

1

Methods of Calorimetry

This chapter provides a brief outline of the principles of heat measurement. A classification scheme will be developed on the basis of simple examples. A more detailed treatment of the procedures and calorimeters involved can be found in the second part of the book.

1.1

Compensation of the Thermal Effect

The heat released from a sample during a process flows into the calorimeter and would cause a temperature change of the latter as a measuring effect; this thermal effect is continuously suppressed by compensating the respective heat flow. The methods of compensation include the use of “latent heat” caused by a phase transition, thermoelectric effects, heats of chemical reactions, a change in the pressure of an ideal gas (Ter Minassian and Milliou, 1983), and heat exchange with a liquid¹⁾ (Regenass, 1977). Because the last three methods are confined to special cases, only the compensation by a physical heat of transition and by electric effects are briefly discussed here.

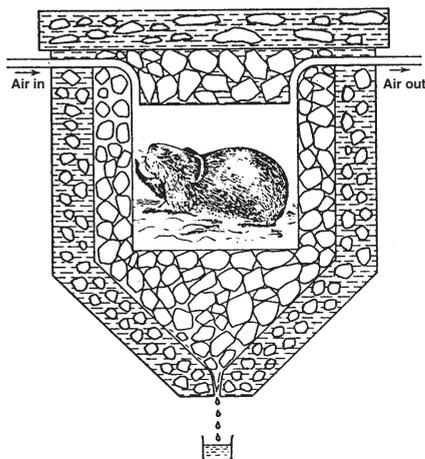
1.1.1

Compensation by a Phase Transition

Around 1760, Black²⁾ (Robison, 1803) realized that the heat delivered to melting ice serves for a transition from the solid to the liquid state at a constant temperature. Indeed, although the melting of ice requires a steady supply of heat, the temperature of the ice–water mixture only begins to rise after all the ice has melted. Black is said to have been the first to have used this “latent heat of fusion” of ice for the measurement of heat. His “phase transition calorimeter” was very simple. He placed a warm sample in a cavity inside a block of ice and sealed the cavity with an

1) For example, “Bench Scale Calorimeter” developed by Ciba-Geigy Ltd., Switzerland, and commercialized by Mettler-Toledo (Schweiz) GmbH, Switzerland, as Reaction Calorimeter RC1.

2) Black only reported his findings verbally; see Encyclopaedia Britannica (2003) or Ramsay (1918).



Working equation:

$$\Delta Q = q_{\text{trs}} \cdot \Delta m$$

ΔQ Heat produced by the sample

Δm Mass of molten ice

q_{trs} Specific heat of fusion of ice

To be determined ΔQ

To be measured Δm

Known q_{trs}

Figure 1.1 Calorimeter of Lavoisier and Laplace (according to Kleiber, 1975).

ice sheet. After the sample had assumed the temperature of ice, he determined the mass of the melted ice by weighing.

The principle of this method is that the heat ΔQ exchanged with the calorimeter is not measured as a heat flow but causes a phase transition in a suitable substance (e.g., ice). If the specific heat of transition q_{trs} of the respective substance is known, the heat involved can be determined because it is proportional to the mass of the transformed substance Δm :

$$\Delta Q = q_{\text{trs}} \cdot \Delta m$$

The mass of the transformed substance Δm is determined either directly by weighing or indirectly (e.g., by measuring the volume change due to the difference between the densities of the two phases).

The first usable calorimeter involving a phase transition – the “ice calorimeter” – was developed by Lavoisier and Laplace (1780). Figure 1.1 schematically shows the design of this device. The sample chamber is completely surrounded by a double-walled vessel containing pieces of ice. This inner ice jacket is surrounded by a second double-walled vessel filled with an ice–water mixture (outer ice jacket). The whole system is in thermal equilibrium at 0°C. The basic idea in this calorimeter is that the measuring system proper (i.e., the inner ice jacket) is insulated by the outer jacket, in which any disturbing influence of heat from the environment on the inner ice jacket is compensated by an ice–water phase transition in the outer jacket. Only heat released inside the sample chamber serves for the melting of ice in the inner ice jacket. Because there is no temperature difference between the inner and outer jackets, no heat exchange between them takes place. Lavoisier and Laplace designated the measured heat as the “mass of melted ice.” The specific heat capacities of solids and liquids, as well as heats of combustion and the production of heat by animals, were measured this way. These measurements were carried out in

