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Comparative measurements in isoperibol calorimetry: uses and misuses

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Abstract

In this paper, the application of comparative measurements in isoperibol calorimetry have been presented. The limitations of the applied mathematical models for calculation of heat effects have been given.

Keywords: Isoperibol calorimetry; Comparative measurements; Mathematical models; Differential and twin calorimeters

1. Introduction

More then 60 years ago the International Conferences of Chemistry [1–4] subdivided the physicochemical measurements into two groups, absolute and comparative. The main principle of comparative measurements is the identity of conditions during the measurements and the system calibration.In calorimetry, the method of comparative measurements may involve [5]

1. the use of twin calorimeters and compensation of the heat developed in one calorimeter by electric energy introduced into the other;
2. elimination of external temperature disturbances using differential calorimeters, where the heat generated is determined based on measured temperature difference between two calorimeters;
3. the use of two successive measurements to reproduce the heat effect by electrical energy and
4. comparison of the heat liberated by a standard thermochemical material.

This paper will discuss some uses and misuses of comparative measurements in isoperibol calorimeters where the calorimetric vessel has surroundings at constant temperature. Mathematical models of isoperibol calorimeters will be developed.

In general, the heat processes that occur in a system are described by the Fourier–Kirchhoff equation coupled with the Navier–Stokes equation and the flux continuity equation to account for mass transport. Calorimetric models are developed on the basis of a simplified Fourier equation with a set of parameters limited to those considered to be of prime importance. The choice of the model is important for an accurate determination of heat effect.

Comparative measurements can help one obtain more accurate results only within the framework of an accepted model of the calorimeter. Thus, it is useful to analyse the assumptions and limitations of the models and methods of measurements applied in calorimetry.

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2. Heat balance equation of a simple body

Let us assume that the heat effect dQ involved in the calorimetric vessel is partly accumulated in the vessel and partly transferred to the isothermal shield. According to the Newton equation, the amount of heat dQ_2 transferred from the calorimetric vessel to the isothermal shield is:

$$\mathrm{d}Q_2 = \alpha S\theta(t)\,\mathrm{d}t \tag{1}$$

where α is the heat exchange coefficient for the surface S of the calorimeter vessel per unit time when the temperature difference between the external surface of the calorimeter vessel and isothermal shield is equal to 1° and where $\theta(t)$ characterises the change in temperature θ of the calorimeter vessel within time t. The amount of heat dQ_1 accumulated in the vessel is:

$$\mathrm{d}Q_1 = C\theta(t) \tag{2}$$

where C is the heat capacity. The heat effect involved in the calorimeter vessel is:

$$\mathrm{d}Q = \mathrm{d}Q_1 + \mathrm{d}Q_2 \equiv C\theta(t) + \alpha S\theta(t)\mathrm{d}t \tag{3}$$

or

$$W(t) = \frac{\mathrm{d}Q}{\mathrm{d}t} \equiv \frac{\mathrm{d}Q_1}{\mathrm{d}t} + \frac{\mathrm{d}Q_2}{\mathrm{d}t} = C\frac{\mathrm{d}\theta(t)}{\mathrm{d}t} + \alpha S\theta(t)\mathrm{d}t \tag{4}$$

According to Eq. (4), a physical system described by this type of equation is characterised by inertial properties of the first order. This is easily recognised, because upon dividing both sides of Eq. (4) by G=αS and setting

$$\tau = \frac{K}{G} \quad \text{and} \quad f(t) = \frac{1}{G}W(t)$$

we arrive at:

$$\tau\frac{\mathrm{d}\theta(t)}{\mathrm{d}t} + \theta(t) = f(t) \tag{5}$$

which indicates that the time constant τ establishes the course of the heat flow. If a Laplace transformation is applied to Eq. (5), the transmittance is:

$$H(s) = \frac{\theta(s)}{Q(s)} \equiv \frac{1}{\tau s + 1} \tag{6}$$

where $\theta(s)$ and $Q(s)$ denote the transforms of the functions $\theta(t)$ and $Q(t)$, respectively, and the resulting quotient represents the transmittance $H(s)$. This function is expressed by the operator 1/(τs+1), which characterises the properties of the calorimeter as those of a first-order inertial object. The time constant t is the parameter that describes the inertial properties of the object. This also means that the value of the time constant determines whether experimental conditions approach more closely isothermal or adiabatic, and the resulting observed temperature follows the course of the function $Q(t)$, which corresponds to the power of the transformation investigated.

