

## **SUGGESTED PRACTICE FOR CLASSIFICATION OF CALORIMETERS \***

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### **ABSTRACT**

The classification proposed here aims at being simple, easy to apply (both for actual and hypothetical calorimeters) and having the minimum overlaps. It starts with the widely accepted heat exchange considerations, paying special attention to the dynamic behaviour of calorimeters. Nevertheless, it was found useful, for the sake of simplicity and sharpness of definition, to base the operational classification on a criterion of temperature control which leads to a clear-cut distinction between "adiabatic", "ordinary" (main class: isoperibol) and "true or extended isothermal" (main classes: phase change, power compensation, heat-flow or conduction) calorimeters. About 100 of them are quoted here.

### **INTRODUCTION**

We know that the accurate measurements of mass and heat were the two prerequisites for the development of modern chemistry [1]. Nevertheless, the somewhat elusive nature of heat, so difficult to store and to measure totally, was, for more than two centuries, a permanent challenge to scientists. The consequence is an extremely large number of calorimeters which have been devised to "track" and measure the heat in a variety of experiments. It follows that the scientist wishing to select a calorimetric system adapted for his particular purpose is faced with a multitude of possibilities. The comparison is usually difficult, especially because the meaning of the terms used to define a calorimeter is somewhat vague and because the criteria used to distinguish the various classes of calorimeters are extremely numerous and

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\* Dedicated to Professor Syûzô Seki in honour of his contribution to Calorimetry and Thermal Analysis.

usually lead to largely overlapping classes. For instance, the Lavoisier [1] or Bunsen [2] ice calorimeter, which is considered by many as the typical isothermal calorimeter, has been classified by others as adiabatic, with, of course, appropriate justification (Sunner and Wadsö [3], Kubaschewski and Evans [4]). Also, depending on the classification used and on the mode of operation, the Tian–Calvet microcalorimeter may be classified as an isothermal, quasi-isothermal (although the temperature gradients are not larger than in an ice calorimeter), power compensated (when used with a Peltier or Joule compensating effect), differential scanning (when temperature programmed), heat-flow (or conduction) calorimeter, etc. Other calorimeters are defined as drop, flame or bomb calorimeters but this of course sheds light on their purpose but not on their principle.

To simplify things we may consider that any description of a calorimetric experiment involves the description of (i) the measuring principle of the calorimeter used, (ii) its operational characteristics (stability, noise level, sensitivity, resolution, accuracy, response time, temperature range, etc.) and (iii) the way the physical, chemical or biological experiment is carried out. Description of (iii) is normally easy, whereas description of (i) and (ii) needs to refer to some generally accepted definitions, especially to improve clarity and save space. This paper, which has its roots in previous work [5,6], aims to help in the description of (i).

#### CHOICE OF A CRITERION

Let us first define a “calorimeter” as an apparatus devised to measure the heat  $Q$  exchanged or stored by the calorimetric vessel (and its contents) in which the transformation studied takes place. As indicated in Fig. 1, in any calorimeter one may distinguish the calorimetric vessel  $V$  (also called sample cell, calorimeter proper or sample container) which is usually in good

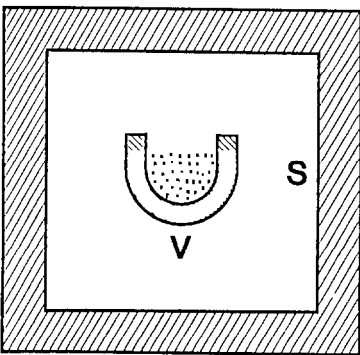


Fig. 1. General representation of a calorimeter (calorimetric vessel  $V$ , surrounding shield  $S$ ).

