefore, the work done by the engine must be just the difference between the heat supplied at T_H and that dumped at T_C .

Now the heat supplied along the initial hot isothermal path ab is equal to the work done along that leg, (from the paragraph above on isothermal expansion):

$$Q_H = nRT_H \ln \frac{V_b}{V_a}$$

and the heat dumped into the cold reservoir along cd is

$$Q_C = nRT_C \ln \frac{V_c}{V_d}.$$

The difference between these two is the net work output. This can be simplified using the adiabatic equations for the other two sides of the cycle:

$$\begin{aligned} T_H V_b^{\gamma-1} &= T_C V_c^{\gamma-1} \\ T_H V_a^{\gamma-1} &= T_C V_d^{\gamma-1}. \end{aligned}$$

Dividing the first of these equations by the second,

$$\left(\frac{V_b}{V_a} \right) = \left(\frac{V_c}{V_d} \right)$$

and using that in the preceding equation for Q_C ,

$$Q_C = nRT_C \ln \frac{V_a}{V_b} = \frac{T_C}{T_H} Q_H.$$

So for the Carnot cycle the ratio of heat supplied to heat dumped is just the ratio of the absolute temperatures!

$$\boxed{\frac{Q_H}{Q_C} = \frac{T_H}{T_C}, \quad \text{or} \quad \frac{Q_H}{T_H} = \frac{Q_C}{T_C}.}$$

Remember this: it'll be *important in developing the concept of entropy*.

The work done can now be written simply:

$$W = Q_H - Q_C = \left(1 - \frac{T_C}{T_H}\right) Q_H.$$

Therefore **the efficiency of the engine, defined as the fraction of the ingoing heat energy that is converted to available work, is**

$$\text{efficiency} = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H}.$$

These temperatures are of course in degrees Kelvin, so for example the efficiency of a Carnot engine having a hot reservoir of boiling water and a cold reservoir ice cold water will be $1 - (273/373) = 0.27$, just over a quarter of the heat energy is transformed into useful work. This is the very same expression Carnot found from his water wheel analogy.

After all the effort to construct an efficient heat engine, making it reversible to eliminate “friction” losses, etc., it is perhaps somewhat disappointing to find this figure of 27% efficiency when operating between 0 and 100 degrees Celsius. Surely we can do better than that? After all, the heat energy of hot water is the kinetic energy of the moving molecules, can’t we find some device to channel all that energy into useful work? Well, we can do better than 27%, by having a colder cold reservoir, or a hotter hot one. But there’s a limit: we can never reach 100% efficiency, because we cannot have a cold reservoir at $T_C = 0K$, and, even if we did, after the first cycle the heat dumped into it would warm it up!

The Laws of Thermodynamics and Limits on Engine Efficiency

The Laws of Thermodynamics

(Picture below from [St. Andrews](#))



In 1850, Rudolph **Clausius**, a German physicist, created the science of *thermodynamics*. He was convinced by Joule’s experiments (he didn’t know about Mayer’s work at the time) that *total energy*, including kinetic, potential, electrical, and, importantly, heat, *was conserved*, he called this:

The first law of thermodynamics: *total energy, including heat energy, is always conserved.*

He explicitly assumed that heat was just the kinetic energy of the moving particles that made up a body. He was the first to make clear that Carnot's analysis of the heat engine (the cycle) was almost right except that the "caloric fluid", meaning heat, wasn't actually conserved—less of it was dumped in the cold reservoir than was taken from the hot one. The difference of course was the work done (in an ideal engine). Engines at the time were so inefficient that this loss of heat energy wasn't obvious.

But abolishing the caloric fluid in favor of overall energy conservation raised another problem. The fluid theory had been highly successful in describing heat flow through solid materials, like electric current flow but with temperature gradients replacing voltage drops, different materials having different *thermal* conductivities, etc.

(*Note*: Fourier revolutionized mathematics by inventing Fourier series, his method of analyzing caloric fluid flow. In fact Kelvin used it in 1862 to estimate the rate of cooling of the earth. Kelvin's conclusion that the earth was twenty million years old or so (much older would be much colder) led to decades of debate with Darwinians and geologists, both of whom needed much more time, for evolution and rock strata formation respectively. The debate went on until the 1890's when the discovery of radioactivity made clear that this unsuspected source of subterranean heat was keeping us all warm. Once this extra heat was included, the heat flow analysis gave a much older earth—and everyone was in agreement.)

In the caloric theory, then, heat flowed naturally from a high temperature to a low temperature, just as a fluid flows downhill, or an electric current to a lower voltage. And, of course, this heat flow is invariably observed in nature.

But the first law makes no such prediction: the conservation of total energy would be equally satisfied if heat flowed from a cold body to a hot body.

Conclusion: since the caloric theory is dead, we need to add this universally observed direction of heat flow *as another law*. Here it is:

The second law of thermodynamics: *heat always flows from a warm body to a cooler one, never the other way. An equivalent statement is that we cannot devise an engine, working in a cycle, that causes heat to flow from cold to warm unless we supply outside energy.*

Translation: your refrigerator won't work if it's not plugged into some power supply, and no-one will ever design one that does.

Unlike the first law, there are many ways of writing this second law: our wording above is a paraphrase of Clausius' original formulation. **Kelvin** gave it a more "engineering" look:

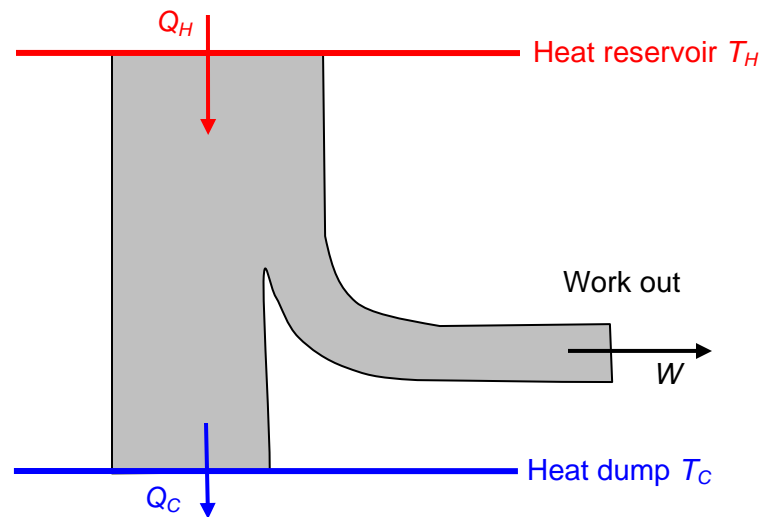
It is impossible to devise an engine which, working in a cycle, shall produce no effect other than the extraction of heat from a reservoir and the performance of an equal amount of mechanical work.

Exercise: think about how you might prove these two definitions amount to the same thing. The second law can also be stated in terms of *entropy*, a concept we'll cover in the next lecture. It's important to note that the first law of thermodynamics, the conservation of total energy including heat, would *not* be violated by an engine that powered a ship by extracting heat energy from the surrounding seawater. *This second law is saying something new: you can't do that!* And, this second law does *not* follow from the first by logical deduction—it *comes* (like the first) *from experiment and observation*.

How the Second Law Limits Engine Efficiency

An important consequence of the second law is that *no engine can be more efficient than the Carnot cycle*. Essentially, this is because a “super efficient” engine, if one existed, could be used to drive a Carnot cycle in reverse, which would pump back to the hot reservoir the heat the super efficient engine dumped in the cold reservoir, and the net effect of the two coupled engines would be to take heat from the hot reservoir and do work, contradicting the second law.

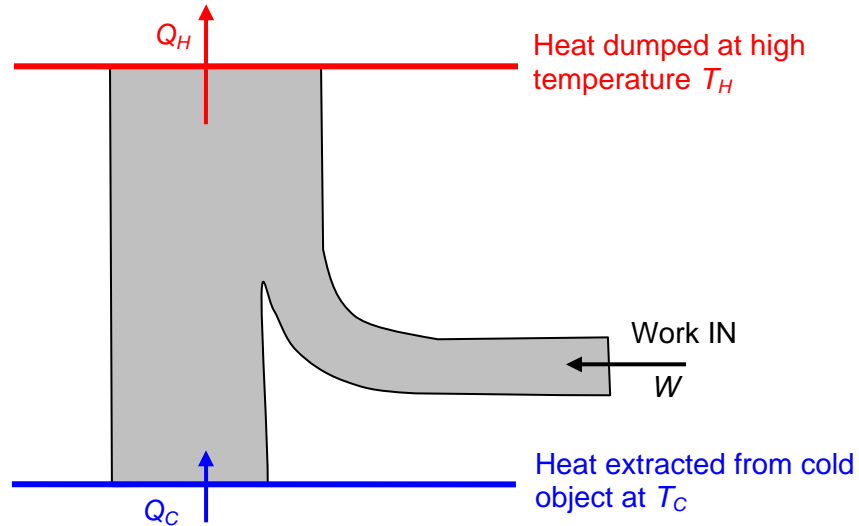
To see this, we plot the heat/energy flow for the Carnot cycle:



Energy flow in a Carnot cycle

Here $Q_H = Q_C + W$ (all expressed in Joules, of course).

Since the engine is reversible, it can also be run *backwards* (this would be a refrigerator): outside work is supplied, and heat is extracted from a cold reservoir and dumped into a hot reservoir:



Energy flow in a Carnot refrigerator

Suppose now we have a *super efficient engine*, represented by the first diagram above, and dumping the same heat per cycle Q_C into the cold reservoir, *but* taking in more heat energy $Q_H + \Delta$ Joules from the hot reservoir, and performing more work: $W + \Delta$.

Now, we hook up our super efficient engine to the “Carnot refrigerator” in the other diagram above. The refrigerator sucks out of the cold reservoir all the heat the super efficient engine dumped there, and needs W Joules of work per cycle to do it. The super efficient engine can provide this, and there are still Δ Joules of work to spare. Of course, the Carnot refrigerator has also dumped Q_H Joules of heat in the hot reservoir. But the bottom line is that between them, the super efficient engine and the Carnot refrigerator have extracted Δ Joules of heat from the hot reservoir and performed Δ Joules of work—contradicting the second law.

The second law therefore forces the conclusion that no amount of machine design will produce an engine more efficient than the Carnot cycle. The rather low ultimate efficiencies this dictated came as a shock to nineteenth century engineers.

Exercise: prove that it is impossible to construct a *reversible engine*, operating between two temperatures, that is *less* efficient than the Carnot cycle. (*Hint:* hook it to a Carnot cycle, drive one backwards.) It follows that although we used an ideal gas in our analysis, that was unnecessary—the same efficiency would result with *any* reversible engine operating between the same two temperatures.

A New Thermodynamic Variable: Entropy

Introduction

The word “entropy” is sometimes used in everyday life as a synonym for chaos, for example: the entropy in my room increases as the semester goes on. But it’s also been used to describe the approach to an imagined final state of the universe when everything reaches the same temperature: the entropy is supposed to increase to a maximum, then nothing will ever happen again. This was called the Heat Death of the Universe, and may still be what’s believed, except that now everything will also be flying further and further apart.

