1.2: Caloric, Calories, Heat and Energy

It has long been understood that heat is a form of energy. But this has not always been so, and indeed it was not generally accepted until the middle of the nineteenth century. Before then, heat was treated as though it were some sort of "imponderable (weightless) fluid" known as caloric, which could flow out of one body into another. It is true that as long ago as 1799 Humphrey Davy showed that ice could be melted merely by rubbing two pieces together without the need of any "caloric", and indeed this could not be explained by the "caloric" theory. Davy argued – quite correctly – that friction between two bodies must generate "a motion or vibration of the corpuscles of bodies", and that the observation of the melting of ice by rubbing alone showed that "we may reasonably conclude that this motion or vibration is heat". Likewise at about the same time Benjamin Thompson, Count Rumford, showed that the boring of cannon continuously produced heat in proportion to the amount of work done in the boring process, and the amount of heat that could be so produced was apparently inexhaustible. This again should have sounded the death knell of the caloric theory, and, like Davy, Rumford correctly suggested that heat is a form of motion.

In spite of this evidence and the arguments of Davy and Rumford, it wasn't until the middle of the nineteenth century that caloric theory finally died, and this was a result of the famous experiments of James Prescott Joule to determine the mechanical equivalent of heat.

There is some question as to whether the name should be pronounced "jool" (to rhyme with fool) or "jowl" (to rhyme with fowl). Joule was from a beer-brewing family in Manchester, in the North of England. In a north of England accent, "jowl" would be a preferred pronunciation, while "jool" would come more naturally in the south of England, although most modern Mancunians, like the rest of us, nowadays say "jool". The uncertainty in the pronunciation is an old one, and was used by the brewery (which no longer exists) in Joule's day as an advertising slogan for the beer. I am indebted to Dr Graham McDonald of the Joule Laboratory, Salford University, who found the actual advertising slogan for Joule's Ales:

> Do you pronounce it Joule's to rhyme with Schools, Joule's to rhyme with Bowls, or Joule's to rhyme with Scowls? Whatever you call it, by Joule's, or Joule's, or Joule's. It's GOOD!

In the nineteenth century (and continuing to today) the metric unit of heat was the *calorie* (the quantity of heat required to raise the temperature of a gram of water through one Celsius degree), and the imperial unit was the *British Thermal Unit* (the quantity of heat required to raise the temperature of a pound of water through one Fahrenheit degree). What Joule did was to show that the expenditure of a carefully measured amount of work always produced the same carefully measured amount of heat. He did this by using falling weights to drive a set of rotating paddles to stir up a quantity of water in a calorimeter, the motion (kinetic energy) of the water being damped by a system of fixed vanes inside the calorimeter. The amount of energy expended was determined by the loss of potential energy of the falling weights, and the amount of heat generated was determined by the rise in temperature of the water. He deduced that the "mechanical equivalent of heat" is 772 foot-pounds per British thermal unit. That is, 772 foot-pounds of work will raise the temperature of a pound of water through one Fahrenheit degree. In more familiar metric units, the mechanical equivalent of heat is 4.2 joules per calorie. He wrote: "If my views be correct,... the temperature of the river Niagara will be raised about one fifth of a degree by its fall of 160 feet."

(*Exercise*: Verify this by calculation or by measurement, whichever you find more convenient.)

Once we have accepted that heat is but a form of energy, there should be no further need for separate units, and the joule will serve for both. That being so, we can interpret Joule's experiment not so much as determining the "mechanical equivalent of heat", but rather as a measurement of the specific heat capacity of water.

In spite of this, the calorie is still (regrettably) used extensively today. Part of the reason for this is that, in measuring heat capacities, we often drop a hot sample into water and measure the rise in temperature of the water. This tells us rather directly what the heat capacity of the sample is in calories – i.e. the heat capacity relative to that of water. I suspect, however, that the calorie remains with us not for scientific reasons, but because old habits die hard. There are several problems associated with the continued use of the calorie. Roughly, the calorie is the heat required to raise the temperature of a gram of water through 1 C$^{\circ}$. For precise work, however, it becomes necessary to state not only the isotopic constitution (and the purity) of the water, but also through which Celsius degree its temperature is raised. Thus in the past we have defined the calorie as "one hundredth of the heat required to raise the temperature of a gram of water from 0°C to 100°C"; or again as "the heat required to raise the temperature of a gram of water from 14.5°C to 15.5°C". This latter is about 4.184 joules, but there is really no need to know this conversion factor, unless you are specially interested in the specific heat capacity of water (which, by the way is rather larger than many common substances). (You may have noticed that I have sometimes written ^{o}C and sometimes C^{o}, and you may have wondered which is correct, or whether the degree symbol should be used at all. This will be discussed in Chapter 3.)

The “calories” that nutritionists quote when talking about the calorific value of foods, is actually the kilocalorie and it is sometimes (but by no means always) written Calorie, with a capital C. How much simpler it would all be if all of us just used joules!

There is yet another problem associated with the continued use of “calories”. That is that we often come across formulas and equations in thermodynamics in which a mysterious factor “J” appears. For example, there is a well-known equation $C_P - C_V = R/J$. This relates the specific heat capacities of an ideal gas at constant pressure and volume to the universal gas constant R. It is supposed to be understood in the equation that C_P and C_V are to be expressed in calories and R is to be expressed in joules. The conversion factor between the two units, J, is the mechanical equivalent of heat, or the number of joules in a calorie. This conversion factor between units will not be used in these notes, and all quantities expressing heat of energy will be measured in the same units, which will normally be joules. The equation quoted above will be rendered simply as $C_P - C_V = R$. (The letter J, not in italics, will, of course, continue to be used to denote the unit the joule, but not J, in italics, for a conversion factor.)