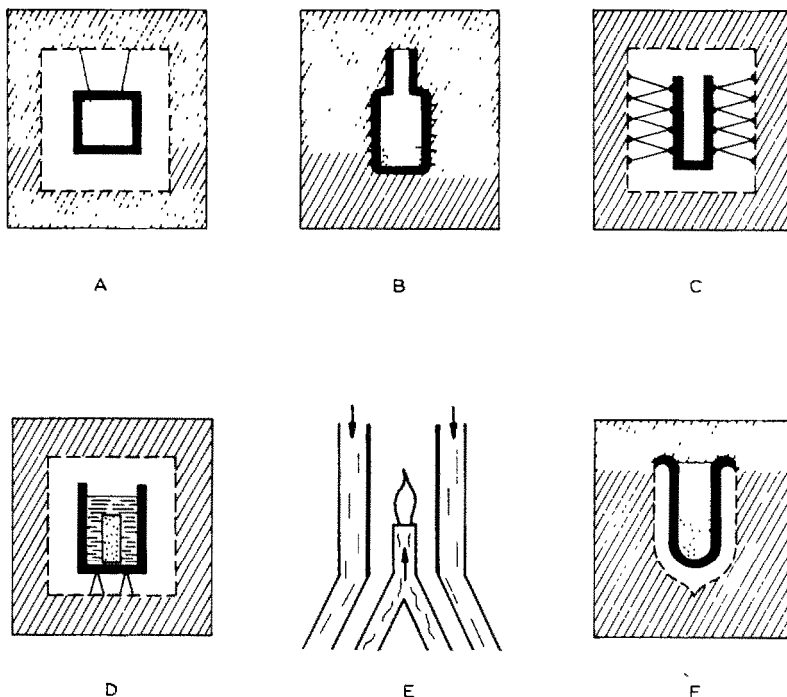


Fig. 2. Location of the "calorimetric vessel" (thick line) in a few typical calorimeters: low-temperature adiabatic (A), phase change isothermal (B), thermopile heat-flow or conduction (C), standard isoperibol (D), flame isothermal (E) and Dewar vessel isoperibol (F).

thermal contact with its content (the sample or reactants) and the surrounding shield S which may be considered as the first thermostat surrounding the calorimetric vessel (some calorimeters may use several thermostats). Since it may be sometimes controversial, Fig. 2 shows the location of the calorimetric vessel, as it will be referred to in the following, in the case of a few calorimeters.

As stated above, the heat to be measured may be stored in the calorimetric vessel and/or exchanged between the calorimetric vessel and shield S:

$$Q_{\text{total}} = Q_{\text{accumulated}} + Q_{\text{exchanged}}$$

This equation naturally leads to three main categories of calorimeters, namely (i) those where all the heat is accumulated ("perfect adiabatic"), (ii) those where all the heat is exchanged ("perfect heat flow") and (iii) those where the heat is partly accumulated and partly exchanged and which we may call "ordinary" calorimeters after the name used by Swietoslowski to designate the Berthelot or Thomsen calorimeters.

Such a classification is simple, logical and comprehensive but still has an important shortcoming, since it is too idealistic. Indeed, perfection never

exists in calorimetry and neither a perfect adiabatic nor a perfect heat-flow calorimeter have ever been built. In these conditions, either we classify all the existing calorimeters within the “ordinary calorimeters” category, so that the classification work still has to be done completely, or we seek for a simple and objective criterion which allows us (i) to apply the definitions to real and imperfect calorimeters and (ii) to avoid the need for any subjective appreciation about the “quality” of the calorimeter.

To reach these goals, we may also think of using the thermal resistance (or thermal insulation) as the selection criterion, but its value is most often unknown either because it was not measured (in the case when it is not needed for a correct calorimeter measurement) or simply because the calorimeter in question does not physically exist. The measured physical property (temperature, heat flow, compensating power, etc.) could also have been thought of as a selection criterion. Unfortunately, overlappings would then be impossible to avoid since two physical properties may be measured at the same time (for instance, the operation of a Berthelot or Thomsen calorimeter needs the determination of both a temperature increase and a heat flow or heat leak, whereas the Tian–Calvet calorimeter may be used with the measurement of both a heat-flow and a Peltier compensating power). A way to make these difficulties less critical could be to combine the “measuring principle” criterion with other criteria like the mode of operation and the construction principle; Hemminger and Höhne recently did this quite comprehensively [7].