So what, exactly, is entropy, where did this word come from? In fact, it was coined by Rudolph Clausius in 1865, a few years after he stated the laws of thermodynamics introduced in the last lecture. *His aim was to express both laws in a quantitative fashion.*

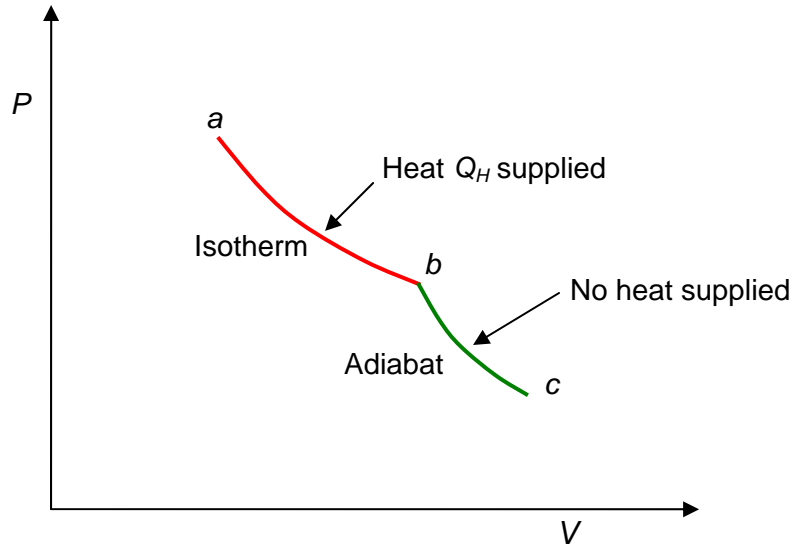
Of course, the first law—the conservation of total energy including heat energy—is easy to express quantitatively: one only needs to find the equivalence factor between heat units and energy units, calories to joules, since all the other types of energy (kinetic, potential, electrical, etc.) are already in joules, add it all up to get the total and that will remain constant. (When Clausius did this work, the unit wasn’t called a Joule, and the different types of energy had other names, but those are merely notational developments.)

The second law, that heat only flows from a warmer body to a colder one, does have quantitative consequences: the efficiency of any reversible engine has to equal that of the Carnot cycle, and any nonreversible engine has less efficiency. But how is the “amount of irreversibility” to be measured? Does it correspond to some thermodynamic parameter? The answer turns out to be *yes*: there is a parameter Clausius labeled entropy that doesn’t change in a reversible process, but always increases in an irreversible one.

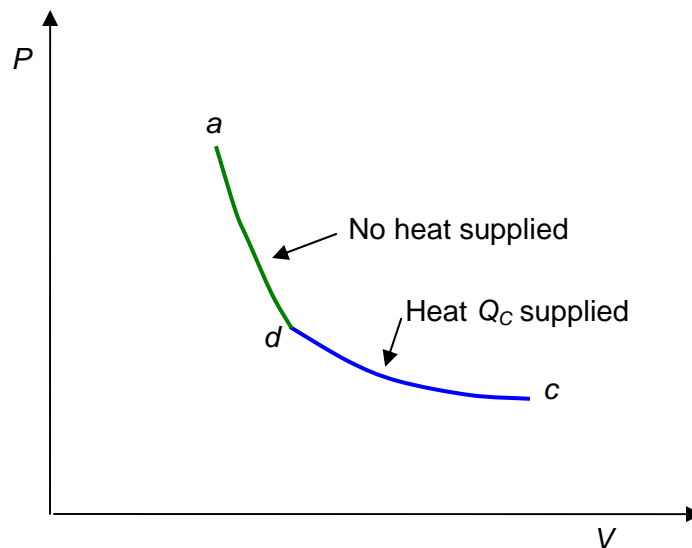
Heat Changes along Different Paths from a to c are Different!

To get a clue about what stays the same in a reversible cycle, let’s review the Carnot cycle once more. We know, of course, one thing that doesn’t change: the internal energy of the gas is the same at the end of the cycle as it was at the beginning, but that’s just the first law. Carnot himself thought that something else besides total energy was conserved: the heat, or caloric fluid, as he called it. But we know better: in a Carnot cycle, the heat leaving the gas on the return cycle is *less* than that entering earlier, by just the amount of work performed. In other words, the total amount of “heat” in the gas is *not* conserved, so talking about how much heat there is in the gas is meaningless.

To make this explicit, instead of cycling, let’s track the gas from one point in the (P, V) plane to another, and begin by connecting the two points with the first half of a Carnot cycle, from a to c :



Evidently, heat Q_H has been supplied to the gas—but this does *not* mean that we can say the gas at (P_c, V_c) has Q_H more heat than the gas at (P_a, V_a) . Why not? Because we could equally well have gone from a to c by a route which is the second half of the Carnot cycle traveled backwards:



This is a perfectly well defined reversible route, ending at the same place, but with quite a *different amount of heat supplied!*

So we cannot say that a gas at a given (P, V) contains a definite amount of heat. It does of course have a definite internal energy, but that energy can be increased by adding a mix of external work and supplied heat, and the two different routes from a to c have the same total energy supplied to the gas, but with more heat and less work along the top route.

But Something Heat Related *is* the Same: Introducing Entropy

However, notice that one thing (besides total internal energy) *is* the same over the two routes in the diagrams above:

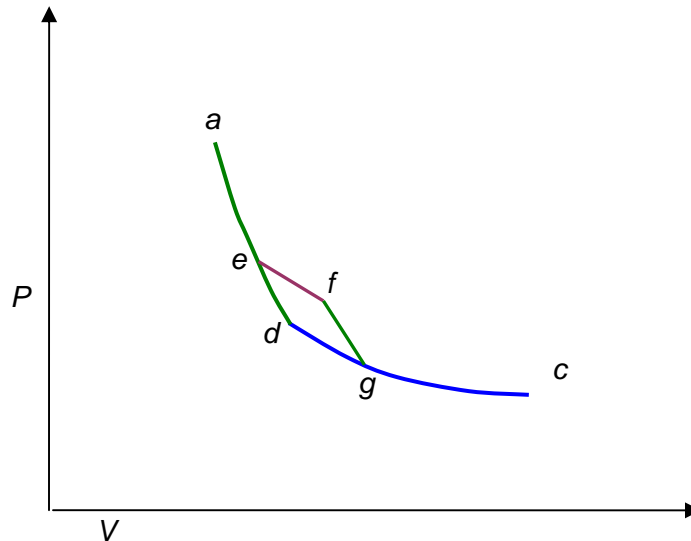
the ratio of the heat supplied to the temperature at which it was delivered:

$$Q_H / T_H = Q_C / T_C.$$

(This equation was derived in the last lecture.)

Of course, we've chosen two particular reversible routes from a to c : each is one stretch of isotherm and one of adiabat. What about more complicated routes?

Let's begin by cutting a corner in the previous route:



Suppose we follow the path $ae fgc$ instead of adc , where ef is an isotherm and fg an adiabat. Notice that $efgd$ is a little Carnot cycle. Evidently, then,

$$\frac{Q_{ef}}{T_{ef}} = \frac{Q_{dg}}{T_C},$$

and

$$Q_C = Q_{dg} + Q_{gc},$$

from which

$$\frac{Q_H}{T_H} = \frac{Q_{ef}}{T_{ef}} + \frac{Q_{gc}}{T_C},$$

But we can now cut corners on the corners: any zigzag route from a to c , with the zigs isotherms and the zags adiabats, in other words, any reversible route, can be constructed by adding little Carnot cycles to the original route. *In fact, any path you can draw in the plane from a to c can be approximated arbitrarily well by a reversible route made up of little bits of isotherms and adiabats.*

We can just apply our “cutting a corner” argument again and again, to find

$$\sum_a^c \frac{Q_i}{T_i} = \int_a^c dQ/T \text{ is the same for all reversible paths}$$

where the i labels intermediate isothermal changes.

We can therefore define a **new state variable**, S , called the **entropy**, such that the difference

$$S(P_2, V_2) = S(P_1, V_1) + \int_{(P_1, V_1)}^{(P_2, V_2)} \frac{dQ}{T}$$

where the integral is understood to be along *any* reversible path—they all give the same result. So knowing $S(P_1, V_1)$ at a single point in the plane, we can find its value everywhere, that is, for any equilibrium state.

This means an ideal gas has four state variables, or thermodynamic parameters: P , V , T , S . Any two of them define the state (for a given mass of gas), but all four have useful roles in describing gas behavior. If the gas is *not* ideal, things get a lot more complicated: it might have different phases (solid, liquid, gas) and mixtures of gases could undergo chemical reactions. Classical thermodynamics proved an invaluable tool for analyzing these more complicated systems: new state variables were introduced corresponding to concentrations of different reactants, etc. The methods were so successful that a hundred years ago some eminent scientists believed thermodynamics to be the basic science, atomic theories were irrelevant.

Finding the Entropy Difference for an Ideal Gas

In fact, for the ideal gas, we can find the entropy difference between two states exactly! Recall that the internal energy of a monatomic gas, the total kinetic energy of the molecules, is $\frac{3}{2}nRT$ for n moles at temperature T . For a diatomic gas like oxygen, the molecules also have rotational energy because they're spinning, and the total internal energy is then $\frac{5}{2}nRT$ (this is well-confirmed experimentally). The standard way to write this is

$$\text{total internal energy} = C_V T$$

because if the gas is held at constant volume, all ingoing heat becomes internal energy. Note that C_V is for the amount of gas in question, it is *not* specific heat per mole.

Suppose now we add heat dQ , but allow volume variation dV at the same time. Then, for n moles of gas,

$$\begin{aligned} dQ &= C_V dT + PdV \\ &= C_V dT + nRT \frac{dV}{V} \end{aligned}$$

so

$$\int_{(P_1, V_1)}^{(P_2, V_2)} \frac{dQ}{T} = C_V \int_{(P_1, V_1)}^{(P_2, V_2)} \frac{dT}{T} + nR \int_{(P_1, V_1)}^{(P_2, V_2)} \frac{dV}{V}$$

and doing the integrals

$$S(P_2, V_2) - S(P_1, V_1) = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}.$$

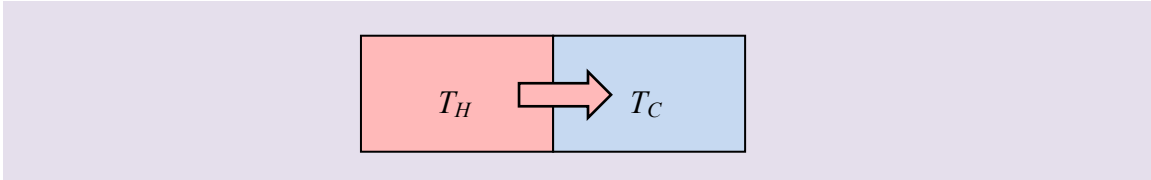
So the entropy change depends only on the final T and V , in other words, the final P and V since we always have $PV = nRT$. This is just restating what we've already established:

S is a state variable,

the (macroscopic) state of the ideal gas is fully determined by P , V (or P , T), and therefore so is the entropy S .

This means we can get to the final state any way we want, *the entropy change is the same*, we don't have to go by a reversible route!

