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DETERMINATION OF SOME PARAMETERS TO BE UTILIZED IN CORRECTING DSC CURVES FOR EFFECTS DUE TO THERMAL LAG

I – THERMAL LAG IN SPECIFIC HEAT MEASUREMENTS

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In many applications of differential scanning calorimetry (DSC), notably the determination of specific heat functions, the analysis of reaction kinetics and the determination of purity, the instantaneous differential heat flow and the instantaneous actual sample temperature are required. The measurement of both is influenced in DSC by thermal lag effects, i.e. signal filtering and thermal gradients. A procedure is proposed which permits, under certains experimental conditions, correction of thermal lag by means of characteristic time constants having material and instrumental components. The validity of the results is enhanced by the comparison with those obtained by other authors.

Owing to the introduction of more advanced DTA and DSC commercial apparatus, it has been possible to extend the applications of thermoanalytical techniques to almost all the fields of chemistry; these techniques have been used chiefly to characterize many kinds of materials by determining either specific transition temperatures or energies associated with them.

In practice, however, there was only little agreement in the data obtained for essentially identical materials from instrument to instrument or from laboratory to laboratory, principally because of the different types and relative locations of components employed in the apparatus. In effect, the comparison of such data would require that the instruments used should be capable of enabling the accurate determination of thermal parameters which affect a DTA or DSC curve of a sample [1]. Normally, such parameters are determined by use of various calibration substances; however, the precision and accuracy in their determination depends on the possibility of controlling them by means of an instrumental control, so that a high degree of standardization may become possible.

The Perkin-Elmer DSC–1B system, for example, to which reference will be made in this paper, has a calorimetric calibration coefficient that meets these requirements: it appears, in fact, to be essentially independent of the temperature and geometry or thermal conductivity of the sample [2]. On the other hand, the calibration of the temperature scale of the same instrument appears to be dependent on sample and sample pan properties, such as the kind of substance analyzed (e.g. metallic or organic), the geometry of sample distribution in the pan and the position of the pan in the holder [3–6].

In effect, as in the DSC system the temperature sensors are external to the sample, and there always exists a thermal lag between sample and sensors, the temperature of the latter being measured and controlled by the instrument.

Various procedures have been proposed for the indirect measurement of sample temperature, by correcting DSC curves for thermal lag [7–10].

In some important applications of DSC, such as reaction kinetics, determination of specific heat functions, purity measurements, the instantaneous actual temperature of the sample and the corresponding power (or energy) input or output are obtained by analyzing DSC curves. Consequently, as a relative temperature accuracy from point to point on the curve is required, the thermal lag must be constant or change in a known manner along the portion of the curve on which measurements are made. It has been shown [5] that, when the heat capacity of the sample changes rather rapidly with the temperature, meaningful errors are made in the determination if effects of thermal lag are not properly considered. Similar errors are possible in purity measurements, since the melting curve of an impure substance can be described by a characteristic specific heat function [7, 11].

In this connection it is interesting to note that, although the method of premelting has long been recognized as the best method for purity determination of crystalline substances [12–13], it has been applied as a routine laboratory method only since the DSC technique has been employed [6, 7, 11, 13–22], thus eliminating complex equipment, large samples, and long analysis time.

In purity determination, as well as in the other above-mentioned applications, the curves to be analyzed reflect a more or less slowly varying heat capacity function dH/dT, since no isothermal transitions are taking place in the sample. With regard to the Perkin-Elmer DSC apparatus it has been claimed [23] that the thermal analyzer is able, in such cases, to track a change in dH/dT accurately, provided that relatively moderate scanning rates are used.

The aim of this paper is to show that, when the above conditions are met, it is possible to correct for dynamic thermal lag in DSC curves with the aid of some parameters: the assumption that they are instrumental parameters is enhanced by comparison of the data obtained with those reported by other authors [5].

Experimental

A Perkin-Elmer differential scanning calorimeter Model DSC–1B was used in this study. The power axis of the instrument was calibrated using a standard sample of indium, as supplied with the apparatus. For calibrating the temperature axis, four RS-Carlo Erba standards (3) (*p*-nitrotoluene, naphthalene, phenanthrene, benzoic acid) were employed in addition to the standards supplied with the instrument (indium, tin, lead).

