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ISOTHERMAL-SURFACE TRANSMITTER WITH THERMALLY INSULATED SAMPLE HOLDER – A NOVEL APPROACH TO QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

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It is demonstrated that quantitative DTA (DSC) must be based on the principle of the isothermal surface of the sample holder. In the known transmitters of DTA instruments of the insulated vessel type the surface of the sample holder is not isothermal, due to the effect of the support which is either a massive ceramic shaft or a support plate. In the transmitter described, the effect of the support is reduced to minimum by substituting it by suspension, for which purpose the sufficiently fine and long wires of the differential thermocouple are used. In this manner a holder with an isothermal surface is obtained and hence one of the fundamental requirements of the theory of heat transfer in systems with no temperature gradient is satisfied. This is experimentally confirmed by the finding that the described transmitter has the following features: first, the instrument constant K coincides with the heat transfer coefficient of the thermal barrier (the working space) of the cell and is independent of the nature of the sample in the holder; secondly, the heat capacity C figuring in the theory is exactly equal to the sum of the heat capacities of the holder and the sample; and finally, the differential curve, after completion of the reaction in the sample, is represented by an exponential expression depending on a single constant, namely the time constant of the cell. A formula for computation which does not contain the instrument constant K, and a new method of instrument calibration utilizing the tail end (the exponential branch) of the differential curve is proposed.

In the practice of differential thermal analysis two main types of signal transmitters are in use: a) the block-type in which the sample holder and the heater are in direct contact, and b) the insulated vessel-type, in which the sample holder is thermally separated (insulated) from the heater by a gas space (the working space of the transmitter) functioning as a heat barrier. The theory developed for the block-type transmitter [1–4] is based on the assumption that the temperature gradient in the sample is described by a cylinder with uniformly rising surface temperature. This theory leads to the formula

$$\Delta H_0 M = 4\pi\lambda l A \tag{1}$$

where ΔH_0 is the specific heat of reaction, M is the sample mass, λ is the thermal conductivity of the sample, l is the height of the sample, and A is the area of the peak in the differential curve.

It follows from Eq. (1) that to determine the heat of reaction by means of the thermoanalytical curve it is indispensable to know the thermal conductivity of the sample, requiring further methods of study. The situation becomes more intricate due to the fact that the value λ in Eq. (1) is not the true value, but is an apparent value depending on the state of the sample and on the closeness of packing within the sample holder. These difficulties arise from the fact that in the block-type transmitter it is the sample itself that forms the heat barrier across which the change of the temperature measured in the experiment takes place, and the nature of the sample is reflected in the calculation formula (1). It is evident that quantitative DTA is impossible with a block-type transmitter.

The drawbacks of the block-type transmitter are largely eliminated in the insulated vessel-type transmitter, owing to the presence of a gaseous heat barrier. The advantages of the latter lie in its extremely low thermal conductivity and heat capacity, these being about three orders of magnitude lower than those in solids. This leads to the following consequences, essential for quantitative DTA:

(i) The high thermal sensitivity of the transmitter, this being the higher, the lower the heat transfer coefficient across the heat barrier.

(ii) The thermal inertia of the transmitter (its time constant) is fully defined by the heat capacity of the sample holder with the sample, since the heat capacity of the barrier connected to the holder is practically zero.

(iii) The temperature difference responsible for heat transfer to the sample holder, and the additional temperature caused by the reaction and measured in the experiment, are totally localized to the thermal barrier of the transmitter; temperature changes in the sample do not affect the temperature of the heater wall.

(iv) When establishing the heat balance of the cell, the heat losses at the heat barrier can be neglected due to the low thermal capacity of the latter.

(v) Temperature gradients in the bulk of the sample holder and on its surface are very small, since they are able to level out owing to the low rate of heat transfer across the barrier, which represents a high thermal resistance.

The above-listed features cause the insulated vessel-type transmitter to approach the gradientless model considered in the theory of DTA [5]; heat transfer in such transmitters may be described by the Newton equation:

$$\frac{dq}{dt} = \alpha S(T_0 - T_S) = K(T_0 - T_S) \tag{2}$$

where dq/dt is the total heat flow transferred from the walls of the heater at temperature T_0 to the sample holder at temperature T_S, α is the heat transfer coefficient, S is the surface area of the sample holder, and K is the instrument constant (in this case, the thermal conductivity of the heat barrier).

