

IS GRADIENTLESS SOLID STATE CALORIMETRY POSSIBLE?

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ABSTRACT

Proceeding from the condition $Bi \rightarrow 0$ which, according to the general theory of heat conduction is a necessary condition for a uniform temperature distribution in a heated (cooled) body, the sufficient conditions for bringing about a gradientless solid state system (construction principles thereof) have been defined and a calorimetric device based thereupon has been elaborated; its conformity to the gradientless theory of differential thermal analysis has been established.

The main problem with which the present day solid state calorimetry is grappling and without the solution of which no further progress of this field of science is possible is the problem of correctly measuring the temperature of the system under study, which is a condition sine qua non for extracting meaningful quantitative information out of the recorded thermoanalytical curves. If the measured quantity depends on poorly controlled factors, such as the position of the temperature detector or the state of the sample in the holder, then the conformity between the process studied and its mathematical model is lost thereby invalidating quantitative determinations. The general source of uncertainty in calorimetry lies in the existence in solids of temperature gradients which cannot be measured or theoretically evaluated; perforce a simplified gradientless theory of DTA has been developed [1, 2] for a DTA cell with uniform temperature distribution. The paradox of the situation is that no such cell actually existed until recently to confirm the theory with the exception of a liquid DTA cell [1] having no great practical value. The tacit conviction of thermoanalysts in the impossibility of a gradientless solid state cell precluded the search for DTA cells of this type. In the theory mentioned the gradientless DTA cell is simply postulated; no hint at concrete measures for bringing it about is given. Such a hint can though be found in a more fundamental theory of heat conduction [3] which among others considers the case of a body heating (cooling) in a medium at a given temperature for three values of the dimensionless criterion Bi :

$Bi \rightarrow 0$, $Bi \rightarrow \infty$ and $0 < Bi < \infty$; $Bi = K_2/K_1$, where K_2 - heat transfer coefficient of the medium, K_1 - same of the body. If $Bi = 0.1 - 0.01$ a nearly homogeneous temperature distribution is established in the body during heating (cooling). This result is a clear indication of the possibility of a gradientless solid state system, the necessary condition for its realization being given by the equation $Bi = 0.1 - 0.01$. Using the criterion Bi , all the calorimetric devices can be divided into three classes: those for which $Bi \rightarrow \infty$ (DSC), those for which $0 < Bi < \infty$ and those for which $Bi \rightarrow 0$; the latter case which corresponds to GSSC seems to have been uninvestigated from the practical point of view.

In order to make GSSC a reality sufficient conditions for its practical realization must be found. These conditions have for the first time been formulated in [4] and in essence boil down to the following.

1. A perfect thermal insulation of the sample holder from the heater and the holder support effected through fixing the holder on sufficiently thin and long wire suspensions in a gaseous medium of the heating block. The wires should lie in the plane of the isothermal surface of the holder.

2. Central-symmetrical arrangement of the holder relative to the heater and symmetrical and compact packing of the sample in the holder.

3. A thin walled metal sample holder of moderate size, low heat capacity and high thermal conductivity.

4. A temperature detector without thermal inertia, with zero contact resistance and of negligible heat capacity, taking no part in heat exchange. It can be obtained by soldering thin thermocouple wires to the outer surface of the holder and placing them close to that surface, i.e. perpendicular to the direction of the heat flow from the heater.

In our studies we use a device with the following parameters: a copper sample holder with walls 0.20 mm thick, 8.0 mm high and 4.4 mm in diameter; the chromel-alumel thermocouple made of 0.20 mm diam. wires; the 0.20 mm wire suspensions 20-40 mm long; the cylindrical heater 140 mm long with the inner diameter 10 mm; nitrogen as the gaseous medium. For this device $Bi = 0.015$. This condition holds mainly for the holder walls for which it was calculated and in a lesser degree for the sample in the holder. Still, provided there is a good thermal contact between the two,

the holder walls assume the temperature very close to that of the sample and this closeness of temperatures is maintained at any time of the experiment including that of the thermal reaction in the sample, and at any point of the holder walls which can thus be regarded as isothermal. This phenomenon of isothermality can best be explained by assuming the existence of large surface heat currents directed towards points of contact of the sample with the holder whose function is to supply heat to the sample and to minimize temperature gradients on the holder walls. Due to surface isothermality a virtual merging of the holder and the sample takes place: the latter takes on the heat absorbing capacity of the former and the former takes on the temperature of the latter. This is especially true for small samples with good thermal conductivity (metals). In our experiments a sample with as low a mass as 5 mg lying as a flat disc on the bottom of the holder imparts its temperature (temperature of a phase transition) to the sample holder whose mass is 250 mg and whose surface is 30-50 times as big as that of the sample. The difference between the measured temperature (that of the holder surface) and the true temperature of the reacting sample may not exceed 0.1-1.0°C depending on heating rate and other factors. The remarkable features of the thermally insulated sample holder delineated above may be said to form the basis of gradientless solid state calorimetry as many important consequences follow from them, the main of which are listed below.

1. The instrument calibration constant K does not depend on thermophysical and geometrical parameters of the sample; this constant is simply the heat transfer coefficient of the gaseous medium of the cell which in principle is a known function of the geometry and heat conductivity of that medium.

2. Ambiguity of temperature measurements is largely eliminated: a single thermocouple placed at no matter what point on the holder surface provides information both about the temperature of the reaction zone of the sample and the heat flow into that zone, which is a fundamental condition for reaction kinetics studies.

3. The operation of the device is adequately described by the basic equation of differential thermal analysis

$$-\frac{d\Delta H}{dt} = K\Delta T + C\frac{d\Delta T}{dt}$$

derived for a gradientless DTA cell [1], provided the internal heat resistance of the holder is small enough. The values K and C in the above equation are true measurable parameters of the cell because they are localized: one at the gaseous thermal barrier of the cell and the other at the holder. This is in sharp contrast to the gradient calorimetry where these parameters are effective values, not directly measurable, being delocalized over the space where the temperature is being measured.

In cases when the internal resistance of the holder (sample) cannot be minimized or is made the object of study, some way of measuring it must be found. For this purpose a two point DTA has been developed [5, 6] in which two DTA curves are simultaneously recorded with the differential thermocouple being periodically switched from the center of the holder (sample) to its surface and vice versa. The distance between the two curves is directly proportional to the internal resistance of the holder enabling the latter to be measured if the heat flow across the sample is known.

Because the gradientless method of DTA described above is so simple and at the same time strictly quantitative, it has decisive advantages over the more cumbersome, expensive and less quantitative methods of gradient calorimetry. It opens up new and as yet unexplored possibilities for raising the theoretical and experimental level of current thermoanalytical research. These are, for example: (i) unification and standardization of DTA equipment and experimental procedures; (ii) a more quantitative approach to solid state reaction kinetics; (iii) determination of thermophysical and thermodynamic parameters of materials under extreme experimental conditions.

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