Their melting points were determined in the "static mode" [5] so as to obtain temperature measurements free of dynamic thermal lag. For the determination of the thermal lag parameters the calorimeter was always used in the "specific heat mode" [23, 24].

Results and discussion

a) *Thermal lag: determination of characteristic time constants*

The linear dependence of the thermal lag δT on the nominal heating rate $\dot{T}_p$, as reported by Richardson and Burrington [5], may be expressed by means of the equation:

$$\delta T = \tau' \dot{T}_p \tag{1}$$

where τ' represents a time constant having either sample or instrument components. The relationship (1) suggests that the value of τ', as determined at a suitable scanning rate, may be used to correct for thermal lag at any other rate.

With regard to Fig. 1, values of time constants may be determined as follows. By scanning sample and blank between the two isotherms T_i and T_f, it is observed, when the program is turned off, that, because of the thermal lag δT, an additional area A is recorded, corresponding to the energy needed to bring the temperature of sample and cells to the final isotherm, relating to the temperature reading T_f.*

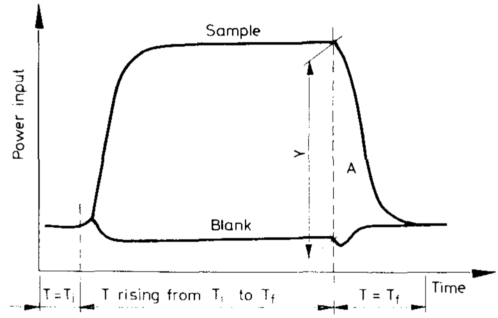

Fig. 1. Typical DSC specific heat determination. T: program temperature

If changes of C_p over the temperature interval δT are reasonably neglected, the area A and the displacement y at T_f are related through the equations: $A = k \cdot C_{p,T_f} \cdot \delta T / v$; $y = k \cdot C_{p,T_f} \cdot \dot{T}$, where k represents the power calibration constant, C_{p,T_f} the sample heat capacity at T_f, v the recording chart speed, and $\dot{T}$ the actual heating rate. Thus, by defining a time constant as $\tau = \delta T / \dot{T}$, the value of the latter at T_f is derived from measurements on the DSC curve, being $\tau = A/(y \cdot v)$. Time constants τ are related to the corresponding τ', defined in

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* Since a steady heat flow is passing in DSC through the calorimeter cells at isothermal equilibrium, a static thermal lag would also be considered, depending on temperature and thermal resistance. However, if reproducible thermal resistances between sample and sample holder are realized, it is automatically corrected for by means of the program temperature calibration.

Eq. (1), through a coefficient given by the ratio between the actual scan speed, $\dot{T}$, and the nominal one, $\dot{T}_p$. In the DSC – 1B the ratio $\dot{T}/\dot{T}_p$ is a nearly linear function of program temperature, with slope and intercept depending upon the temperature calibration curve. Dependence of τ', and hence of δT, on program temperature should therefore be expected, too.

In Table 1 the values of τ, as determined for two alumina (synthetic sapphire) discs, having comparable masses but different diameters and thicknesses, are shown. The discs were placed directly in the calorimeter holder and the final temperature was set to 370 K. Each value reported is the mean (95% confidence limits) of at least four measurements.

Table 1

Values of τ for two alumina discs: m (mass), Φ (diameter), h (thickness)

$\dot{T}_p$ nominal heating rate, K · min^{-1}	τ, sec	
	m = 29.15 mg Φ = 3.20 mm h = 0.92 mm	m = 31.70 mg Φ = 6.40 mm h = 0.25 mm
0.5	11.45±0.54	11.77±0.53
1	11.55±0.32	11.85±0.36
2	8.81±0.14	8.75±0.21
4	8.75±0.14	8.84±0.14
8	8.76±0.11	8.88±0.12
16	8.66±0.20	8.94±0.18
32	8.74±0.19	8.91±0.19
64	8.83±0.21	8.84±0.15

As may be seen, the time constant τ appears to be substantially independent of the program rate for $\dot{T}_p \geq 2$ K · min^{-1}, according to the linear relationship between δT and $\dot{T}_p$ already found [5]. Moreover, a discontinuity in the values of τ is evident, for both samples, when the program rate has changed from $\dot{T}_p \geq 2$ K · min^{-1} to $\dot{T}_p \leq 1$ K · min^{-1} or vice versa. A similar discontinuity has been found for other samples that it has been possible to analyze at the lowest scan speeds, consistently with the sensitivity limitations of the instrument. Although the lack of data gives no allowance to compare these results with others obtained by means of a similar apparatus, this apparent anomaly seems to be due to instrumental factors, as will be discussed later.

