

13.3: Heat and the First Law

"Direct Exchange of Thermal Energy" and Early Theories of Heat

In the previous section I have considered the possibility of “direct exchange of thermal energy” between two objects. This is a phenomenon with which we are all familiar: when a colder object is placed in contact with a warmer one, the warmer one cools off and the colder one warms up. This “warmth” that seems to flow out of one object and into the other is conventionally called “heat.”

Naturally, this observation was made long before the concept of “energy” was even developed, and so heat was thought of, for a time, as an “invisible fluid” (called, at one point, “caloric fluid”), a sort of indestructible “substance” that literally passed from one body to another. By “indestructible” I mean that they had a notion of this caloric fluid being conserved: it was not created or destroyed, only exchanged from one body to another. This makes sense, in a way: if it was really something material, how could it be created or destroyed? Conservation of matter was pretty much accepted scientific “dogma” already by the end of the 18th century.

This idea of conservation of the caloric fluid led to the whole field of “calorimetry,” as essentially a way to try to quantify (that is, measure) the amount of “caloric” that materials would take in or give off. The connection with temperature led directly to the definition of heat capacities and specific heats, just as I have introduced them above (in [section 2.1](#)); only instead of “change in energy” you would use “change in caloric content.” This would be measured in units, called calories, defined by the amount of caloric that led to a given temperature change in a reference substance, such as water.

To be precise, let 1 calorie be the amount of “caloric” needed to raise the temperature of one gram of water by one degree Celsius at a pressure of one atmosphere. This makes the specific heat of water, by definition, 1 calorie/°C·gram. Now imagine you place a hot object in a container of water, insulated from the rest of the world, and wait until thermal equilibrium is reached. Then you can calculate the “amount of caloric that flowed into the water,” from the change in its temperature, and if you assume that all this came from the hot object then you can calculate its heat capacity (in calories/°C) from the change in *its* temperature. By proceeding in this fashion, scientists developed tables of specific heats that do not need any change today—only the recognition that “caloric” is not really a fluid at all, but a form of energy, and can, therefore, be measured in energy units.

Clearly, conservation of caloric was a very good idea in its own way, since much of what was established back then still works if you simply replace the word “caloric” or “heat” by “thermal energy.” It was, however, ultimately unsatisfactory precisely because it restricted itself to what we would today recognize as just one kind of energy, and so it failed to recognize thermal energy as something that could be converted into, or from, other kinds of energy

In hindsight, it is a bit surprising that the belief in the conservation of caloric could have held for so long. What today appear to us like obvious instances of the transformation of (macroscopic) mechanical energy into thermal energy, such as the warmth generated when you rub two objects together, were explained away as instances of mechanically “squeezing” caloric fluid out of the objects. Around the turn of the 19th century, an American expatriate, Count Rumford, observed one of the most egregious instances of this in the enormous amount of “heat” that was generated in the boring of cannons (which involved, basically, a huge metal tool drilling a hole in a large metal cylinder). He noticed that the total mass of the metal, including all the shavings, did not appear to change in the process, and concluded that caloric had to be virtually massless, since enormous quantities of it could be “squeezed” out without an appreciable mass loss. He speculated that caloric was not a fluid at all, but rather “a form of motion,” since only something like that could be made to increase without any apparent limit.

Rumford’s theory was not generally accepted at the time, but later in the 19th century the direct conversion of mechanical energy into thermal energy was established beyond a doubt by James Prescott Joule in a series of painstaking experiments in which he used a system of weights to turn some vanes, or paddles, that stirred water in a container and eventually caused its temperature to rise. By measuring the mechanical energy deficit (gravitational plus kinetic) of his system of weights and paddles, he could tell how much energy the water must have gained, and by measuring the water’s change in temperature he could then establish the equivalent “amount of caloric” that had gone into it. He thus established what was called “the mechanical equivalent of heat,” which we would express today by saying that a calorie does not measure the amount of some (nonexistent) caloric fluid, but simply an amount of energy equal to 4.18 joules (and yes, the Joule is named after him!).

The First Law of Thermodynamics

The upshot of all this experimentation was the full development of the concept of energy as a conserved quantity that manifested itself in different ways and could be “converted” among different kinds. To the observation, already familiar from macroscopic

mechanics, that the energy of a system could be changed by doing work on it (or letting it do work on its environment) was added the observation, coming from thermal physics, that *thermal energy* could also be directly exchanged between two objects merely by placing them in contact, without any macroscopic work being involved. The two things taken together led to the principle of conservation of energy in its most general (pre-relativistic) form:

$$\Delta E = W + Q \quad (13.3.1)$$

which says simply that a change in the total energy of a system may result from work (W) or from “heat exchange” (Q). “Heat,” in physics usage today, is simply what we call the thermal energy that is directly transferred from one object to another, typically by contact; the convention used for this term is the same as for the work term, that is, Q is positive if thermal energy flows into the system and negative if thermal energy leaves the system.

Equation (13.3.1) is the *first law of thermodynamics*. Note that, in terms of Q , the precise definition of a system’s heat capacity is $C = Q/\Delta T$, and so this will only be equal to $\Delta E/\Delta t$ when the system does no work, which is why I was careful to include that condition in the derivation of Equation (13.2.2).

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