Thermochimica Acta, 188 (1991) 315–319
Elsevier Science Publishers B.V., Amsterdam

Note

DTA—why small samples ?

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(Received 14 January 1991)

Abstract

The accuracy of DTA peak shapes and associated parameters is assessed when using large samples.

INTRODUCTION

Thirty years ago, when the twin techniques of differential thermal analysis and thermogravimetry were comparatively new, sample sizes were much larger than they are now. With the growing interest in the use of DTA for calorimetric studies, sample sizes have become smaller and the large DTA unit has largely disappeared. Whilst in some areas of calorimetry this has been a good thing, the loss of larger cell systems has meant that studies of reaction chemistry in mixtures has been made more difficult. Reaction studies in mixtures usually involve the study of multicomponent mixtures, often with each constituent having a different grain size. Attempts to represent such a mixture in a 50 μg sample is doomed to failure. Thus there is still a need for apparatus in which the sample size is much larger, say of the order of 0.5 g.

It has always been thought that larger samples do not give "true" DTA curves owing to the large temperature gradients that exist within the sample, but no proof of this statement has ever been forthcoming. One problem associated with larger samples is that of gas evolution. The mass of material can act as a barrier to the release of gases, altering the kinetics of the reaction process and so affecting the resultant DTA curve. However, mixtures studied by thermal techniques are often representative of even larger industrial processes, where the large mass of reacting mixture will itself act as a barrier to the release of gas, so that often the DTA curve is more representative of the industrial process.

In studying reaction chemistry by DTA, the most important information required is the peak temperatures (peak temperature is defined as the

0040-6031/91/$03.50

temperature at which the deviation from the base-line during a DTA peak is a maximum) and shapes of the various peaks on the DTA curves. These can then be used to identify the possible reactions occurring within the mixture, using phase diagrams etc. If the peak shape is disorted, and the peak temperatures shifted, by the use of large samples, then this DTA information could lead to erroneous conclusions.

USING LARGER SAMPLES

A test is needed to assess the accuracy of peak shape and peak temperature when using large samples. This could be done by comparing results from different apparatus using large and small samples. However, the problem of mixing will still be present. There may be different equipment factors which will lead to different results, quite apart from sample size.

Some years ago the present author and colleagues produced a mathematical theory of DTA [1] which indicated those sample and instrumental factors which may affect the peak shape and peak temperature of a typical DTA peak. Generally it was shown that, if temperature measuring thermocouples were located in the center of both samples and reference materials, then the area of a typical DTA peak was inversely proportional to the thermal conductivity of the sample material, and such a design could not be used as a calorimeter.

However, a criterion for peak shape and temperature is required to decide the most suitable "large" cell design for reaction mixture studies.

ASSESSMENT

To assess peak temperature and shape in the mathematical model, the sample was assumed to react according to a given reaction mechanism, the form of which could be expressed as a mathematical equation. To link this equation into those of heat transfer, it was assumed that the heat generated by reacting material was directly proportional to the rate of reaction. It was then possible to generate mathematical temperature profiles within both sample and reference materials and so produce mathematical DTA curves. These curves were then compared directly with the rate of reaction curve versus temperature, using the same rate of temperature rise for the production of both curves. These curves were normalized on the ΔT and $\mathrm{d}\alpha(y)/\mathrm{d}t$ axis and drawn on a common temperature axis. Thus any variations due to instrumental factors (including heat transfer) will show up as differences in peak shape and peak temperature between the two curves.

RESULTS

In many earlier designs of DTA equipment, the large (≈ 1 g) samples were held in cylindrical wells within a fairly solid container, with the measuring thermocouples mounted axially along the center line of the well. The container or "holder" usually had a high density and thermal conductivity. It was heated by an electrical heater, mounted peripherally or within another well within the holder (e.g. Du Pont).

Another design consisted of a cylindrical furnace tube, the sample and reference materials being held in metal cups on a platform centered on the axis of the furnace tube. If the cups containing the sample and reference materials were thin walled, then mathematically the "holder" could be considered as the gaseous space between samples and the furnace wall. This space would have both a low conductivity and a low density. These two configurations will now be analyzed using the mathematical model described elsewhere [1].

HIGH CONDUCTIVITY HOLDER — WELLS IN HOLDERS

The following results were obtained for a holder of diameter 2 cm while the sample and reference materials were assumed to be contained in wells of various diameters from 0.7 to 1 cm. The conductivity of the holder material was high, being 4.18 W m^{-1} K^{-1}, while the conductivity of the sample and reference materials was purposely kept to a low value of 0.209 W m^{-1} K^{-1}, as previous studies with this model [1] had shown that such sample conditions produced the most curve distortion.