For our part, we preferred to look to another criterion which, even when applied alone, would lead to clear-cut boundaries between already widely known categories. This finally lead us to the simple relationship between the temperature of the calorimetric vessel  $V$  and that of the surrounding thermal shield  $S$ : as we shall explain in more detail in the following, three main categories of calorimeters may indeed be easily defined and distinguished unambiguously:

(1) The adiabatic calorimeters, where the thermal shield temperature is controlled after that of the calorimetric vessel (“sample following” temperature control)

(2) The ordinary calorimeters where there is neither control nor fixed relationship between the thermal shield temperature and that of the calorimetric vessel and whose practically unique existing class is that of isoperibol calorimeters (thermal shield kept, or considered to be, at constant temperature)

(3) The true or extended isothermal calorimeters, which exactly fill the image ensemble of that of adiabatic calorimeters, since their definition is perfectly symmetrical: here, it is the calorimetric vessel temperature which is controlled after the temperature of the thermal shield (“shield following” temperature control). The main classes are those of the phase change, power compensated extended isothermal and heat-flow or conduction calorimeters.

Table 1 stresses the “separating power” of the various criteria given above. The dashed lines indicate “floating boundaries” (labelled a to j) which are in some respect unsatisfactory since they are actually crossed by a number of existing calorimeters which may therefore be considered on both sides of the so-called “boundary” and which are, for instance:

- a, b calorimeters whose “perfection” is a matter of personal appreciation, goal, and experimental procedure
- c “isoperibol” calorimeters used in a simplified way, i.e. without heat loss correction
- d, j calorimeters which may be used either in the isoperibol or in the heat-flow mode, because their time constant is either adjustable or set at an intermediate value (ca. 10 min)
- e calorimeters where both a heat flow and a compensating power are measured (for example, the Tian–Calvet calorimeter used with a Peltier or Joule power compensation)
- f calorimeters which are both isoperibol and power compensation (for example, the Perkin-Elmer DSC)
- g power compensated adiabatic calorimeters
- h, i calorimeters of actual unknown thermal resistance (either because the calorimeter was designed but not built or because the thermal resistance was simply not measured because its knowledge is not needed for calibration)

We think that among the criteria examined in Table 1 the first and last are especially worth being selected:

- (1) the dynamic behaviour criterion, in order to understand more deeply and to figure out the behaviour of a calorimeter;
- (2) the temperature control criterion, for the sake of a simple and clear classification.

The classification which is now looked at in more detail gives priority to the second criterion above (since only one criterion must be selected) but makes use of the first one as far as it remains compatible with the other. The basic equations describing the thermal behaviour of the various types of calorimeters will be given here in their simplest form but their explicit derivation and generalization can be found elsewhere [8]. Of course, to illustrate the relatively straightforward and unambiguous application of this classification we find it useful to quote a number of representative calorimeters. Nevertheless, we must point out that we are not at all comprehensive: the quotations would have to be at least twice as numerous. Also in order to be as operational as possible, we shall directly consider the five main classes of existing calorimeters into which we may conveniently (and realistically, we hope) split the three main categories defined with the help of the temperature control criterion:

- (1) adiabatic (adiabatic category)
- (2) isoperibol (main class in ordinary category)