The common application of this model, based of the heat balance equation of a simple body, in isoperibol calorimetry is generally familiar. Eq. (4) is a basis for determination of the heat involved in Calvet microcalorimeters [6] and is known as the Tian–Calvet equation. It is the basis of the static–dynamic method of Swietoslawski and Salcewicz [5]. Most corrections applied to an ordinary calorimeter, for example the Regnault–Pfaundler correction [7,8], are based on this model. The integral of Eq. (4) is described by:

$$\Delta Q = C\Delta\theta \equiv (\Delta\theta_\mathrm{c} + \Delta\theta_\mathrm{p}) \tag{7}$$

where C is the heat capacity; $C\Delta\theta$=ΔQ corresponds to the amount of heat generated in the calorimeter; $\Delta\theta_\mathrm{c}$ the change in the calorimeter temperature; $\Delta\theta_\mathrm{p}$ a 'temperature correction' which corresponds to the integral

$$\int_{t_1}^{t_2} \theta_\mathrm{c}(t)\,\mathrm{d}t \tag{8}$$

which can be determined on the basis of the Regnault–Pfaundler correction.

The model is also used for calculation of the total heat effect and thermokinetics $W(t)$ in conduction calorimeters. When the values of temperature initially and finally for an experiment are equal the integral of the second term of Eq. (4) is determined. Additionally, assuming that the first term of the right side of Eq. (4) can be neglected, $W(t)$ is expressed by the second term of the right side of this equation and $W(t)$ corresponds to the course of $\theta(t)$ with accuracy up to the factor G.

The applications of the model of a simple body to isoperibol calorimetry make it necessary to consider the conditions in which this model is valid [8]. Let us transform the Fourier–Kirchhoff equation

$$C_\mathrm{p}\rho\left(\frac{\partial T}{\partial t} + w\,\mathrm{grad}\,T\right) - \left(\frac{\partial p}{\partial t} + w\,\mathrm{grad}\,p\right) = \mathrm{Div}\,(\mathrm{grad}\,T) + g \tag{9}$$

into the heat balance equation of a simple body in order to indicate the simplifications and limitations assumed in the definition of Eq. (4).

Let us assume that heat processes take place in isobaric conditions p=const ($\mathrm{d}p/\mathrm{d}t$=0 and grad p=0), without mass exchange, and the thermal parameters, namely C_p the heat capacity, ρ the density, G the heat loss coefficient and V the volume, are constants. Then, Eq. (9) can be written as:

$$C_\mathrm{p}\rho\frac{\partial T}{\partial t} = \mathrm{Div}(\lambda\,\mathrm{grad}\,T) - C_\mathrm{p}\rho\,\mathrm{grad}\,T + g \tag{10}$$

where T is the temperature, and g the density of inner heat sources (amount of heat developed per unit volume in unit time). Integrating the particular terms of Eq. (10) with respect to volume V of a body of external surface S we obtain:

$$\iint_V\!\!\int C_\mathrm{p}\rho\frac{\partial T}{\partial t} = C_\mathrm{p}\rho V\frac{\partial T}{\partial t}V \tag{11}$$

$$\iint_V\!\!\int \div\,(\mathrm{grad}\,T)\,\mathrm{d}V = -G(T_\mathrm{s} - T_0) \tag{12}$$

$$\iint_V\!\!\int C_\mathrm{p}w\,\mathrm{grad}\,T\mathrm{d}V = wC_\mathrm{p}\rho V\frac{\mathrm{d}T_\mathrm{V}}{\mathrm{d}t} \tag{13}$$

$$\iint_V\!\!\int g\,\mathrm{d}v = \frac{\mathrm{d}Q(t)}{\mathrm{d}t} \equiv W(t) \tag{14}$$

where T_v is the average temperature of the calorimeter vessel of total volume V, T_s the average temperature of the external surface S of the calorimeter vessel, T_0 the temperature of the isothermal shield and w a velocity vector. Assuming additionally that w=0, and T_v=T_s and $T-T_0=\theta$, Eq. (10) becomes:

$$C_\mathrm{p}\rho V\frac{\mathrm{d}\theta(t)}{\mathrm{d}t} + G\theta(t) = W(t) \tag{15}$$

which is equivalent to Eq. (4).

The heat balance equation of a simple body (Eq. (4)) and the Fourier–Kirchhoff Eq. (10) are identical, when:

1. temperature in the total volume is homogenous and a function of time only;
2. temperature on the whole surface is homogenous and a function of time only;
3. the above temperatures are equal, and are the same at all times; and
4. the heat capacity C and heat loss coefficient G are constant and are not functions of time or temperature.