Entropy in Irreversible Change: Heat Flow Without Work



Irreversible processes are easy to find—just hold something hot. When heat Q flows from a body at T_H to one at T_C , simply by thermal contact, by definition the entropy change is:

$$\Delta S = \frac{\Delta Q}{T_C} - \frac{\Delta Q}{T_H} > 0$$

since the temperatures must be different for heat to flow at all. There is *no energy loss* in this heat exchange, but there *is* a loss of *useful* energy: we could have inserted a small heat engine between the two bodies, and extracted mechanical work from the heat flow, but once it's flowed, that opportunity is gone. This is often called a *decrease in availability* of the energy. To get work out of that energy now, we would have to have it flow to an even colder body by way of a heat engine.

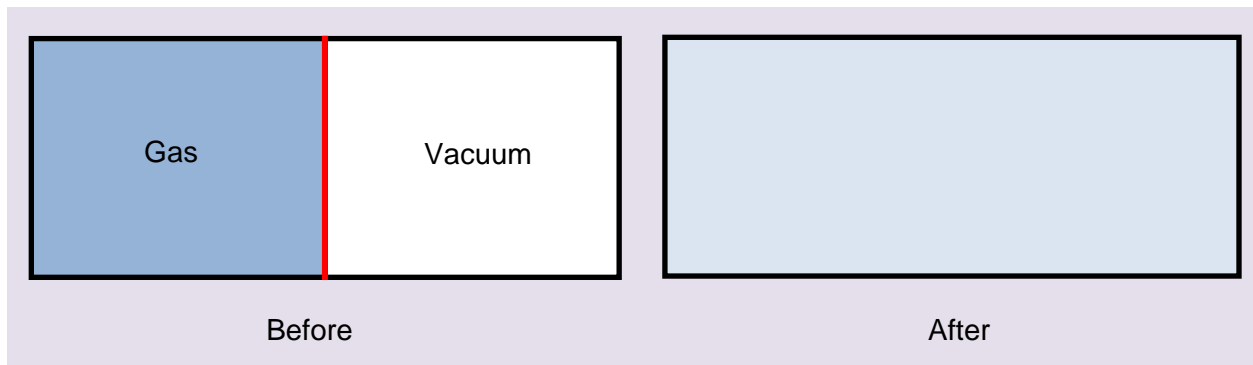
Note that the increase in entropy is for *the two bodies considered as a single system*. The hot body does of course lose entropy. Similarly, when a heat engine has less than Carnot efficiency, because some heat is leaking to the environment, there is an overall increase in entropy of the *engine plus the environment*. When a reversible engine goes through a complete cycle, its change in entropy is zero, as we've discussed, *and* the change in entropy of its environment, that is, the two reservoirs (hot and cold) taken together is *also* zero: entropy is simply transferred from one to the other.

The bottom line is that *entropy change is a measure of reversibility*:

- for a reversible process, total entropy change (system + environment) $\Delta S = 0$,
- for an irreversible process, total entropy *increases*, $\Delta S > 0$.

Entropy Change without Heat Flow: Opening a Divided Box

Now consider the following scenario: we have a box of volume $2V$, which is two cubes of volume V having a face in common, and that face is a thin partition in the box.



At the beginning, n moles of ideal gas are in the left-hand half of the box, a vacuum in the other half. Now, suddenly, the partition is removed. What happens? The molecules will fly into the vacuum, and in short order fill the whole box. Obviously, they'll never go back: this is irreversible.

Question: What happens to the temperature of the gas during this expansion?

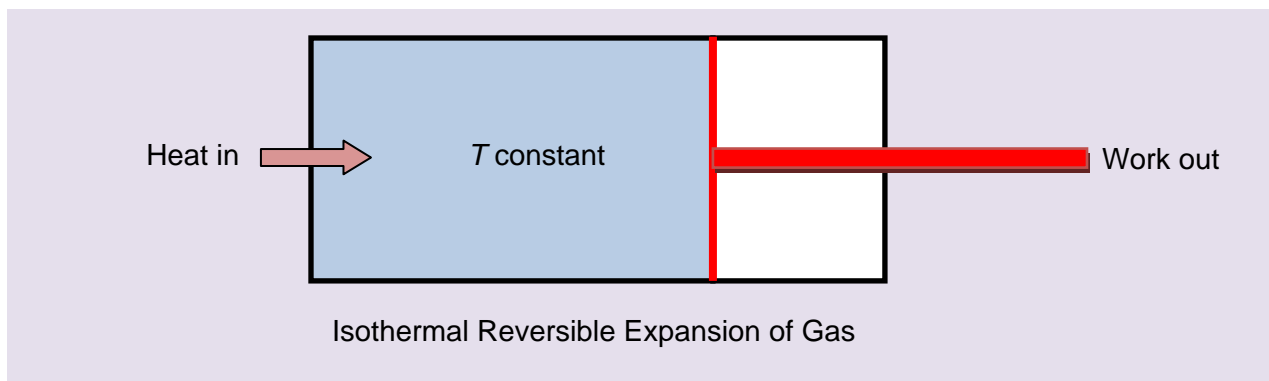
Answer: Nothing! There's no mechanism for the molecules to lose speed as they fly into the new space. (*Note:* we don't need a molecular model to see this—an ideal gas expanding against nothing does no work.)

Question: What happens to the pressure? Can you explain this?

Question: What is the entropy change? It is $nR \ln 2$.

But no heat flowed in on this route!

If we had followed a *reversible* route, for example moving slowly along an isothermal, letting the partition gradually retreat to one end of the box like a piston in a cylinder, we would have had to supply heat.



That supplied energy would have all been used in pushing the cylinder, the gas itself ending up in the same state as just removing the partition. But we would have had a nonzero $\int dQ/T$.

Just removing the partition quickly there is *no* heat transfer, and **this action doesn't correspond to any path in the P, V plane**, since each point in that plane represents a gas in equilibrium at that P, V . Nevertheless, the initial and final states *are* well defined (after the partition-removed state has reached equilibrium, which will happen very quickly) and they're the same as the initial and final states in the isothermal expansion. So, even though there's no heat transfer during the expansion into a vacuum, there *is* an increase in entropy, and this increase is the same as in the isothermal expansion.

Clausius realized that the entropy measured both something to do with heat content, but also how “spread out” a system was. This is clear for the ideal gas: the entropy change formula has two terms, one depending on the temperature difference, the other the volume difference. We shall return to this in the next lecture, when we examine entropy in the kinetic theory.

The Third Law of Thermodynamics

Notice the argument above only tells us entropy *difference* between two points, it's a bit like potential energy. Actually, though, there *is* a natural base point: a system at absolute zero temperature has zero entropy. This is sometimes called the *Third Law of Thermodynamics*, or Nernst's Postulate, and can only be really understood with quantum mechanics. We don't need it much for what we're doing here, we only work with entropy differences, but it makes things convenient because we can now write $S(P, V)$ without ambiguity.

Entropy and the Kinetic Theory: the Molecular Picture

Searching for a Molecular Description of Entropy

Clausius introduced entropy as a new thermodynamic variable to measure the “degree of irreversibility” of a process. He believed that his two laws of thermodynamics (conservation of energy and that entropy never decreases) were profound and exact scientific truths, on a par with Newton's laws of dynamics. Clausius had also made contributions to kinetic theory, publishing work as early as 1857, although unlike Maxwell he did not adopt a statistical point of view—he took all the molecules to have the same speed. (Actually, this work inspired Maxwell's first investigations of kinetic theory and his discovery of the velocity distribution.) Clausius was the first to attempt a semiquantitative analysis of the effects of molecular collisions (see later).

Obviously, if the kinetic theory is correct, if heat *is* motion of molecules, the fundamental laws of thermodynamics must be expressible somehow in terms of these molecular motions. In fact, the first law of thermodynamics *is* easy to understand in this way: heat is just kinetic energy of

molecules, and total energy is always conserved, but now instead of having a separate category for heat energy, we can put the molecular kinetic energy together with macroscopic kinetic energy, it's all $\frac{1}{2}mv^2$ with the appropriate masses.

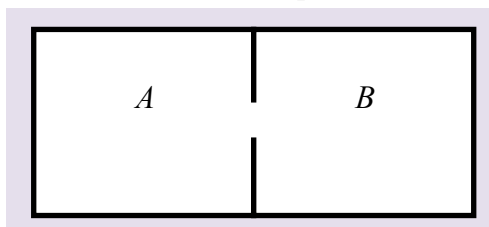
(*Note: What about potential energy? For the ideal gas, potential energy terms between molecules are negligible, by definition of ideal gas. Actually, potential energy terms are important for dense gases, and are dominant during phase changes, such as when water boils. The extra energy needed to turn water into steam at the same temperature is called the latent heat. It is simply the energy required to pull the water molecules from each other working against their attraction—in other words, for them to climb the potential energy hill as they move apart. The term “latent heat”—still standard usage—is actually a remnant of the caloric theory: it was thought that this extra heat was caloric fluid that coated the steam molecules to keep them away from each other!*)

But how do we formulate *entropy* in terms of this molecular mechanical model? Boltzmann, at age 22, in 1866, wrote an article “On the Mechanical Meaning of the Second Law of Thermodynamics” in which he claimed to do just that, but his proof only really worked for systems that kept returning to the same configuration, severely limiting its relevance to the real world. Nevertheless, being young and self confident, he thought he'd solved the problem. In 1870, Clausius, unaware of Boltzmann's work, did what amounted to the same thing. They both claimed to have found a function of the molecular parameters that increased or stayed the same with each collision of particles and which could be identified with the macroscopic entropy. Soon Boltzmann and Clausius were engaged in a spirited argument about who deserved most credit for understanding entropy at the molecular level.

Enter the Demon

Maxwell was amused by this priority dispute between “these learned Germans” as he termed them: *he knew they were both wrong*. As he wrote to Rayleigh in December 1870: “if this world is a purely dynamical system and if you accurately reverse the motion of every particle of it at the same instant then all things will happen backwards till the beginning of things the raindrops will collect themselves from the ground and fly up to the clouds &c &c men will see all their friends passing from the grave to the cradle...” because in a purely *dynamical* system, just particles interacting via forces, *the system will run equally well in reverse*, so any alleged mechanical measure of entropy that always supposedly increases will in fact *decrease* in the equally valid mechanical scenario of the system running backwards.

