Review

TOWARDS CLASSIFICATION OF CALORIMETERS

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Classification based on thermal properties and temperature conditions of heat transfer between proper calorimeter andsurrondings was presented.The dynamic properties of distinguished groups of calorimeters were determined.

Keywords: classification of calorimeters, thermal and dynamics properties of distinguised groups of calorimeters

Introduction

In the papers that consider determination of the heat effects that are accompanying physical and chemical process is presented a wide spectrum of the types of calorimeters. These devices have been given various names by the authors, which made their choice basing on different premises. Such names like: low temperature calorimeters, high temperature calorimeters and high pressure calorimeters come from the conditions of temperature and pressure in which the measurements are performed. In some cases decisive is a type of investigated process – calorimeters for heat of mixing, heat of evaporation, specific heat measurements and the others. Very often names of calorimeters have to contain information about their construction features, for example: labyrinth flow calorimeter, calorimetric bomb, drop calorimeter, stopped flow calorimeter. Sometime the origin of the device's name stems from the name of its creator. As such examples can be cited here following instruments: calorimeter of Lavoisier, of Laplace, of Bunsen, of Calvet, of Świętosławski, of Junkers and the others. Presented by then diversity of the premises used to create names of the calorimeters give a reason for finding the features that will univocal classify the devices.

An interesting proposal of standardization of calorimetric nomenclature was presented in the papers of Hansen [1] and Hansen and Hart [2]. These works inspired this proposal of classification of calorimeters. It has long been the subject of the author's interest to work out such classification [3–5]. In the works [4, 5] the proposed division of calorimeters was based on two criteria: 1) heat transfer exchange conditions between the calorimetric vessel and the shield (surroundings), 2) dynamic properties of the calorimeters [6]. The present work significantly supplements the classification presented in [5].

Before we begin to discuss the classification, let us present some definitions and terms used for the description of the calorimetric devices.

The term 'calorimeter' is used for the description of an instrument devised to determine heat, whereas the term 'microcalorimeter' should be used for such calorimeters in which microcal (or microjoules) quantities of heat are determined. In this work term 'microcalorimeter' have not always been distinguished from the devices called 'calorimeters'.

In the literature the word 'calorimeter' is used in two meanings. Firstly, it refers to a part of a calorimetric device in which the change of the energy takes place. This part of the calorimeter is the calorimetric vessel in which the sample is located. It is also referred to by the following terms: calorimetric vessel, proper calorimeter, reaction vessel, cell, container, and others. In this work the names calorimetric vessel and proper calorimeter will be used interchangeably.

The calorimetric vessel and contents constitute the system and everything outside the calorimetric vessel constitutes the surroundings. In the literature among the various names for the surroundings are shield, jacket, guard, envelope, thermostat, others. In this work two terms will be used interchangeably: surroundings and shield. Various types of shields are used. There are adiabatic shields which are always maintained at the temperature of the calorimeter

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proper. There are shields with programmed temperature in time, e.g. with linear rise temperature change in time as in the case of scanning calorimeters. There are shields of constant temperature. Calorimeters in which the calorimetric vessel is surrounded by a constant temperature shield are called, according to the term coined by Kubaschewski and Hultgren [7], isoperibol calorimeters. 'Isoperibol' is a Greek word meaning 'constant environment' and in this meaning the term 'isoperibol' will be used in order to determine calorimeters with constant temperature of the shield.

The term 'calorimeter' (or 'calorimetric system') sometimes denotes a system consisting of calorimeter proper, sensors for the determination of the changes of measured parameters (temperature, volume, pressure, etc.), shields, thermostat and a set of devices used for the measurements, automatic regulation as well as data acquisition and data processing. The use of this reference term 'calorimeter' was useful in this work when the examples of known or commercialized calorimeters were given.

It can be generally assumed that the contents of the calorimetric vessel can be constant or may vary during the measurement. We shall name a calorimeter with mass exchange an open system; the one in which mass exchange does not occur is called a closed system. In literature [8] a closed calorimetric system is also named a 'batch' – a term referring to any calorimetric determination where no external mass is introduced across the vessel boundaries during the determinations. The group of open calorimeters often includes those instruments, in which the following techniques for manipulating the solutions are used: titration, direct titration and flow [8].

