Sander van Herwaarden. "Calorimetry Measurement."

# Calorimetry Measurement

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*Xensor Integration*

## 36.1 Heat and Other Thermal Signals

Calorimetry is the science of measuring heat or thermal signals. This chapter begins by explaining thermal and other signals. For a correct understanding of calorimetry, knowledge of thermodynamics is necessary; however, space permits an introduction only. An overview of the most important types of calorimeters, followed by some of the many applications, will then be presented. For those who want to do measurements without having to make their own devices, an overview of the most important calorimeters, and their vendors and approximate prices will be given. The chapter concludes with some

hints on present and future developments, and on further reading, since there is a large amount of literature on calorimeters.

## Signal Domains

In measurement science, physical quantities can be distinguished by six different so-called signal domains [1]. All signals in calorimeters are either thermal signals or other signals that are transduced into thermal signals. The thermal signal (heat, for example) is then transduced into an electrical signal. In addition to the domains of thermal and electric signals, there is also the domains of the chemical, the mechanical, the magnetic, and the radiant signals. Calorimetric measurement of signals occurs from all domains [2]. Many of them are described in different sections of this Handbook. Calorimeters usually measure the thermal effects of (bio)chemical or mechanical processes, or they measure the thermal effect of temperature changes on matter.

## Heat and Temperature

One of the forms in which energy can be present in a system is the random, internal kinetic energy of the particles (molecules or atoms) of a system, which can intuitively be called "thermal energy." This is to be distinguished from the average, external movement of a system of particles as a whole, which can be called the "mechanical energy" of the system. For gases, thermal energy is closely related to the random velocity of the molecules; and in the case of multi-atom molecules, the rotations and vibrations of the atoms within the molecules. The zeroeth law of thermodynamics states that, if two systems are each in equilibrium with a third system, they will be in equilibrium with each other. They are said to have the same temperature. For gases, statistical mechanics shows the direct relation between the thermal energy (or heat) stored in the system and temperature [3]. This law, however, also applies to liquids and solids, although the quantitative relation between thermal energy (agitation of the particles) and temperature is less straightforward and not so easy to calculate as for gases. Temperature and thermal energy distribution can be viewed as the result of statistical processes, such as diffusion. Diffusion ensures that if ever there is a surplus of thermal energy (i.e., of fast molecules or electrons, or a higher density of phonons) in some area, some of it will flow toward areas with a lower thermal energy density until thermal equilibrium has been established. This flow of energy $P$ (in W = J s$^{-1}$) is called heat flow. Heat flow is therefore the transfer of (thermal) energy from one (part of a) system to another. Note that heat is not conserved, because a change in thermal energy of a system may be achieved by heat exchange with the environment, but also by mechanical interaction, and heat can be used to do mechanical work (motor!) just as well as heating up a system. Heat can be viewed as "thermal energy on the move," but whether it ends up as thermal, mechanical or another form of energy depends on the circumstances.

## Work and Enthalpy

The first law of thermodynamics is also of importance for calorimetry. In a simple form, in the absence of other forms of energy exchange, it states that the change in internal energy $\Delta U$ of a system is equal to the heat $Q$ supplied by the ambient to the system, minus the work (mechanical energy) $p\Delta V$ done by the system on the ambient:

$$\Delta U = Q - p\Delta V \qquad (36.1)$$

This is of importance when measuring the specific heat capacity $c$ (in J kg$^{-1}$ K$^{-1}$) of matter. This measurement can be performed under two conditions: at constant volume $V$ and at constant pressure $p$. At constant volume, no work will be done by the system, since $p\Delta V = 0$. So, the specific heat capacity at constant volume $c_v$ is simply the change in internal energy. The specific heat capacity of a system at constant pressure $c_p$ is (usually) higher, since additional energy (heat) is needed to perform work on the ambient: $p\Delta V$. The quantity combining these contributions to the energy at constant pressure is called

**TABLE 36.1**  Overview of the Classification Criteria for Calorimeters

| Relation to surroundings | Heat measurement |
|---|---|
| Isothermal | Phase-transition compensation of heat |
| | Thermoelectric compensation of heat |
| Adiabatic | Measurement of temporal temperature difference |
| Isoperibol | Measurement of spatial temperature difference |

enthalpy $H$, and the change in enthalpy vs. temperature (in $J\,K^{-1}$) at constant pressure is the specific heat capacity $C_p$ of a sample at constant pressure: $C_p = (dH/dT)_p$.

# 36.2 Calorimeters Differ in How They Relate to Their Surroundings

In essence, a calorimeter performs three functions: it encloses a chamber in which a thermal experiment is carried out; it measures the heat exchange between the sample under test and the calorimeter (and often other quantities are being measured as well, such as temperature and amount of substance); and it thermally separates the experimental chamber from its surroundings. There exist many types of calorimeters. They all have an experimental chamber. Apart from this, four essential criteria can be used to classify calorimeters [4, 5]. The first criterion is, what does the calorimeter do with the heat that is generated (or absorbed) by the experiment? The second criterion is, how does the calorimeter relate to its surroundings? The third criterion is, does it measure a single experimental sample, or is it a twin design with a reference compensating for common mode errors? The fourth criterion is, does the calorimeter function at a fixed temperature, or can it scan a temperature range? Table 36.1 lists the various possibilities for the relation to the surroundings, and for the heat measurement. In principle, almost every combination is possible. In practice, some combinations naturally go together because they compensate for their strengths and weaknesses. For example, calorimeters in which the experimental temperature is scanned often use a twin configuration to eliminate the common mode errors arising from the continually changing temperature.