Heat transferred to the sample holder is consumed in the reaction and in increasing the temperature of the sample holder with the sample:

$$C\frac{dT_S}{dt} + \frac{d\Delta H}{dt} = K(T_0 - T_S) \tag{3}$$

When a linear temperature rise of the transmitter is established, the following equations are valid [6]:

$$T_S = \varphi t + \Delta T \tag{4}$$

$$T_0 = \varphi t + \varphi \tau \tag{5}$$

where φ is the pre-set constant heating rate, ΔT is the additional temperature at the thermal barrier, equal to the peak height of the thermal transformation, and $\tau = C/K =$ const. is the time constant of the cell.

By introducing Eqs (4) and (5) into Eq. (3), one obtains

$$-\frac{d\Delta H}{dt} = K\Delta T + C\frac{d\Delta T}{dt} \tag{6}$$

an equation which is strictly applicable only to systems without temperature gradients, but frequently used without taking account of this condition.

Equation (6) was derived in [7] for a transmitter with a liquid sample and a liquid heat transfer medium, in which temperature gradients were reduced to a minimum by stirring. Up to the present this is the only known example of a gradientless system to which Eq. (6) may be applied without reserve. The situation with solids – in which temperature gradients cannot be eliminated by stirring – is much less clear. For such systems, other ways must be found to reduce temperature gradients.

As shown above, the separation of the sample holder from the heater by a gaseous barrier having a high thermal resistance and a low thermal conductivity promotes lowering of thermal gradients in the sample holder and sample. This is true, however, only if a satisfactory separation is achieved, when the only path of heat transfer into the sample is across the gas barrier, i.e. the working space of the transmitter. This is equivalent to the condition that there is no direct contact of the sample holder with other elements of the transmitter.

In the known transmitters of DTA instruments, sample holder supports are used in the form of ceramic shafts or support plates. Their presence has the following consequences, resulting in deviation from the ideal model:

(i) The thermal sensitivity of the transmitter is reduced, owing to the lowered thermal resistance of the heat barrier.

(ii) The value of C in formula (6) becomes undefined, owing to some unknown proportion of the heat capacity of the support being added to the heat capacity of the sample holder.

(iii) The heat flow into the sample consists of two components: flow through the support and flow across the working space; these flows will depend differently on the experimental conditions (temperature) and cannot be evaluated theoretically with the required accuracy.

(iv) The heat flow through the support upsets the symmetry of the temperature gradients in the sample holder and renders its surface non-isothermal.

It is obvious from the above that, in order for a transmitter to approach to the theoretical gradientless model, one should eliminate the support of the sample holder.

This is impossible, of course; however, very good thermal insulation of the sample holder from the heater can be attained by replacing the support with a suspension. For this purpose the wires of the differential thermocouple itself are well suited; if the wires are thin and long enough, one may obtain a thermal resistance higher by several factors as compared to the resistance of the gaseous heat barrier. Further advantages of a suspension are a low thermal capacity and a very small contact area with the sample holder. In the case of necessity, rigidity can be increased by placing the sample holder on the points of steel support pins and rigging it to them by the wires of suspension. In this variant, suspension is combined with support, but the thermal resistance is high owing to the very small contact area with the sample holder, and the thermal inertia is low owing to the small mass and heat capacity.

The degree of insulation of the sample holder from the heater can be estimated by the ratio of the thermal conductivities of the working space and the suspension (support). Starting with the assumption that satisfactory insulation corresponds to a value of 20 or more for this ratio, one can find acceptable parameters of the cell.

For the thermal conductivity of a cylindrical space, the following expression is valid [8]:

$$K_1 = \frac{2\pi h \lambda_g}{\ln \frac{R_0}{R_i}} \tag{7}$$

and for the thermal conductivity of the support (suspension) [1]:

$$K_2 = \frac{\pi d^2 \lambda_\omega}{2l} \tag{8}$$

where h is the height of the sample holder, R_0 is the radius of the cylindrical cavity of the heater, R_i is the radius of the sample holder, λ_g is the thermal conductivity of the gas in the working space, λ_ω is the thermal conductivity of the wires of the thermocouple, d is the diameter of the wire, and l is the length of the suspension.