Operation of titration calorimeters consists in introducing a titrant into the reaction vessel at a known constant rate (continuous titration) or in small equal-volume amounts (incremental titration).

The direct injection consists in injecting quickly an excess of titrant into the reaction vessel and measuring the amount of heat caused by the added titrant.

The flow technique consists in introducing two or more streams of reactants into the calorimetric vessel where they mix and react.

The term 'drop calorimeter' is used to describe the type of calorimeters in which a sample is heated to a known temperature and then dropped into a proper calorimeter which provides measurement of the heat evolved by sample in cooling to the calorimeter temperature.

The calorimeters are constructed as single, differential or twin units. There is no agreement in the literature as to what type of calorimetric system is described as 'differential calorimeter' or 'twin calorime-ter'. In this work, similarly as in [5, 9], they were defined as below.

The differential calorimeters consist of two proper calorimeters (let us call them I and II), placed in a common shield (thermostat). It is assumed that proper calorimeters I and II have identical construction and the same thermal properties. In one of them is located the object generating the heat effect, in the other a thermally passive object of the same heat capacity. The course of temperature changes of the internal part of calorimeter, in which there is an active source of heat, is defined on the basis of the measured temperature difference between temperatures of both proper calorimeters, I and II. At the same time it is assumed that the effect of disturbance occurring in the environment on proper calorimeter I and II is the same, and also that the applied method of temperature measurement makes possible its elimination. One of the first differential calorimeters was the calorimeter constructed by P. Curie and Laborde [10].

Twin calorimeters comprise two proper calorimeters placed in a common shield, in which the measurement consists in compensation of heat developed in one calorimeter by a well-known heat effect introduced into the other. One of the first twin calorimeters was the calorimeter constructed by Ångström [11].

Fundamental assumptions of the presented classification of calorimeters

The proposed classification has been elaborated on the basis of the following assumptions: 1) heat balance equation of simple body Eq. (1) was treated as a general mathematical model of the closed calorimeters, which is equivalent to the Fourier-Kirchhoff equation if several simplifying assumptions are made (Appendix); 2) particular forms of Eq. (1) were set out on the basis of the distinguished temperature conditions of the courses of heat transfer in the calorimeter. Those equations were accepted as general mathematical models for particular groups of calorimeters; 3) the distinguished groups of calorimeters had the properties of dynamic objects ascribed to them [5, 6].

Equation (1) was given in the form

$$C\frac{\mathrm{d}T_c(t)}{\mathrm{d}t} + G(T_c(t) - T_0(t)) = P(t) \qquad (1)$$

where C is heat capacity, G is a heat loss coefficient, T_c is temperature of the calorimetric vessel with contents, T_0 is the temperature of the surroundings (shield), $P(t)$ is function characterizing the changes of heat power within time. It was assumed that heat power $P(t)$ can be generated in calorimetric cell or on calorimetric shield or both in calorimetric cell and ca-

lorimetric shield. Consequently it was assumed that the heat power $P(t)$ {Eq. (1)} can be equal to: 1) the heat power $P_1(t)$ generated by transformation studied; 2) the heat power $P_2(t)$ generated additionally for conducting the process in a desired manner e.g. for compensating the heat power $P_1(t)$; and 3) the heat power $P_3(t)$ involved in the calorimetric shield, causing the conditions of the process to be different from isothermal or 4) the sum of particular heat powers.

Particular forms of Eq. (1) were given for various temperature conditions of the courses of heat transfer between the calorimetric vessel and shield. It was assumed that we can establish: 1) isothermal or non-isothermal conditions for the process occurring in the calorimetric vessel of temperature T_c; 2) the temperature T_0 of the external shield as well as the temperature difference $(T_c–T_0)$ can be established in a desired manner and, 3) the temperatures T_c and T_0 can change in time t. In this manner the following cases of temperature conditions can be enumerated (Table 1).