In addition to this, it is interesting to observe from the data of Table 1 that, in spite of the notable difference between their geometrical dimensions, the two sapphire discs show very close time constants, the time constant of the one with larger mass being slightly greater on the average.

The dependence of thermal lag on sample mass has already been considered to obtain an instrumental thermal lag, by extrapolating to zero mass thermal lag values calculated for a given material [5]. If different materials are to be taken into consideration, a relationship between thermal lag (or time constant) and sample heat capacity, rather than mass, seems to be more reasonable.

For this purpose, samples of different thermal conductivity, size, geometry and packing were analyzed by DSC–1B so as to determine their time constants and heat capacities. In order to compare the results with the data reported in [5], the samples were scanned up to the final temperature of 370 K. The results, obtained at the scan speeds of 1 K · min^{-1} and 8 K · min^{-1}, respectively, for the two scan ranges $\dot{T}_p \leq 1$ K · min^{-1} and $\dot{T}_p \geq 2$ K · min^{-1} are shown in Table 2 (for the samples of Table 1 the values of τ reported are the average ones for both ranges).

Table 2

Heat capacities (C_p) and time constants (τ) of various samples

Sample	C_p, mcal · K^{-1}	τ, sec	
		$\dot{T}_p \leq 1$K · min^{-1}	$\dot{T}_p \geq 2$K · min^{-1}
Alumina disc (8.56 mg)	1.85	—	8.02
Standard sample pan (Al)	3.65	—	8.32
Alumina disc (8.56 mg) in standard pan	5.47	—	8.63
Volatile sample pan	5.51	—	8.57
Indium (6.56 mg) encapsulated in standard pan	5.85	11.40	8.74
Alumina disc (29.15 mg)	6.31	11.51	8.76
Alumina disc (31.70 mg)	6.85	11.81	8.86
Benzoic acid (3.27 mg) encapsulated in volatile sample pan	8.05	12.74	8.97
Alumina disc (29.15 mg) in standard pan	9.84	13.90	9.30
Alumina disc (31.70 mg) in standard pan	10.39	14.09	9.44

By plotting τ vs. C_p, two distinct linear trends are found for the two scan ranges, as shown in Fig. 2.

A linear regression analysis applied to the experimental points appears to be significant to a high level of confidence corresponding to F [25] values of 1000 and 600 for $\dot{T}_p \geq 2$ K · min^{-1} and $\dot{T}_p \leq 1$ K · min^{-1}, respectively. The time constant appears consequently to be linearly dependent on the heat capacity of the sample (including eventual pan), whereas, in considering the different thermal contacts made with the holder by the various samples, no dependence on thermal resistance between sample and holder appears. This conclusion is enhanced by

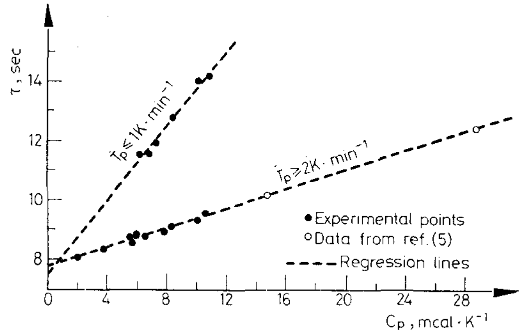

Fig. 2. Time constant as a function of heat capacity

the fact that the time constants, as calculated by means of Eq. (1) from the thermal lag data of Ref. [5], fit very well the regression line for $\dot{T}_p \geq 2$ K · min^{-1}. The slopes of both regression lines represent, therefore, really or apparently, two instrumental thermal resistances: their values calculated by regression analysis are 0.161 ± 0.012 and 0.633 ± 0.070 deg · sec · mcal^{-1} (95% confidence limits) for the scan ranges $\dot{T}_p \geq 2$ K · min^{-1} and $\dot{T}_p \leq 1$ K · min^{-1}, respectively.