In this work a transmitter was studied in which the sample holder was a thin-walled silver crucible (wall thickness 0.15–0.2 mm), 8 mm high and 4 mm in diameter; the chromel-alumel themocouple made of 0.2 mm diam. wires and serving as suspension was soldered to the side wall of the crucible; the length of the suspension was 15 mm; the gas in the working space was nitrogen. The values λ_g and λ_w at 100° are 0.031 and 24.4 Wm^{-1} degree^{-1}, respectively. The reference junction was located in the wall of the heater, i.e. thermal curves were recorded in the DTA regime with no reference material. The heating rate was 12 degree min^{-1}. With these parameters, the value of K_1 is 2.24 mW degree^{-1}, and that of K_2 is 0.1 mW degree^{-1}, demonstrating that the chosen parameters are acceptable.

Experimental data obtained with this transmitter allowed the assumption that it has the following characteristics:

(i) The surface of the sample holder is isothermal both before and during the reaction.

(ii) Heat flows to the sample holder preferentially across the working space; heat flow through the support is negligible.

(iii) The thermal capacity C figuring in the formulas of the theory is exactly the sum of the thermal capacities of the sample holder and the sample.

From these characteristics, certain conclusions can be made which can be confirmed experimentally.

Conclusion 1. The peak area in the differential curve is independent of the position of the hot junction on the surface of the sample holder.

Conclusion 2. The peak area is directly proportional to the mass of the sample and to the specific heat of the reaction, according to the integrated form of Eq. (6):

$$\Delta H_0 M = KA_t \tag{9}$$

and hence the peak area and the instrument constant K will be independent of the form, state and thermal conductivity of the sample.

Conclusion 3. The instrument constant coincides with the heat transfer coefficient of the heat barrier. According to Eq. (7), it is directly proportional to the height (to the surface area) of the sample holder. Since the value of $\Delta H_0 M$ is constant for a given reaction, the peak area is inversely proportional to the instrument constant K, which may be considered a measure of the thermal sensitivity of the transmitter.

Conclusion 4. It follows from Eq. (6) that from the moment when the reaction in the sample is completed, i.e. when the condition $\mathrm{d}\Delta H/\mathrm{d}t = 0$ begins to be satisfied, the differential curve is a graphical representation of the function $\Delta T_n = \Delta T_0 e^{-t/\tau}$, which is the solution of the differential equation:

$$K\Delta T_n + C\frac{\mathrm{d}\Delta T_n}{\mathrm{d}t} = 0 \tag{10}$$

Using the calculated value of the thermal capacity C (characteristic (iii) of the transmitter), one can find the constant K directly from Eq. (10) by measuring the values ΔT_n and $\mathrm{d}\Delta T_n/\mathrm{d}t$ at any point of the differential curve after completion of the reaction, or, after integration of Eq. (10), from the resulting formula:

$$K = \frac{C\Delta T_n}{A_n} \tag{11}$$

where A_n is the area of the peak demarcated by the differential curve, the baseline and the height of the peak ΔT_n at the point from which integration is performed.

Thus, Eqs (10) and (11) allow the thermal curve by which the kinetic and thermodynamic parameters of the reaction are being studied to be used for calibration too. The advantage of this mode of calibration – in addition to its simplicity – is that all variable factors of the experiment (temperature, gaseous medium) are automatically included, and the value K is very close to the true value, i.e. to the value directly at the moment of thermal transformation.

Introducing the value of K from Eq. (11) into Eq. (6) yields

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = \frac{C\Delta T_n}{A_n}\Delta T + C\frac{\mathrm{d}\Delta T}{\mathrm{d}t} \tag{12}$$

or, in the integrated form

$$\Delta H = \frac{C\Delta T_n}{A_n}A + C\Delta T \tag{13}$$

and for the total heat of reaction

$$\Delta H_t = \frac{C\Delta T_n}{A_n}A_t \tag{14}$$

In Eqs (12)–(14), the instrument constant K is not involved. These equations demonstrate that, theoretically, the DTA method does not require special calibration using a reference material. The role of the calibration constant can be taken over by the heat capacity of the sample holder with the sample. This is the main advantage of the DTA method over other thermoanalytical methods.

