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Calculation of smoothing factors for the comparison of DSC results

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Abstract

The subjective selection of smoothing factors for the analysis and comparison of DSC results is addressed. Four key equations are shown to relate the heating rate and the smoothing factor. The equations allow a comparison of data acquired i) at different heating rates and plotted against temperature, ii) at a single heating rate and plotted against both time and temperature, iii) at different heating rates and plotted against both time and temperature, and iv) at different heating rates, and shown exclusively in the time domain. The equations apply equally well to DSC and modulated DSC results, including derivative curves.

Keywords: differential scanning calorimetry (DSC); modulated differential scanning calorimetry (MDSC); smoothing; data analysis; bitumen.

1. Introduction

Differential scanning calorimetry (DSC) is used to measure the enthalpy of transitions and the heating capacity of materials [1, 2]. The method has a long history [3, 4], with its foundation in thermodynamics firmly established by the turn of the 20th century [5]. Despite this long history and the widespread use of the method, it can be difficult to acquire the knowledge for proper DSC. Formal training is possible at less than 4% of science and engineering departments in the USA [4], and day- or week-long courses are often limited to basic techniques and analysis. The identification of artefacts is seldom discussed in the literature [6], and the issue of smoothing is absent from textbooks [2, 3].

In DSC, the heating flow from the sample is superimposed with a random signal, best described as noise. Figure 1 shows, for instance, data acquired at 1, 3 and 5 °C/min, where the slower the heating rate, the greater the noise. The problem of noise is especially acute in modulated DSC [7] when the derivative of the heating capacity is used to identify multiple glass transitions [8]. The unsmoothed derivative is very noisy (Figure 2).

Generally, the removal of noise (smoothing) requires filtering, or digital processing, of the signal either in the time or the frequency domain [9]. In the frequency domain, smoothing is applied to the Fourier transform of the signal, a common method to filter spectroscopic data [10]. In DSC, heating flow is monitored against time and temperature, but smoothing is done in the time domain on data acquired at regular time intervals, where the most common methods of smoothing are the n -point moving average and the method of least squares [11, 12].

In this paper, the issue of smoothing DSC data is addressed, particularly the choice of smoothing factors such that data acquired under different conditions or displayed in different domains (time or temperature) can be compared on an equal basis to avoid possible misinterpretation. In this respect, the choice of appropriate smoothing factors for three scenarios is presented: a) data acquired at different heating rates; b) data compared across time and temperature domains; and c) combinations of a) and b). It was found that four key equations exist for the calculation of smoothing factors.

2. Experimental Section

The data were acquired with a DSC-2910 from TA Instruments. The data collection rate was 5 points/second, and the heating rates were 1°C/min, 3°C/min, and 5°C/min. The results were those for a bitumen after a second heating run between –100°C and 150°C, where the signal is a complex superimposition of transitions [8, 13] and where the degree of smoothing may affect the interpretation of the results.

The DSC signals were smoothed with software from TA Instruments, Universal Analysis 2000, version 4.1d, for which smoothing is based on the method of least-squares and a minimum of five data points are used for calculations. The input for smoothing was the width of the region to be smoothed, either in min or in °C.

3. Results and Discussion

Fig. 1 shows the heating flow in the temperature domain for heating rate of 1, 3 and 5 °C/min. The faster the heating rate, the smoother the data. In such a comparison, it is difficult to determine the effect of heating rate on a transition that may be of interest, and to avoid interpreting noise. For an identical level of noise, the unsmoothed data must be in the time domain (Fig. 3), but such representation is not conducive to an easy comparison of the results because of the differences in scale.

With results such as those in Fig. 1, various smoothing factors can be applied to the curves by trial and error until they appear to have a uniform smoothness. This subjective approach can be problematic because the results are often inconsistent and depend on the operator and/or the time of analysis.

3.1 Smoothing for different heating rates

To compare data in the temperature domain acquired at different heating rates (Fig. 1), there must be an equal basis for comparison. In a manner analogous to n -point averaging, a possible basis of comparison might be to select an equal number of data points (N^T) for each curve, as calculated from

$$I/H = G \quad (\text{Eq. 1}).$$

$$G \cdot S(T) = N^T \quad (\text{Eq. 2}).$$

where I is the fixed instrument sampling rate in points (pt)/min, H is the heating rate in °C/min, G is the experimental sampling rate in pt/°C, and $S(T)$ is the smoothing interval

in the temperature domain in °C. On the basis of Eq. 2, the number of data points is equal for two different conditions (i, j) if

$$G_i \cdot S(T)_i = G_j \cdot S(T)_j = N^T \quad (\text{Eq. 3})$$

Table 1 shows the results obtained from the application of Eq. 3 on the three heating rates illustrated in Figure 1. These results show that an increase in heating rate would require greater smoothing, which is contrary to experience.

The roughness of the curves in Fig. 1 suggest that less smoothing would be required with an increase in heating rate. The DSC curve obtained at the highest heating rate appears smoother because there are fewer data points. With the instrument sampling rate, $I = 300$ pt/min, Table 1 shows that the number of data points in the temperature domain (G) was 300, 100, and 60 after one minute at the respective rates of 1, 3 and 5°C/min.