Further, the intercepts of such lines, corresponding in turn to 7.73 ± 0.08 and 7.59 ± 0.57 sec (95% confidence limits), may be regarded as coincident within the precision limits of their experimental determination, and be identified with an instrumental time constant τ_0; a value of this may be obtained as the weighted mean of the above values, that is: $\tau_0 = 7.73 \pm 0.10$ sec. Interestingly, the values of the instrumental thermal lag, as determined by Richardson and Burrington [5] for four different substances, yield, after transformation by Eq. (1), an average instrumental time constant corresponding to 7.74 ± 0.26 sec, very close to the one determined in this work.

A characteristic instrumental time constant of the DSC–1B apparatus may therefore be supposed, and moreover time constants having sample and instrumental components are easily calculated by means of the equation:

$$\tau = \tau_0 + \rho C_p \tag{2}$$

which arises from the straight lines of Fig. 2, where ρ takes on two different values depending upon the scan range used. Values of C_p to be substituted into Eq. (2) may be determined with sufficient accuracy from DSC ordinate displacements and scanning rates corrected for non-linearities in the temperature program [9, 24].

Time constants, once known, allow correction of thermal lags, concerning either the ordinate displacement of DSC traces [9, 10], or, on account of the relation between τ and δT, the abscissa temperature [5].

The dependence of τ on temperature must finally be considered. A slow increase of δT with temperature has, indeed, already been observed for a given material [5].

Apart from non-linearities in the temperature program, which affect the actual heating rate, and variations of the sample heat capacity, possible changes in the values of τ_0 and ρ must also be taken into account.

For this purpose, indicative measurements of τ were made on five samples (four sapphire discs of different diameters and masses, and one aluminium reference pan) at the final temperatures 500 K and 600 K, respectively, by utilizing a scan speed of 8 K · min^{-1}. The results are shown in Fig. 3. The linear trend τ versus C_p, already found at 370 K, appears to hold still at these considerably higher temperatures. Furthermore, the values of τ_0 and ρ arising from the regression analysis at 500 K (7.77 sec, 0.147 deg · sec/mcal) and 600 K (7.63 sec, 0.161 deg · sec/mcal), indicate, together with those already determined at 370 K, the substantial independence of both parameters on temperature, thus supporting the assumption of their electric-instrumental nature.

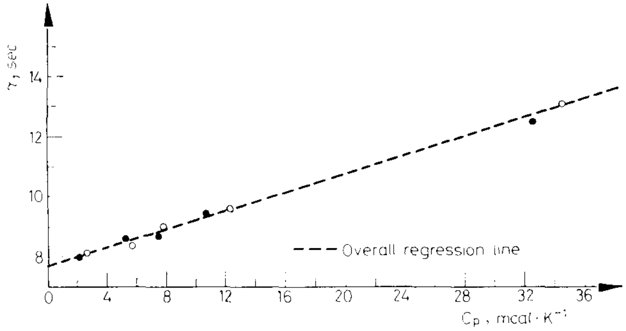

Fig. 3. Relation between τ and C_p at 500 K (●) and 600 K (○)

Because the thermal capacities of the samples analyzed are very slowly varying functions of temperature, only a small increase is found in time constants when passing from 370 K to 600 K, as may be inferred from Fig. 2 and Fig. 3. The greater increase of δT with temperature, as found in [5], should be principally due, therefore, to changes of the ratio $\dot{T}/\dot{T}_p$.

b) *Relation between the parameters* τ_0 *and* ρ *and the function of the electrical loops in the DSC–1B*

The correction for thermal lag of measurements on DSC curves always requires knowledge of the filtering effects, either instrumental or not, that influence the shape of the curve itself [9, 10, 26].