Table 1 The temperature conditions of the heat transfer between the proper calorimeter and the shield

No.	$T_c(t)$	$T_0(t)$	ΔT
1	$T_c(t) \neq$const.	$T_0(t) \neq$const.	$T_c(t) - T_0(t) = \Delta T = 0$
2	$T_c(t) =$const.	$T_0(t) =$const.	$T_c(t) - T_0(t) = \Delta T = 0$
3	$T_c(t) =$const.	$T_0(t) =$const.	$T_c(t) - T_0(t) = \Delta T = T_t$
4	$T_c(t) \neq$const.	$T_0(t) \neq$const.	$T_c(t) - T_0(t) = \Delta T = T_t$
5	$T_c(t) \neq$const.	$T_0(t) =$const.	$T_c(t) - T_0(t) \neq \Delta T \neq 0$
6	$T_c(t) \neq$const.	$T_0(t) \neq$const.	$T_c(t) - T_0(t) \neq \Delta T \neq$const.

According to the temperature conditions presented in Table 1 let us first of all distinguish two groups of calorimeters:

- adiabatic calorimeters in which the temperature gradient between the temperature T_c of the calorimeter proper and the temperature T_0 of the shield is equal to zero ($\Delta T=0$); no heat transfer occurs between the calorimetric vessel and the shield during the calorimetric measurement.
- nonadiabatic calorimeters in which the temperature gradient between the calorimeter proper and the shield is different from zero ($\Delta T \neq 0$); heat transfer occurs between the calorimetric vessel and the shield during the calorimetric measurement.

If we assume the temperature conditions listed in Table 1, particular solutions of Eq. (1) are as follows:

1. When $T_c(t) \neq$const., $T_0(t) \neq$const., $T_c(t)–T_0(t)=\Delta T=0$, Eq. (1) has the form

$$C \frac{dT_c(t)}{dt} = P(t) \qquad (2)$$

Calorimeters that are described by Eq. (2) are characterized only by heat accumulation. The process in such calorimeters takes place under non-isothermal conditions. They have dynamic properties of integral objects. They are adiabatic calorimeters [12–22] as well as scanning adiabatic calorimeters [23, 24].

2. When $T_c(t)=$const., $T_0(t)=$const., $T_c(t)–T_0(t)=\Delta T=0$, then both terms of the left-hand side of Eq. (1) should equal zero.

$$C \frac{dT_c(t)}{dt} = 0 \quad G(T_c(t) - T(t)) = 0 \qquad (3)$$

These conditions can be fulfilled when the produced heat effect is compensated at the moment of its generation. It happens when two heat processes of the same value but of the opposite sign $P_1(t)$ and $P_2(t)$ occur

$$P(t) = P_1(t) + P_2(t) \equiv 0 \qquad (4)$$

where $P_1(t)$ is the heat power of the process studied and $P_2(t)$ is the compensating heat power. In order to fulfil the condition set by Eqs (3) and (4) compensation of the investigated heat effect should occur in the whole calorimetric vessel or at least on its surface. Such compensation is obtained by: a) putting in direct contact with the external vessel's walls a substance in which, at a given temperature, phase transition occurs, *e.g.* solid–liquid. Such calorimeters are often called 'phase change compensation calorimeters' [1, 2], b) the action of a different kind of heat source, *e.g.* the Peltier or Joule effects. These calorimeters are named 'power compensation calorimeters'.

The best known such phase change compensation calorimeters are those [3] 'of Lavoisier and Laplace (determination of the mass of melted ice), Bunsen (picnometric determination of the volume change of the liquid water-ice system), Dewar (volumetric determination of the air vaporized) or Jessup (room temperature operation based on melting of diphenylether)'. In all these devices there were determined changes of measured quantity that has been a result of the phase transformation. However, in this case it is very difficult or impossible to obtain conditions that respond to the thermodynamic equilibrium [25].

In the development of adiabatic-isothermal calorimetry an unusual role played the idea of Tian that has materialized in what is known as the Tian calorimeter [26–29]. To compensate the thermal effect produced in the calorimeter proper, Tian has made use of the Peltier and Joule's effects. At present modern electronic and steering devices applied for generation of these effects allow to realize the measurements with high accuracy. A good illustration for the last sentence is ITC MicroCal microcalorimeter [30].