To provide for a proper normalization of the data sets with the application of smoothing in accordance with the experiment, G must be divided by S such that

$$G_i/S(T)_i = G_j/S(T)_j = v \quad (\text{Eq. 4})$$

where v is the normalized number of data points per °C, with units of pt/°C². With a substitution for G from Eq. 1, Eq. 4 is conveniently written in terms of heating rate as

$$H_i \cdot S(T)_i = H_j \cdot S(T)_j \text{ (units of } ^\circ\text{C}^2/\text{min)} \quad (\text{Eq. 5})$$

This equation can be used to calculate the smoothing factors for the proper comparison of data in the temperature domain and obtained at different heating rates (Table 2). Fig. 4 shows data acquired at different heating rates and plotted with equal smoothness based on Eq. 5.

3.2 Smoothing across the time and temperature domains

It is sometimes necessary to compare two DSC curves, one represented in the time domain and the other in the temperature domain. Most often the tendency is to use the same smoothing factor for each curve, but then the smoothness of the curves are such that the comparison of data is difficult, if not completely inadequate. To compare data from one heating rate across time and temperature domains, the number of data points in both domains must be equal, $N^T = N^t$, or

$$G \cdot S(T) = I \cdot S(t) \quad (\text{Eq. 6})$$

With a substitution for G from Eq. 1, Eq. 6 can be written

$$H = S(T) / S(t) \quad (\text{Eq. 7})$$

Eq. 7 allows for the selection of proper smoothing factors to compare data from a single heating rate across the time and temperature domains. The equation is most useful, however, for the comparison of time and temperature derivative curves from modulated DSC. For examples, Figure 5 shows dC_p/dt and dC_p/dT curves with respective $S(t)$ and $S(T)$ factors calculated based on Eq. 7.

To further compare data from different heating rates across the time and temperature domains, one smoothing factor in Eq. 5 is substituted for its equivalent in Eq. 7 to give

$$H_i \cdot S(T)_i = (H_j)^2 \cdot S(t)_j \quad (\text{Eq. 8})$$

Eq. 8 is most useful to compare dC_p/dt and dC_p/dT curves, but unlike Eq. 7, it allows for the comparison of data acquired at different heating rates (Figure 6).

3.3 Smoothing of derivative curves in the time domain

Given Eq. 5 for the temperature domain, one might assume that it could apply equally well to the time domain, but this is not the case. The substitution of the remaining $S(T)_i$ in Eq. 8 for its equivalent in Eq. 7, leads to an equation expressed exclusively in the time domain

$$(H_i)^2 \cdot S(t)_i = (H_j)^2 \cdot S(t)_j \quad (\text{Eq. 9})$$

This equation is analogous to Eq. 5 except that the heating rates are squared. Although Eq. 9 may be used to compare in the time domain the total heating flow acquired at different heating rates, it is most useful to compare the dC_p/dt derivatives of data acquired at different heating rates.

As shown above, there are four key equations to select appropriate smoothing factors. With the factors in Table 3, for instance, Eq. 5 and 9 are used to move vertically in the temperature and time domains, respectively. Equation 7 is used to move horizontally from $S(T)$ to $S(t)$ and vice-versa, whereas Eq. 8 is used to move diagonally from one column to the next.

4. Summary and Conclusion

DSC results acquired at different heating rates and represented in the time or the temperature domains are generally compared after a trial and error selection of smoothing factors. To circumvent the subjectivity of this process, four equations that relate the heating rate and the smoothing factor were developed. These equations allow an easy

conversion of the results from the temperature to the time domain, and vice-versa, and an equal basis to compare data acquired at different heating rates. They apply equally well to DSC and modulated DSC data, including dC_p/dT and dC_p/dt derivatives.

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Table 1. Calculation of the smoothing factor based on Eq. 3.

Table 2. Calculation of smoothing factors based on equations 4 and 5.

Table 3. Representative sets of smoothing factors for various heating rates.

Fig. 1. Unsmoothed heating flows from DSC experiments at 1, 3, and 5 °C/min.

Fig. 2. Unsmoothed heating capacity and its derivative from a modulated DSC experiment at 1°C/min, a modulation of $\pm 0.16^{\circ}\text{C}$ and a period of 60 s.

Fig.3. Unsmoothed heating flows in the time domain after acquisitions at 1, 3, and 5 °C/min.

Fig.4. Heating flows in the temperature domain. The smoothing factors were calculated based on Eq. 5.

Fig. 5. Time and temperature derivatives of the heating capacity acquired at 5°C/min. The smoothing factors were calculated with Eq. 7.

Fig. 6. Time and temperature derivatives of heat capacity acquired at 3°C/min and 5°C/min. The smoothing factors were calculated with Eq. 8.

Table 1. Calculation of the smoothing factor based on equation 3.

H	I	G	S(T)	N ^T
°C/min	pt/min	pt/°C	°C	pt
1	300	300	3	900
3	300	100	9	900
5	300	60	15	900

Table 2. Calculation of smoothing factors based on equations 4 and 5.

H	G	S(T)	v
°C/min	pt/°C	°C	pt/°C ²
1	300	5.0	60
3	100	1.6	60
5	60	1.0	60

Table 3. A set of smoothing factors for various heating rates.

H	S(T)	S(t)
°C/min	°C	min
1	10	10
2	5	2.5
3	3.3	1.1
4	2.5	0.7
5	2	0.4

Fig. 1. Unsmoothed heating flows from DSC experiments at 1, 3, and 5 °C/min.

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Fig. 6. Time and temperature derivatives of heat capacity acquired at 3°C/min and 5°C/min. The smoothing factors were calculated with equation 8.