Time constants as calculated by means of Eq. (2), and concerning filtering effects due to instrumental and sample limitations may be explained by considering the function of two electrical control loops in DSC [2]. The loops operate on a time-sharing basis on two nominally identical cells, the sample and reference holders. An average temperature loop operates by comparing the average temperature of the cells to the one demanded by the programmer, and the power required is always provided equally to both cells as needed; the program temperature is marked out on the abscissa of the DSC recorder. The other, the differential temperature loop, controls temperature differences between the cells, by supplying the differential power needed to compensate for any difference; this is the power input recorded as DSC ordinate.

With regard to the time-sharing operation of the two loops, it has been observed [19] that the power supply for the average temperature loop is an order of magnitude larger than that of the differential temperature loop. As a consequence, the power transfer by the differential loop always lags the power input by the average one; in other words, the temperature difference to be compensated for is always due to a different uptake of the average power in sample and reference. Since the temperature marked out on the abscissa is the one of the programmer, while the ordinate is the differential read-out, the temperature lag of any point of the DSC curve will depend partly on how much the average temperature is delaying the program temperature, and partly on how much power variations in the differential loop are delaying the corresponding ones in the average loop. With regard to conditions in which Eq. (2) retains its validity, the two partial lags appear to be expressed through the time constants τ_0 and ρC_p, respectively. The apparent value of ρ seems to be dependent either on intrinsic thermal resistances in the circuit or on the response time of the two loops to the required power variations. The constancy of the ρ value over both scan ranges is indicative of a constant ratio between the rate of average power input and the rate of differential power transfer. On the other hand, the discontinuity in the ρ value, when passing from one range to the other, is probably due to a different instrumental filtering that occurs in the average loops, as may be inferred from an analysis of the DSC circuitry.

Although Eq. (2) has been derived from measurements on DSC curves unperturbed by phase changes, we should expect that it will also hold for correction of thermal lag when the sample is undergoing non-isothermal transitions, as occurs in the fusion of an impure crystalline substance or of a polymeric material one. In such cases, indeed, the thermal capacity of the sample may be made to vary slowly enough, by choosing a suitable heating rate, to realize a constant ratio between the rate of average power input and the rate of differential power transfer.

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Résumé — Dans de nombreuses applications de l'analyse calorimétrique différentielle, par ex. les déterminations de chaleur spécifique, de cinétiques réactionnelles et de pureté, il est nécessaire de connaître les valeurs instantanées du flux de chaleur différentiel ainsi que la température réelle de l'échantillon. En DSC, la mesure de ces deux valeurs est influencée par des effets d'inertie comme le filtrage du signal et les gradients thermiques. On propose un procédé qui permet, dans certaines conditions expérimentales, de corriger ce retard de transmission du signal thermique par des constantes de temps caractéristiques du matériau et de l'instrument. La validité des résultats est mise en valeur par comparaison avec ceux obtenus par d'autres méthodes.

Zusammenfassung — Bei vielen Anwendungen der Differentialabtastkalorimetrie, besonders bei der Bestimmung der spezifischen Wärme, der Analyse der Reaktionskinetik sowie bei der Reinheitsbestimmung werden die momentane differentiale Wärmeströmung und die momentane Probentemperatur benötigt. Die Messung beider Größen wird bei der DSC durch thermische Verzögerungs-Effekte, d. h. Signalfiltrierung und thermische Gradienten beeinflußt.

Es wird ein Verfahren vorgeschlagen, das unter gewissen Versuchsbedingungen die Korrektur des thermischen Verzögerungs-Effekts durch charakteristische, aus Material- und Instrumentalkomponenten bestehende Zeitkonstanten, ermöglicht. Die Gültigkeit der Ergebnisse wird durch Vergleiche mit den von anderen Autoren erhaltenen besonders betont.

Резюме — Во многих применениях дифференциальной сканирующей калориметрии, особенно при определении функций удельных теплоемкостей, анализе кинетики реакций и определении чистоты вещества, требуется знание мгновенного перепада теплового потока и действительной температуры образца. Измерение обоих параметров в ДСК затрагивается термическими индукционными эффектами, как например, фильтрацией сигнала и температурными градиентами. Предложен метод, позволяющий при определенных экспериментальных условиях проводить корректирование термического запаздывания посредством характерных постоянных времени, имеющих вещественную и инструментальную компоненты. Обоснованность результатов усилена путем сравнения с результатами, полученными другими авторами.