## Isothermal Calorimeters

In the isothermal calorimeter, the experiment is always kept at a fixed temperature. This is attained by instantly removing (or supplying) any heat that the experiment releases (or absorbs). The isothermal calorimeter was the first to be developed. In 1780, Lavoisier and Laplace made the "ice calorimeter" in which the heat generated by the experiment is used to melt ice into water. If enough ice is available, the calorimeter will remain at 0°C, regardless of the progress of the experiment. The experimentally generated heat $Q$ (J) is calculated by weighing the mass $m$ (kg) of the melt water and multiplying by the heat of the ice-water transition $q_{fus}$ ($J\,kg^{-1}$):

$$Q = m\,q_{fus} \tag{36.2}$$

The experiment with the melting ice is enveloped within a thermostat, which consists of a double-walled vessel with melting ice between the walls, which is always at 0°C as well. Thus, the isothermal calorimeter has a perfect thermal isolation between experiment and surroundings in the form of a second guard-vessel that buffers all the heat coming from the surroundings.

## Phase-Transition or Thermoelectric Compensation of the Heat

In the isothermal calorimeter, the heat generated by the experiment is immediately absorbed by the calorimeter. This can be accomplished by phase-transition compensation of the heat, e.g., by melting of

solids or evaporation of liquids. But nowadays, compensation by electrical means is preferred because it can be measured so easily. Thus, heat $Q$ (J) absorbed by the experiment is replaced using Joule heating (dissipation of heat by a current $I$ (A) through an electric heater with resistance $R_h$ ($\Omega$)), while heat generated by the experiment is absorbed by Peltier coolers:

$$Q = \int I^2 R_h \, dt \tag{36.3}$$

## 36.3 Adiabatic Calorimeters Often Measure Time-Dependent Temperature Differences

In the adiabatic calorimeter, no heat exchange with the surroundings is allowed, and all the heat generated by the experiment is used to increase the temperature of the calorimeter. The amount of heat $Q$ (J) generated follows from the temperature increase $\Delta T$ (K), divided by the heat capacity of the calorimeter $C_c$ (K J$^{-1}$):

$$Q = \Delta T \big/ C_c \tag{36.4}$$

The absence of heat exchange with the surroundings of the calorimeter is obtained by immersing the experimental chamber of the adiabatic calorimeter in an outer vessel; see Figure 36.1. The temperature of the outer vessel is kept at the same (increasing) temperature as the experimental chamber by means of electronic feedback, heating the outer vessel to maintain a practically zero temperature difference. In the adiabatic calorimeter, one must wait a few minutes after the experiment has finished to allow the heat to spread itself uniformly over the chamber and to obtain the final temperature. In Figure 36.1, the experimental chamber is a so-called "calorimetric bomb" in which fuel is fully burned to measure its heat of reaction. The bomb is immersed in a vessel filled with water — the inner vessel. A stirrer assures fast heat exchange between the bomb and the inner vessel, thermometers measure the temperature of the inner vessel and the outer guard vessel. The outer vessel is regulated to the inner-vessel temperature by means of electrical heaters and refrigerator coolers.

### Isoperibol and Heat Flux Calorimeters

The term *isoperibol* was devised to indicate a calorimeter having "uniform surroundings." In this calorimeter, the outer shell provides a reference temperature, and customarily, the experiment starts at the same temperature. The experimental chamber is connected to the outer shell by a well-defined thermal conductance. Any heat generated by the experiment will cause a well-defined temperature difference $\Delta T$ (K) across the thermal conductance $G_{th}$ (W K$^{-1}$), and this temperature difference is subsequently measured as a "local temperature difference." Calorimeters utilizing this way of measuring the heat are referred to as "heat flux calorimeters," and often measure the power $P$ (J s$^{-1}$ or W) generated by the experiment, rather than the energy:

$$P = \Delta T \, G_{th} \tag{36.5}$$

### Scanning Calorimetry Sweeps the Experiment Temperature

While calorimeters are over 200 years old, a recent innovation is that of the *scanning calorimeter*. In the scanning calorimeter, the experimental chamber is not kept at (approximately) one temperature, but it is swept over a temperature range. The temperature is increased at given rate (e.g., 10 K min$^{-1}$) by electric heating, or decreased by, for example, cooling with liquid nitrogen. To achieve the temperature sweep, the experiment is placed inside a computer-controlled oven. To compensate for common-mode errors
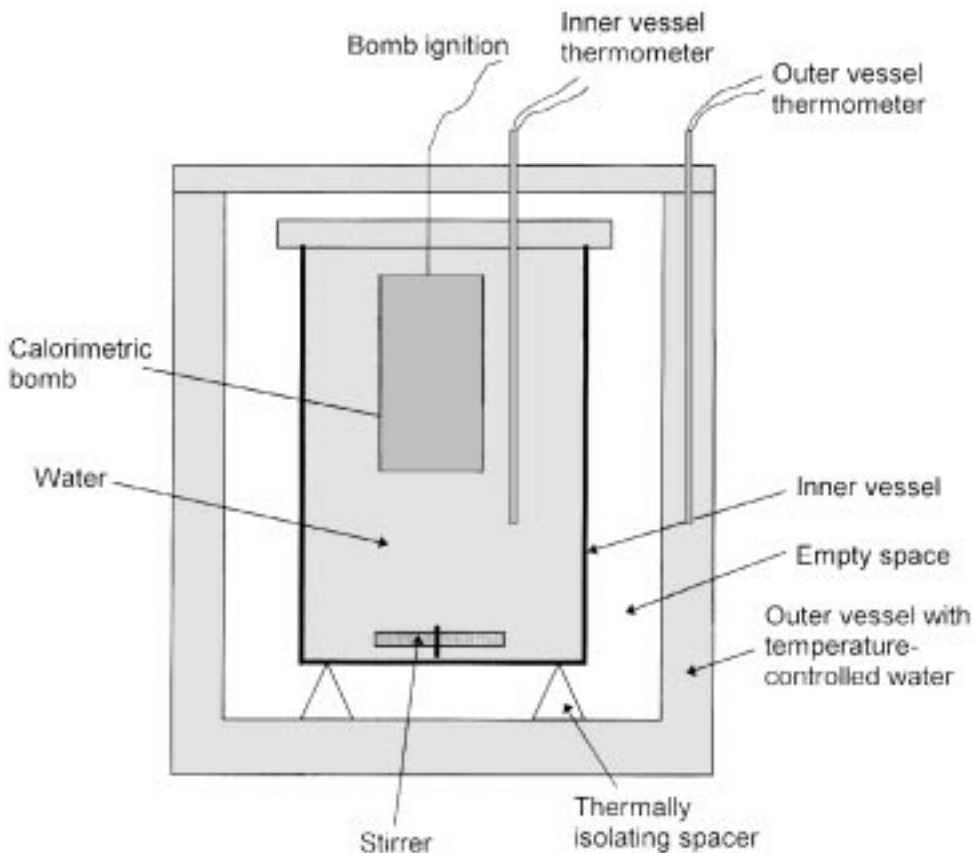
**FIGURE 36.1** Adiabatic calorimeter, with inner experimental vessel being heated by a chemical reaction in the calorimetric bomb, and outer guard vessel electronically adjusted to the temperature of the inner vessel to prevent heat loss of the inner vessel. The temperature increase of the inner vessel is a measure of the heat of burning of fuel in the bomb.