Application of various criteria for the classification of calorimeters, their ability to heat to heating (heating times) or heat-out (cooling times) boundaries between the various classes of calorimeters	
<p>First criterion (useful to analyse behaviour of calorimeter): The heat exchange mode and dynamic behaviour</p> <p><i>Perfect adiabatic</i> Integrating system, characterized by heat accumulation in calorimetric vessel</p> <p><i>Ordinary</i> Inertial system, characterized by time constant</p> <p><i>Perfect heat flow</i> Proportional system, characterized by excellent heat exchanges with surroundings, or phase change or power compensation</p> <p>Third criterion: the measured property <math>T_{\text{vessel}}</math> = temperature of calorimetric vessel <math>\phi(t)</math> = thermal flux between calorimetric vessel and surroundings <math>P(t)</math> = power compensation within calorimetric vessel (Joule or Peltier effect, gas compression, etc.) <math>n</math> = amount of matter undergoing phase change</p>	<p>Second criterion: the thermal resistance (<math>R</math>) between calorimetric vessel and surroundings</p> <p><i>Adiabatic</i> <math>R &gt;</math> arbitrary value <math>R_h</math></p> <p><i>Isoperibol</i> <math>R_h &gt; R &gt; R_l</math></p> <p><i>Conduction</i> <math>R &lt;</math> arbitrary value <math>R_l</math></p> <p>Fourth criterion (selected for operational classification): The temperature control, relative to each other, of: <math>T_{\text{vessel}}</math> = temperature of calorimetric vessel <math>T_{\text{shield}}</math> = temperature of surrounding shield</p>
<p><i>Power compensation</i> In single or differential assembly <math>P(t)</math> is measured</p> <p><i>Adiabatic</i> <math>T_{\text{vessel}}</math> is measured</p> <p><i>Isoperibol</i> (isothermal surrounding shield) <math>T_{\text{vessel}}</math> is measured <math>\phi(t)</math> is measured or taken into account</p> <p><i>Heat flow</i> <math>\phi(t)</math> is measured</p> <p><i>Phase change</i> <math>n</math> is measured</p>	<p><i>Adiabatic</i> <math>T_{\text{shield}}</math> controlled by <math>T_{\text{vessel}}</math> (sample following temperature control)</p> <p><i>Ordinary</i> No control between <math>T_{\text{shield}}</math> and <math>T_{\text{vessel}}</math> Main existing sub-class:</p> <p><i>Isoperibol</i> <math>T_{\text{shield}}</math> = constant</p> <p><i>True or extended isothermal</i> <math>T_{\text{vessel}}</math> controlled by <math>T_{\text{shield}}</math> { True isothermal: <math>T_s</math> constant extended isothermal: <math>T_s</math> changing</p> <p>(shield following temperature control)</p> <p><i>Phase change</i> true isothermal only</p> <p><i>Power compensation</i> true or extended isothermal</p> <p><i>Heat flow</i> or <i>conduction</i> with <math>\tau &lt; 10</math> min true or extended isothermal</p>

- (3) phase change (true isothermal)
- (4) power compensated true or extended isothermal
- (5) heat flow or conduction (true or extended isothermal)

### *Adiabatic calorimeters*

This is the easiest class to define. Generally speaking, an adiabatic calorimeter is a calorimeter where provision is made for minimizing the heat flow between the calorimetric vessel and the surrounding shield. In terms of heat exchange and dynamic properties such a device operates as an integrating system. Its basic equation may be written as

$$C \frac{dT_V(t)}{dt} = P(t)$$

where  $P(t)$  is the input function describing the generation of thermal power within the sample cell and where  $C$  is the heat capacity of the calorimetric vessel and its contents (i.e. the sample). It must be noted that since absolute thermal insulation does not exist, the ultimate way to reach that goal would be to keep the shield at the same temperature as the calorimetric vessel, by appropriate thermal control. This was the method first used by Person in his calorimeter “with cancelled heat losses” [9] and then by Richards [10] and Swietoslowski [11]. This control is indeed the characteristic feature of any adiabatic calorimeter. This is why we practically define an adiabatic calorimeter as a calorimeter where the temperature of the first thermal shield (that surrounding the calorimetric vessel) is controlled by that of the sample.

Contrary to a definition using the thermal insulation criterion (second criterion in Table 1) this definition does not require any arbitrary boundary between the adiabatic and isoperibol calorimeters and it effectively includes all these calorimeters which are usually considered as adiabatic. Among them we may quote:

(1) Low temperature ones like those of Westrum [12], Hoagland et al. [13], Busey [14], Stull [15], Furukawa et al. [16], Martin [17], Morrison and Los [18], Suga and Seki [19], Gmelin and Rödhammer [20], Downie and Martin [21] or Kleinclaus et al. [22].

It is also in this sub-class that we must mention an interesting high resolution calorimeter by Seki and co-workers [23] where separate thermometers measure the absolute temperature and the temperature increases, or an alleviated calorimeter by Suga and co-workers [24] where a reference cell receives the mass and leads of the calibrated thermometric resistance, or another twin adiabatic calorimeter by Marx [25] where the heat compensation is obtained by thermal connection of the two cells through a heat flow meter, or the differential scanning calorimeters of Bonjour [26] designed to study irradiated materials, and Arntz [27] designed for pressures up to 4 kbar.

