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The role of heat transfer in the production of DSC curves

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Abstract

The influence of heat transfer on heat measurements is discussed and it is demonstrated that the contact between sample and pan, as well as that between pan and heat source, must be maintained constant if reproducible results of heat changes are to be achieved. Where there are difficulties of contact, techniques must be employed which will reduce the possible errors to a minimum. This may necessitate using statistical methods of analysis on a large number of experiments in order to obtain reliable and reproducible results.

INTRODUCTION

Recently, there has been considerable interest focussed on some of the technical difficulties observed when using the DSC technique. These include problems associated with the measurement of the true sample temperature and the area of the resulting DSC peak, and how this area is related to the heat absorbed or released during the reaction. This latter problem is noticed particularly when studying reactions which end abruptly, such as meltings and first-order reactions, but the problem also occurs with other forms of reaction where the consequences are not so obvious in the DSC curve. The two problems, namely sample temperature measurement and distortion of the DSC peak, are both associated with the thermal "resistance" formed by the contact between sample pan and sample, as well as that between sample pan and heat source. This contact can vary, particularly if care is not exercised in ensuring that the pans make good contact both with the sample and the heat source. Some theoretical models have been produced [1–4] but most of these have used lumped parameter models to analyse the heat transfer into the sample from the source of heat via the sample pan and the sample itself, and thus are not able to generate the resulting form of the DSC curve produced. This shows more realistically the effect of poor contact between the sample and pan and between

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

pan and heat source. The changes in the size and shape of the DSC curve caused by these effects, together with the effect on area measurement, can be demonstrated using the model set up some years ago by one of the present authors and his colleagues [5]. This technique was used to investigate the influence of low conductivity or "thermal resistance" within a DTA system [6,7]. The results given in these papers can be applied directly to the problems outlined above. However, the original model only applies to a single interface, as for example between the sample pan and the sample. Further work is continuing to also study the additional influence of the contact between the heat source and the pan on the resulting DSC curve, as well as the measurement of heat (by area measurement) and the onset and maximum temperatures.

PROBLEMS ASSOCIATED WITH DSC

In the more usual heat-flux type DSC, heat is supplied to the periphery of a constantan disc which has known heat transfer characteristics. The pan containing the sample rests on one of the twin platforms, located near the centre of the disc, the pan being used to avoid contamination of the disc. The second platform is often left without a pan. Temperatures are usually measured beneath each platform. It is the thermal contact between the pan and the platform and that between the pan and sample which can be the cause of variation in the resulting DSC curve. The heat transfer from the heat source to the platform on which the sample pan rests, is defined by the construction of the instrument and, apart from ageing over time, this remains fairly constant.

If the contact between the pan and platform varies, then the heat transfer across this gap will also vary, i.e. the thermal "resistance" across this gap will vary, increasing as the contact becomes less perfect. The same will be true for variations in contact between the sample and the pan. Although it is generally easier to ensure good contact between pan and platform than between sample and pan, particularly where powdered solids or fibres are concerned, there are still some difficulties. There can be changes in the pan contact due to expansion during heating. When using aluminium pans it is very difficult to ensure that the pan makes identical contact with both the heat source and sample in every experiment. Hence, area measurements and peak temperatures may not be reproducible owing to these changing heat transfer conditions. Ideally the pan should make good and identical contact with both heat source and sample in every experiment in order to eliminate this variable from the results. The thermal "resistance" between the sample pan and heat source and that between the sample pan and sample, produce lags in the system which can be clearly seen on a DSC curve for a reaction which ceases abruptly, namely a melting or first-order reaction (Fig. 1). This curve was generated using the

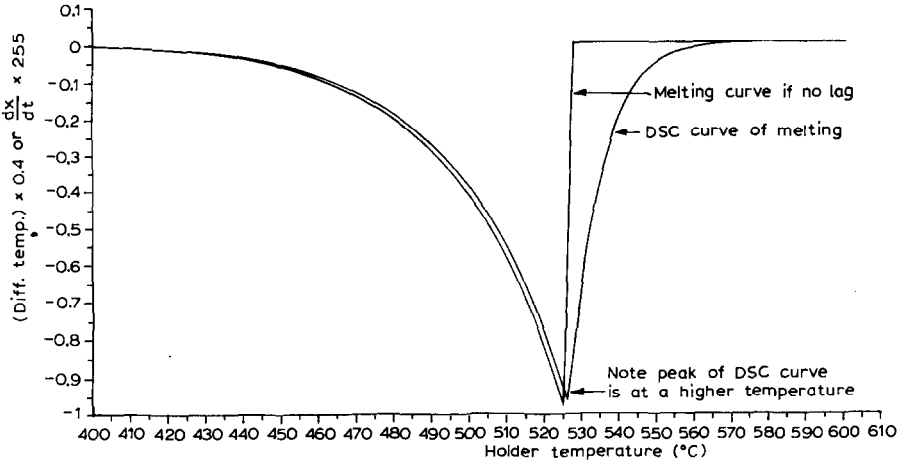

Fig. 1. Melting DSC curve in a low-conductivity cell.