Experimental confirmation of the conclusions

Conclusion 1 was confirmed by soldering the hot junction of the thermocouple to the sample holder at various heights. In these tests, no essential difference was found in the peak areas recorded.

Conclusion 2 was confirmed by varying the mass of the sample (the height of filling the sample holder crucible), its form (powder, pieces of various shape) and its nature (metal, organic compound). In all cases, the direct proportionality of the peak area and the sample mass was obtained, in full agreement with Eq. (9). In Fig. 1 the relationships for the calibration materials listed in Table 1 are shown. For comparison, the relationship peak area *versus* sample mass for naphthalene, obtained with a block-type transmitter, is also plotted in Fig. 1. (The sample holder in this experiment was a 4 mm internal diam. glass tube fitted into the cavity of the heater block.) The latter relationship (curve 1′) is clearly non-linear; from 100 mg sample masses on, the peak corresponding to the melting process of naphthalene does not change. Similar relationships were observed in [9–11].

To confirm Conclusion 3, we used a 4 mm high sample holder, besides the 8 mm high one. As seen from Fig. 2, the values of K differed by a factor of 2 in all studied temperature intervals, i.e. an identical difference as for the surface areas of the two sample holders. The sensitivity of the transmitter with the lower sample holder is twice as high as that of the bigger sample holder. Hence, Conclusion 3 of the theory may be considered to be fully confirmed.

Conclusion 4 was checked by calculating the constant K by two independent methods, by utilizing Eq. (9) and (11). The results, together with the standard deviation of the experimental measurements, are listed in Table 1. The mean values for K

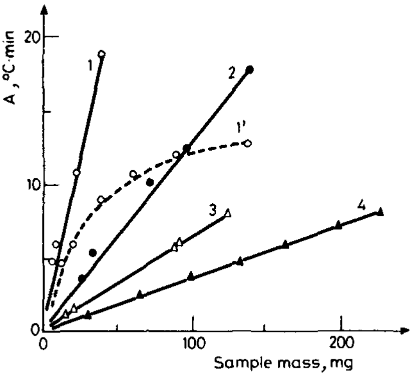

Fig. 1 Area of melting peak *versus* sample mass; 1 — naphthalene, 1 ' — naphthalene recorded with a block-type transmitter, 2 — zinc, 3 — indium, 4 — lead

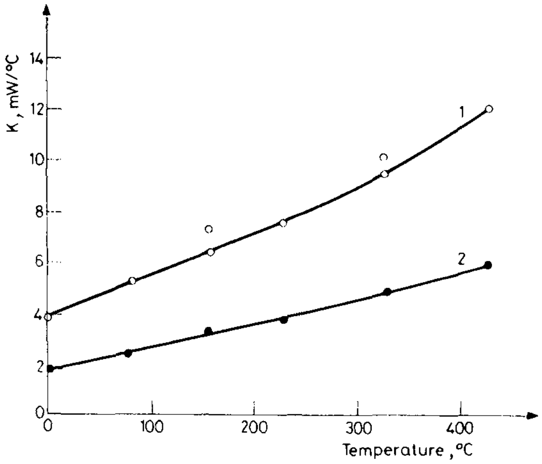

Fig. 2 Instrument constant *versus* temperature; 1—4 mm diameter, 8 mm height sample holder, 2—4 mm diameter, 4 mm height sample holder

were calculated from five values for each material, obtained by varying the sample mass from 10 to 140–230 mg.

In three of the five cases, practically full agreement of the values found for *K* with the two methods is observed; in the cases of indium and lead, however, the difference is around 10%, i.e. higher than the experimental error of from 1.5 to 5.0% for these substances. The experimental error presumably depends on the state of the sample in the holder, to the degree to which this state affects the isothermalness of the surface area of the sample holder. The error, however, does not exceed 5.0% for the most adverse cases.