But Maxwell had a simpler illustration of why he couldn't accept always increasing entropy for a



mechanical system: his **demon**. He imagined two compartments containing gas at the same temperature, connected by a tiny hole that would let through one molecule at a time. He knew, of course, from his earlier work, that *the molecules on both sides had many different velocities*. He imagined a demon doorkeeper,

who opened and closed a tiny door, only letting fast molecules one way, slow ones the other way. Gradually one gas would heat up, the other cool, contradicting the second law. But the

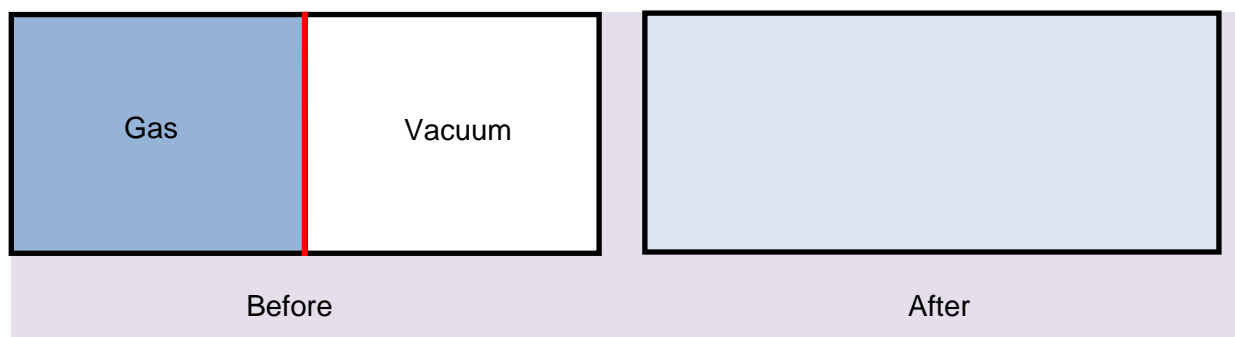
main point is *you don't really need a demon*: over a short enough time period, say, for twenty molecules or so to go each way, a random selection passes through, you won't get an exact balance of energy transferred, it could go either way.

Maxwell's point was that **the second law is a statistical law**: on average over time, the two gases will stay the same temperature, but over short enough times there will be fluctuations. *This means there cannot be a **mechanical** definition of entropy that rigorously increases with time.* The whole program of formulating the entropy in terms of mechanical molecular variables is doomed! Evidently, it isn't at all like the first law.

Boltzmann Makes the Breakthrough

Despite Maxwell's deep understanding of the essentially statistical nature of the second law, and Boltzmann's belief into the 1870's that there must be a molecular function that always increased and was equivalent to entropy, Boltzmann was the one who finally got it. In 1877, eleven years after his original paper, his senior colleague at the University of Vienna Josef Loschmidt got through to him with the point Maxwell had been making all along, that a mechanical system can run backwards as well as forwards. At that point, it dawned on Boltzmann that entropy can only be a *statistical measure*, somehow, of the state of the system.

The best way to get a grip on what this statistical measure must be is to take a very simple system, one where we already know the answer from macroscopic thermodynamics, and try to see how the known macroscopic entropy relates to what the molecules are doing. The example we choose is the ideal gas expanding to twice its original volume by removal of a partition:



Recall that we established in the last lecture that the change in entropy of n moles of an ideal gas on going from one state (specified uniquely by P, V) to another to be:

$$S(P_2, V_2) - S(P_1, V_1) = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}.$$

For expansion into a vacuum there will be no temperature change, the molecules just fly through where the partition was, they can't lose any kinetic energy. The volume doubles, $V_2 = 2V_1$, so the entropy increases by

$$\Delta S = nR \ln 2.$$

So what's going on with the molecules? When the volume is doubled, each molecule has twice the space to wander in. The increase in entropy per molecule is simply expressed using Boltzmann's constant k , and the gas constant $R = N_A k$, where N_A is Avogadro's number (molecules in one mole).

On doubling the volume,

there is an entropy increase of $k \ln 2$ per molecule.

So part of the entropy per molecule is evidently Boltzmann's constant k times the logarithm of how much space the molecule moves around in.

Question: but from the equation above, you could also increase the entropy by keeping the volume fixed, and increasing the temperature. For a monatomic gas, $C_V = \frac{3}{2}nR$, doubling the temperature will increase the entropy by $\frac{3}{2}k \ln 2$ per molecule! Does *that* relate to "more space"?

Answer: Yes. Remember the lecture on the kinetic theory of gases. To specify the state of the system at a molecular level at some instant of time, we need to say where in the box every molecule is located, *plus* giving its velocity at that instant.

So the gas fills up *two* kinds of space: the ordinary space of the box, but also *a sphere in velocity space*, really a sphere with a fuzzy edge, defined by the Maxwell distribution. It's a good enough approximation for our purposes to replace this fuzzy sphere with the sharp-edged sphere having radius the root mean square velocity $v_{rms} = \sqrt{v^2}$. Therefore the volume of the sphere is $\frac{4}{3}\pi v_{rms}^3$, and this measures how much velocity space a given molecule wanders around in over time and many collisions.

Now, if we heat up the gas, the molecules speed up—which means they spread out to take up more volume in the velocity space. If we double the temperature, since $\frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT$, v_{rms}^2 is doubled and the volume of velocity space the gas occupies, measured by the sphere, must go up by a factor of $2^{3/2}$.

But $\ln 2^{3/2} = \frac{3}{2} \ln 2$, so the entropy increase $\frac{3}{2}k \ln 2$ on raising the temperature is *exactly* a measure of the increase in velocity space occupied by the gas, that is, *the increase in entropy per*

molecule is evidently Boltzmann's constant k times the logarithm of the increase in the velocity space the molecule moves in, exactly analogous to the simple volume increase for the box.

Epitaph: $S = k \ln W$



The bottom line, then, is that for the ideal gas *entropy is a logarithmic measure of how much space a system is spread over, where space is both ordinary space and velocity space*. This total space—ordinary space plus velocity space—is called “**phase space**”.

Boltzmann used W as a measure of this total phase space, so the entropy is given by

$$S = k \ln W.$$

This discovery of the molecular meaning of entropy was his greatest achievement; the formula is on his grave.

But What Are the Units for Measuring W ?

We've seen how $S = k \ln W$ relates to Clausius' thermodynamic entropy by looking at the entropy *difference* between pairs of states, differing first in volume, then in temperature. But to evaluate the entropy for a particular state we need to have a way of explicitly measuring phase space: it would appear that we could move a molecule by an infinitesimal amount and thereby have a different state. Boltzmann himself resolved these difficulties by dividing space and velocity space into little cells, and counting how many different ways N particles could be arranged among these cells, then taking the limit of cell size going to zero. This is of course not very satisfactory, but in fact the ambiguities connected with how precisely to measure the phase space are resolved in quantum mechanics, which provides a natural cell size, essentially that given by the uncertainty principle. Nernst's theorem, mentioned in the last lecture, that the entropy goes to zero at absolute zero, follows immediately, since at absolute zero any quantum system goes into its lowest energy state, a single state, the ground state: $W = 1$, so $\ln W = 0$.

Exercise: recall that an adiabat has equation $TV^{\gamma-1} = \text{constant}$. Show using the equation above that entropy remains constant: as the spatial volume increases, the velocity space volume shrinks.

A More Dynamic Picture

We've talked interchangeably about the space occupied by the gas, and the space available for one molecule to wander around in. Thinking first about the space occupied by the gas at one instant in time, we mean where the molecules are at that instant, both in the box (position space) and in velocity space. We're assuming that a single molecule will sample all of this space eventually—in air at room temperature, it collides about ten billion times per second, and each

collision is very likely a substantial velocity change. Evidently, the gas as a whole will be passing rapidly through *immense* numbers of different states: a liter of air has of order 10^{22} molecules, so the configuration will change of order 10^{33} times in each second. On a macroscopic level we will be oblivious to all this, the gas will appear to fill the box smoothly, and if we could measure the distribution in velocity space, we would find Maxwell's distribution, also smoothly filled. Over time, we might imagine the gas wanders through the whole of the phase space volume consistent with its total energy.

The entropy, then, being a logarithmic measure of all the phase space available to the molecules in the system, is a logarithmic measure of the total number of microscopic states of the system, for given macroscopic parameters, say volume and temperature. Boltzmann referred to these many different microscopic states as different “complexions”, all of them appearing the same to the (macroscopic) observer.

The Removed Partition: What Are the Chances of the Gas Going Back?

We've said that any mechanical process could run in reverse, so, really, why shouldn't the gas in the $2V$ enclosure happen to find itself at some time in the future all in the left hand half? What are the odds against that, and how does that relate to entropy?

We'll assume that as a result of the huge number of collisions taking place, the gas is equally likely to be found in any of the different complexions, or molecular configurations—another common word is *microstates*—corresponding to the macroscopic parameters, the *macrostate*. (*Note*: A further mechanism for spreading the gas out in phase space is interaction with the container, which is taken to be at the same temperature, but individual molecular bounces off the walls can exchange energy, over time the exchange will average zero.)

Thus the gas is wandering randomly through phase space, and the amount of time it spends with all the molecules in the left-hand half is equal to the corresponding fraction of the total available phase space. This isn't difficult to estimate: the velocity distribution is irrelevant, we can imagine building up the position distribution at some instant by randomly putting molecules into the container, with a 50% chance of the molecule being in the left-hand half. In fact, we could just pick a state by flipping a coin, and putting the molecule somewhere in the left-hand half if it comes up heads, somewhere on the right if it's tails, and do this N times. (Well, for small N .) Suppose as a preliminary exercise we start with 20 molecules. The chances that we get twenty heads in a row are $(1/2)^{20}$, or about 1 in 1,000,000. For 40, it's one in a trillion. For 100 molecules, it's 1 in 10^{30} .

Question: What is it for a million molecules?

But a liter of air has of order 10^{22} molecules! This is never going to happen. So the states having the gas all in the left-hand half of the box are a *very* tiny fraction of all the states available in the whole box—and the entropy is proportional to the logarithm of the number of available states, so it increases when the partition is removed.

Demon Fluctuations

Recall in the above discussion of Maxwell's demon the point was made that for two boxes with a small interconnection, assuming molecules hit the connecting hole randomly from both sides, the energy flow will in fact fluctuate—and clearly so will the number of molecules in one half.

Obviously, then, with our volume $2V$, with free access from the left hand half to the right-hand half, the number of molecules in the left-hand half will be constantly fluctuating. The question is: how much? What percentage deviation from exactly 50% of the molecules can we expect to find to the left if we suddenly reinsert the partition and count the molecules?

We can construct a typical state by the coin-toss method described in the previous section, and this is equivalent to a random walk. If you start at the origin, take a step to the right for each molecule placed in the right-hand half, a step to the left for each placed to the left, how far from the origin are you when you've placed all the molecules? The details are in my [Random Walk Notes](#), and the bottom line is that for N steps the deviation is of order \sqrt{N} . For example, if the container holds 100 molecules, we can expect a ten percent or so deviation each time we reinsert the partition and count.

