LEARNING ABOUT CALORIMETRY

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Abstract

Calorimetry deals with the energetics of atoms, molecules, and phases and can be used to gather experimental details about one of the two roots of our knowledge about matter. The other root is structural science. Both are understood from the microscopic to the macroscopic scale, but the effort to learn about calorimetry has lagged behind structural science. Although equilibrium thermodynamics is well known, one has learned in the past little about metastable and unstable states. Similarly, Dalton made early progress to describe phases as aggregates of molecules. The existence of macromolecules that consist of as many atoms as are needed to establish a phase have led, however, to confusion between colloids (collections of microphases) and macromolecules which may participate in several micro- or nanophases. This fact that macromolecules can be as large or larger than phases was first established by Staudinger as late as 1920. Both fields, calorimetry and macromolecular science, found many solutions for the understanding of metastable and unstable states. The learning of modern solutions to the problems of materials characterization by calorimetry is the topic of this paper.

Keywords: calorimetry, glass transition, heat capacity, history, melting transition, nonequilibrium, temperature modulated calorimetry, TMC

Introduction

In this lecture, a summary will be given of the subjects that must be learned to understand the application of calorimetry to materials characterization. Today, we know that atomic motion is the source of heat, \( Q \) (unit: joule, J), and its intensive parameter is temperature, \( T \) (unit kelvin, K). The exchange of heat is measured by calorimetry. The total heat content or internal energy of a substance is, however, more difficult to assess. We have learned by now that to find the heat content, one must remove all energy, i.e., cool the substance to the absolute zero of temperature, and then add heat successively under measuring conditions until one reaches the starting temperature again. The sum of the added \( Q \) is the internal energy \( U \) (at con-
stant volume) or heat content $H$ (at constant pressure). It is very much easier to measure the total mass, $m$. A single weighing yields $m$. Perhaps this difference in ease of measurement of $m$ relative to $Q$ is one reason for a lag in learning about matter via energetics based on calorimetry relative to structural science, which was originally based on thermogravimetry.

Another reason for a lag in learning about matter via energetics relative to structural science can be found in the distance between the macroscopic, human, and the microscopic, atomic, scales in the two fields of knowledge. The fundamental length-scale of structural science is set by the atoms and is the Ångstrom unit (0.1 nm). The smallest visible length unit, the micrometer, is about $10^4$ times larger. The atomic motion, on the other hand, was linked by Einstein and Debye early this century to the heat capacity, $C_p$, the basic quantity of calorimetry [1, 2]. The time scale of atomic motion is the picosecond ($10^{-12}$ s), much further removed from the fastest event macroscopically perceivable time, the millisecond (by a factor of $10^9$). Perhaps the disparity in difficulty of measurement and the distances from human level of experience are the cause that learning about calorimetry must continue at a rapid pace to match our knowledge about structure.

**Experimental details**

Good calorimetry was already made in the 18th century, as shown in Fig. 1 [3]. Heat was measured, for example, in the ice calorimeter of de la Place by finding the heat flow to the measuring ice in volume $HGbbd$ from a sample of known, higher temperature $T_1$, in basket LM which is inserted into the calorimeter cavity $ft$. The whole calorimeter was kept adiabatic by a second, insulating layer of ice in FFaaaa. After equilibration, which for larger samples might take as much as 12 h, the water was drawn through the stopcock $y$ and weighed to yield its mass $m_{water}$. The average specific heat capacity of the sample, $c_p$, was then for a given mass $m_{sample}$:

$$
c_p = \frac{m_{water}L}{m_{sample}(T_1 - T_o)}
$$

where $L$ is the latent heat of fusion of the unit mass of ice and $T_o$, the melting temperature of ice. Many materials and even biological specimens, like living mice, were studied in this fashion.

Modern calorimetry is based on the adiabatic calorimeter designed by Nernst [4]. This type of calorimeter, decreased somewhat in size, automated, and computerized, is still the best tool to measure heat capacities from perhaps 10 K to room temperature. The specific heat capacity of the sample is in this case calculated from the heater input $\Delta Q$, measured electrically, and the temperature increase, $\Delta T$:

$$
c_p = \frac{\Delta Q_{corrected} - C'\Delta T_{corrected}}{\Delta T_{corrected} \times m_{sample}}
$$

where $C'$ is the heat capacity of the empty calorimeter, its 'water value'. In the last 40 years a much more expedient method, differential scanning calorimetry (DSC),