(i.e., back-logging or deviation of the sample temperature from the oven temperature, and imperfections in the oven temperature profile with respect to time and location), scanning calorimeters are often built with twin experimental sites for which the difference is measured. One site is for the sample under test; the other site serves as reference, which is either left empty or contains material resembling the sample under test as much as possible, except for the phenomena to be measured. Such calorimeters are called *differential scanning calorimeters*, DSCs (see "Further Information" for a general book on DSC). Three different types of DSCs are common. The first type is the DSC based on heat flux measurement; see Figure 36.2. In this, the reference and the sample are both heated by the oven through a thermal resistance (gaseous or a solid circular disk). In Figure 36.2, the heating block is the oven, while the (constantan) disk is the path from oven to sample and reference, assuring both heat conduction from oven to sample/reference. The disk also forms a well-defined heat resistance from sample to oven, to measure the heat generation and absorption in the sample using thermocouples that measure the resulting temperature differences. Because of the small size of the experimental site and sample (typically less than 1 cm diameter and 0.1 mL volume), the DSC is usually very fast, and the temperature curve is an accurate representation of the momentaneous heat production in the sample. In the second type of DSC — the power compensation DSC — the temperature of the sample and the reference are both measured with platinum resistors. Sample and reference each have an individual heating source, which is electronically
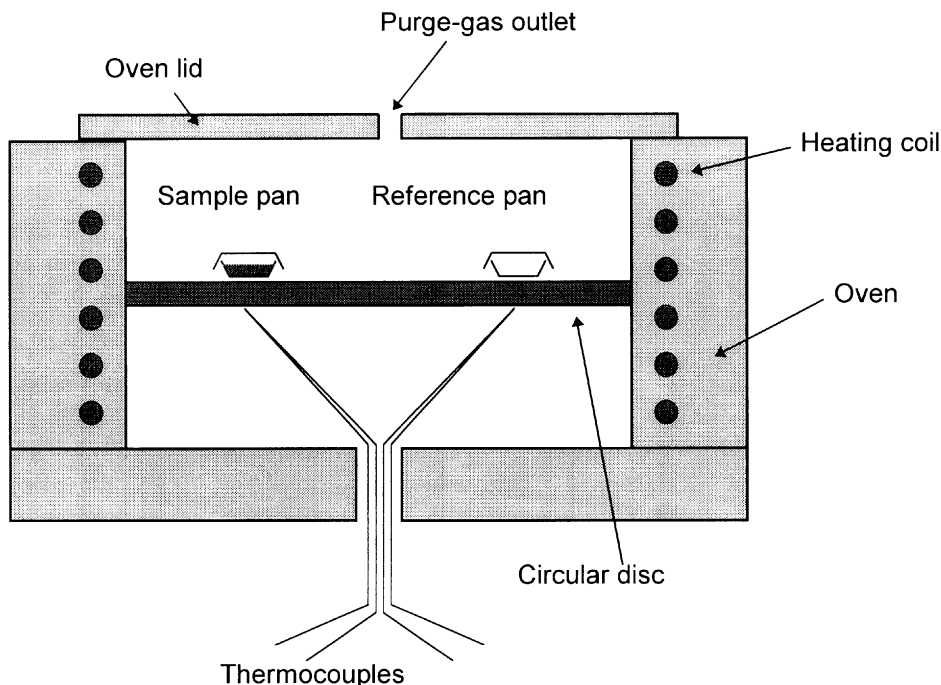
**FIGURE 36.2** The heat flux differential scanning calorimeter (DSC) consists of two experimental sites on a heat-conducting disk. Heat generation in the sample pan results in a temperature increase of the sample with respect to the reference, measured by thermocouple (the disk being one part of the couple).

controlled to maintain sample and reference on the required temperature course. The difference between reference and sample heating power immediately gives the experimental heat. In the third (less accurate) type, only the temperature at which phenomena occur is registered. This type can be used for bigger samples (2 to 3 mL against 0.1 mL for the heat-flux DSC), or at very high temperatures up to 2000°C.

## Converting the Measured Curve to the Actual Progress of the Experiment

Due to the thermal resistance and the heat capacitance inside the experimental chamber of a calorimeter, there is a time constant associated with distributing the experimental heat over the chamber, and reaching the final temperature. A heat pulse does not create a temperature pulse, but rather a smeared-out curve. In a DSC, this smearing-out is usually not significant because of the small time constant (1 to 3 s). For some other instruments, so-called *curve desmearing* has to be carried out using convolution integrals to extract all the information from the measurement curve. With commercially available instruments, software is often supplied that does the job for you, but the accuracy of this software is not satisfactory in all cases, so one might need to do some further study on desmearing [4].