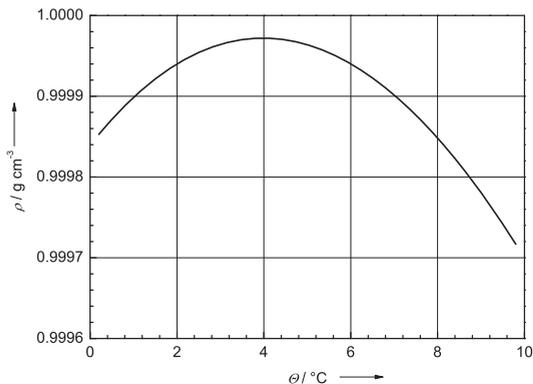


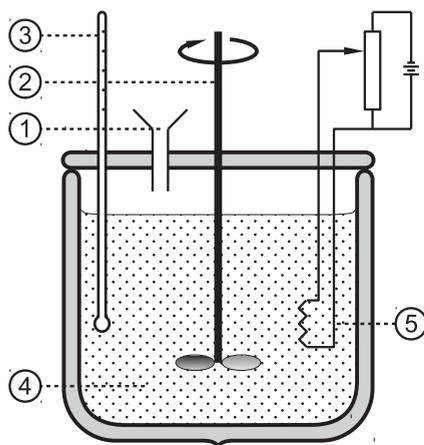
Figure 1.2 The density of water as a function of temperature.

winter when low environmental temperatures allowed experiments to be carried out over longer periods of time (up to 20 h) in order to measure relatively small heat from animals, for example. The ice calorimeter of Lavoisier and Laplace is very bulky; moreover, the inner ice jacket must be carefully prepared before each test. In addition, it suffers from a systematic error that stems from the influx of relatively warm air at the lid. This air cools down in the calorimeter, thus releasing heat, and escapes with the downward flow of ice water. Another systematic error that affects the accuracy results from the fact that the water layer located in the inner jacket between the pieces of ice may attain a local temperature of several degree C, depending on the magnitude of the heat and the rate of its release. These layers may rise because of density differences (Figure 1.2) and transfer part of their heat to the outer jacket (lid). This latter heat thus escapes being measured.

Bunsen (1870) was the first to describe an ice calorimeter that was free from these errors and allowed precise and reliable measurements (see Section 7.8.1.1).

A disadvantage of all phase transition calorimeters stems from the fact that the experimental temperature is determined by the transition temperature. Consequently, a variety of experimental temperatures can only be obtained in such calorimeters by using substances other than water. Very high sensitivity can be attained by using the liquid–gas phase transition (e.g., liquid nitrogen–gaseous nitrogen). The advantages of phase transition calorimeters lie in their relatively simple construction, their great sensitivity, and the possibility of enclosing the calorimeter in a vessel in which a phase transition identical to that occurring in the calorimeter takes place. This approach compensates for disturbances from the surroundings and creates “adiabatic” conditions (see Section 5.3).

For quantitatively determining heats with phase transition calorimeters, the specific heat of transition of the phase changing substance must be known. To calibrate such a calorimeter, a known amount of (electrical) energy E_{el} is supplied to the inside of the calorimeter via a heating wire, and the mass of substance undergoing the transition is measured. The energy supplied divided by the mass of



① Reactant (salt), ② stirrer, ③ thermometer, ④ calorimeter liquid, ⑤ electric heater

Figure 1.3 Brönsted's calorimeter (shown schematically).

Working equation:

$$q_{\text{sln}} \cdot m = \int U(t) \cdot I(t) dt$$

q_{sln} Heat of solution of the salt
(endothermic)

m Mass of dissolved salt

U Voltage

I Current

t Time

Boundary condition: Constant
temperature T_0 of the
calorimeter liquid

To be determined q_{sln}

To be measured $U(t), I(t)$

Known m

substance transformed gives the specific heat of transition:

$$q_{\text{trs}} = \frac{E_{\text{el}}}{\Delta m}$$

1.1.2

Compensation by Electric Effects

This method was applied for the first time by von Steinwehr (1901) and Brönsted (1906). This measuring procedure is best illustrated by the experiment performed by Brönsted. The device shown schematically in Figure 1.3 served for the measurement of the endothermic heat of solution of a salt in water. An amount of salt is dissolved endothermically in a Dewar vessel containing water, and the contents are steadily mixed by means of a stirrer. An electric heater yields a heat output that is regulated so as to leave the solution temperature unchanged. If the voltage $U(t)$ and the current $I(t)$ are constantly recorded, then $\Delta Q = \int U(t) \cdot I(t) dt$ (the electrically generated compensatory heat) equals the heat of solution of the salt.

