Award Lectures

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 ff. 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}:

$$c_p = \frac{m_{\text{water}}L}{m_{\text{sample}}(T_1 - T_o)} \tag{1}$$

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 ΔQ, measured electrically, and the temperature increase, ΔT:

$$c_p = \frac{\Delta Q_{\text{corrected}} - C'\Delta T_{\text{corrected}}}{\Delta T_{\text{corrected}} \times m_{\text{sample}}} \tag{2}$$

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),

has replaced in many cases the classical adiabatic calorimetry despite the lower precision of DSC [5]. Its major application is in the temperature range from 200 to 1000 K. In DSC the lengthy correction procedure of the adiabatic calorimeter is simplified. Under the usual condition that sample and reference calorimeters (usually aluminum pans) are identical, and that the reference pan is empty, one finds the sample specific heat capacity as:

$$c_p \approx \frac{K\Delta T}{mq} \qquad (3)$$

where K is the Newton's law constant, ΔT is the temperature difference between reference and sample $(T_r - T_s)$ and q is the heating rate. Equation (3) is exact if the sample and reference calorimeters are heated at the same rate (resulting in a horizontal DSC-curve for steady state and constant c_p). For the case of changing heating rate of the sample due to a slowly changing heat capacity, easy corrections are available [5], but often neglected.

An exciting development added recently to DSC is temperature modulation [6] (temperature-modulated calorimetry, TMC, temperature-modulated differential scanning calorimetry, TMDSC). One uses a sinusoidal or other periodic temperature modulation that is superimposed on an underlying heating rate $<q>$. The modulated sample temperature is:

$$T_s(t) = T_0 + <q>t - <q>\frac{C_s}{K} + A\sin(\omega t - \varepsilon) \qquad (4)$$

where T_0 is the temperature at the start of the experiment; C_s, the heat capacity of the sample calorimeter (sample + pan); A, the maximum amplitude of the sample-temperature modulation; and $\omega = 2\pi/p$, the angular modulation frequency (p = modulation period in seconds), and ε is the phase lag relative to ω. Analogous equations hold for the reference temperature, T_r (maximum amplitude A_r and phase
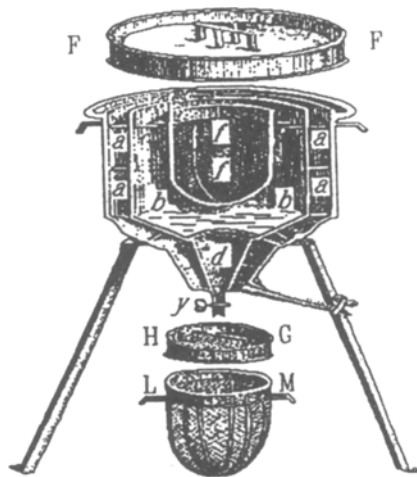

Fig. 1 Historical ice calorimeter of de la Place. For a description see [3]

shift φ) and the temperature difference, $\Delta T = T_r - T_s$ (maximum amplitude A_Δ and phase shift δ). The standard DSC of Eq. (3) can be thought of as TMDSC without modulation ($A = 0$). Small samples can be studied by TMDSC over at least one order of magnitude of change in time scale. Experiments with modulation and an underlying linear heating rate, as shown in Eq. (4), have two time scales, one due to the underlying heating rate and one due to the modulation. Each can be used for measurement of heat capacity. As long as the heat capacity is independent of time, as is usually the case, both evaluations give the same result.

The determination of the heat capacity from the modulation alone is carried out by a pseudo-isothermal analysis. The effect of modulation is separated for this analysis from the total change in temperature difference $<\Delta T>$ and underlying heating rate $<q>$. The averages $<>$ are carried always over $\pm 1/2p$, so that any sinusoidal effect averages to zero. Inserting the averages in place of ΔT and q in Eq. (3) gives the 'total heat capacity'. The difference in ΔT due to modulation alone is given by $\Delta T(t) - <\Delta T>$. Evaluation of the calibration constant and the maximum amplitude of the temperature difference, A_Δ, which is proportional to the maximum heat flow amplitude A_{HF}, gives the heat capacity [7]:

$$mc_p = \frac{A_\Delta}{A}\sqrt{\left(\frac{K}{\omega}\right)^2 + C'^2} = \frac{A_{HF}}{A} \times K' \tag{5}$$

where A and ω are parameters set at the beginning of the experiment, and C' is the heat capacity of the empty reference pan of identical mass to the empty sample pan. The calibration constant K is independent of modulation frequency and reference heat capacity. The commonly measured calibration constant K' changes for runs with different ω and C' (K' is sometimes also written as K''/ω). Equation (5) represents the 'reversing' heat capacity. It can then be compared to the heat capacity measured from Eq. (3). In case there is a difference between the result of Eqs (3) and (5), this is the 'nonreversing' heat capacity, connected to a slow or irreversible process within the sample. With these techniques materials characterization can be attempted.

Results

Heat exchanged with a sample can have two different functions. It can change the kinetic energy of the atoms, and is then considered a heat capacity, or it can act as 'latent heat' (of transition or reaction) which causes no change in total kinetic energy. A series of important equilibrium and nonequilibrium experiments that taught us calorimetry are demonstrated next.

Equilibrium heat capacities are illustrated in Fig. 2 for crystalline and amorphous polyethylene as measured by adiabatic calorimetry and DSC [8]. Equilibrium melting occurs at $T_m = 414.6$ K and the glass transition at $T_g = 237$ K [9]. Note that no latent heat shows in a heat-capacity plot. Below the equilibrium melting transition the amorphous data refer to a (metastable) supercooled liquid, below the glass transition temperature, to a (metastable) glass. To go from one of these states to the other, the latent heat of fusion is exchanged with the calorimeter (4.11 kJ mol^{-1} of CH_2 at T_m [9]). It produces mainly the effects needed to change order into disorder

or vice versa. The heat capacity of the solid states (glass and crystal) are well understood and agree quantitatively with calculations from an approximate vibrational frequency spectrum [10]. The frequency spectrum is derived from the group vibrations available from IR and Raman spectra (7 modes), and the skeletal vibrations (2 modes), fitted to the low-temperature heat capacity with two characteristic frequencies (Θ values). Calculations for polyethylene are shown in Fig. 3 [11]. A data bank exists for over 200 polymer and polymer-related compounds [12]. Even the heat capacities of solid proteins with thousands of group vibrations can be computed in this way. The liquid heat capacities, in contrast, are more difficult to assess fully [13], but they can be derived empirically from the various groups that make up the molecule, as shown in Fig. 4 for a series of polyoxides. The reason for this additivity is the almost full excitation of the skeletal vibrations when the liquid state is reached and additivity of group vibrations and other contributions.

Deviations from the vibrational heat capacity are seen when large-amplitude motions become possible. For glassy polyethylene this occurs before the glass transition. The enthalpy of this motion is given by the shaded area in Fig. 2. For crystalline polyethylene the same occurs at somewhat higher temperature, before melting, as shown in Fig. 3. The detailed motion could be simulated by molecular dynamics calculations [14]. It involves frequent flips of the trans conformations in the crystal to gauche. At room temperature, the rate of flips is about 10^9 per second per bond. Despite this fast rate, the total gauche concentration at any one time is less than 1% because of their short life time. The importance of this effect, measurable by calorimetry, is that the gauche defects play an important role in the deformation mechanisms of polymers.
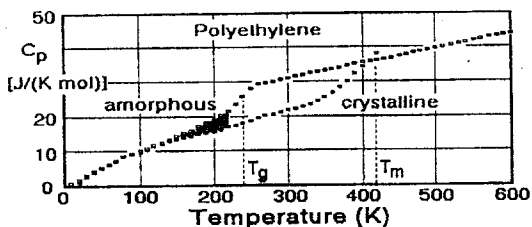

Fig. 2 Heat capacity of fully amorphous and crystalline polyethylene [8]
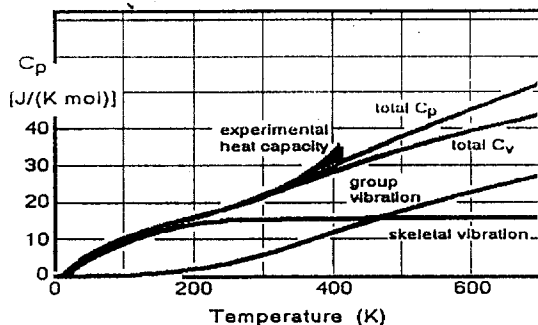