But what deviation in density can we expect to see in a container big enough to *see*, filled with air molecules at normal atmospheric pressure? Let's take a cube with side 1 millimeter. This contains roughly 10^{16} molecules. Therefore, the number on the left-hand side fluctuates in time by an amount of order $\sqrt{10^{16}} = 10^8$. This is a pretty large number, but *as a fraction of the total number, it's only 1 part in 10^8 !*

The probability of larger fluctuations is *incredibly* small. The probability of a deviation of m from the average value $N/2$ is (from Random Walk notes):

$$P(m) = Ce^{-\frac{2m^2}{N}}.$$

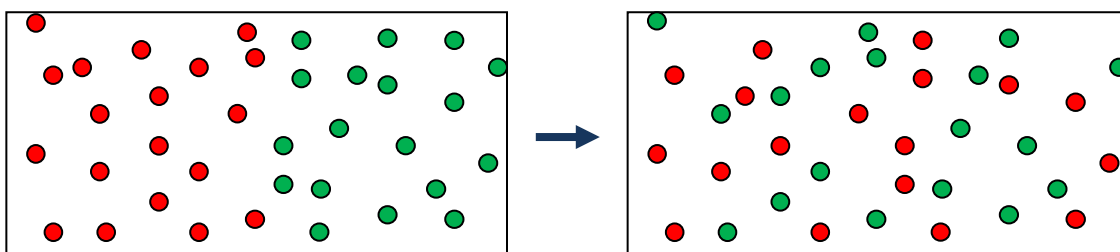
So the probability of a fluctuation of 1 part in 10,000,000, which would be $10\sqrt{N}$, is of order e^{-200} , or about 10^{-85} . Checking the gas every trillionth of a second for the age of the universe wouldn't get you close to seeing this happen. That is why, on the ordinary human scale, gases seem so smooth and continuous. The kinetic effects do not manifest themselves in observable

density or pressure fluctuations—one reason it took so long for the atomic theory to be widely accepted.

Entropy and “Disorder”

You have probably seen it stated that entropy is a measure of “disorder”. We have defined it above in terms of the amount of phase space the system is moving around in. These are not really different concepts. If we pinned a little label on the molecules, l or r depending on whether it was in the left or the right hand side of the box, the original state had all the labels l . The final state has a random selection of l 's and r 's, very close to equal in numbers.

Another way to say the same thing is to visualize an initial state before removing the partition where the left hand half has “red” molecules, the right hand side “green” molecules (we’re making up these names for visualization purposes, they could be any two gases). If the gases are ideal (or close enough) after removal of the partition both will have twice the volume available, so for each gas the entropy will increase just as for the gas expanding into a vacuum. Thinking about what the state will look like a little later, it is clear that it will be completely disordered, in the sense that the two will be thoroughly mixed, and they are not going to spontaneously separate out to the original state.



How much did the entropy increase?

Boltzmann himself commented on order versus disorder with the example of five numbers on a Lotto card. Say the ordered sequence is 1,2,3,4,5. The particular disordered sequence 4,3,1,5,2 is just as unlikely to appear in a random drawing as the ordered sequence, it’s just that there are a lot more disordered sequences. Similarly, in tossing a coin, the exact sequence H, H, T, H, T, T, T, H is no more likely to appear than a straight run of eight heads, but you’re much more likely to have a run totaling four heads and four tails than a run of eight heads, because there are many more such sequences.

Summary: Entropy, Irreversibility and the Meaning of Never

So, when a system previously restricted to a space is allowed to move into a larger space, the entropy increases in an irreversible way, irreversible meaning that the system will never return to its previous restricted configuration. *Statements like this are always to be understood as referring to systems with a large number of particles. Thermodynamics is a science about large*

numbers of particles. Irreversibility isn't true if there are only ten molecules. And, for a large number, by "never" we mean it's extremely unlikely to happen even over a *very* long period of time, for example a trillion times the age of the universe.

It's amusing to note that towards the end of the 1800's there were still many distinguished scientists who refused to believe in atoms, and one of the big reasons why they didn't was thermodynamics. The laws of thermodynamics had a simple elegance, and vast power in describing a multitude of physical and chemical processes. They were of course based on experiment, but many believed such power and simplicity hinted that the laws were exact. Yet if everything was made of atoms, and Newton's Laws applied to interactions between atoms, there was a problem. Any dynamical process will run equally well backwards in time. But we always see heat flow from a hot object to a cold object, never the reverse. How could this lack of symmetry come about in an atomic picture? Boltzmann answered this with arguments similar to those given above in the example of the gas initially confined to one half of a box, then allowed to spread out against no resistance. But this meant that ultimately the second law was a statistical statement, not an absolute truth; and, for small enough systems, it isn't true. But that's the way it is.

Everyday Examples of Irreversible Processes

Almost everything that happens in everyday life is, thermodynamically speaking, an irreversible process, and increases total entropy. Consider heat ΔQ flowing by direct thermal contact from a hot body at T_H to a cold one at T_C . The hot body loses entropy $\Delta Q/T_H$, the cold one gains entropy $\Delta Q/T_C$, so the net entropy increase as a result is $\Delta Q/T_C - \Delta Q/T_H$, a positive quantity. The heat flow in the Carnot cycle did *not* increase total entropy, since it was isothermal—the reservoir supplying the heat was at the same temperature as the gas being heated (an idealization—we do need a slight temperature difference for the heat to flow).

Friction, or an inelastic collision such as dropping a ball of clay on the floor, converts kinetic energy to heat—so there is a nonzero ΔQ of heat entering some body, entropy is being generated. Since heat involves random motions of the particles involved, this is sometimes stated as a transformation of ordered energy (a falling ball, with the molecules all moving in the same direction) into disordered motion. Yet another phrasing is that potentially useful energy is being degraded into less useful energy: the falling ball's kinetic energy could have been utilized in principle by having it caught by a lever arm which could then do work. The slight heat in the floor is far less useful energy, some of it could theoretically be used by a heat engine but the temperature difference to the rest of the floor will be very small, so the engine will be very inefficient!

Molecular Collisions

Difficulties Getting the Kinetic Theory Moving

Oddly, the first published calculation of the average speed of a molecule in the kinetic theory of gases appeared in the *Railway Magazine*, of all places, in 1836. Why there? Well, the calculation was by John Herapath—he owned the magazine. He was definitely not part of the scientific establishment: a previous paper of his on the kinetic theory had been rejected by the Royal Society. But the calculation of molecular speed was in fact correct. Another outsider, John James Waterston, submitted an excellent paper on the kinetic theory to the Royal Society in 1846, to have it rejected as “nonsense”. This was evidently still the age of the caloric theory, at least in the Royal Society. In 1848, Joule (who had worked with Herapath, and was also something of an outsider) presented a paper at a meeting of British Association where he announced that of the speed of hydrogen molecules at 60F was about 1 mile per second, close to correct. Again, though, this did not excite wide interest...

Finally, in 1857, a pillar of the scientific establishment—Clausius—wrote a paper on the kinetic theory, repeating once more the calculation of average molecular speed (around 460 meters per second for room temperature oxygen molecules). He mentioned the earlier work by Joule, and some more recent similar calculations by Krönig. Suddenly people sat up and took notice! If a highly respected German professor was willing to entertain the possibility that the air molecules in front of our faces were mostly traveling faster than the speed of sound, perhaps there was something to it...

How Fast Are Smelly Molecules?

But there were obvious objections to this vision of fast molecules zipping by. As a Dutch meteorologist, C. H. D. Buys-Ballot, wrote: [if the molecules are traveling so fast] how does it then happen that tobacco-smoke, in rooms, remains so long extended in immovable layers?” (Nostalgia trip for smokers!) He also wondered why, if someone opens a bottle of something really smelly, like ammonia, you don’t smell it across the room in a split second, if the molecules are moving so fast. And, why do gases take ages to intermingle?

These were very good questions, and forced Clausius to think about the theory a bit more deeply. Buys-Ballot had a point: at that speed, the smelly NH_3 's really would fill a whole room in moments. So what was stopping them? The speed of the molecules follows *directly* from measuring the pressure and density—you don’t need to know the size of molecules. If the kinetic theory is right at all, this speed has to be correct. Assuming, then, the speed *is* more or less correct, the molecules are evidently not going in straight lines for long. They must be bouncing off the other molecules. Still, the standard kinetic theory pressure calculation assumed each molecule to be bouncing from wall to wall inside the box, collisions with the other molecules had always been ignored, because the molecules were so tiny. Evidently, though, they weren’t.

The Mean Free Path

Clausius concluded that the molecules must be big enough to get in each other's way to some extent. He assumed the average speed calculation was still about right, and that the molecules only interacted when they were really close. So, watching one molecule, most of the time it's going in a straight line, not influenced by the other molecules, then it gets close to another one and bounces off in a different direction. He termed the average distance between collisions the **mean free path**.

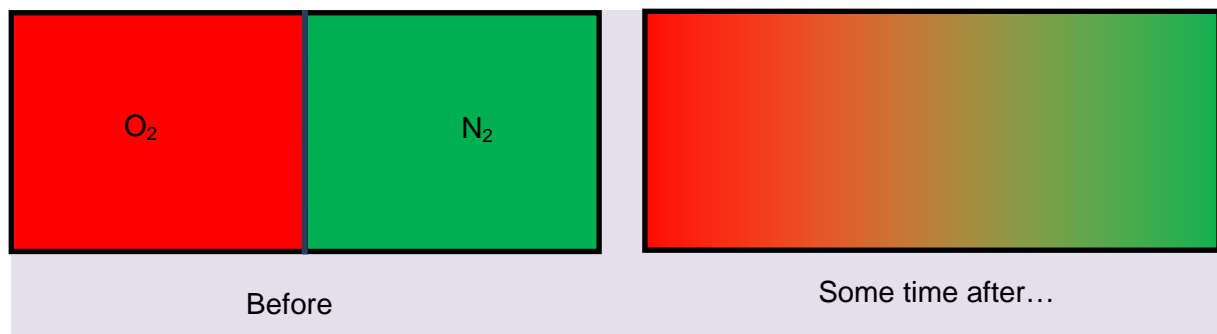
But how could this be reconciled with the pressure calculation, the pressure from a single molecule being found by counting the times per second it bounced off a given wall? Evidently each molecule will now take a lot longer to get across the container—will that lower the pressure? The answer is no: although molecules now take a long time to do the round trip, they don't have to—a molecule bouncing off the wall can hit another nearby molecule and go straight back to the wall. The pressure on a wall depends on the *density of molecules close to the wall* (less than a mean free path away), and their velocity distribution. This won't be too different from the no-collisions case.

Gas Viscosity Doesn't Depend on Density!

This fixed up the theory in the sense of answering Buys-Ballot's objections, but it turned out to do much more. Maxwell took the concept of mean free path, and used it to prove *the viscosity of a gas should be independent of density* over a very wide range. (Viscosity arises when fast molecules move into a slower stream: halving the density halves the number of fast molecules getting over, but they get twice as far, so penetrate into even slower streams. For a much more detailed explanation, see my [lecture on viscosity](#).) Maxwell was startled (his word: *Phil. Mag*, Jan Jun 1860, p 391) by this result, and thought it probably spelled doom for the kinetic theory, because it contradicted experimental findings. But the experiments, it turned out, were not very good, and had found the (wrong) answer they expected. Maxwell did the experiments more carefully himself, and found agreement with the kinetic theory—the viscosity really *didn't* depend on density! Usually in physics good experiments knock down bad theories—this time it was the other way round.