(2) Room-temperature calorimeters, like those of Swietoslowski [11], Zlotowski [28], Mosselman et al. [29], Prosen and Kilday [30] and like the differential, power compensated, scanning calorimeter of Privalov et al. [31], designed to measure the heat capacity of biological solutions.

(3) High-temperature calorimeters like those of Kubaschewski and Walter [32], West and Ginnings [33], Dench [34], Sale [35], with spherical symmetry, Rogez and Le Coze [36], Sandrock [37], for pressures up to 6 kbar, Haki [38] and Townsend and Tou [39], the last two being specially designed for the evaluation of thermal hazards, which is an interesting application of the adiabatic operation, or Inaba [40] who shows the drastic increase of the heat transfer coefficient from  $0.2 \text{ mW K}^{-1}$  (at 100 K) to  $40 \text{ mW K}^{-1}$  (at 700 K).

### *Isoperibol calorimeters*

These are, or at least have been for a long time, the most popular calorimeters. They are “ordinary” calorimeters (i.e. in which there is no temperature control between the calorimetric vessel and the shield) but in which, to simplify the things, the surrounding shield is maintained at a constant temperature, hence the names of “isoperibol” calorimeter coined by Kubaschewski and Hultgren [41] and “isothermal jacket” calorimeter, are also used.

From the thermodynamic and heat exchange points of view, these are calorimeters in which the heat is partly accumulated in the calorimetric vessel and partly exchanged with the surrounding shield. The relevant equation, sometimes known as Tian’s equation [42,43] is of the following form:

$$C \frac{dT_v(t)}{dt} + G \Delta T(t) = P(t)$$

where  $\Delta T$  stands for the (varying) temperature difference between the calorimetric vessel and the surrounding shield.

This heat balance equation is that of an inertial system characterized by a time constant  $\tau = C/G$ . Actually, the same equation also holds to describe the thermokinetics in conduction calorimeters (Tian’s calorimeter was indeed of the latter type). Nevertheless, these calorimeters have a much shorter time constant, in order to allow a satisfactory return to the starting temperature of the calorimetric vessel within the duration of one measurement (“complete” return to the baseline), so that the first term of the equation may be dropped (its integral over time being equal to zero) except if one is interested in a kinetic treatment of the data. In isoperibol calorimeters the time constant is longer and one does not wait for the return to the baseline. Therefore, the whole equation must always be used, i.e. one must calculate both the heat accumulated in the calorimetric vessel (first term of the equation) and the heat exchanged between the calorimetric vessel and the surrounding shield (second term, also known as the corrective term) using



for instance the well-known Regnault–Pfaundler equation. Since in isoperibol calorimeters one tries to keep at a minimum the “corrective term”, it follows practically that the time constant of these calorimeters is always larger than 10 min. We therefore suggest that this time-constant is considered as the lowest limit under which we pass from isoperibol to heat-flow or conduction calorimeters (cf. boundary *j* in Table 1). Rather fortunately, most heat-flow or conduction calorimeters have a time constant smaller than 4 min so that there is no practical “boundary problem”. The best known isoperibol calorimeters in the past were those of Favre and Silbermann [44], Berthelot [45] or Thomsen [46]. Also for operation around room temperature we may quote those of Armstrong [47] and of Abramowitz et al. [48], the latter being to study combustion in a flow of oxygen. Other versions of the isoperibol calorimeter are also:

(1) Dewar vessel calorimeters, in a more or less sophisticated form, like the well-known Nernst low-temperature calorimeter [49] or like that of Zielenkiewicz and Kurek [50] in which the inner wall of the Dewar vessel acts as the sample cell, whereas its external wall acts as the surrounding shield (cf. scheme F in Fig. 2). A vacuum jacket of special design (but without silver coating, so that it is actually a “d’Arsonval” vessel) is also used in the accurate instrument of Sunner and Wadsö [51].

(2) High temperature calorimeters like those of Eckman and Rossini [52] or Mathieu et al. [53].