Fig. 3 Graph of the heat capacity of crystalline polyethylene, showing the contributions of skeletal and group vibrations and a comparison with experimental data [11]

Mesophases are common in modern materials. Figure 5 shows a summary of mesophases and their transitions by calorimetry. By analysis of the latent heats and the corresponding entropies, a first characterization of any two phases linked by a first order transition is possible ($\Delta H/T=\Delta S$) [15]. Similarly, the jump in heat capacity at the glass transition ΔC_p can be used to estimate the number of parts of the molecule that become mobile ('beads'). For an amorphous polymer one can, thus, estimate the number of beads in the melt from ΔC_p. Crystallizing the same polymer, the various entropies of disordering must give the same number of beads when adding all transition entropies up to isotropization. Since mesophases have usually drastically different properties, calorimetry can play a vital role in the characterization of materials.

The kinetics of the transitions can naturally also be followed. As calorimetry is developing to measure increasingly smaller samples, short time-scales can be covered. Well-known are the studies of crystallization at fixed degrees of supercooling, summarized in Ref. [16]. The new TMDSC can even follow glass transitions directly as a function of modulation frequency, as will be discussed in detail later in this meeting.

Nonequilibrium transitions are very common in the calorimetry of materials. Naturally, the crystallization mentioned above occurs usually at a lower temperature than equilibrium melting. The resulting crystals may, as a result, not be equilibrium crystals and on fusion yield different melting points. Even worse, the metastable crystals may on heating become unstable and reorganize to better crystals. Calorimetry without considering nonequilibrium effects would thus be of little value. By using the independently gained information on equilibrium as a baseline, the characterization by calorimetry can be extended to irreversible processes, and the unlimited variety of nonequilibrium states is open for analysis. Figure 6 permits, for example, the measurement of the lamellar thickness l from the irreversible melting temperatures T_m, and the surface free enthalpy γ from the slope of the line $[\gamma=0.627/(2\Delta h_f)=87.4 \text{ erg/cm}^2]$.
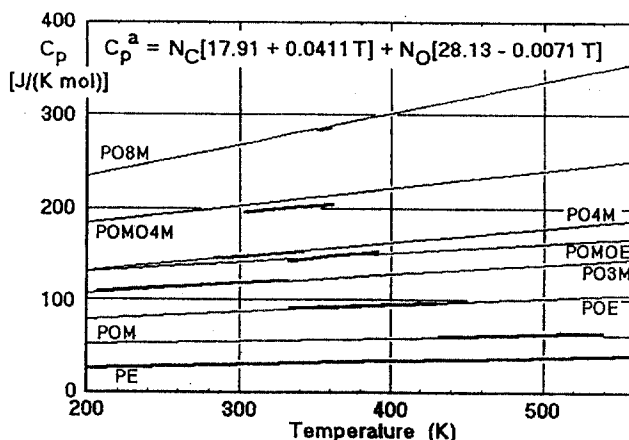

Fig. 4 Heat capacity of liquid polyoxides. Thin lines are given by the equations, thick lines are available experimental data. Nomenclature: P stands for poly, O for oxy, M for methylene, E for ethylene, 3 for tri, 4 for tetra, and 8 for octa

Broad transitions are frequently observed as a result of nonequilibrium. By calorimetry a full stability diagram can be derived as shown in Fig. 7. The free enthalpy distribution was derived from the melting under zero-entropy-production conditions, i.e. the transition is done sufficiently fast so that the metastable crystals could not anneal, and the crystals melted to a supercooled liquid of identical metastability as the crystals [17].