The process in such adiabatic calorimeters takes place under isothermal conditions. They are adiabatic-isothermal calorimeters.

3. When $T_c(t)$=const., $T_0(t)$=const., $T_c(t)-T_0(t)$=$\Delta T=T_t$, the process in the calorimeter takes place under conditions close to isothermal. In this case it is assumed that the accumulation of heat during the calorimetric measurement does not occur, the first term of the right-hand side of Eq. (1) is equal to zero.

$$C\frac{dT_c(t)}{dt}=0 \qquad (5)$$

whereas between the proper calorimeter and the isothermal shield a constant temperature difference $\Delta T=T_t$ is maintained. In this case the second term of Eq. (1) takes the form

$$G(T_c(t)-T_0(t))=GT_t \qquad (6)$$

Methods of determination of heat effects in these types of calorimeters are based on the assumption that

$$P(t)=P_1(t)+P_2(t)\equiv GT_t \qquad (7)$$

where $P_1(t)$ is the heat power generated during the process investigated; $P_2(t)$ is compensating heat power, generated additionally to carry out the calorimetric measurements in isothermal but nonadiabatic conditions. The word 'isothermal' in this context is normally not used in a strict sense but is merely an indication that the temperature of the calorimeter is constant enough not to affect the course of the investigated change. Their advantage, similarly as that of adiabatic-isothermal calorimeters, is that they allow to avoid the necessity to determine the heat capacity of the calorimetric system. They are nonadiabatic-isothermal calorimeters. In this class there are the calorimeters of Olhmeyer [31], Kisielev *et al.* [32, 33], Wittig and Schilling [34], Zielenkiewicz and Chajn [35], Hansen *et al.* [36], Christiansen and Izaat [37].

The above-presented adiabatic-isothermal and nonadiabatic-isothermal calorimeters are often called 'compensation calorimeters' [38]. The dynamic properties of these calorimeters are similar to the properties of dynamic proportional objects.

4. $T_c(t)\neq$const., $T_0(t)\neq$const., $T_c(t)-T_0(t)=T_t=\Delta T$=const. In calorimeters of this type the temperature difference between the calorimeter proper and the shield is constant, whereas the temperature of both the shield and the calorimeter proper are changing in time. This occurs for instance in the case of temperature scanning. In order to fulfill such temperature conditions, it is necessary that the heat power $P(t)$ should be

$$P(t)=P_1(t)+P_2(t)+P_3(t) \qquad (8)$$

a superposition of at least three heat forcing functions that are the result of: the heat power $P_1(t)$ generated
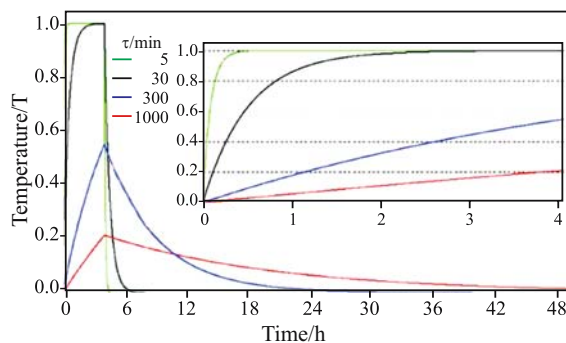

Fig. 1 The curves $T=f(t)$ of calorimeters with various time constants

by the investigated process; the compensating heat power $P_2(t)$ and the heat power $P_3(t)$ generated in the shield in order to keep its temperature in compliance with the programmed changes.

5. $T_c(t)\neq$const., $T_0(t)$=const., $T_c(t)-T_0(t)\neq0$. The general mathematical model of this type of calorimeters is Eq. (1) in the form

$$C\frac{dT_c(t)}{dt}+G(T_c(t)-T_0)=P(t) \qquad (9)$$

This group of nonadiabatic calorimeters, in which the heat transfer occurs in nonisothermal conditions, includes the majority of different types of calorimeters and methods of determination of heat effects. In this class of calorimeters there are instruments that have the time constant of about thousand minutes and several hundreds seconds. How significant are the differences caused by different inertia of these devices is illustrated on Fig. 1. The curves $T=f(t)$ result from a constant heat effect with amplitude of one and the time of duration 300 min calorimeters having time constants: 1000, 300, 30, 5 min calorimeters having high time constants are often referred to as quasi-adiabatic or adiabatic; those of low time constants as quasi-isothermal or isothermal.