A major advantage of this procedure is that the conditions of heat transfer to the surroundings (heat leakage; see Chapter 4) remain unchanged during the measurement. Consequently, a highly sensitive but not necessarily calibrated thermometer can be used as a zero change indicator. The only correction to be made is to the heat generated by the stirrer; this is determined separately in a blank run. Because a resistor can only produce heat, this method is restricted to the measurement of *endothermic* effects. The compensation of *exothermic* effects is possible, in principle, by the use of electric cooling using the Peltier effect. The applications of Peltier cooling are discussed in greater detail in Chapter 7. Calorimeters involving an electrical compensation of the thermal effect are

advantageous because the calibration of the calorimeter is necessary only for the determination of the sensitivity of the apparatus, and the electrical quantities voltage U and current I can be measured with great accuracy.

1.2

Measurement of Temperature Differences

Every exchange of heat needs a temperature difference to enable a heat flow. Therefore, the measurement of heats and heat flow rates can be reduced to the measurement of temperature differences (i) as a function of time, that is, $\Delta T = T(t_2) - T(t_1)$, inside a calorimeter, or (ii) as a function of position, $\Delta T = T(x_2) - T(x_1)$, along a heat conducting path.

1.2.1

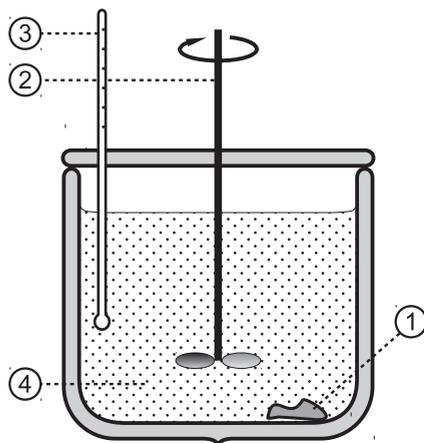
Measurement of Time-Dependent Temperature Differences

The oldest method for the indirect determination of heat consists of measuring the change of temperature of a given mass of water after the introduction of a hot sample. This approach to the measurement of heat emerged with the development of reproducible, graduated thermometers (approximately since 1700); it is based on the principle that a given heat, ΔQ , always changes the temperature of a given mass of water by the same amount, that is, $\Delta T = \Delta Q / C_w$. This is true only if the heat capacity of water C_w does not depend on temperature, which is only roughly correct. A way out of this difficulty would be to confine the use of the calorimeter to a narrow temperature range, say, between 14.5 and 15.5 °C, to give a historical example. By means of this “mixing calorimetry” method, Wilcke (1781) and Crawford (1788) determined the specific heat capacities of various substances.

Calorimeters with a liquid calorimeter substance can be made in a variety of designs (see Chapter 7). Using a version known as a combustion calorimeter, Crawford (1788) also measured the heats of combustion of various substances and compared these with the heat generated by a guinea pig.

The *calorimeter substance* used for this purpose does not have to be water. Other liquid and even solid substances are also suitable. If the calorimeter substance is a solid (usually a metal), the calorimeter is referred to as “aneroid” (nonliquid).

In all calorimeters based on this principle (Figure 1.4), the heat exchange between the sample and the calorimeter substance alters the temperature of the latter from $T(t_{\text{ini}}) = T_{\text{ini}}$ to $T(t_{\text{fin}}) = T_{\text{fin}}$. The change of temperature $\Delta T = T_{\text{fin}} - T_{\text{ini}}$ is measured. The quantity of heat to be determined is $\Delta Q = C_{\text{cal}} \cdot \Delta T$. The “heat capacity” C_{cal} of the calorimeter, which represents the sum of the heat capacity of the calorimeter substance and the heat capacities of other instrument components (stirrer, thermometer, vessel) involved to a greater or lesser extent in the temperature change ΔT , must be known. This “heat capacity” is an instrument-



① Sample, ② stirrer, ③ thermometer, ④ calorimeter liquid

Figure 1.4 Calorimeter for the measurement of a time-dependent temperature difference (classical calorimeter with liquid calorimeter substance).