(3) Power compensated isoperibol calorimeters which may be either single, like that of Battino and Marsh [54], designed to study the solution of gases in liquids, or differential in which case they may be for use around room temperature [55] or as differential scanning calorimeters (“power compensation DSC”, to distinguish them from the “heat-flux DSC”, as recommended by the Nomenclature Committee of the International Confederation for Thermal Analysis [56]; the latter class of DSC will be found in the class of heat-flow or conduction calorimeters). Watson et al.’s DSC, which makes use of a symmetrical Joule effect compensation is widely known [57]. Along the same lines, an equipment working under pressures up to 10 kbar has been recently proposed [58]. A light beam compensation was also interestingly used by Hill and Slessor [59]. In both apparatuses, it is only the sample and reference which are temperature programmed, whereas the surrounding shield (here, a bell) remains unheated, hence their classification among the isoperibol calorimeters.

(4) A number of “quasi-adiabatic” calorimeters, which are actually isoperibol calorimeters built and/or used in such a way that the corrective term (heat exchange term) can be forgotten. These are, e.g., the flash calorimeters of Rosencwaig [60] and Callis et al. [61], the photo-acoustic pulse calorimeter of Zielenkiewicz and co-workers [62], the flow calorimeters of Roughton [63] and Bateman and Roughton [64] and finally the stop-flow calorimeters of Berger and co-workers [65,66].

### *Phase change calorimeters*

These are of course in the “true isothermal” category: the calorimetric vessel follows the shield temperature which is itself kept constant due to the phase change. We may consider that the phase change plays the part of a “heat-flow integrator” around the calorimetric vessel, since at any time the amount of substance which has undergone the phase change is, ideally, proportional to the integral of the heat flow over time. It should be noted that, in this type of calorimeter, the same container usually has its internal wall acting as the sample cell and its external wall acting as the surrounding (and isothermal) shield. The best known such calorimeters are those of Lavoisier (determination of the mass of melted ice [1]), Bunsen (pycnometric determination of the volume change of the liquid water–ice system [2]), Dewar (volumetric determination of the amount of air vapourized [67]) or Jessup (room temperature operation based on the melting of diphenyl ether [68]).

Another way to look at these calorimeters could be to include the phase change system within the calorimetric vessel and to consider the inner surface of the second thermostat as the “surrounding shield” (kept at the same temperature by means of the same phase change), which is nearly always used here. This representation leads to the idea that these are adiabatic calorimeters (since, ideally, there is no heat exchange between the inner and outer thermostat which are at the same temperature), which is somewhat puzzling, since this tends to bring to the second position what we feel to be the fundamental character (and limitation) of these calorimeters, which is isothermicity. Incidentally, in our classification, the above location of the calorimetric vessel would bring these calorimeters among the isoperibol calorimeters (no mutual temperature control between calorimetric vessel and shield, since they are independently kept at the same temperature) which also tends to show the inadequacy of this second representation.

### *Power compensated isothermal (or extended isothermal) calorimeters*

The word “isothermal” is an integral part of the name of these calorimeters, since, as we saw above, power compensation is also used in adiabatic and isoperibol calorimeters but with a rather different control loop. Here, the calorimetric vessel temperature is forced, by means of the power compensation, to “follow” that of the surrounding shield. There are four possibilities.

(1) The temperature difference between calorimetric vessel and shield is virtually cancelled and the shield is kept at constant temperature. We then have a truly isothermal power compensated calorimeter. If we assume that  $P_1(t)$  is the heat power of the process studied and  $P_2(t)$  the compensating heat power, the relevant equation is:

$$P_1(t) + P_2(t) = 0$$

Both powers are shown here to be proportional to each other at any time. This is because this equation does not take into account any heat transfer kinetics within the calorimetric cell, nor any time constant of the electronic control loop. Nevertheless it is true that these parameters may be adjusted so that they lead to an overall experimental time constant [figuring out the time lag between the  $P_1(t)$  and  $P_2(t)$  functions] which is easily one or two orders of magnitude smaller than that observed with conventional heat-flow or conduction calorimeters, so that in most experiments it may be forgotten.