These calorimeters have different construction and find various applications. Among them these are:

- Dewar vessel calorimeters in a more or less sophisticated form, like the well known Nernst low-temperature calorimeter [39] or the Curie and Laborde twin calorimeter. Dewar vessel calorimeters found numerous applications in the determination of heat effects of various phenomena [9].
- Vacuum vessels of special design used in *e.g.* Randzio and Zielenkiewicz microcalorimeter [40] for measuring the heat of chemisorption of gases on thin metal films.
- Calorimeters with vacuum jacket or jacket filled with water or air used, among others, in combustion calorimeters [41–44] or solution calorimeters [45, 46]. These calorimeters are frequently referred to in the literature as 'isoperibol' calorimeters. It

happens almost always when total heat effect involved in the calorimeter is determined using the method of corrected temperature rise given by Regnault and Pfaundler [47–51].

- Conduction calorimeters and microcalorimeters, e.g. [52–54], in which the conditions of the heat exchange between the calorimetric vessel and the shield are good enough for the accumulation term in Eq. (1) to be neglected as in flux method. These calorimeters are often called isothermal calorimeters [55]. It does not mean, however, that these calorimeters have no properties of inertial objects. They are incredibly important in the determination of thermokinetics of fast reactions [5]. It is frequent though scarcely understandable and incorrect to refer to those calorimeters as fluxmeters. Let us cite the opinion of the late Prof. McGlashan, presented in the paper entitled 'The Use and Misuse of the Laws of Thermodynamics' published on the occasion of an inaugural lecture delivered in the University of Exeter on 18 January 1965: 'Exposition of calorimetry especially in textbooks of physics, are still hedged about unique concepts like the so-called mechanical equivalent of heat which belong, like phlogiston, to the time when the first law of thermodynamics was not yet understood. It is commonly wrongly supposed that calorimetry measures heat. On the contrary, the whole art of calorimetry depends on making the heat as small as possible or at least as reproducible as possible, and preferably both. In a calorimeter experiment one measures only the changes of temperature and amounts of work and then uses the first law to derive the values for heat changes. The key to understanding calorimetry is, as usual in science, to think exactly what one does in real experiment in a real laboratory'.
- Calorimeters where the heat generated is transferred to the liquid that flows around the outside surface of the calorimetric vessel, as in Junkers [56] and labyrinth flow calorimeters [57, 61].

6. $T_c(t) \neq$ const., $T_0(t) \neq$ const., $T_c(t) - T_0(t) \neq$ const. This group includes the calorimeters in which there occurs a change in time of both the temperatures of calorimeter proper and the shield, as well as of the temperature difference between them. These calorimeters form a group of nonisothermal calorimeters described by the Eq. (1). In order to fulfil the temperature conditions of the experiment it is necessary that the heat power $P(t)$ should be equal to

$$P(t) = P_1(t) + P_3(t) \tag{10}$$

a superposition of at least two heat forcing functions that are the result of the heat power $P_1(t)$ generated by the studied process and heat power $P_2(t)$ generated in

the shield, caused e.g. linear rise of the shield temperature. To this group of nonadiabatic-nonisothermal calorimeters of dynamic properties of inertial objects belong devices applied in thermal analysis, as well as in differential scanning (DSC) calorimeters [62–65].

Suggested classification of calorimeters

On the basis of the above-described classification of calorimeters being the closed systems there were distinguished: a) two kinds of adiabatic calorimeters: adiabatic-nonisothermal (group 1a), scanning adiabatic (group 1b) being integral dynamic objects; b) adiabatic-isothermal (group 2), nonadiabatic-isothermal (group 3) and nonadiabatic-nonisothermal e.g. scanning calorimeters (group 4) being the heat power compensation calorimeters; c) nonadiabatic-nonisothermal calorimeters of both isoperibol (group 5) and changing temperature of the shield as in scanning nonisothermal-nonadiabatic calorimeters (group 6). The division of presented calorimeters is shown in Fig. 2.