These conditions can be met in all calorimetric measurements, including calibration and determination of heat effects. As was mentioned before, the main principle of comparative measurements is the identity of the conditions during the measurements and calibration. Applying this model, it is assumed that G and C are the same in all the measurements and that temperature gradients do not occur. To preserve these conditions in real calorimeters is enormously difficult.

3. Differential and twin calorimeters

Differential isoperibol calorimeters have found a wide range of applications. Such calorimeters consist of two calorimeters (I and II) placed in common shield. One vessel contains localised heat source and the other — thermally passive. It is assumed that the static and dynamic properties of both the calorimeters are identical. The course of temperature changes of calorimeter I, in which the heat effect is generated, is based on the measured temperature difference between calorimeters I and II. It is assumed that the influence of external disturbances is the same in both the calorimeters and that temperature difference measurements enable us to eliminate these disturbances. From a consideration of the dynamic properties of differential calorimetric systems it is clear that the influence of disturbances can be eliminated only when transmittances of calorimeters I and II are the same. This means that time constants and heat loss coefficients should be equal. It is very hard to fulfill this condition from the principle of comparative measurements. Because of this it is useful to determine, for a given differential calorimeter, an acceptable range of difference of time constants of calorimeters I and II for which, for a given disturbance, the required accuracy of $\theta(t)$ measurement is fulfilled [8].

Another type of calorimetric system is called twin calorimeters. In these devices, it is necessary to obtain equal temperatures of the inner parts of calorimeters I and II in such a way that a heat effect of the same magnitude and course is generated in calorimeters I and II. It is obvious that, for twin calorimetric systems, as in differential calorimetric systems, the dynamic properties of both the calorimeters should be the same.

4. Invariance of the transmittance of the calorimeter

There exist a number of methods based on the 'black box' notion to determine the thermokinetics $W(t)$ [9,10] (e.g. dynamic optimisation, harmonic analysis, state variables, numerical correction), where a consideration of the physical parameters of the system is abandoned, and the dependence between the heat effect $Q(t)$ corresponding to changes in temperature θ in time t is searched for. If the results of calibration $Q(t)$ and $\theta(t)$ are known, the transfer function of the calorimeter, which represents the dynamic properties of the system, can be found. It is possible to evaluate the course of unknown heat effects on the basis of the changes of the temperature $\theta(t)$ in the transmittance of the calorimeter during calibration and measurement are the same. For example, a change in the calorimetric vessel contents, and thus its heat capacity, can cause errors in the determination of the heat effect.

5. Mutual localisation of heat sources and the temperature sensor in proper calorimeter vessel

In the investigations on heat of combustion at the US National Bureau of Standards, it was stated [11,12] that the calculated heat capacity of the calorimetric bomb as the sum of heat capacities of the particular parts of the calorimeter was not equal to the experimentally determined heat capacity of the system. This phenomenon cannot be explained when using an equation for a simple body. King and Grover [11] replaced that model with a two-body model which can be described by the following differential equations:

$$C_1\frac{d\theta_1(t)}{dt}+G_{01}\theta_1(t)+G_{12}[\theta_1(t)-\theta_2(t)]=W_1(t) \tag{16}$$

$$C_2\frac{d\theta_2(t)}{dt}+G_{12}[\theta_2(t)-\theta_1(t)]=W_2(t) \tag{17}$$

where C_1, C_2 are heat capacities of the two bodies; G_{01} the heat loss coefficient between the outer body and the environment; G_{12} the heat loss coefficient between the two bodies; $W_1(t)$, $W_2(t)$ the heat powers generated in the two distinguished bodies and $\theta_1(t)$, $\theta_2(t)$ the temperatures of these bodies.

It was shown [11,12] that, for this model, the energy equivalent of the system depends on the values of heat capacities C_1, C_2 of distinguished bodies as well as on the value of heat loss coefficient between these bodies. Margas and Zielenkiewicz [13] analysed this two-body model and demonstrated that two cases can be given when the energy equivalent corresponds to the sum of the heat capacities of the parts of the calorimeter. This takes place, when the no heat exchange between the calorimeter and shield occurs and when intensive heat exchange between the distinguished bodies occurs.

The detailed considerations of the models of two and three bodies of different configurations demonstrated [8,14–17] that transfer functions of the system also depend on the mutual localisation of heat sources and temperature sensors as well as on the values of heat loss coefficients between the bodies. This suggests that during the calibration the determination of heat effects and the localisation of the temperature sensor with respect to the heat source must be guaranteed.