In this sub-class we may quote the Kanbour and Joncich calorimeter [69], used with a Joule effect compensation and, more recent, several liquid flow calorimeters by Christensen et al. [70–73] which all make use of a Peltier effect compensation and the “pneumatic calorimeter” of Ter Minassian and Milliou [74] where both the differential thermometer and the power compensating device are based on the expansion or compression of gases.

(2)  $\Delta T$  is still cancelled, as above, but the shield is temperature programmed, so that, at any time, the power compensation has to bring the calorimetric vessel temperature at the (changing) temperature of the shield:

$$C \frac{dT_V(t)}{dt} = P_1(t) + P_2(t) \neq 0$$

This is the case for the apparatuses of Sykes [75], the first power compensation scanning calorimeter described in the literature (single, with electrical compensation but manually operated); of Eyraud [76], using an electrically conducting sample (if necessary, by mixing it with graphite powder for instance) in order to develop an homogeneous power compensation; or of Speros and Woodhouse [77] using a differential assembly but with only one compensating heat source (Joule effect), on the sample side.

(3)  $\Delta T$  is now brought at a constant value of usually several Kelvin but the shield temperature is constant. One interest of the resulting steady heat flow (or heat leak) between the calorimetric vessel and surrounding shield is that a mere Joule effect allows the study of either endothermal or exothermal effects (in the latter case, the power compensation initially needed to ensure the steady  $\Delta T$  has only to be lowered). The appropriate equation here is:

$$G \Delta T = P_1(t) + P_2(t) = \text{constant}$$

In this sub-class we find the calorimeters of Ohlmeyer [78], Kiselev et al. [79], Dzhigit et al. [80], Pankratiev [81], Zielenkiewicz and Chajn [82], and the high temperature calorimeters of Wittig and Schilling [83], Hansen et al. [84] (their “battery calorimeter”) or Christensen and Izatt [85] (their high-pressure, liquid flow calorimeter).

(4)  $\Delta T$  is still different from zero but the surrounding shield is now temperature programmed. The equation here is:

$$C \frac{dT_V(t)}{dt} + G \Delta T = P_1(t) + P_2(t)$$

Depending on the accuracy required and on the use of a differential assembly or not, one may or may not consider that  $G$  is independent of temperature and therefore of time.

### *Heat-flow or conduction calorimeters*

Since both names correctly describe these calorimeters and since they are both in use in the literature, we have no reason to drop either of them. Let us only point out the uncertainty which could stem from the use of the word "flow" alone, since we know that heat flow, liquid flow and gas flow are all employed in calorimetry. As we have already seen, Tian's equation, previously given for the isoperibol calorimeters, is also appropriate for the heat-flow or conduction calorimeters where good thermal exchanges (through a heat flow meter) between the calorimetric vessel and surrounding shield bring the former to the temperature of the latter which is either constant (true isothermal) or programmed against time (extended isothermal).

For various reasons (sensitivity, wide temperature range, long-term stability with the differential assembly and, maybe overall, good adaptation for the study of open systems) these heat-flow calorimeters now exist in a large number of types. Most of them make use of thermoelectric heat flowmeters (thermopiles) in a differential assembly, following the lines of the Tian-Calvet microcalorimeter [43]. This is the case for the apparatuses devised by Petit et al. [86], Kleppa and Mraw [87,88], Radenac et al. [89] or Barberi [90] which, like the Tian-Calvet one, may be used either as true isothermal or as scanning calorimeters. A number of miniature heat-flow differential scanning calorimeters, based on the same principle but using simplified flow meters (sometimes obtained by a technique of vapour deposition of thermocouples or thermometric resistances) are commercially available today.

Other heat-flow calorimeters were developed for true isothermal use only, like those of Wadsö et al., using semiconductor Peltier elements as thermopiles [91–93], Benzinger and Kitzinger specially suited for mixing experiments [94], Reggiani et al. [95], Capelli et al. [96], Kaminski and Zielenkiewicz used to follow the slow hydration of cements [97], Rouquerol et al. to study either gas adsorption at 77 or 87 K [98] or liquid adsorption by a flow-through procedure [99], Zielenkiewicz [100], Wertenstein [101], Evans et al. [102], Becker and Malicke [103], Tenoutasse [104] or Stein [105].