Let us discuss the information included in Fig. 2. In adiabatic calorimeters there occurs only the accumulation of the produced energy. These are integral objects. In heat power compensation calorimeters through the compensation of heat effects one aims at the creation of conditions in which the difference in temperatures between the proper calorimeter and the shield remains the stable. It occurs when there is a zero temperature gradient maintained between the proper calorimeter and the shield or a temperature gradient with a determined value. Dynamic properties of this group of calorimeters are similar to the properties of dynamic proportional objects. In case of compensation calorimeters with constant temperature of the shield the conditions of the course of heat of transformation are similar to isothermal conditions (group 2, adiabatic – isothermal, group 3 nonadiabatic – isothermal); whereas in case of compensation calorimeters with variable temperature of the shield (group 6) a constant gradient of temperature is maintained between the calorimeter proper and the shield.

The group of calorimeters, in which inertial properties are taken into account in the methods of determination of heat effects, includes calorimeters with different heat inertia ranging from scarce (conduction calorimeters) to so significant that the properties of those calorimeters hardly differ or do not differ at all from calorimeters referred to as adiabatic calorimeters. In this group of calorimeters there is the largest number of methods of determination of heat effects based on the heat balance equation of simple body (Eq. (1)) and its simplified forms. Total heat effects are determined with the use of the temperature cor-
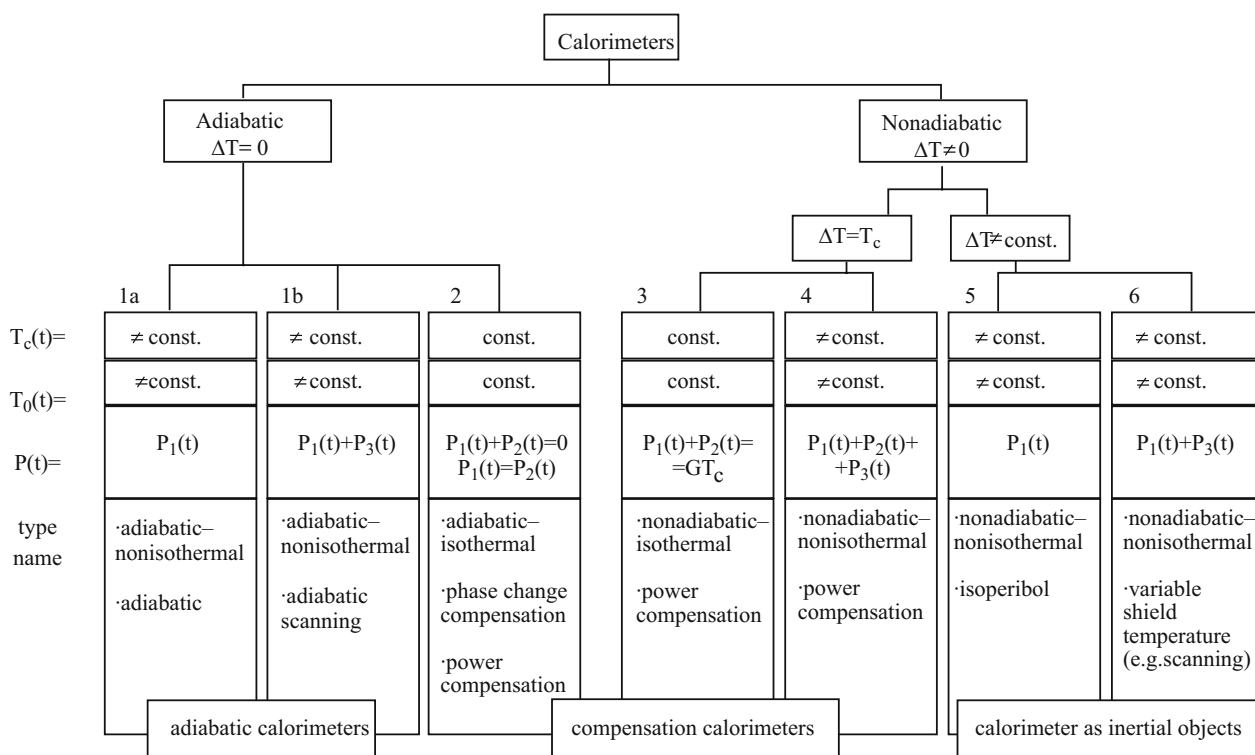
Fig. 2 The division of calorimeters