theory referred to above [5] and shows that if the thermal "resistance" between either sample and pan or pan and platform is high, then there is a lag in the return of the DSC curve to the baseline. However, if the contact is improved, that is the thermal "resistance" is much lower, then the return of the DSC to the baseline is much faster, and the DSC curve is more representative of the melting curve (Fig. 2). In this case the thermal "resistance" was reduced by a factor of ten compared with that used for the curve of Fig. 1. Note also that the maximum of the DSC curve is higher than that of the melting curve when the thermal "resistance" is high. This lag has been reported to be as much as 4 seconds for a commercial apparatus, and was determined by plotting the melting temperature for

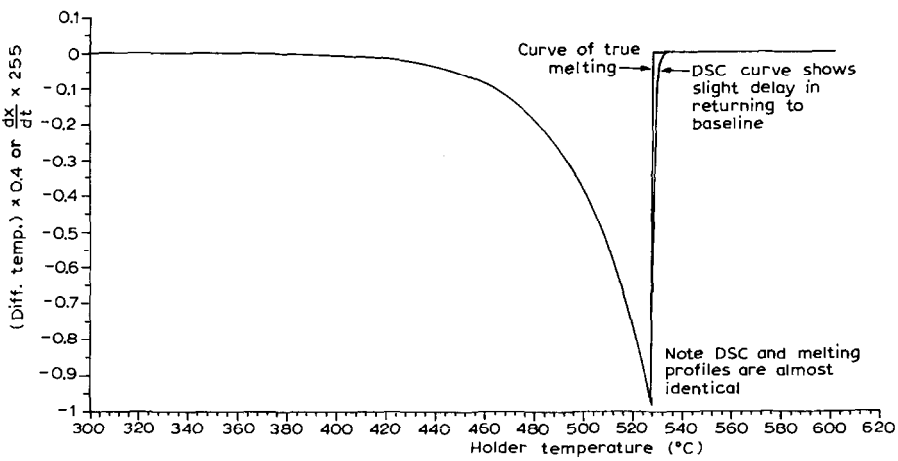

Fig. 2. Melting DSC curve in a high-conductivity cell.

indium at various heating rates [4]. This slower return to the baseline increases the area under the DSC curve leading to incorrect energy values. In addition, if the thermal resistance varies from experiment to experiment, then the area of the peak will also vary. However, because the temperature is measured beneath the platform and not in the sample, then the peak area will be independent of the physical properties of the sample [7,8]. It is important therefore that the contact between the pan and platform and that between sample and pan be kept as constant as possible from experiment to experiment. Some authors have developed various techniques to overcome this problem [9] which may or may not be applicable in specific cases.

When using DSC to determine reaction kinetics, particularly those of polymers where the sample conductivity is low, Batch and Macosko [4] found it necessary to be able to determine the time lag of the control mechanism, the heat-flow limit for a 1°C mean temperature change for a given sample and pan geometry, the mean temperature increase for a given exothermic heat flow, and a correction for the time lags in both the sample and instrumentation. They found that dynamic DSC runs which involve large sample temperature increases can distort the calorimetric data. Their findings indicate that the average time lag due to instrumentation, together with that due to pan and sample thermal resistance, was usually of the order of 5 seconds.

BASELINE CHANGE

This is brought about by the changing thermal properties of the cell system as heating proceeds. The most important change usually occurs in the sample as it undergoes transformation or melting. The change, for example in sample thermal conductivity, can be quite dramatic when a sample melts. In the earlier large sample DTA systems, where temperatures were often measured in the sample (and reference), the baseline shift during a reaction was quite pronounced and reflected the changes in the thermal characteristics of the sample as it underwent the reaction. Usually these changes were not known, making it difficult to define the true baseline. Some years ago, one of the present authors (F.W.W.) developed a baseline construction based on the model used here [10]. Because, however, temperatures in heat-flux DSC are usually measured beneath the platform, changes in the sample thermal properties do not have such a dramatic effect on the baseline of the resulting DSC curve. If necessary, the baseline construction mentioned above can be used, should the baseline of the peak be non-linear, in order to define the bounded area of the peak in question.

CONCLUSIONS

When using heat-flux DSC for heat measurements, it is important to ensure that, as far as possible, the contact between the platform and pan, as well as that between the pan and sample, is as good as possible. If it should be impossible to ensure good contact, then means should be found to produce repeatable contact arrangements in order to ensure reproducible results from repeated experiments. In any case, experiments should be repeated to gain an insight into the possible accuracy of the result.

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