Working equation:

$$C_S \cdot (T_S - T_{\text{fin}}) = C_{\text{cal}} \cdot (T_{\text{fin}} - T_{\text{ini}})$$

C_S	Heat capacity of the sample
C_{cal}	Heat capacity of the calorimeter
T_S	Initial temperature of the sample
T_{ini}	Initial temperature of the calorimeter substance
T_f	Final temperature of the calorimeter substance
To be determined	C_S
To be measured	$T_{\text{fin}}, T_{\text{ini}}, T_S$
Known	C_{cal}

associated factor (determined by a proper *calibration procedure*) that can assume a variety of values depending on the experimental conditions (e.g., the magnitude of ΔT , the duration of the investigation, etc.). Moreover, part of the entire heat ΔQ escapes directly into the surroundings by heat transfer via “heat leaks” and does not contribute to the temperature change ΔT . This heat loss must be determined. Hence, there is the need for a *calibration* of the calorimeter. For this purpose, a known quantity of heat ΔQ is introduced, and the resulting temperature change ΔT is measured to get $C_{\text{cal}} = \Delta Q / \Delta T$.

The effective “heat capacity” of the calorimeter C_{cal} determined in this manner represents a *calibration factor* valid only for specific conditions of the respective experiment. The historic term for this quantity is “water value,” namely, the mass of water possessing the same heat capacity as that of the calorimeter components, partly or entirely, involved in the temperature change. Thus, the water value reflects the sensitivity of the calorimeter because it indicates the heat necessary to obtain a given temperature change. A large water value consequently means low sensitivity, and vice versa. The term “energy equivalent” is also used. The term “heat capacity” will be used here in the sense of an instrument-associated or calibration factor. The experimental determination of this factor is best performed using electric heating because electric energy can be conveniently released at the desired site and measured with great accuracy.

The advantage of these calorimeters is their simple construction. However, precise determinations require the use of special arrangements (see Chapter 7).

One of the major applications of calorimeters with measurement of temperature differences as a function of time is the determination of specific heat capacities by measuring the rise of the sample temperature following the supply of a known amount of electric energy. A number of versions of these devices are described in Chapter 7.

1.2.2

Measurement of Local Temperature Differences

This method consists of the simultaneous measurement of temperature at two positions, x_1 and x_2 , usually as their difference. It is illustrated by the following examples.

1.2.2.1 First Example: Flow Calorimeter

Two liquids capable of reacting with one another and possessing the same known temperature T_1 (at position x_1) flow into a reaction tube (Figure 1.5). There they react. At the measuring position for T_2 (i.e., at position x_2), where the reaction is assumed to be already completed, the liquid flows out of the tube. The calorimeter operates continuously. With the establishment of a thermal steady state between the liquid-containing reaction tube and the surroundings, a constant temperature difference $\Delta T = T(x_2) - T(x_1) = \Delta T(x_1, x_2)$ is established that is proportional to the heat of reaction. The proportionality factor has to be determined by proper calibration. This can be done in a subsequent experiment in which the collected reaction product flows with the same flow rate and temperature around an electric heater inside the reaction tube.

1.2.2.2 Second Example: Heat Flow Rate Calorimeter

In this type of calorimeter, a sample container is connected to a thermostat via a certain heat conducting body (e.g., a bar) (Figure 1.6). Initially, the entire device has the temperature T_0 . However, the occurrence of a thermal process (reaction) in the sample alters its temperature. This generates an equalizing heat flow rate $\Phi = dQ/dt$ through the bar and under ideal circumstances only through the bar (no heat leaks). In the steady-state case, the heat flow rate between two adjacent cross sections of the bar is associated with a temperature difference $\Delta T = \Phi/G$ (see Section 4.1), where G is the thermal conductance between the sites where the