rected rise method. Frequently, the calculations are made with the use of the Calvet equation, which is particularly useful for calculating changes of heat power within time. This equation is given both in thermal power and temperature [52]. The method of determination of heat effects and thermokinetics using the Calvet equation is called by the author a dynamic method. For conduction calorimeters the flux method is usually applied. In a number of cases it is also assumed that in conduction the course of changes resulting from the changes of temperatures between the proper calorimeter and the shield follows with sufficient accuracy the course of changes of the heat power in time. Power compensation, dynamic and flux methods are applied both in isothermal and in calorimeters with variable temperature of the shield (*e.g.* scanning calorimeters).

It can be mentioned that the assumption that there are isothermal, adiabatic as well as proportional and integral dynamic objects is only a kind of idealization. All physical objects have properties of inertial objects. This feature is particularly noticeable in non-stationary conditions of calorimetric work. In calorimetry the terms 'adiabatic' and 'isothermal' are also usually used with intentional assumption that both in adiabatic and isothermal calorimeters the conditions, set out in thermodynamics as corresponding to those terms, are not completely fulfilled [38, 66].

The presented classification has a number of limitations. It is based on the model of a simple body. It does not offer specific dependencies concerning open calorimetric systems. It does not present mathematical models of nonisothermal-nonadiabatic calorimeters described by n-order differential equations. However, this fact does not affect the division of calorimeters.

The above-described classification is similar to the one given in 1930 by Lange and Mishchenko [67] who distinguished four groups of calorimeters: 1) isothermal–adiabatic; 2) isothermal–nonadiabatic; 3) nonisothermal–adiabatic, and 4) nonisothermal–nonadiabatic. Both in the present work and in the one by Lange and Mishchenko a calorimeter is treated as an object in which heat processes occur. However, in the majority of the existing classifications no attention is paid to the conditions of heat transfer but rather to temperature conditions of the process and the methods of performing the heat process.

The task of presenting a classification that would be generally accepted by everyone is very difficult because of such aspects as tradition, habits and various opinions as to which of the properties of those instruments should be considered important. It would be possible only if the interested scientific organizations made certain arrangements in this scope.

Appendix

Let us assume, that region D corresponds to the proper calorimeter (Fig. 1) of volume V and of external surface S bounded by a shield B of temperature $T_0(t)$. For each element of the region D according to First Law of thermodynamics we can describe
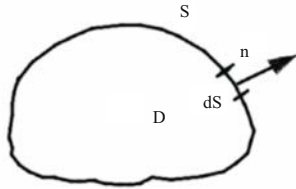
$$dQ = dh - Vdp \qquad (1)$$

Fig. 1

where: dQ, dh, dp – differentials of heat, specific enthalpy and pressure, respectively. Heat flux through a surface element dS in the time dt, according to Fourier's Law corresponds to

$$d^2Q_1 = qdSdt \qquad (2)$$

where: $dS=ndS$ – normal vector to a surface element dS in external direction; qdS – scalar product of heat flux vector q and vector dS.

The heat transported through the whole surface S in the time dt is

$$dQ_1 = dt\iint_S qdS \qquad (3)$$

and

$$dQ_1 = dt\iint_S q_ndS \qquad (4)$$

where q_n is the normal component of vector q with respect to element dS.