## Calibration of Calorimeters

The inaccuracy of the calorimeter can be reduced by *calibration*. Heat production can easily be simulated electrically. Unfortunately, the thermal leakage of the electric leads reduces the accuracy of this method. More common, therefore, is the use of reference materials with a known heat of transition or reaction for calibration. For bomb calorimeters, the response can be calibrated using the heat of reaction of benzoic acid, which has been carefully determined to be 26,457 J $g^{-1}$ [6]. For a DSC, a range of materials can be used for calibration. This is due to the wide range of applications, and also to the wide range of

temperatures used. Generally, one or more metals are used for calibration of both the power and the temperature scale; for example, indium, which has a melting point of 156.6°C, and an enthalpy of melting of 28.6 J g$^{-1}$. The uncertainty of the value for the heat of fusion (in this case, of melting) is about 0.5%. This is the limit when calibrating in this manner. Basically, DSC inaccuracy is around a few percent. For up-to-date details on calibration and the calibration materials, please consult [7, 8], the references given there, and the most recent data published, since calibration procedures for the DSC are still improving. Specific heat capacity measurements are often performed in three steps. First, the baseline-offset of the DSC is measured with empty reference and empty sample sites (one measures the difference between sample and reference baseline, i.e., the systematic asymmetry of the instrument). Then, a measurement of a reference material with accurately determined specific heat capacity is made; for this, sapphire (crystalline $Al_2O_3$) is often used. Finally, a measurement of the unknown sample is carried out. By correcting for the baseline-offset, and division of the measurements of the known and the unknown samples, the specific heat capacity of the unknown sample can be determined. Currently, these corrections are all made by the computer controlling the DSC [9].

## 36.4   Typical Applications of Calorimeters

### Specific Heat, Transition Heat and Temperatures

Specific heat capacity can be measured by accurate point-wise measurements, but measurement with a DSC is much more efficient. With the DSC, one also obtains the temperature and heat of phase transitions by enthalpy measurement at the transition temperature. Many materials also exhibit changes in crystallization at some given temperature (e.g., glass transition points). Also, these are transition points with their specific heat and temperature, and these can be measured with DSC as well.

### Analysis of Chemical and Physical Reactions

Calorimetry is very well suited for analysis of chemical reactions. In particular, the heat of exothermic and endothermic reactions can be determined. An important example is the calorific value of fuels. Households and factories buying fuels are primarily interested in the calorimetric value of their purchases. The so-called oxygen bomb calorimeter is indispensable for primary calibration in this application. The oxygen bomb is usually an adiabatic calorimeter, in which a sample of the fuel (such as solid coal, liquid oil, or gaseous methane) is brought together with an excessive amount of oxygen (e.g., at a pressure of 30 bar). Then, the mixture is ignited, and the heat of burning will spread over the bomb, until equilibrium is reached. The temperature increase of the bomb, divided by the heat capacity of the device, gives the heat of reaction. In general, corrections have to be made for volume and pressure changes (work!) as liquids or solids are burned and converted to gases and liquids, and also for the additional heat capacity and for the transition heat of the reaction products. Of course, chemical reactions other than burning of fuel can be analyzed in this way as well. In a slightly modified version, the adiabatic calorimeter can also serve to analyze, for example, weak bases and weak acids that do not easily respond to other analysis methods. Similarly, the heat of mixing two solutions, of dissolving a solid in a solvent, of diluting a mixture, and even the heat of wetting can be determined in this so-called *solution calorimeter*.

## 36.5   Thermal Analysis of Materials and Their Behavior with Temperature

Apart from directly measuring chemical reactions, one can also analyze materials by exposing them to a temperature sweep, either in an inert atmosphere (nitrogen or helium) or in an oxidizing atmosphere.

**Schematic Diagram STA 409 EP**   furnace

purge gas

metallic heater

DTA-TG sample carrier

DSC-TG sample carrier

sample carrier

radiation shield
protective tube

TG sample carrier

purge gas
thermostat

inductive displacement
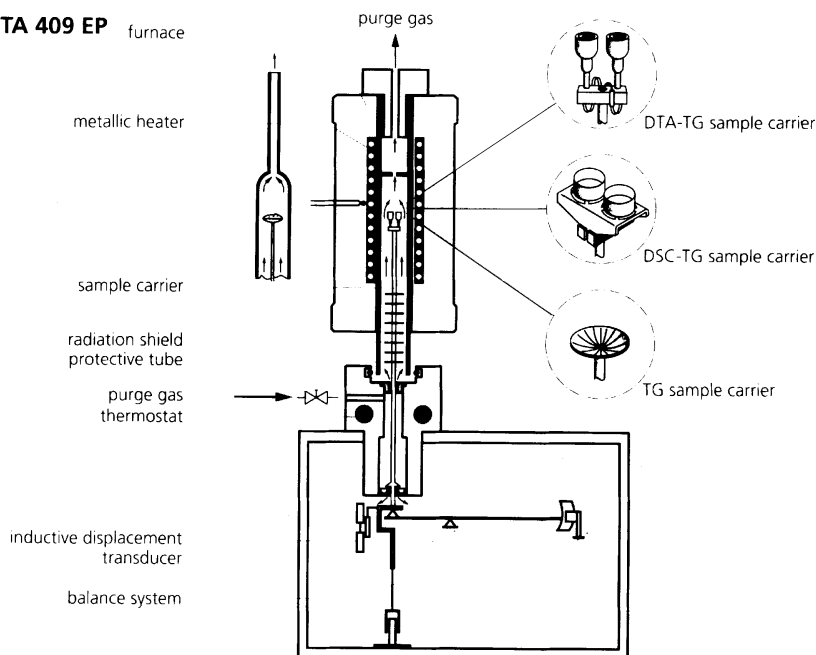transducer

balance system

**FIGURE 36.3**   In a DSC-TG combined thermal analysis instrument, heat is transferred to the sample from the oven by the enveloping purge gas, with radiation shields to diminish heat loss by infrared radiation. The entire sample carrier is placed on a balance to enable thermogravimetric analysis. (Drawing courtesy of Netzsch GmbH.)