The reaction equation used for the tests was a combination of two first order Arrhenius type equations, which because they overlap give a "shoulder" on the high-temperature side of the $d\alpha/dt$ curve. It was felt that any change in shape or position of this shoulder would be a good indicator of curve distortion. In the model, temperatures within the sample parallel to the central axis are assumed to be uniform, that is, there are no end effects, so that to express the volume of a sample within a given radius it is necessary to assume a unit length. This gives sample volumes from 0.38–0.78 cm^3. If we assume a sample density of 1000 kg^{-3}, this represents sample masses from 0.38–0.78 g. The holder density of 2500 kg m^{-3} represents a heavy block typical of the older type of holder.

Holder details: radius 1 cm; density 2500 kg m^{-3}. Thermal conductivity 4.18 W m^{-1} K^{-1}; specific heat 0.836 J kg^{-1} K^{-1}. Sample (and reference) details: radius varied between 0.35 and 0.5 cm; density 1000 kg m^{-3}.Thermal conductivity 0.209 W m^{-1} K^{-1}. specific heat 0.836 J kg^{-1} K^{-1}. Reaction equation details:

Form: $d\alpha/dt = A_1(1-\alpha)\exp(-E_1/RT) + A_2(1-\alpha)\exp(-E_2/RT)$ where $A_1 = 1.26 \times 10^7$ (s^{-1}); $A_2 = 2.40 \times 10^6$ (s^{-1}); $E_1 = 1.7556 \times 10^4$ J mol^{-1}; $E_2 = 1.7556 \times 10^4$ J mol^{-1}; R is the gas constant and T is the absolute temperature (K), increasing at 10 K min^{-1}; α is the fraction reacted at a given time and $d\alpha/dt$ is the rate of reaction.

TABLE 1

Data for high conductivity holder — wells in the holder

Test	Peak temperature (°C)		
	Sample radius		
	0.35 cm	0.45 cm	0.5 cm
Sample	496.2	497.3	498.0
Reference	497.5	499.3	500.4
Reaction equation	495.8	495.8	495.8

As stated previously, the curves of $d\alpha/dt$ and the computed DTA curves were plotted on the same temperature axis, each curve being normalized on the ordinate of the graph. This method of presentation facilitates easy comparison of peak shapes and peak temperatures. Table 1 presents the relevant peak temperature data. Comparison of the peak sample temperatures with the temperature of the point of maximum rate of $d\alpha/dt$ shows that, even with quite large samples, the difference between the two is small and is never greater than 3°C.

Observations of typical DTA peaks indicate that shape distribution is minimal, the high temperature end of the curve being delayed by not more than 10°C and any "shoulder" present remaining clearly defined. The results would suggest that for reaction studies, i.e., where data on peak temperatures and peak shapes only are required, instantaneous temperatures of sample and reference materials should be measured along the central axis of the materials.

One of the authors (F.W.W.) used the Roberts DTA holder [2] for many years in the study of the chemistry of the glass-making process, and was able to correlate many of the peaks on DTA curves for glass-forming mixtures with the eutectic on the relevant phase diagrams [3].

LOW CONDUCTIVITY HOLDER — SAMPLES IN CUPS IN GASEOUS SPACE

Holder details: radius 1 cm; density 1000 kg m^{-3}. Thermal conductivity 0.0418 W m^{-1} K^{-1}; specific heat 0.836 J m^3 K^{-1}. Sample (and reference) details: radius varied between 0.35 and 0.5 cm; density 1000 kg m^{-3}. Thermal conductivity 0.209 W m^{-1} K^{-1}; specific heat 0.836 J m^3 K^{-1}. Reaction equation details as for Table 1.

The data for this kind of DTA arrangement are given in Table 2. The data indicate that, for this cell arrangement, there are marked differences between the peak temperature and that given by the maximum of the reaction equation. The DTA curves show very great distortion. There is a distorted

TABLE 2

Data for low conductivity holder — samples in cups in gaseous space

Test	Peak temperature (°C)	
	Sample radius	
	0.35 cm	0.5 cm
Samples	524.3	527.8
Reference	532.0	539.1
Reaction equation	495.8	495.8

peak and a slow return to the base-line. Thus this design cannot be recommended for chemical reaction studies.

CONCLUSIONS

The above results show that large samples can be used in suitably designed DTA apparatus if the information required from the curves is qualitative rather than quantitative. Indeed, for reaction studies on multi-component reaction mixtures, the larger sample type DTA equipment is more suitable than the modern miniature types now readily available.

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