Gas Diffusion: the Pinball Scenario; Finding the Mean Free Path in Terms of the Molecular Diameter

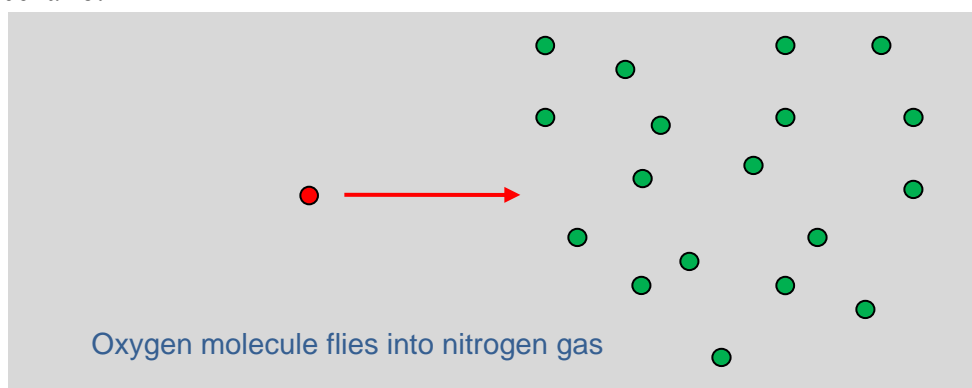
How does the mean free path picture handle mutual diffusion of two gases, say oxygen and nitrogen, when a partition initially separating them is removed?



For a box holding a few liters, it takes of the order an hour or so for the gases to mix. (We're assuming the temperature is kept constant so that convection currents don't arise—such currents would reduce the time substantially.) Obviously, the rate of mixing must depend on the mean free path: if it was centimeters, the mixing would be pretty complete in milliseconds. In fact, as we shall see, the mean free path can be deduced from the measured rate of penetration of one gas by the other.

First, though, we'll show how to derive the mean free path in units of the diameter of the molecules, taking O_2 and N_2 to be spheres of diameter d . (You're used to seeing them pictured like dumbbells and that's true of the two nuclei, but the surrounding electron cloud is in fact close to spherical.)

Think of one of the oxygen molecules moving into nitrogen. So now visualize the little O_2 sphere shooting into this space where all these other spheres are moving around. *Temporarily, for ease of visualization, let's imagine all the other spheres to be at rest.* This is a pinball machine scenario:



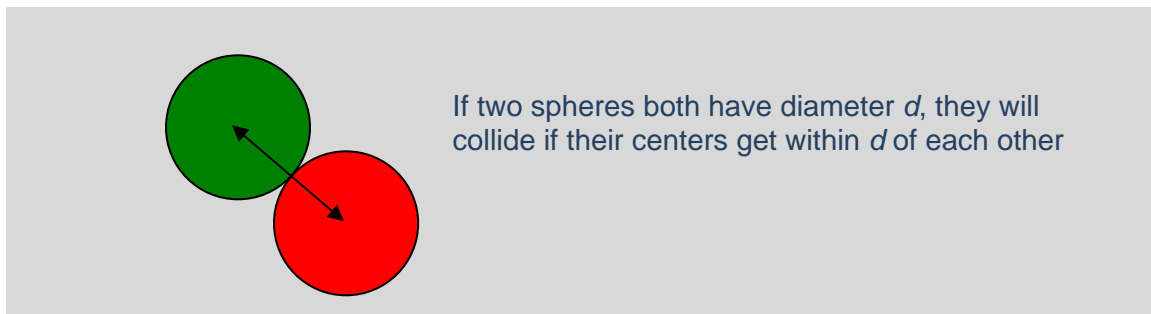
How far can we expect the O_2 to get before it hits an N_2 ? The *average* distance before a collision is the mean free path. Let's try to picture how much room there is to fly between these fixed N_2 spheres. (Bear in mind that the picture above should be three-dimensional!) We do know that if it were *liquid* nitrogen, there would be *very little* room: liquids are just about incompressible, so the molecules must be touching. Roughly speaking, a molecule of diameter d will occupy a

cubical volume of about d^3 (there has to be some space left over—we can pack cubes to fill space, but not spheres.)

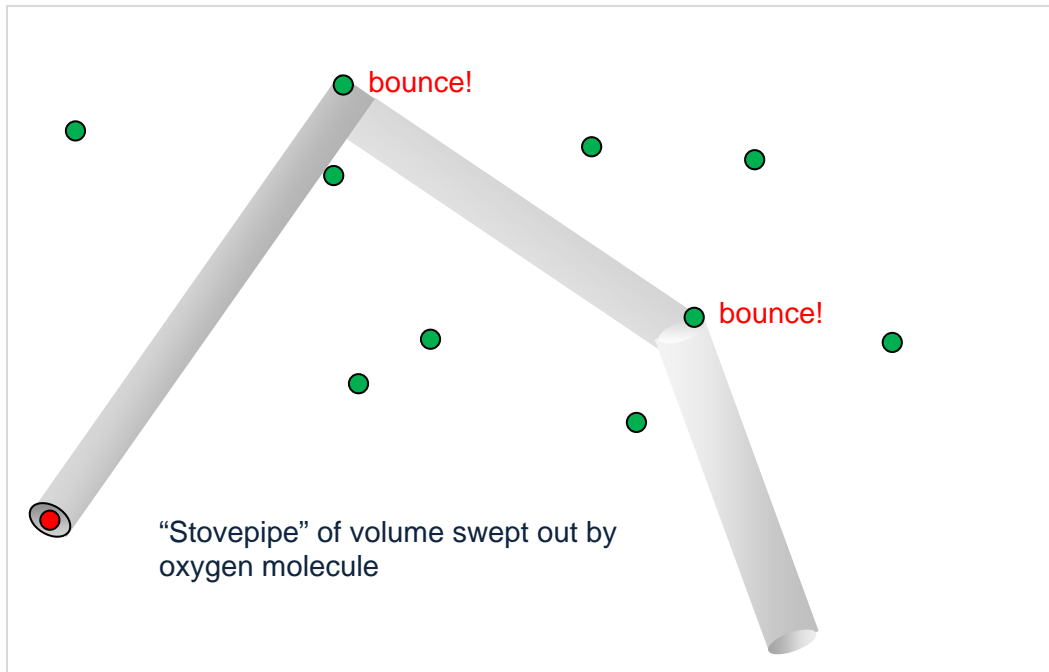
We also know that liquid nitrogen weighs about 800 kg per cubic meter, whereas N_2 gas at room temperature (and pressure) weighs about 1.2 kg per cubic meter, a ratio of 670. This means that *on average each molecule in the gas has 670 times more room*—that is, it has a space 670 times the volume d^3 we gave it in the liquid. So in the gas, the average center-to-center separation of the molecules will be the cube root of 670, which is about $8.75d$. So the picture is a gas of spheres of diameter d , placed at random, but separated on average by distances of order $10d$. It's clear that shooting an oxygen molecule into this it will get quite a way. Let us emphasize again that this picture is independent of the actual *size* of d : we're only considering the *ratio* of mean free path to molecular diameter.

We now estimate just how far an O_2 will get, on average, as it shoots into this forest of spheres. Picture the motion of the center of the oxygen molecule. Before any collision, it will be moving on a straight-line path. Just how close does the O_2 center have to get to an N_2 center for a hit? Taking both O_2 , N_2 to be spheres of diameter d , if an N_2 center lies within d of the O_2 center's path, there will be a hit.

Note: this picture is simplified in that we're taking the molecules to be hard spheres. This is not a bad approximation, but the repulsive potential does not fall quite that suddenly, and consequently the effective scattering size varies somewhat with speed, i.e. with temperature. This turns out to be important in finding the temperature dependence of viscosity, for example.



So we can think of the O_2 as sweeping out a volume, a cylinder of *radius* d centered on its path, hitting and deflecting if it encounters an N_2 *centered within that cylinder*. So how far will it get, on average, before a hit? In traveling a distance x , it sweeps out a volume $\pi d^2 x$. Now picture it going through the gas for some considerable length of time, so there are many collisions. The volume swept out will look like a stovepipe, long straight cylindrical sections connected by elbows at the collisions. The total volume of this stovepipe (ignoring tiny corrections from the elbows) will be just $\pi d^2 L$, L being the total length, that is, the total distance the molecule traveled.



If the density of the nitrogen is n molecules per cubic meter, the number of N_2 's in this stovepipe volume will be $\pi d^2 L n$, in other words, this will be the number of collisions. Therefore, the average distance *between* collisions, the mean free path l , is given by:

$$\text{mean free path } l = \frac{\text{total distance traveled}}{\text{number of collisions}} = \frac{L}{\pi d^2 L n} = \frac{1}{\pi d^2 n}$$

So what is n ? We estimated above that each molecule has space $670d^3$ to itself, so n is just how many of those volumes there are in one cubic meter, that is, $n = 1/670d^3$.

Therefore, the mean free path is given by

$$l = \frac{1}{\pi d^2 n} = \frac{670d^3}{\pi d^2} \approx 200d.$$

(We can see from this that the average length of stovepipe sections between elbows is 200 times the pipe radius, so neglecting any volume corrections from the elbows was an excellent approximation, and our diagram has the sections far too short compared with the diameter.)

Notice that this derivation of the mean free path *in terms of the molecular diameter* depends *only* on knowing the *ratio of the gas density to the liquid density*—it does *not* depend on the *actual size of the molecules*!

But it *does* mean that if we can somehow measure the mean free path, by measuring how fast one gas diffuses into another, for example, we can deduce the size of the molecules, and historically this was one of the first ways the size of molecules was determined, and so Avogadro's number was found.

But the Pinball Picture is Too Simple: the Target Molecules Are Moving!

There is one further correction we should make. We took the N_2 molecules to be at rest, whereas in fact they're moving as fast as the oxygen molecule, approximately. This means that even if the O_2 is temporarily at rest, it can undergo a collision as an N_2 comes towards it. Clearly, what really counts in the collision rate is the *relative* velocity of the molecules.

Defining the average velocity as the root mean square velocity, if the O_2 has velocity \vec{v}_1 and the N_2 \vec{v}_2 , then the square of the relative velocity

$$\overline{(\vec{v}_1 - \vec{v}_2)^2} = \overline{v_1^2} - 2\overline{\vec{v}_1 \cdot \vec{v}_2} + \overline{v_2^2} = \overline{v_1^2} + \overline{v_2^2},$$

since $\overline{\vec{v}_1 \cdot \vec{v}_2}$ must average to zero, the relative directions being random. So the average *square* of the relative velocity is twice the average square of the velocity, and therefore the average root-mean-square velocity is up by a factor $\sqrt{2}$, and the collision rate is increased by this factor. Consequently, the mean free path is *decreased* by a factor of $\sqrt{2}$ when we take into account that *all* the molecules are moving.

Our final result, then, is that the mean free path

$$l = \frac{1}{\sqrt{2}\pi d^2 n}.$$

Finding the mean free path is—literally—the first step in figuring out how rapidly the oxygen atoms will diffuse into the nitrogen gas, and of course vice versa.

If Gases Intermingle 0.5cm in One Second, How Far in One Hour?

What we really want to know is just how much we can expect the gases to have intermingled after a given period of time. We'll just follow the one molecule, and estimate how far it gets. To begin with, let's assume for simplicity that it takes steps all of the same length l , but after each collision it bounces off in a random direction. So after N steps, it will have moved to a point

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots + \vec{l}_N,$$

where each vector \vec{l}_j has length l , but the vectors all point in random different directions.