Then, all effects — such as glass transition, crystallization, melting, evaporation, decomposition, and even oxidation — can be detected. For this, a DSC is again utilized. In the more expensive analysis systems, DSC instruments often offer the possibility of incorporating other techniques. Mass changes due to oxidation and evaporation are detected by thermogravimetry (TG). This is accomplished by placing the entire experimental chamber on a balance, that continuously measures the sample mass. These data are available as a function of temperature as well, parallel to the heat data. The DSC inner gas atmosphere is usually refreshed continuously using purge gas. This makes it possible to collect the gases coming from the calorimeter furnace and subject them to further analysis, such as mass spectrometry (MS), gas chromatography (GC), Fourier transform infrared analysis (FTIR), and other analysis methods. With sensitive DSC, it is thus possible to detect almost any structural change in matter as a function of temperature. Figure 36.3 shows a drawing of a combined DSC and TG instrument, capable of analyses up to 2000°C. The DSC-TG sample carrier is accurate up to 1500°C, using heat transfer from oven to samples carrier by the surrounding purge gas. Radiation shields are required to reduce heat losses by infrared radiation, which is significant at high temperatures.

## Biological Analysis from Cells to Entire Human Beings

Calorimetry is not just the measurement of thermal effects in 1-mL samples. Calorimeters receiving entire human beings are available as well. In practice, there is a wide range of application of calorimeters to biology. This is not surprising, since all forms of live produce heat in activity and often also in rest. The first calorimeters were already used to measure the heat produced by animals. But also, the study of cells (with their heat production of about 1 pW [10]) and the efficiency of enzymatic conversions can be studied using calorimetry. Microcalorimetry is used for very small effects, sometimes using micro-technology to fabricate very small and very sensitive calorimeters [11, 12]; see [10] for an overview and
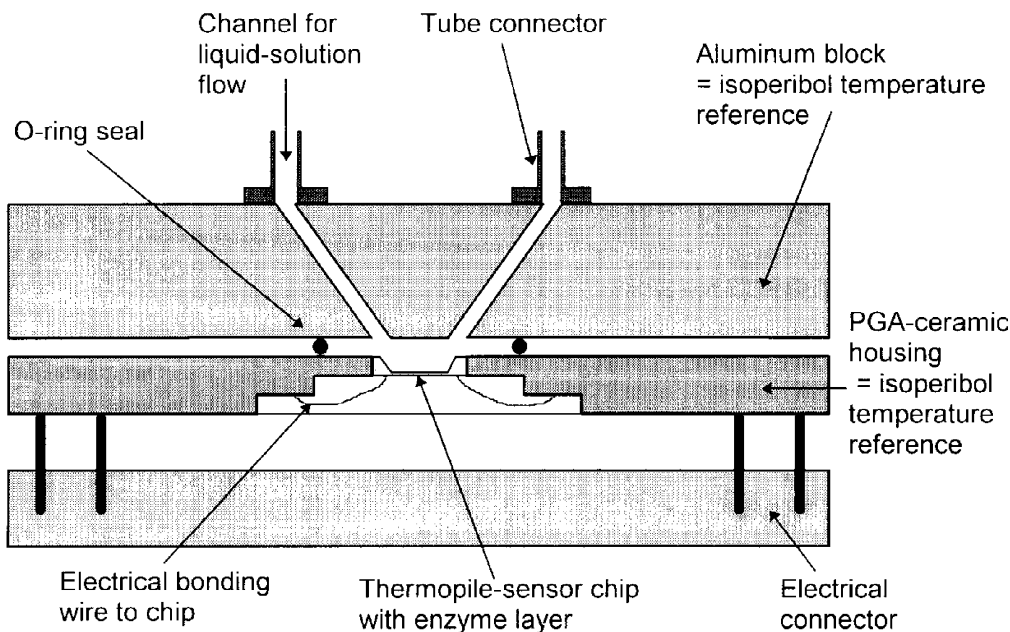
**FIGURE 36.4** In microcalorimetry for (bio)chemical analyses, flow-through systems allow continuous, on-line measurement of (bio)chemical quantities in microliter reaction chambers, using $5 \times 5$-mm silicon microchips coated with enzymes or living cells.

many references. Some microcalorimeters are already being commercialized, using integrated-circuits technology to make very sensitive sensors. Figure 36.4 shows such microcalorimeters encapsulated in a ceramic housing. So far, the use of these sensors is restricted to isoperibol operation around room temperature [11], using aluminum heat sinks to provide the reference temperature. Applications of calorimetry are also found in the food industry, for routine analyses, ecology, plants, etc. See [13, 14] for collections of papers on these subjects.

## Summary

The applications of thermal analysis are overwhelming in number. In many cases, when wanting to learn more about materials, thermal analysis can add insight. Some applications were mentioned above. In Table 36.2 some of the often-encountered applications for various disciplines are listed.

## 36.6 Choosing the Proper Calorimeter for an Application

When faced with a practical analysis problem, one can choose between many instruments. The three main categories are the DSC, the calorimetric bomb or solution calorimeter, and the large reaction or fermentation calorimeter.

### What Do You Want To Measure?

If one wants to measure specific heats of reaction, of oxidation, solution, etc., at room temperature, a calorimetric bomb or a solution calorimeter might be the first choice. They are accurate and economical. If one wants to optimize a chemical or biological process, reaction calorimeters or fermentation calorimeters might be the choice. In almost all other cases, a DSC will be the most effective instrument. A

**TABLE 36.2**  Applications of Calorimeters

| Area of interest | Parameter that can be measured with calorimeters |
|---|---|
| Material characterization and all other areas listed below | Specific heat |
| | Melting and boiling temperature and behavior |
| | Fusion and reaction heat and kinetics |
| | Heat of solution, dilution, mixing, wetting |
| | Thermal safety |
| | Glass transition |
| | Rate and degree of cure |
| | Crystallization time, temperature, and percentage |
| | Purity and solid–liquid ratios |
| | Thermal and oxidative stability |
| | Identification of multicomponent systems |
| | Dehydration |
| Polymers | Effect of the thermomechanical history |
| | Compatibility tests |
| | Effects of additives |
| Pharmaceuticals/Cosmetics | Purity and compatibility of active ingredients |
| | Polymorphism |
| | Effects of storage and hydrolysis |
| | Tablet-compression characteristics |
| | Influence of emulsifiers |
| | Concentration of medicines in polymers |
| | Melting and crystallization behavior of waxes |
| Foods | Melting, solidification behavior, and specific heat of fats and oils |
| | Polymophism |
| | Denaturation of proteins |
| | Gelatinization of starch |
| | Freezing-thawing behavior |
| Biology | Metabolism of cells, organs, animals, and human beings |
| | Influence of nutrition, toxins, and others on organisms |
| | Enzymatic efficiency and selectivity |
| | Concentration of solutions using enzymes or organisms |
| | Environmental monitoring |

