previous index next

Heat

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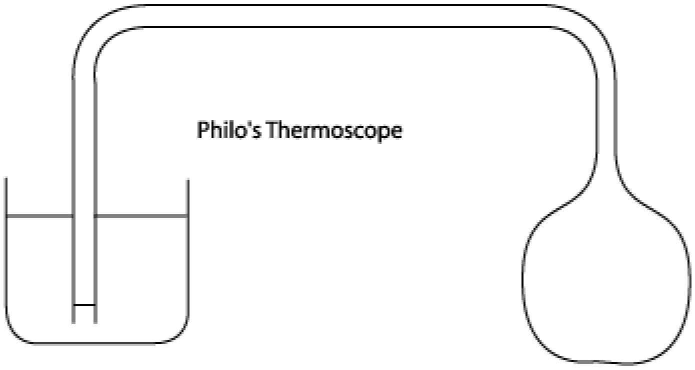
Feeling and seeing temperature changes

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 …"

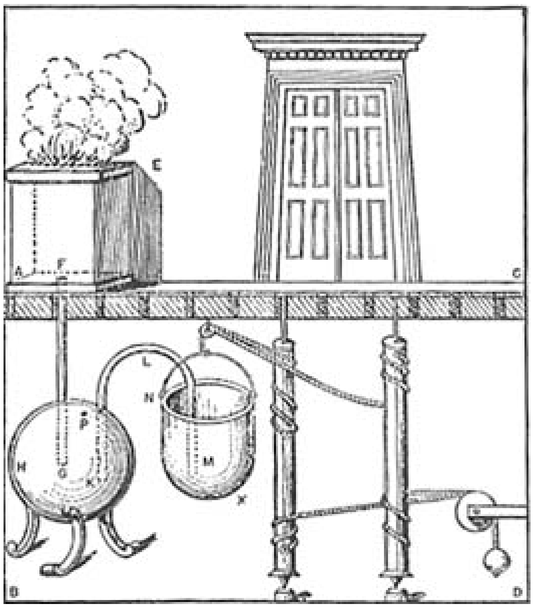
"*No matter how many times you repeat the operation, the same thing will happen.*

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.

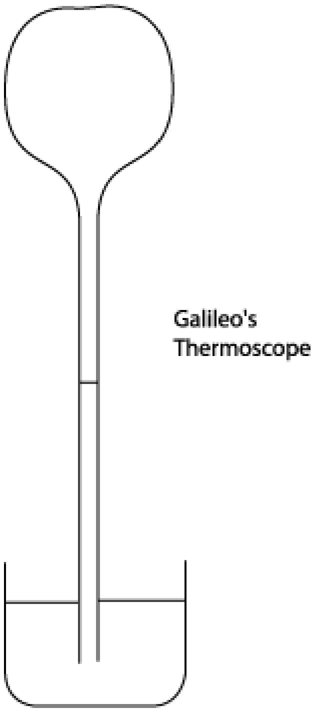


The altar is a large airtight box, with a pipe leading from it to another enclosed container filled with water. When the fire is set on top of the altar, the air in the box heats up and expands into a second container which is filled with water. This water is forced out through an overflow pipe into 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.

Torricelli, 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 327C, whereas 8x37=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 e*xactly 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 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.

previous **index** **next**

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.