Another group of heat-flow or conduction calorimeters is those derived from the DTA principle, i.e. with a punctual and differential determination of the temperature drop through the thermal resistance surrounding the calorimetric vessel. They are most often true isothermal, like the batch reaction calorimeters of Borchardt and Daniels [106] or Baumgartner and Duhaut [107], like the adsorption liquid flow equipment of Groszek [108] or still like the liquid flow reaction calorimeter of Picker et al. [109] where the

liquid mixture is rapidly brought, through a countercurrent heat exchange, to the initial temperature of a water flow whose temperature increase is a measure of the heat flow. In some respects this is a fine development for the case of liquid mixtures of the gas flow calorimeter designed long ago by Junkers [110] to measure continuously the enthalpy of combustion of fuel gases. The latter calorimeter, whose principle is given in Fig. 2 (scheme E) is of course not truly isothermal since the flame temperature is far above that of the water countercurrent. Nevertheless, through the heat exchanges undergone by the combustion gases, we may say that the "gas sample" is eventually (and rather quickly) brought back to the temperature of the shield, so that this flame calorimeter is really an extended isothermal calorimeter, like the Fisk and Gusinov calorimeter, designed to "trap" high energy, pulsed laser signals in order to calibrate them after energy exchange with a water flow [111]. Here also we must mention the "labyrinth flow calorimeter" of Swietoslowski and Zielenkiewicz [112]. The high temperature "tandem" calorimeter (used up to 1600 K) devised by Hoster and Kubaschewski [113] is of the heavy DTA type (metal samples of ca. 10 cm<sup>3</sup>) and is still used isothermally.

It is extremely seldom that a heat-flow calorimeter is not differential; nevertheless, this is the case for the reaction calorimeter devised by Regenass [114] for the study and development of chemical processes. Due to the large amount of reactants (a 2-l volume is available), sensitivity and stability conditions are less stringent so that a twin assembly is not needed. Another feature of this calorimeter is that it can also be operated as an adiabatic calorimeter (although it is designed to be used primarily as an isothermal heat-flow calorimeter) in order to evaluate thermal hazards. Another single isothermal heat-flow calorimeter is the gas/solid "calorimetric bead system" of Jones et al. [115] where the unique temperature sensor (which may also be used to release compensating energy) is embedded in a bead of solid absorbent, directly cooled by the surrounding gas medium.

## DESCRIPTION OF A CALORIMETRIC EXPERIMENT

To present the various aspects of a calorimetric experiment it may be worthwhile to consider a form of checklist. The following goes through the three aspects considered in the introduction:

- (1) Principle and design of the calorimeter proper:
  - (a) fundamental class (adiabatic, isoperibol, phase change, power compensated isotherm, heat flow or conduction, as defined above);
  - (b) simple or differential assembly;
  - (c) designed for temperature scanning or not;
  - (d) measured quantity and measuring device (temperature increase measured with the help of a thermistor, compensating power measured

- by Joule or Peltier or gas compression–expansion effect, heat flow measured by means of a semiconductor thermopile, phase change in the ice–liquid water system, etc.);
- (e) characteristics of the thermal shield or thermostat (metal, liquid or gas medium, phase equilibrium, etc.);
  - (f) type and details of calibration;
  - (g) destination (combustion, mixture or reaction, heat capacity, adsorption, thermal dissociation, sublimation, melting or multipurpose).
- (2) Operational characteristics of the calorimeter:
    - (a) stability, noise level, sensitivity (overall or specific, i.e. per gram of the maximum size sample which may be conveniently accommodated by the calorimetric vessel), resolution, accuracy, etc.;
    - (b) temperature and pressure range;
    - (c) dynamic behaviour (time constant, heat capacity of the calorimetric vessel, etc.).
  - (3) The experiment itself:
    - (a) the system and the transformation studied;
    - (b) the way used to start and to carry out the experiment: mixing, drop, flame, gas or liquid flow calorimetry, open or closed system, constant or scanning temperature, etc.

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