If we now imagine many of the oxygen molecules following random paths like this, how far on average can we expect them to have drifted after N steps? (Note that they could with equal likelihood be going backwards!) The appropriate measure is the root-mean-square distance,

$$\overline{L^2} = \overline{(\vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots + \vec{l}_N)^2} = Nl^2 + \sum_{i,j} \overline{\vec{l}_i \cdot \vec{l}_j}$$

Since the direction after each collision is completely random, $\overline{\vec{l}_i \cdot \vec{l}_j} = 0$, and the root-mean-square distance

$$\sqrt{\overline{L^2}} = \sqrt{N} l.$$

If we allow steps of different lengths, the same argument works, but now l is the root-mean-square path length. *The important factor here is the \sqrt{N} .*

This means that the average distance diffused in one second is $\sqrt{10^{10}} l = 10^5 l$, say half a centimeter (justified in the next section). The average distance in one *hour* would be *only* 60 times this, or 30 cm., and in a day about a meter and a half—the average distance traveled is only increasing as the *square root* of the time elapsed!

This is a very general result. For example, suppose we have a gas in which the mean free path is l and the average speed of the molecules is v . Then the average time between collisions $\tau = l/v$. The number of collisions in time t will be t/τ , so the average distance a molecule moves in time t will be $r = l\sqrt{t/\tau}$.

Actually Measuring Mean Free Paths

It should be clear from the above that by carefully observing how quickly one gas diffuses into another, the mean free path could be estimated. Obviously, oxygen and nitrogen are not the best candidates: to see what's going on, a highly visible gas like bromine diffusing into air would be more practical. However, there's a better way to find the mean free path. As we proved in the [lecture on viscosity](#), the viscosity coefficient $\eta = \frac{1}{3}nmvl$, where n is the number density, m the molecular mass, v the average speed and l the mean free path. The viscosity can be measured quite accurately, the mean free path in air was found to be $l \approx 60 \text{ nm}$, or $6 \times 10^{-8} \text{ m}$.

In 1865, Josef Loschmidt gave the first good estimate of the size of molecules. He used the viscosity data to find the mean free path, assumed as we did above that the molecules were more or less touching each other in the liquid, then used the geometric argument above to nail down the ratio of molecular size to mean free path. He overestimated by a factor of three or so, but this was much closer to the truth than anyone else at the time.

Here are some numbers: for O_2 , N_2 , $d \approx 0.3 \text{ nm}$, $l \approx 60 \text{ nm}$, the speed of the molecules at room temperature v is approximately 500 meters per sec., so the molecule has of order 10^{10} collisions per second.

Why did Newton get the Speed of Sound Wrong?

A famous mystery cleared up by arguments like this was that Newton predicted the speed of sound would be given by $c^2 = B / \rho$, as we discussed earlier in the course, with B the bulk modulus. But when B was measured carefully by slowly compressing air, the result was in error by about 30%! The speed of sound predicted a higher (stiffer) bulk modulus.

The explanation turned out to be that in a slow measurement of the bulk modulus, the gas stays at the same temperature—the heating caused by slow compression leaks away. But if the compression is rapid, the gas heats up and so the pressure goes up more than if it had stayed at the same temperature. So the question is whether the compression and decompression as a sound wave passes through is so rapid that the heated-up gas doesn't have time to spread to the cooled regions. For sound at say 1000Hz, the wavelength is 34 cm. If compression heats gas locally, the hot molecules will diffuse away in a similar manner to that discussed above. They will be slightly faster than the average molecules. In 1/1000 th of a second, they will have 10^7 collisions, so will travel about $\sqrt{10^7} l \times 3000l \times 0.2 \text{ mm}$. This tiny distance compared with the wavelength of the sound wave means that during the compression/decompression cycles as the wave passes through, the heat has no chance to dissipate—so, effectively, it's like compressing a gas in an insulated container, it's harder to compress than it would be if the heat generated could flow away, and the bulk modulus is higher by an amount (around 30%) we shall work out in a forthcoming lecture.

Brownian Motion

See Applet [here!](#)

Introduction: Jiggling Pollen Granules

In 1827 Robert Brown, a well-known botanist, was studying sexual relations of plants, and in particular was interested in the particles contained in grains of pollen. He began with a plant (*Clarcia pulchella*) in which he found the pollen grains were filled with oblong granules about 5 microns long. He noticed that these granules were in constant motion, and satisfied himself that this motion was not caused by currents in the fluid or evaporation. Smaller spherical grains,

which at first he took to be oblongs end-on, but later realized weren't, had even more vigorous motion. He thought at first that he was looking at the plant equivalent of sperm—they were jiggling around because they were alive. To check this, he did the same experiment with dead plants. There was just as much jiggling. Perhaps all organic matter, everything that ever was alive, still contained some mysterious life force at this microscopic level? Sure enough, he found the movement in tiny fragments of fossilized wood! But then he went on to find it in matter that never was alive—tiny particles of window glass, and even dust from a stone that had been part of the Sphinx. The movement evidently had nothing to do with the substance ever being alive or dead, much to Brown's surprise. So what was causing it? Perhaps it *was* evaporation currents, or the incident light energy, or just tiny unnoticed vibrations. But none of these explanations was very satisfactory.

Half a century later, a new possible explanation emerged. The kinetic theory of heat developed by Maxwell, Boltzmann and others was gaining credence. If all the molecules in the fluid were indeed in vigorous motion, maybe these tiny granules were being moved around by this constant battering from all sides as the fluid molecules bounced off. But there was a problem with this explanation: didn't it violate the second law of thermodynamics? It had been well established that energy always degrades, as friction slows movement kinetic energy goes to heat energy. This seemed to be the other way round—the molecular battering was certainly disorganized heat energy, but when the granule moved it had evidently gained kinetic energy. Since many scientists regarded the second law as an absolute truth, they were very skeptical of this explanation.

In 1888, French experimentalist Léon Guoy investigated the movement in detail, finding it to be more lively in low viscosity liquids. He established that it was unaffected by intense illumination or by strong electromagnetic fields. Despite the second law, Guoy believed—correctly—the random motion was indeed generated by thermal molecular collisions.

It's easy to see the Brownian movement, or Brownian motion (it's called both) by looking through a microscope at tobacco smoke in air. We have a movie [here](#).

Einstein's Theory: the Osmosis Analogy

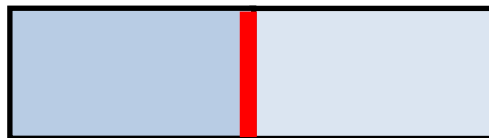
In 1905, Einstein published a theoretical analysis of Brownian motion. He saw it as a crucial test of the kinetic theory, even of the atomic/molecular nature of matter. Previous discussions of the phenomenon had all been qualitative—Einstein demonstrated that careful observation of Brownian motion could reveal the actual size of molecules, that is, find Avogadro's number.

If the results of such experiments were consistent with other estimates of Avogadro's number, based on unrelated phenomena such as gas viscosity measurements and van der Waal's equation fit to isotherms of real gases, it would be a powerful argument for the kinetic theory. On the other hand, if there was real disagreement then the kinetic theory was in serious trouble.

Einstein's approach was based on an analogy with osmosis: recall that osmosis involves one substance (the solute) dissolved in another, the solvent. The solute has larger molecules. Now imagine a container divided in two by a semipermeable membrane, meaning the solvent molecules can pass through the tiny holes in it, but the solute molecules are too big to get through. Suppose on one side of the membrane there's pure solvent, on the other side solvent plus solute (assumed fairly dilute), and initially the pressure on the two sides of the membrane is the same. The pressure on the side with solute is generated by both solvent and solute molecules bouncing off the membrane, so necessarily the rate at which *solvent* molecules are hitting the membrane on this side is less than on the other side. Some percentage of the solvent molecules hitting the membrane pass through the little holes, so what will happen is that more will pass through from the pure solvent side, and gradually pressure will build up on the solvent + solute side until equilibrium is reached, meaning equal numbers of solvent molecules going each way on average.

Einstein's insight was that a liquid containing a large number of tiny identical particles, such as those observed in Brownian motion, was really no different from a solvent containing solute molecules. True, the Brownian particles were a lot bigger than molecules, but they were buzzing around, and would therefore bounce off the walls of a container, generating pressure. The formal analysis should be the same: the kinetic theory, with equipartition of energy, predicted they would have kinetic energy $1.5k_B T$. If the concentration of particles varied spatially, they would flow to even it out.

Here again he used an osmosis analogy: think of a cylindrical container, with a semipermeable membrane which is like a piston, free to move. The solute concentration is initially greater to the left of the piston.



Semipermeable membrane piston free to move
Color represents solute concentration

From the previous discussion, it's clear that the solvent will flow to the left, raising the pressure there, so the piston will move to the right. The solute molecules cannot cross the piston, so the piston will move until the solute concentrations on the two sides are equal.

The rather surprising result is that if one assumes equipartition of energy, *the pressure on the piston from the solute on one side is the same as if those solute molecules were freely moving in a vacuum.*

Their greatly reduced mean free path *doesn't matter*: the pressure depends only on the concentration in the immediate neighborhood of the piston, and the speed of the molecules. And, this is equally true if the solute molecules are replaced by tiny but macroscopic spheres. At least, this is what Einstein asserted, and he gave a formal proof based on an evaluation of the free energy, assuming a dilute system (meaning interactions between the spherical granules could be neglected).

So we can think of the little spheres as *moving freely through space* (!), and although their paths will actually be very different, calculations of local pressure based on this should be correct: the pressure on the walls from the granules is therefore given by the ideal gas law, that is,

$$P = \frac{1}{3} mn\overline{v^2} = \frac{2}{3} n\overline{\frac{1}{2}mv^2} = \frac{2}{3} n\overline{K.E.} = \frac{2}{3} nW$$

where the average kinetic energy is written W , and—if the kinetic theory is correct—this should equal $1.5k_B T$.

An Atmosphere of Yellow Spheres

So how is this to be checked experimentally? As we shall see in a moment, the first experiment used uniformly sized tiny *spheres* in place of granules. The first obvious thought is that if $\overline{\frac{1}{2}mv^2}$ is predicted to be $1.5k_B T$, perhaps one can measure the jiggling velocity of the tiny sphere a few times and take an average. This, however, misunderstands the nature of the motion: a molecule will bounce off the sphere around 10^{20} times per second, and although that only makes a tiny difference to the sphere's velocity, in one hundredth of a second the average imbalance, \sqrt{N} , will be of order 10^9 , enough to make a change in a small sphere's velocity. And all the successive changes are completely random in direction, so it's as hopeless as attempting to measure the velocity of H_2S molecules in air by releasing a few and measuring the time for the smell to reach the far end of a room.

A slightly less direct method of finding $\overline{\frac{1}{2}mv^2}$ is needed. Now, it is well-known that in an isothermal atmosphere of an ideal gas under gravity the density falls off exponentially with height, this is established by balancing the gravitational force on a thin horizontal slice against the pressure difference between top and bottom. It occurred to the French experimentalist Jean Perrin that this same argument should apply to a "gas" of tiny uniform spheres in a fluid: their pressure is generated by the Brownian motion. In 1908, he chose gamboge, an emulsion used for water color, which contains bright yellow spheres of various sizes. By various ingenious tricks described in his book he was able to separate out spheres all close to the same size. He was able

to measure the size, he knew the density—and that of the “solvent”—so he could compute the gravitational pull. He could also measure the decrease in density with height in isothermal equilibrium.