DSC is especially useful when one wants to obtain the thermal behavior of materials as a function of temperature. In turn, the temperature-dependent behavior of materials can tell a lot about their structure, their properties, and even their thermomechanical history. Important is the scanning range and rate of the DSC. In some cases, the measurement problem cannot be solved by a standard available calorimeter, and one is forced to either use an experimental calorimeter or develop a special-purpose calorimeter.

## Budget, and the Need of Pre- and After-Sales Service

A cost-effective DSC will cost about $25,000, the most expensive models can cost up to $150,000 and include thermogravimetric measurement. Calorimetric bombs are somewhat cheaper, starting at $18,000. The large reaction calorimeters are more costly, at about $120,000 and above. Finally, one can buy experimental instruments or make one's own system. An adiabatic system consisting of a Dewar in a polystyrene housing, using a commercially available stirrer and platinum resistance (measured with any 5½ digit DMM) will put you in business, although at reduced accuracy. However, the budget for this will not need to exceed much more than about $1000 (excluding the DMM). It is less advisable to make one's own DSC (for cost reasons) or calorimetric bomb (for cost and safety reasons).

## 36.7   Can the Instrument of Choice Measure
##        the Signals Desired?

Here, various parameters must be considered. Accuracy, the degree to which an instrument reading approaches the true value, lies around a few percent for DSCs and parts-of-percent for adiabatic calorimeters. Repeatability of the major calorimeter measurement results — such as heat peak area and peak starting temperature — depends, among other things, on such matters as baseline noise/drift, influence of sample preparation, and positioning in the DSC sample site. Resolution should be considered for two parameters: heat and temperature. First, there is the sensitivity of the instrument for generated heat or power, related to its noise. For DSCs, resolution for power is usually around 0.1 µW to 10 µW; for bomb calorimeters, resolution for heat is around 0.1 J to 10 J. But there is also the resolution of a DSC for separating two heat pulses at two nearby temperatures. This can be designated as the temperature resolution, and depends on time constant and heating rate. Finally, there is the point of linearity and time constant. In case the time constant of the instrument is much larger than that of the process, good linearity is required if one wants to "desmear" the measured curve and obtain the actually produced heat as a function of time. But, a current DSC is a very fast instrument, and desmearing is not really necessary anymore. So, linearity is less important for fast DSCs.

### Instrument Control and Data Management

Software is becoming more and more important. Since it will control the measurement, its user-friendliness determines how easy and how error-free one can operate the instrument. It also can take care of analysis of the measurement results, and graphical and numerical presentation of the results. The software can also take care of quality-control aspects of analysis, such as writing to file all the measurement details (not only what was measured, but also how it was measured). Presently, top models of all three types described above will perform these functions. With DSC instruments, software can often be used to control all kinds of thermal analysis instruments apart from the DSC, such as TG, DMA, etc., and merge results obtained with DSCs, TG, DMA, and other analysis techniques. This facilitates interpretation of measurements.

## 36.8   Commercially Available Calorimeters

Tables 36.3 and 36.4 describe the different instruments and vendors. Table 36.3 gives an overview of instruments and some characteristics, while Table 36.4 gives vendor information. Tables 36.3 and 36.4 are (necessarily) incomplete since only the major vendors have been listed; thus, if looking for a calorimeter, please complete the list with local (and up-to-date) information.

## 36.9   Advanced Topic: Modulated or Dynamic
##        DSC Operation

### Modulating the Temperature Scan Improves Insight into the Measurement

One of the recent developments in DSC is the use of a nonuniform temperature scan. On the standard temperature increase (for example, 1 K min$^{-1}$), an alternating fast temperature change is superimposed, which can be a sinusoidal signal. Alternatively, a stepped temperature profile can be used. Here, the temperature is increased during, for example, 0.5 min with 2°C, and then stabilized for 0.5 min, resulting in an overall scan rate of 2°C min$^{-1}$. In fact, the scan is now modulated with a block wave of amplitude 2°C min$^{-1}$, see Figure 36.5(a). For an instrument with small time constant, such as the DSC-7 of Perkin