The generated heat in region D in time dt is equal to

$$dQ_2 = dt\iint_D gdV \qquad (5)$$

where g is the volume density of the generated heat. Then, the increase of heat dQ in region D in time dt equals

$$dQ = -dQ_1 + dQ_1 \qquad (6)$$

or

$$dQ = -dt\iint_S q_ndS + dt\iiint_D gdV \qquad (7)$$

From the Gauss–Ostrogradzki theorem, we obtain

$$\iint_S q_ndS = \iiint_D \mathrm{div}gdV \qquad (8)$$

then

$$dQ = -dt\iiint_D \mathrm{div}qdV + dt\iiint_D gdV \qquad (9)$$

Second-order differential of enthalpy corresponding to temperature increase dT and volume dV is equal to

$$d^2h = C_p\rho dTdV \qquad (10)$$

where: C_p – specific heat; ρ – density. The increase of enthalpy in the whole region D equals

$$dh = dT\iiint_D C_p\rho dV \qquad (11)$$

We can also write

$$Vdp = dp\iiint_D dV \qquad (12)$$

Taking into account the relations (9), (11), (12), Eq. (1) can be given in the form (13)

$$dt\iiint_D (-\mathrm{div}q + g)dV = dT\iiint_D C_p\rho dV - dp\iiint_D dV \qquad (13)$$

Equation (13) is valid in any region D, if

$$dt(-\mathrm{div}q + g) = dTC_p\rho - dp \qquad (14)$$

Assuming that temperature T is the function of localization and time, changes of temperature of the medium of region D depend on the field of vector of medium velocity. According to this, we can note the differential of the function $T=T(x, y, z, t)$ as follows

$$dT = \frac{\partial T}{\partial x}dx + \frac{\partial T}{\partial y}dv + \frac{\partial T}{\partial z}dz + \frac{\partial T}{\partial t}dt \qquad (15)$$

we obtain

$$dT = \left(\frac{\partial T}{\partial x}\frac{dx}{dt} + \frac{\partial T}{\partial y}\frac{dy}{dt} + \frac{\partial T}{\partial z}\frac{dz}{dt} + \frac{\partial T}{\partial t}\right)dt \qquad (16)$$

then

$$dT = \left(w\mathrm{grad}T + \frac{\partial T}{\partial t}\right)dt \qquad (17)$$

where

$$w = \left(\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}\right) \qquad (18)$$

is the medium velocity vector.

In a similar way we can determine the dependence between velocity of pressure changes p and velocity of medium transfer from D and we obtain

$$dp = \left(w\mathrm{grad}p + \frac{\partial p}{\partial t}\right)dt \qquad (19)$$

Introducing dependences (17) and (19) into (14) we can obtain a relationship corresponding to the Fourier–Kirchhoff equation

$$C_p\rho\left(\frac{\partial T}{\partial t} + w\mathrm{grad}T\right) - \left(\frac{\partial p}{\partial t} + w\mathrm{grad}p\right) = -\mathrm{div}q + g \qquad (20)$$

Assuming that the process takes place under isobaric conditions and multiplying both sides of Eq. (20) by volume V, we obtain

$$C\left(\frac{\partial T}{\partial t} + w\mathrm{grad}T\right) = -\mathrm{div}qV + P \qquad (21)$$

where: $C=C_p\rho V$ – heat capacity; $P=gV$ – heat power. Furthermore, assuming the boundary conditions of the third kind (Newton's Cooling Law), we obtain

$$V \operatorname{div} q = G(T_S - T_0) \tag{22}$$

where: G – heat loss coefficient; T_S – surface temperature; T_0 – shield temperature. Taking into account (22), relationship (21) can be given in the form

$$C\left(\frac{\partial T}{\partial t} + w \operatorname{grad} T\right) = -G(T_S - T_0) + P \tag{23}$$

Assuming additionally that mass transport takes place only in direction x, then temperature T and heat power P are the functions of one coordinate x and time t, e.g.: $T=T(x, t)$, $P=P(x, t)$. If surface temperature T_S is equal to temperature T and represents the calorimeter temperature $T_c(x, t)$ Eq. (23) can be described in the form

$$C\left(\frac{\partial T_c(x,t)}{\partial t} + w\frac{\partial T_c(x,t)}{\partial x}\right)$$
$$+ G(T_c(x,t) - T_0(x,t)) = P(x,t) \tag{24}$$

When the velocity vector is equal to zero, Eq. (24) can be given in the form of the heat balance equation of simple body.

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