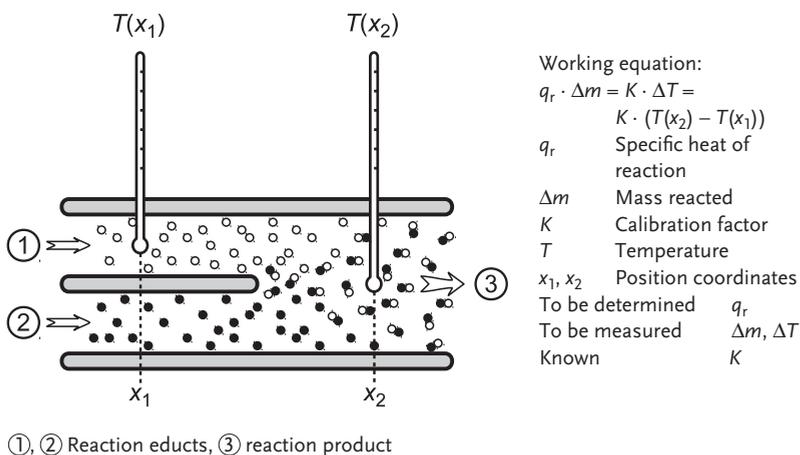
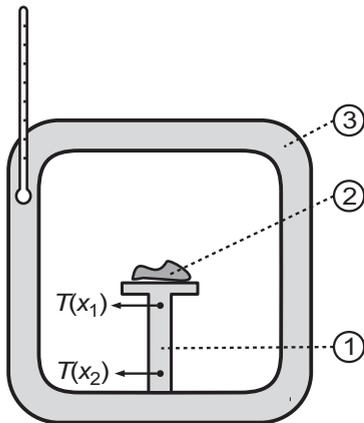


Figure 1.5 Calorimeter for the measurement of a local temperature difference (flow calorimeter).



Working equation:

$$Q = K(T_0) \cdot \int \Delta T(t) dt$$

$$= K(T_0) \cdot \int (T(x_2, t) - T(x_1, t)) dt$$

Q Heat produced by the sample

$K(T)$ Calibration factor

T Temperature

t Time

x_1, x_2 Position coordinates

To be determined Q

To be measured $\Delta T(t)$

Known $K(T_0)$

① Heat conduction path with temperature measurement points, ② sample, ③ thermostat

Figure 1.6 Calorimeter for the measurement of a local temperature difference (heat flow calorimeter).

temperature is measured located at a distance Δx from one another. Thus, $G = \lambda \cdot A / \Delta x$ (where λ is the thermal conductivity of the bar material and A the cross-sectional area of the bar). In the steady state, the temperature difference between two adjacent cross sections of the bar is thus proportional to the heat flow rate (for non-steady-state conditions, see Section 4.1). To determine an unknown heat flow rate, this temperature difference is measured as a function of time: $\Delta T(t) = T(x_2, t) - T(x_1, t)$. If the entire system reverts to the constant temperature T_0 , the entire heat has flowed through the bar. The total heat exchanged through the bar can be determined from the integral $\int \Delta T(t) dt$ together with the thermal conductivity and the geometry of the bar. This, however, applies only to the ideal case in which the entire heat flows only through the bar without any losses caused by radiation, convection, or parasitic heat transfer (heat leakage). Under actual experimental conditions, there is always a certain leakage of heat, and the integral $\int \Delta T(t) dt$ is proportional to the heat exchanged with an unknown proportionality factor $K(T)$, which must be determined by proper *calibration*, whereupon $Q = K(T_0) \cdot \int \Delta T(t) dt$.

1.3

Summary of Measuring Principles

A brief overview of measuring principles is given below.

- i) Measurement of the heat exchanged by compensation, that is, suppression of any temperature change of the calorimeter caused by the thermal effect of the sample.
 - 1) Compensation by a phase transition and measurement of the mass of transformed substance.

- 2) Compensation by electric cooling (Peltier effect) or heating (Joule effect) and measurement of the respective electric energy.

Compensation principle	
By endothermic effect	By exothermic effect
Phase transition (solid–liquid; liquid–gaseous)	Phase transition (liquid–solid; gaseous–liquid)
Electric cooling (Peltier effect)	Electric heating (Joule effect)

- ii) Measurement of the heat exchanged by measurement of a temperature difference.
- 1) Measurement of a time-dependent temperature difference and of the effective heat capacity of the calorimeter.
 - 2) Measurement of a local temperature difference along a well-defined heat conducting path and of a calibration factor.

This classification covers all the types of calorimeters that are of relevance in practice. It provides the basis for Chapter 7, which describes instruments operating in accordance with these methods.

It is noteworthy that any exact measurement of heat consists essentially of the measurement of electric energy or is traceable to electric energy determinations because the latter form of energy is easy to release, can be measured with great accuracy, and is directly connected to the base unit of the SI (Système international d'unités) for the electric current, the ampere. Accordingly, all calorimeters are calibrated either directly by the use of electricity or by means of precisely known heats of reaction or transition, which in turn are measured in electrically calibrated or electrically compensated calorimeters.

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