The calculation is as follows: for a horizontal slice of thickness dh , with n spheres per unit volume, each of volume φ and density Δ , in a liquid of density δ (I’m using Perrin’s notation here), the gravitational downward force on the slice is $ndh\varphi(\Delta - \delta)$, this is balanced by the pressure difference:

$$-\frac{2}{3}Wdn = ndh\varphi(\Delta - \delta).$$

This is easily integrated to give the exponential vertical density profile.

$$\frac{dn}{dh} = -\frac{n\varphi(\Delta - \delta)}{\frac{2}{3}W}, \quad n(h) = n(0)\exp\left(-\frac{\varphi(\Delta - \delta)}{\frac{2}{3}W}h\right).$$

Perrin could establish by observation and measurement every term in this equation except W , so this was a way of measuring W , assuming of course the validity of the kinetic theory.

Now equating W to $1.5k_B T$ gives a value for Boltzmann’s constant, and hence via the known gas constant $R = N_A k_B$, a value for Avogadro’s number.

Perrin repeated the experiment with a wide variety of different substances, the experiments were very challenging, his results for Avogadro’s number were consistently between 5×10^{23} and 8×10^{23} . He remarked that for the largest granules behaving like a perfect gas, *a gram molecule would weigh 200,000 tons!* The results were consistent with the other quite different ways of finding Avogadro’s number, and these experiments convinced even the most recalcitrant anti-atomic theory skeptics. The kinetic theory was fully established.

Langevin’s Theory

In 1908, Langevin gave a more direct treatment of Brownian motion. He focused on following one particle as it jiggled around. We’ll follow him in restricting the motion to one dimension—assuming the molecular collisions driving the motion are completely random, the motions in the three directions are uncorrelated, so can be treated separately and added. Finally, we’ll neglect gravity and any other external force fields.

Let’s assume, then, that we’re tracking a small spherical object, of mass m and radius a . It will experience a viscous drag force $-6\pi a\eta v$ (Stokes’ formula). We’ll denote the random thermal molecular collision force by X , which clearly averages to zero.

Assuming the equipartition of energy applies also to the kinetic energy of our sphere,

$$\overline{m \left(\frac{dx}{dt} \right)^2} = k_B T$$

where the average is over a long time.

The equation of motion $ma = F$ is:

$$m \frac{d^2 x}{dt^2} = -6\pi a \eta \frac{dx}{dt} + X.$$

Multiplying throughout by x ,

$$mx \frac{d^2 x}{dt^2} = -6\pi a \eta x \frac{dx}{dt} + Xx$$

which can be written

$$m \frac{d}{dt} \left(x \frac{dx}{dt} \right) - m \left(\frac{dx}{dt} \right)^2 = -3\pi a \eta \frac{d}{dt} x^2 + Xx.$$

Now we'll average over a long time:

$$\overline{m \frac{d}{dt} \left(x \frac{dx}{dt} \right) - m \left(\frac{dx}{dt} \right)^2} = -3\pi a \eta \overline{\frac{d}{dt} x^2} + \overline{Xx}.$$

Since X is random, $\overline{Xx} = 0$. Also, $\overline{m \left(\frac{dx}{dt} \right)^2} = k_B T$. The operations of averaging and taking the time derivative commute, so we can write the equation:

$$\frac{m}{2} \frac{d^2}{dt^2} \overline{x^2} + 3\pi a \eta \frac{d}{dt} \overline{x^2} = k_B T.$$

To solve this differential equation, write $\frac{d}{dt} \overline{x^2} = y$.

The equation becomes:

$$\frac{dy}{dt} + \frac{6\pi a \eta}{m} y = \frac{2k_B T}{m}$$

The solution is

$$y(t) = \frac{k_B T}{3\pi a \eta} + C \exp\left(-\frac{6\pi a \eta}{m} t\right).$$

For the actual systems examined experimentally, the exponential term dies off in far less than a microsecond, so for a particle beginning at the origin:

$$\frac{d}{dt} \overline{x^2}(t) = y(t) = \frac{k_B T}{3\pi a \eta},$$

so

$$\overline{x^2}(t) = \frac{k_B T}{3\pi a \eta} t$$

Hence by doing multiple experiments and averaging, Boltzmann's constant k_B can be found, and from that Avogadro's number, as before.

Note that the constancy of $(d/dt)\overline{x^2}(t)$ also appears in discussions of random molecular motion and the random path—this is all the same thing.

Exercises:

1. Estimate the decay time of the exponential term in the integrated expression for $y(t)$ above. You'll need to find the viscosity of water, and estimate the sphere size as a few microns.
2. Estimate how rapidly density of yellow spheres drops with height in Perrin's "atmosphere".
3. Notice the average distance traveled in the last equation above depends on the kinetic energy, the size, and the viscosity. This means a tiny lead sphere would diffuse the same distance, on average, as a tiny sphere of oil of the same size. But isn't the lead moving a lot more slowly, since it has the same average kinetic energy? Explain.

References

For Brown's work, see *A Source Book in Physics*, W. F. Magie, Harvard, 1963, page 251, where several pages from the original pamphlet are reproduced.

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Heat Transport: Conduction, Convection, Radiation

Conduction

If different parts of an isolated solid are at different temperatures, heat will flow from the hot places to the cold ones until eventually all is at the same temperature. By “isolated” here we mean that the solid is not able to exchange heat with the outside world.

Experimentally, it is found that for most substances the rate of heat flow at any point is proportional to the temperature gradient—how fast the temperature is changing with position. To give an example, consider heat flowing down a thin rod, heated at one end, and assume the rod is wrapped in insulation so all the heat flows *down* the rod, none escapes from the surface. The natural unit of heat flow down the rod is how many joules per second pass a fixed point in the rod. It is found that:

$$\frac{dQ}{dt} \propto \frac{dT}{dx}$$

where Q is in joules, T in degrees Kelvin, x is meters down the rod. The heat flow rate is then in joules per second, or watts. It is evident from this equation that if heat is supplied at a steady rate to one end of the rod, and drains from the other end, the temperature distribution will ultimately settle down to $dT/dx = \text{constant}$, a linear drop along the rod from one end to the other.

It is also found experimentally that a rod of double the cross-section carries twice the heat current at the same temperature difference. (This is also true for electric current, but remember it is not true for water in a pipe—the “caloric” fluid evidently doesn’t act like a viscous liquid.)

This makes it possible to define a *coefficient of thermal conductivity* κ for a particular material by

$$\frac{dQ}{dt} = \kappa A \frac{dT}{dx}$$

for heat flow across an area A (in square meters) for a given temperature gradient dT/dx .

The units of κ are watts/K·meters. Some values: copper 390, stainless steel 13, glass around 0.8, white pine 0.11, air 0.026.

Microscopic Picture of Conduction

When a solid is warmed, the atoms jiggle around more—the heat energy is partially their kinetic energy of motion, partly the extra energy stores in the springy bonds between them as a result of their motion. If one end of a solid is heated, the more vigorously moving atoms there bounce against their neighbors, which then begin to move more vigorously, and the motion diffuses

down the line. Obviously, this cannot be the whole story, because if we hit one end of the rod, a sound wave travels down by neighbor hitting neighbor, and moves far faster than heat. A more accurate picture (for a nonmetal) is that when one end is heated, tiny sound waves (called phonons) are generated by the fast moving atoms near the surface. These phonons travel into the solid at the speed of sound, but, unlike the massive compression wave when the end of the rod is hit, these phonons bounce off impurities or imperfections in the solid and follow random paths, only a few tens of atomic spaces between hits, typically. This, then, is very like the diffusion of a molecule in a gas we studied earlier, and it takes several minutes for heat to make its way through, say, half a centimeter of glass. The picture is different for metals: the electrons which conduct electricity so efficiently do the same for heat. However, heat transport by electrons cannot be understood without quantum mechanics: Pauli's Exclusion Principle means only about 1% of the electrons take part in the heat conduction, but it also means that they travel far faster. The thing to remember at this stage is that the electrons carry the heat, phonons do too, but make a negligible contribution. As you might expect, good conductors of electricity are also good conductors of heat. This is why copper is used in saucepans (also, it doesn't corrode too badly).

Conductivity in liquids and gases can be measured—but usually heat transport in fluids is dominated by convection, see below. Exceptions are, for example, a fluid heated from above, or a pond below 4 degrees Celsius being cooled from above on a winter night.

American Units

In the real world out there, the units are different. Heat flow (in construction jobs, for example) is measured in BTU's per hour, temperature gradients in degrees Fahrenheit per inch thickness and cross-section area in square feet! The R -value of "thermal resistance" is the inverse of the thermal conductivity. For one square foot of material, one inch thick, R relates the heat current to the temperature drop by an Ohm's Law equation $\Delta T = IR$. Different areas and thicknesses scale in the obvious way. For a wall made of layers of different materials, the R -values just add.

Convection

Convection is gravitationally-induced heat transport, driven by the expansion of a fluid on heating. The hot expanded fluid has lower density, so will rise to the top of colder, and therefore denser, fluid. The simplest example is water in a kettle heated from below: hot water will rise in a central column, spread through the top layer, cooling, then flow back down around the outside. The pattern becomes more complicated if a fluid is being heated over a large area, with no obvious center. Convection cells can arise, each having a pattern like that in the kettle, the cells in a hexagonal pattern. This can happen in weather: a storm can be such a cell. However, many patterns are possible: the fluid mechanics is extremely complex. One important example of convection currents is inside the earth. Such currents deep inside are believed drive the surface movement of plates, causing earthquakes, tsunamis, etc.

Radiation

Heat from the sun reaches us as radiation, much of it visible light, the rest similar electromagnetic waves but at wavelengths our eyes are not sensitive to. All bodies not at absolute zero temperature radiate, at room temperature the radiation is in the infrared, wavelengths longer than those of the visible spectrum. Microscopically, the radiation comes about because the oscillating ions and electrons in a warm solid are accelerating electric charges, and as you will find next semester, such charges radiate. Different substances radiate with different efficiencies, those that radiate better also absorb incoming radiation better. A perfect absorber is called a black body (such perfection is not found in nature, but some things are close). This, then, is also a perfect radiator. It was found experimentally that for a perfect black body at an even temperature, the radiant energy output in watts per square meter of surface went as the fourth power of the absolute temperature:

$$P = \sigma T^4$$

P being power per square meter, σ is Stefan's constant, 5.67×10^{-8} Watts/sq.m./K⁴.

For a given T , the radiant power peaks at a certain wavelength, $\lambda_{\max} T = \text{constant}$. This was well established: on heating a piece of metal, say, such as turning a dimmer on an ordinary light bulb, the first visible radiation is in the red, and an extremely hot object becomes white or even bluish. However, this was theoretically incomprehensible without quantum mechanics, and in fact the mystery of black body radiation led Planck to the first formulation of the idea of the quantum.

I have a detailed discussion of black body radiation [here](#).

Exercises:

1. Estimate the sun's surface temperature knowing the heat received here is about one kilowatt per square meter.
2. Estimate the rate of heat loss from a naked body at skin temperature 33 degrees C in a room with walls at 20 degrees C. (It would be zero for a body at 20 degrees!)