**TABLE 36.3**  Some Commercially Available Calorimeters and Their Specifications

| Type | Instrument | Vendor | Cost[a] ($1000) | Range[b] (°C) | Scan rate[c] (K min⁻¹) | Resolution[d] |
|---|---|---|---|---|---|---|
| PC DSC[e] | Pyris | Perkin Elmer | 55 | −170 to +725 | 500 | 0.2 μW |
| CHF DSC[f] | DSC 12E | Mettler | 20 | −40 to 400 | 20 | 10 μW |
| | DSC 821 | Mettler | 30 | −150 to 700 | 100 | 0.7 μW |
| | DSC 200 | Netzsch | 45 | −170 to 530 | 40 | 4 μW |
| | DSC 6 | Perkin Elmer | 25 | −120 to 450 | 50 | |
| | Exstar 6000 | Seiko | 40 | −150 to 1500 | 100 | 0.2 μW |
| | DSC 141 | Setaram | 40 | −150 to 600 | 100 | 10 μW |
| | DSC 50 | Shimadzu | 30 | 20 to 725 | 100 | 10 μW |
| | DSC 2920 | TA Instr | 45 | −180 to 725 | 200 | 0.2 μW |
| | DSC 2010 | TA Instr | 30 | −180 to 725 | 200 | 1 μW |
| FFHF DSC[g] | DSC 404 | Netzsch | 60 | −120 to 1500 | 50 | 8 μW |
| FFHC DSC + TG | STA 409 | Netzsch | 70 | −160 to 2000 | 100 | 8 μW |
| | Labsys | Setaram | 45 | 20 to 1600 | 100 | 10 μW |
| C DSC[h] | DSC VII | Setaram | 55 | −45 to 120 | 1.2 | 1 μW |
| | DSC 111 | Setaram | 80 | −120 to 830 | 30 | 5 μW |
| Bomb | 1425 | Parr | 18 | Ambient | — | 4 J |
| | 1271 | Parr | 45 | Ambient | — | 2 J |
| | C 5000 | IKA | 33 | Ambient | — | 6 J |
| | C 7000 | IKA | 35 | Ambient | — | 0.5 J |
| Solution | 1455 | Parr | 18 | 0 to 70 | — | 0.4 J |
| Calvet | MS 80D | Setaram | 95 | 20 to 200 | — | 0.1 μW |
| | HT 1000 | Setaram | 220 | 20 to 1000 | 1 | 10 μW |
| Process | RC1 | Mettler | 120 | −50 to 300 | 30 | |
| | BFK | Berghof | 150 | 20 to 60 | | 40 mW |
| Micro | LCM-2526 | Xensor | — | Ambient | — | 0.1 μW |

[a] Cost: simplest complete system.
[b] Range: addition of the widest ranges available.
[c] Scan Rate: the highest controlled scan rate (usually for heating).
[d] Resolution: vendor specification or 2x rms noise, for the most accurate system.
[e] PC DSC: Power-Compensated DSC.
[f] CHF DSC: Circular-Disk Heat-Flux DSC.
[g] FFHF DSC: Floating-Foil Heat-Flux DSC.
[h] C DSC: Calvet DSC.

Elmer at about 1 to 2 s, this means that the heat flow for increasing the experiment temperature in the stabilization time will be completely stopped. Any heat flows remaining result from processes in the sample itself; see Figure 36.5(a). Proper interpretation of the measurement results obtained by this method is still under discussion by Reading [15], Schawe [16], and many others.

## PET Is Often Used as Example

Figure 36.5(b) gives the analysis of PET (**p**oly**e**thylene **t**erephthalate), a polymer often used as a reference material because of its convenient and exemplary behavior in polymer analysis [17]. The curve is that of shock-cooled PET, i.e., the PET (from an ordinary beverage bottle) is heated to 300°C in a nitrogen atmosphere, and then quench-cooled in 1 min to maintain an amorphous structure. Six regions can be seen. From 50°C to about 75°C, the heat capacity of the PET sample requires power to achieve the temperature increase. At about 75°C, the so-called "glass transition" takes place, where reordering of the PET molecules takes place, increasing the specific heat of PET (an endothermic process), as can be seen from the lifting of the baseline (even at zero temperature increase, heat has to be supplied to the PET). Then follows a region with increased specific heat, caused by the higher freedom of movement of the

**TABLE 36.4**  Companies That Sell Calorimeters
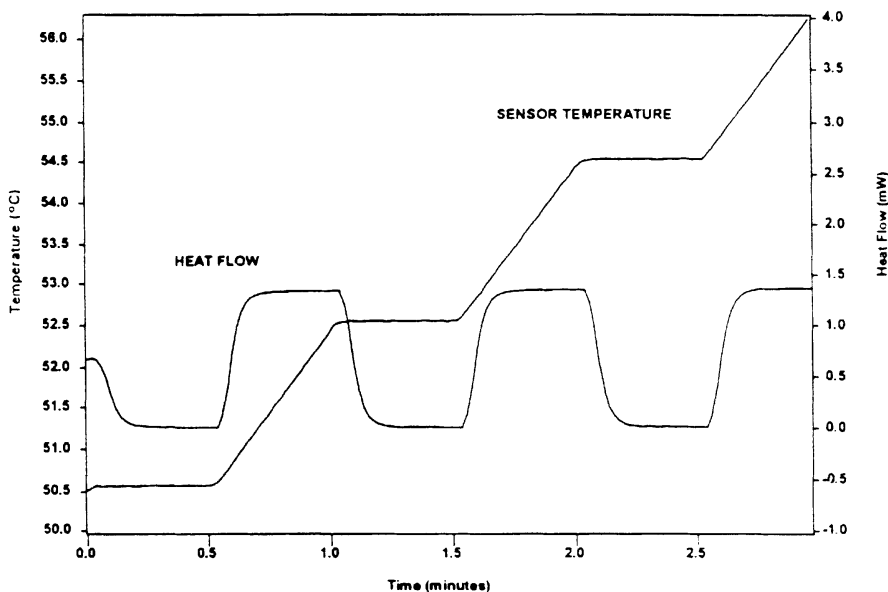
| | |
|---|---|
| Berghof GmbH<br>Harretstrasse 1<br>D-72800 Eningen/Reutlingen, Germany<br>Tel: + 49-7121-8940, Fax: + 49-7121-894100 | Perkin-Elmer Corp.<br>761 Main Ave.<br>Norwalk, Connecticut 06859-0012<br>Tel: + 1-203-762-1000, Fax: + 1-203-762-6000 |
| IKA Analysentechnik GmbH<br>P.O. Box 1240<br>D-79420 Heitersheim, Germany<br>Tel: + 49-7633-8310, Fax: + 49-7633-83198 | Seiko Instruments<br>1-8, Nakase, Mihami-Ku, Chiba-shi<br>Chiba 261, Japan<br>Tel: + 81-43-211-1340, Fax: + 81-43-211-8067 |
| Linseis GmbH<br>P.O. Box 1404<br>D-95088 Selb, Germany<br>Tel: + 49-9287-8800, Fax: + 49-9287-70488 | Setaram<br>7, rue de l'Oratoire, BP 34<br>F-69641 Caluire Cedez, France<br>Tel: + 33-72 10 2525, Fax: + 33-78 28 6355 |
| Mettler Toledo AG Analytical<br>Sonnenbergstrasse 74<br>CH-8603 Schwerzenbach, Switzerland<br>Tel: + 41-1-806-7711, Fax: + 41-1-806-7350 | Shimadzu Corp.<br>3. Kanda-Nishikicho 1-chome, Chiyoda-ku<br>Tokyo 101, Japan<br>Tel: + 81-3-3219-5641, Fax: + 81-3-3219-5710 |
| Netzsch Gerätebau GmbH<br>P.O. Box 1460<br>D-95088 Selb/Bavaria, Germany<br>Tel: + 49-9287-8810, Fax: + 49-9287-88144 | TA Instruments Inc<br>New Castle, Delaware 19720<br>Tel: + 1-302-427-4000, Fax: + 1-302-427-4001 |
| Parr Instrument Company<br>211 Fifty-Third Street<br>Moline, Illinois 61265<br>Tel: + 1-309-762-7716, Fax: + 1-309-762-9453 | Xensor Integration<br>P.O. Box 3233<br>2601 DE Delft, the Netherlands<br>Tel. + 31-15-2578040, Fax: + 31-15-2578050 |