Multiple-phase structures in equilibrium follow the phase rule (number of stable phases = number of components – number of degrees of freedom +2). Typical homopolymers (one component) should, as a result, have only one phase under conditions of variable pressure and temperature (two degrees of freedom). Many polymers are, however, semicrystalline and have thus two phases present, amorphous
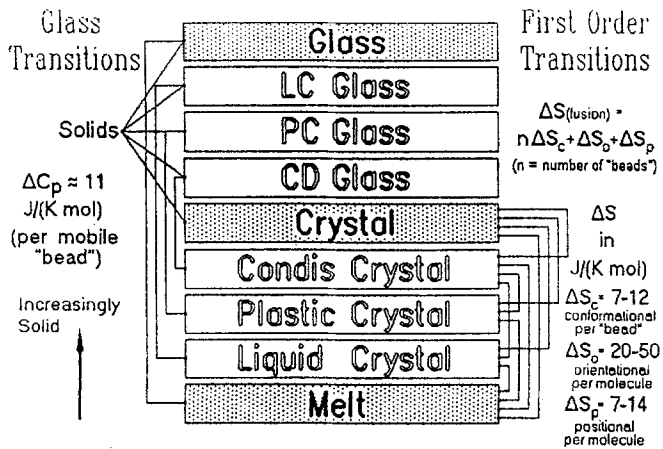

Fig. 5 Schematic of the classical phases (shaded boxes) and the mesophases. Transitions are indicated by the connections between the boxes. Orientational and positional entropy contributions refer to the whole molecule and are negligible for macromolecules

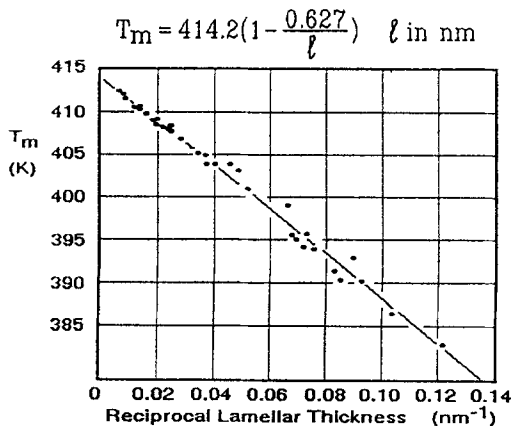$$T_m = 414.2 \left(1 - \frac{0.627}{\ell}\right) \quad \ell \text{ in nm}$$

Fig. 6 Irreversible melting temperatures of lamellar crystals of polyethylene (under conditions of zero-entropy-production) [17]

and crystalline. Such two-phase systems must necessarily be metastable and may even become unstable at higher temperature. Although calorimetry becomes difficult when the material becomes unstable, it is still possible to analyze the metastable state. Through kinetics studies even the unstable states may be followed.
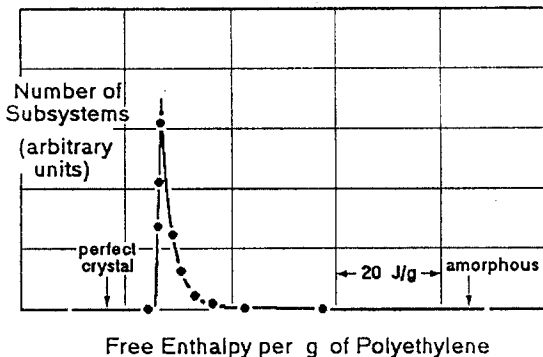

Fig. 7 Free-enthalpy distribution of melt-crystallized polyethylene $(\Delta g = \Delta h_f \Delta T_m)$ [17]

A rigid amorphous fraction was found in many semicrystalline polymers in addition to the mobile amorphous fraction [18]. This increases the number of phases to three (or more). The semicrystalline polymers not only have a broader and higher-temperature glass transition, but also the fraction of the noncrystalline material which becomes mobile at T_g is less than expected from the crystallinity, i.e. the missing part of the amorphous phase remains rigid, often up to melting region. The rigid amorphous fraction contributes to the strength of the material and plays an important part in the structure–property–processing triangle. While crystallinity increases on annealing, the rigid amorphous fractions decreases; while crystallinity decreases on faster cooling, the rigid amorphous fractions increases. To follow the balancing of these effects for optimal performance, one needs high-precision calorimetry.