6. The multi-body model

The real calorimeter is composed of many parts. To describe the flow of heat in such a system, the multi-body model of the calorimeter was elaborated [8,17,18].

The basic postulates of the multi-body model are as follows: Each of the separate bodies has a uniform temperature over its entire volume, the temperature is a function of time t only, and the heat capacity of the body is constant. Temperature gradients appear only in the media separating the bodies, and the heat capacities of these media are, by assumption, negligibly small. The amount of heat exchanged between bodies through these media is proportional to the difference in the temperatures of the bodies; the proportionality constants are the appropriate heat loss coefficients. Furthermore, a heat source or a temperature sensor may be positioned in any of the bodies. The system of bodies is placed in a medium with a constant temperature. The generalised heat balance equation derived with these assumptions is

$$C_j\mathrm{d}\theta_j(t) + G_{0j}\theta_j(t)\,\mathrm{d}t + \sum_{\substack{j=1\\ j\neq 1}}^{N} G_{ij}[\theta_j(t) - \theta_i(t)\,\mathrm{d}t$$
$$= \mathrm{d}Q_j(t), \quad j = 1, 2, \ldots, N \tag{18}$$

where N is the number of bodies, C_j the heat capacity of body j, $G_{0\mathrm{j}}$ the coefficient of heat loss between body j and the environment, G_{ij} the coefficient of heat loss between bodies i and j, $\theta_j(t)$ describes the variation in time of the temperature of body j in relation to the ambient temperature which is constant, $\mathrm{d}Q_j(t)$ the amount of heat evolved in time dt in body j; $C_j\mathrm{d}\theta_j(t)$ the amount of heat accumulated in body j in time dt; $G_{0\mathrm{j}}\theta j(t)\mathrm{d}t$ the amount of heat exchanged between body j and the environment in time dt and $G_{ij}[\theta_j(t){-}\theta_i(t)]\mathrm{d}t$ the amount of heat exchanged between bodies j and i in time dt.

The particular form of these equations for a calorimetric system depends on the number of distinguished bodies, on the heat interactions between those bodies, and on mutual localisation of heat sources and temperature sensors. The determination of the particular form of these equations is equivalent to the determination of the transmittance of the calorimetric system. It is necessary to describe the heat capacities, C_p, of the bodies and characterise the heat interactions between these bodies by heat loss coefficients, G_{ij}, and also heat interactions between these bodies and the environment by heat loss coefficients, G_{0j}. The values of coefficients G_{ij}, $G_{\mathrm{j}0}$ and heat capacities, C_j are determined from a knowledge of physical parameters of the calorimetric system (e.g, thermal conductivity, volume specific heat). Thus, the values of the transmittance of the system can be determined. The transmittance of the system is accepted when optimisation and stability conditions of numerical solution are fulfilled [19,21]. If any of the time constants of the calorimetric system does not satisfy the stability condition, then a new model of the system must be devised to decrease the number of time constants which satisfy the stability condition. Next, the temperature is compared with the experimental response. If the result is consistent, we can accept the elaborated model. This method was used with success to identify existing calorimetric devices [20,22]. Such a model of calorimeters makes it easy to determine the total heat effect and thermokinetics of the process studied. Let us determine a domain (domains) whose heat capacity corresponds to the heat capacity of the substance examined (or substance and calorimetric vessel). Then Eq. (18) takes the form

$$C_j\frac{\mathrm{d}\theta_i(t)}{\mathrm{d}t} + G_i\theta_i(t) - \sum_{\substack{j=1\\ j\neq 1}}^{N} G_{ij}\theta_j(t) = W_i(t),$$
$$j = 1, 2, \ldots, p-1,\ p+1, \ldots, N \tag{19a}$$

$$C_p\frac{\mathrm{d}\theta_p(t)}{\mathrm{d}t} + G_p\theta_p(t) - \sum_{\substack{j=1\\ j\neq p}}^{N} G_{pj}\theta_j(t) = W_p(t) \tag{19b}$$

Eq. (19b) describes the so-called ‘changeable’ part of the calorimetric system. The remaining part of the calorimetric system described by Eq. (19a) corresponds to an ‘empty’ calorimeter. This part can be called the ‘non-changeable part’ of the calorimetric system. The method of calculation of heat effects permits elimination of the effect of changing the dynamic properties of a calorimetric system, e.g. in titration calorimeters in which each injection of liquid changes C_p of calorimetric vessel.

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