# Early Attempts to Understand the Nature of Heat

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## 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.

## 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.

Painting by Joseph Wright, Wikimedia Commons.

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.

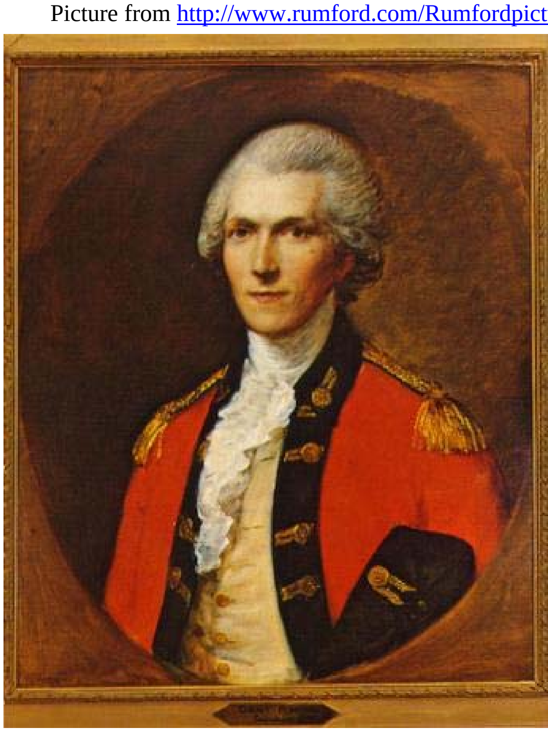
For a given temperature difference, then, a given amount of heat can only deliver so much work. And, this is quite independent of the materials used in constructing the engine, including the gas itself.

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 curricle, the only other curricle 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 the 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 ¾ inch candles burning continuously. Long before the concept was formulated, Rumford had measures 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.

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