Table 1 Calibration data obtained by two independent methods *

Substance	$T_{\text{melt.}}$, °C	ΔH, J/g	K, mW/°C from Eq. (9)	S_n	K, mW/°C from Eq. (11)	S_n
Naphthalene	80.2	146.55	5.08	0.07	5.07	0.174
Indium	156.2	28.21	7.23	0.15	6.47	0.24
Tin	231.9	59.52	7.74	0.136	7.70	0.32
Lead	327.5	23.01	10.37	0.28	9.50	0.40
Zinc	419.6	101.97	12.37	0.6	12.20	0.17

* Data for calibration computations (heats of transformation, temperatures of transformation, heat capacities) were taken from [12].

All in all, it may be stated that the experimental data confirm all the fundamental conclusions of the theory (within an error limit of 5%), and that consequently the operation of the transmitter with a thermally insulated sample holder is adequately described by the theory of heat transfer for gradientless systems (elementary theory of thermal inertia). This finding opens up wide prospects for the development of quantitative aspects of DTA, for the unification and standardization of the method, and for its applicability in many novel research areas.

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Zusammenfassung — Es wird gezeigt, dass die quantitative DTA (DSC) auf dem Prinzip der isothermen Oberfläche des Probenhalters beruhen muss. In den bekannten Transmittern von DTA-Instrumenten mit isoliertem Gefäss ist die Oberfläche des Probenhalters nicht isotherm, was auf den Effekt des Trägers zurückzuführen ist, der entweder eine massive Keramikstange oder eine Trägerplatte ist. In dem beschriebenen Transmitter wird die Wirkung des Trägers auf ein Minimum reduziert, indem er durch eine Aufhängung ersetzt wird, zu der die genügend feinen und langen Drähte des Differentialthermoelements verwendet werden. Auf diese Weise wird ein Träger mit einer isothermen Oberfläche erhalten und damit eine der fundamentalen Erfordernisse der Theorie des Wärmeübergangs in Systemen mit keinem Temperaturgradienten erfüllt. Dies wird experimentell dadurch bestätigt, dass der beschriebene Transmitter die folgenden charakteristischen Züge aufweist: Erstens stimmt die Instrumentenkonstante *K* mit dem Wärmeübergangskoeffizienten der thermischen Barriere (des Arbeitsraumes) der Zelle überein und ist unabhängig von der Natur der Probe auf dem Träger; zweitens ist die in der Theorie auftretende Wärmekapazität *C* genau gleich der Summe der Wärmekapazitäten des Trägers und der Probe; drittens ist die differentielle Kurve nach Beendigung der Reaktion in der Probe durch einen exponentiellen Ausdruck zu beschreiben und abhängig von einer einzigen Konstante, nämlich der Zeitkonstante der Zelle. Eine die Instrumentenkonstante nicht enthaltende Berechnungsformel und eine neue Methode zur Kalibrierung des Instruments, zu der der exponentielle Zweig der differentiellen Kurve herangezogen wird, werden vorgeschlagen.

Резюме — Показано, что в основе количественного ДТА (ДСК) должен лежать принцип изотермичности поверхности держателя. В известных датчиках приборов ДТА типа изолированного контейнера поверхность держателя не изотермична из-за влияния опоры держателя, имеющей вид массивного керамического стержня или опорной плиты. В описываемом датчике влияние опоры сведено к минимуму путем замены ее подвесом, в качестве которого используются достаточно тонкие и длинные провода измерительной термопары. В результате получен держатель с изотермической поверхностью и тем самым выполнено одно из основных требований теории теплопередачи в системах без температурных градиентов. Это подтверждается экспериментально тем, что, в полном согласии с теорией, описываемый датчик обнаружиавет следующие замечательные свойства: 1) константа прибора К совпадает с коэффициентом теплопередачи теплового барьера (рабочего зазора) ячейки и не зависит от свойств образца в держателе; 2) теплоемкость С, фигурирующая в теории, в точности равна суммарной теплоемкости держателя и образца; 3) дифференциальная кривая после момента окончания реакции в образце выражается экспонентой, зависящей от одной константы — постоянной времени ячейки. Предложена расчетная формула ДТА, не содержащая константы прибора К, а также новый способ калибровки прибора по хвостовой (экспоненциальной) ветви дифференциальной кривой.