Nanophase separation is a new term, describing an old phenomenon in macromolecular materials. The crystals and the amorphous areas (rigid and mobile) are
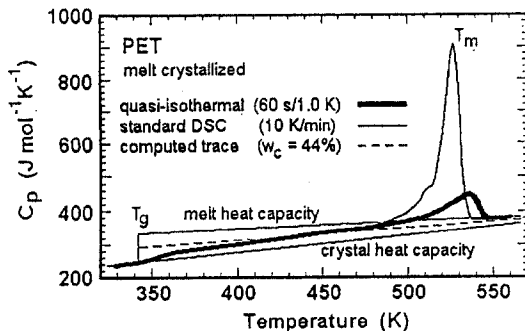

Fig. 8 Melting of poly(ethylene terephthalate). Thin lines: equilibrium heat capacities; Thicker line: measurement by standard DSC. Heavy line: measurement by TMDSC under quasi-isothermal condition in steps of 2 K

often less than 10 nm in size in one or more dimensions. This formation of nano-phase-separated materials is at the root of much of the above-mentioned nonequilibrium. Combining calorimetry with X-ray structure analysis and solid-state NMR for mobility-analysis permitted us to identify the load-bearing phase in polymer fibers. Again, it shows that the calorimetry with its link to large-amplitude molecular motion is a valuable tool for materials characterization. For the first time this link was established for drawn poly(ethylene terephthalate) fibers and gel-spun polyethylene of high molar mass [19, 20].

The detection of equilibrium on a molecular level is the most recent effect we learned from calorimetry. Using TMDSC, a polymer sample was quasi-isothermally analyzed within the melting range of poly(ethylene terephthalate). After steady state was reached, a small amount of reversible latent heat was observed when all nonequilibrium melting had disappeared [21]. This must refer to a local melting/crystallization equilibrium on a molecular level. Figure 8 shows the first data. These experiments connect to earlier efforts trying to extract molten polymer in the melting region [17]. The fraction of molecular segments that can achieve local (restrained) equilibrium is dependent on the crystallization history. One has thus learned yet another characterization method based on calorimetry.

Conclusions

Any research laboratory dealing with materials needs, thus, at least one thermal analyst who has learned all the intricacies of the macroscopic and microscopic energetics and motion of matter to get to the ultimate understanding of structure–property–processing interrelations. The training of these scientists has run in the past into difficulties by the limited attention paid to teach and learn about thermal analysis and macromolecules.

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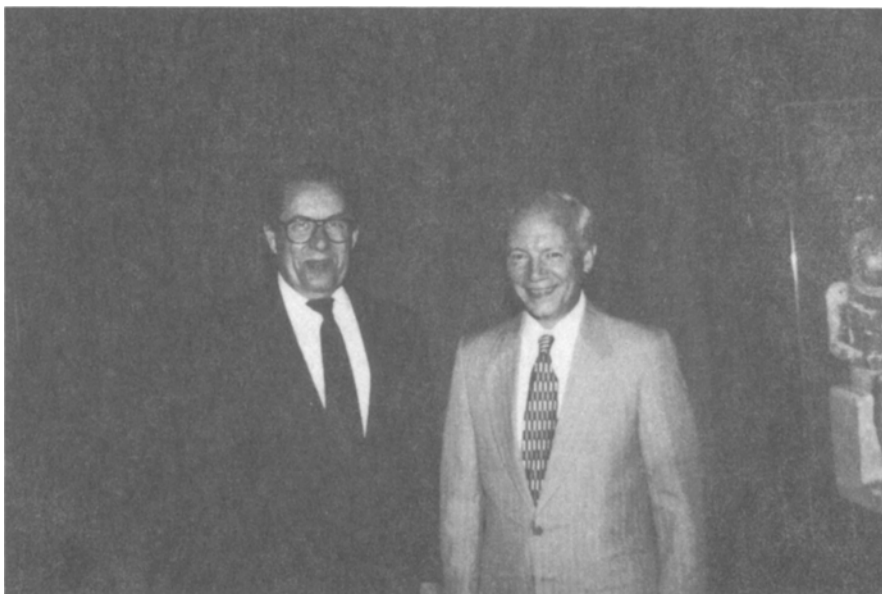
Presentation of ICTAC-TA Instruments Award.
The recipient was Professor B. Wunderlich. The award was presented by Dr. David J. Chalmers,
the President of TA Instruments. Congratulations!