18.5: Specific Heat Capacities of Solids and Liquids

In elementary instructional methods often used at high school, the method of mixtures is generally used. For example, to measure the specific heat capacity of copper, one would need a calorimeter (a small cup) made of copper, and of known mass. Pour a measured mass of boiling water (100 °C) into this. The temperature of the copper rises from room temperature, t_1 °C, to a final temperature, t_2 °C, while the temperature of the copper falls from 100 °C to t_2 °C. The specific heat capacity of the copper is then given by $m_{\mathrm{Cu}}\, C_{\mathrm{Cu}}\, (t_2 - t_1) = m_{\mathrm{H2O}}\, (100 - t_2)$. Since the specific heat capacity of water is, by definition, 1 cal g^{-1} $C^{\circ -1}$ (at least to the precision expected at this level of experimentation), the specific heat capacity of the copper is determined.

To determine the specific heat capacity of another liquid, you could pour a measured mass of the hot liquid into the calorimeter (whose heat capacity is now known), and measure the fall in temperature of the liquid and the rise in temperature of the calorimeter, and hence deduce the specific heat capacity of the liquid by means of a similar equation to the above.

To determine the specific heat capacity of another metal, for example, iron, one can warm an iron specimen (of measured mass) to 100 °C, and then drop it into the copper calorimeter, which contains water at room temperature, t_1 °C, and then measure the final temperature t_2 °C to which the iron cools down and the copper and water heat up. Then $m_{\mathrm{Cu}}\, C_{\mathrm{Cu}}\, (t_2 - t_1) + m_{\mathrm{H2O}}\, C_{\mathrm{H2O}}\, (t_2 - t_1) = m_{\mathrm{Fe}}\, C_{\mathrm{Fe}}\, (100 - t_2)$.

In all such experiments, precautions must be taken to minimize heat losses, and to allow for such heat losses as remain. Most of us will remember such experiments from our schooldays, and will remember how difficult it was to get reliable results, and will be aware that there are much more accurate methods available. Furthermore, the method of mixtures measures the relative values of the specific heat capacities of the materials being mixed, rather than their absolute specific heat capacities. This is all right if we accept that the specific heat capacity of water is unity by definition, but, as soon as it is recognized that heat is a form of energy, we want to be able to measure heat capacities in joules rather than in calories, and the method of mixtures does not do this.

It must not be supposed, however, that the method of mixtures is confined to the schoolroom, and is never used in professional research laboratories. It has been found particularly useful in the measurement of heat capacities at high temperatures. While the details of such experiments are much more sophisticated than as described above, the principle of the method of mixtures still remains.

Nevertheless it remains true that the method of mixtures is really a method of comparing the specific heat capacities of different materials, or of *comparing* the specific heat capacity of a substance with that of water. The first reasonably accurate direct determination of the amount of energy needed to raise the temperature of a measured mass of water through a measured temperature rise was Joule’s famous experiment. In Joule's experiment, water was warmed by stirring it with paddles, which were operated by a set of falling weights, and the amount of work done by these falling weights could be accurately calculated in units of work (which, to Joule, were foot-pounds, but which today, we would calculate in joules.) To Joule, the object of the experiment was to demonstrate that a given amount of work always produced the same amount of heat, and hence to determine what he called the *mechanical equivalent of heat*. Today, we recognize the experiment as a direct measurement, in units of mechanical work, of the specific heat capacity of water, no longer defined to be 1 calorie per gram per degree, but measured to be 4184 joules per kilogram per kelvin. We can look back today at Joule's experiment in amazement – amazement not only at how difficult it must have been and what great experimental skills it entailed, but amazement, too, at how accurate a result he obtained. He wrote: "After reducing the result to the capacity for heat for a pound of water, it appeared that for each degree of heat evolved by the friction of water, a mechanical power equal to that which can raise a weight of 890 lbs to the height of one foot had been expended." Bearing in mind that his "degree of heat" would have been a Fahrenheit degree, this is equivalent to 4790 joules per kilogram per Celsius degree. In addition to his famous paddle-wheel experiment, Joule performed two other experiments - of a quite different nature – to determine the "mechanical equivalent of heat", and he took, as the average of the three experiments, a figure of 817 pounds, which, in modern units, would be equivalent to 4398 joules per kilogram per Celsius degree – only five percent greater than the modern value.

Of course much more accurate measurements of the energy required to raise the temperature of a solid or a liquid can be made by *heating the sample electrically* – that is, in the case of a liquid, immersing a heating coil in the liquid, or, in the case of a solid, wrapping a heating coil around the solid. Admittedly, this does not have the direct frontal approach of heating the sample by mechanical work, but at least the heat input (I^2R) can be accurately measured. Of course, as in all thermal measurements, precautions must be taken to minimize heat losses, and to allow for what heat losses remain, and these considerations must go into the detailed design of the experiment and its procedures. One technique is to surround the calorimeter by an outer vessel, which, by means of suitably-designed thermostats, is kept always at the same temperature as the calorimeter itself, thus (at least in principle) avoiding heat losses from the calorimeter altogether.

Quite precise measurements of the specific heat capacities of solids and liquids (relative to that of water) can be made with the *Bunsen Ice Calorimeter*, which is described in Section 18.7.