PET molecules compared to the structure below glass transition. Around 140°C, cold crystallization of the material occurs: again a reordering of the material. This is a strongly exothermic process, which again displaces the baseline. The power to be supplied to the sample then steadily increases, and also, with rising temperature, the baseline starts to fall again until a maximum just below melting at 250°C. This is the result of further crystallization, which is facilitated by the higher energy in the sample, and the much better mobility of the molecules just before melting. In the modulated DSC, recrystallization and melting are two concurring phenomena that can be distinguished. Similarly, the hope is that glass transition and cold crystallization can be better distinguished in materials where they overlap (in PET, they are clearly distinct).
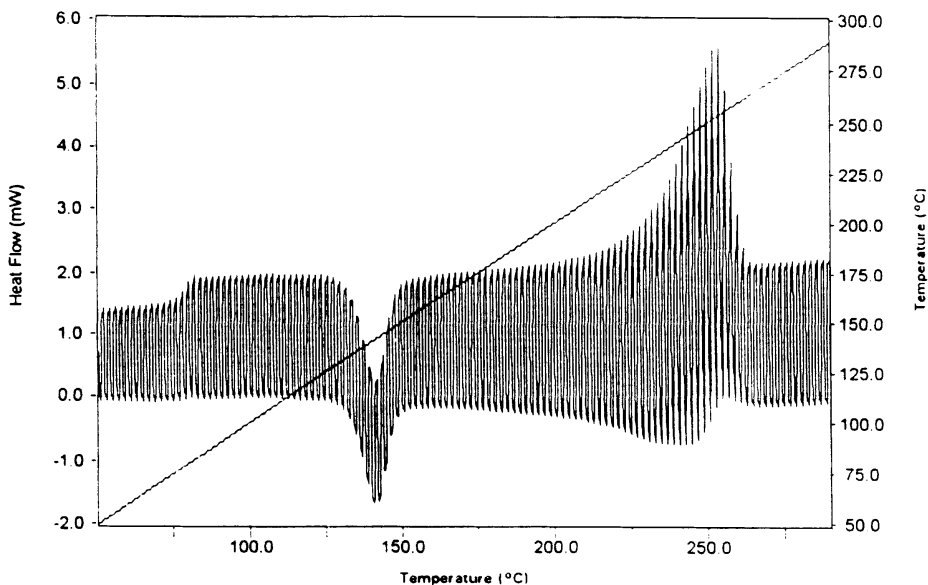
# Acknowledgments

## Close-up of DDSC Primary Signals



(a)

## DDSC of Shock Cooled PET: Primary Signals



(b)

**FIGURE 36.5**  In modulated or dynamic DSCs, the temperature is not increased at a given rate, but modulated with a sinusoidal or stepwise deviation (a) to separate heat transfer due to temperature increase (specific heat), and heat transfer due to phase-changes in the material (glass transition, crystallization, melting). The heat flow in dynamic a DSC for shock-cooled PET (b) clearly shows the absence of heat flow in regions without material change (only temperature increase), and also the residual heat flow when not increasing temperature due to glass transition ($\approx$75°C), cold crystallization ($\approx$140°C), and melting ($\approx$250°C). (Drawings courtesy of Perkin Elmer.)

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## Further Information

Much is being published on Calorimetry each year. Some very good books to obtain a basic understanding of calorimetry are:

W. Hemminger and G.W.H. Höhne, *Calorimetry — Fundamentals and Practice*, Weinheim, Verlag Chemie, 1984.

V.B.F. Mathot (ed.), *Calorimetry and Thermal Analysis of Polymers*, Munich, Hanser Publishers, 1994.

B. Wunderlich, *Thermal Analysis*, San Diego, CA, Academic Press, 1990.

M. Brown, *Introduction to Thermal Analysis,* London, Chapman and Hall, 1988.

On DSC, an up-to-date book is:

G.W.H. Höhne, W. Hemminger, and H.-J. Flammersheim, *Differential Scanning Calorimetry: An Introduction for Practitioners*, Berlin, Springer-Verlag, 1996.

Apart from these, many relevant papers appear in:

*Thermochimica Acta*, Amsterdam, Elsevier Science Publishers.
*Journal of Thermal Analysis,* Chichester, U.K., John Wiley & Sons.

Leafing through the latest volumes will bring one up to date on calorimetry research. Regular conferences on Calorimetry and Thermal Analysis are being held, organized by local and global institutes, such as the ICTAC (International Confederation on Thermal Analysis and Calorimetry). Proceedings of these conferences are often published in *Thermochimica Acta* or the *Journal of Thermal Analysis.*

Very interesting is the publication of ICTA from 1991, which contains significant information on nomenclature, literature, suppliers of instrumentation, etc.:

J.O. Hill (ed.), *For Better Thermal Analysis and Calorimetry, Edition III,* ICTA, 1991.