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A STUDY ON THE HEAT TRANSFER GEOMETRY IN MBDTA

B. Erdogan[1] *and O. Alpaut*[2]

[1]GAZI UNIVERSITY, FACULTY OF SCIENCE, ANKARA, TURKEY
[2]HACETTEPE UNIVERSITY, FACULTY OF ENGINEERING, ANKARA, TURKEY

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This paper presents the quantitative application of the Metal Blocked Differential Thermal Analysis (MBDTA). Calibrations have been electrically carried out by using three types of calibration heaters (pen, ring and spiral), which are placed inside the sample. By means of this arrangement, thermophysical properties of the samples make the quantitative evaluation of the results easy. The influence of the size and sample diameter, the types of heater, the space between heater and thermocouple, in other words, the factors affecting calibration and the effect of the heat transfer geometry on the determination of the fusion heat have been investigated.

Keywords: heat transfer geometry, Metal Blocked Differential Thermal Analysis

Introduction

Several reports on heat measurement with DTA have been published [1–4]. Many theoretical and empirical equations have been derived to determine the relationship between the peak area of a DTA curve and the value of heat of reaction. The theoretical approach requires the solution of differential equations and it is necessary to introduce the simplifying assumptions which enable them to be solved. The parameters involving samples and apparatus have various effects on DTA curves. These effects are complex and generally interactive [5]. Therefore the majority of the methods used for the determination of the heat of the reaction from the peak area are comparative and empirical. The theoretical and empirical relations between the peak area, S, of the DTA curve and the heat transferred, Q, in the thermal event may be given by the general form,

$$Q = K S \tag{1}$$

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where K is known as calibration constant or proportionality constant, determined experimentally. The proportionality constant is affected by extremely high number of factors, such as experimental conditions, design properties of the system, thermophysical properties of the sample and operating parameters [6–9].

For the determination of K, calibration may be done either electrically or by using substances known by heat of reaction. Electrical calibration may be carried out by supplying a known amount of heat to the sample by incorporating a small electrical heater. This heat effect is obtained as a peak very close to the peak of the thermal event on the DTA curve. Quantitative evaluation is accomplished by comparing these peaks. The calibration is, of course, specific to one apparatus and one set of the operating conditions. The detailed description of the calibration technique by using an electrical heater and arrangements necessary for quantitative studies can be found in several papers [10–13].

Some attempts to overcome the effects of thermophysical properties of the sample have been made [12, 14, 15]. Boersma gives reasons that DTA cannot be used for precise quantitative analysis owing to the inherent limitations of the DTA method. Egunov [15] expresses that the DTA curves contain all information about the transformations occurring in the sample and all the conditions of the experiment. Wittels [16] studied the effect of the sample size on the peak area and observed deviations on (peak area/mass) ratio. He explained these pertaining to the thermal gradients in the large samples, in our opinion the geometrical dimensions of the sample will ordinarily change the heat transfer surface so that peak area variation will occur. Sample size and heat transfer pattern change during the transformation. Therefore it is important to investigate the heater type, geometry and sample size for calibration arrangement. In this study MBDTA apparatus [17] has been used. It is difficult to use the commercial DTA apparatus for such a study. The influence of the sample and heater geometry on the measurement of heat have been studied thoroughly. Investigations involving different geometrical dimensions for sample and heaters did not take place in the literature due to constructional difficulties.

Experimental

In this study, MBDTA apparatus was used (Fig. 1). The sample is put into a pyrex tube and inserted in the big cavity of the cylindrical aluminum block. The reference is the metal block itself. The thermocouples are located symmetrically in the sample and in the small cavity of the metal block. They are covered by ceramic tubes. This arrangement is illustrated schematically in Fig. 1. A calibration heater is also inserted in the sample to supply a given amount of electrical

energy. The shape of the sample is cylindrical with a flat bottom. Its diameter is large enough to accommodate the heater and thermocouple for calibration.

DTA curves are obtained under dynamic N_2 atmosphere. Runs are made at a heating rate of 3–5 deg·min^{-1}. Electrical energy for calibration supplied from a direct current source which consists of battery provided from the market. Rheostat, voltmeter, ammeter and heater are also used in the circuit. The voltage applied to the heater is at a level of 4–5 Volts and adjusted by a rheostat. The current of the electricity for the heater is provided at a rate of 60 –100 mA. The heater resistance is about 50 –60 ohm. These operation parameters are selected so as to avoid the heater from excessive heating resulting in oxidation. The voltmeter and the milliammeter are both AEG and both have a precision of ±0.5%. The power supply period is measured by a stopwatch with a precision of 0.1 sec.

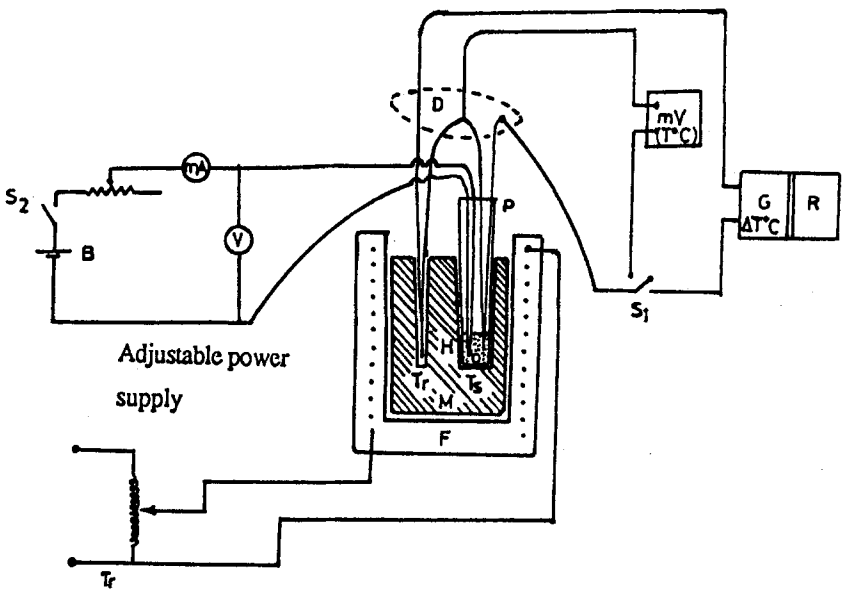

Fig. 1 MBDTA apparatus used for this study F: Furnace, Tr: Transformer, mV: Mili voltmeter, G: Galvanometer, R: Recorder, S and Sz; Switches, Ts and Tr: Thermocouples of the sample and referent materials, M: Metal block, H: Heater, P: Pyrex sample container, D: Dewar flask, B: Battery, mA: Milliammeter, V: Voltmeter, Ö: sample

The energy injected into the sample is controlled by S_2 switch (Fig. 1). The amount of heat delivered to the sample can be measured by the adjustable power supply unit. The calibration was done by using three different types of home-made heaters. These are pen, ring and spiral (Fig. 2). The heating wire of the heater is made of kanthal with a diameter of 0.15 mm. It is covered by a pyrex

capillary tube. Dimensions of the heaters are changed according to size of the sample and the sample tube. The leads are connected to the resistance by spot-welding. Differential temperature (ΔT) and temperature (T) are measured by Ni–NiCr thermocouples, 0–2 mm in diameter manufactured by Degussa.

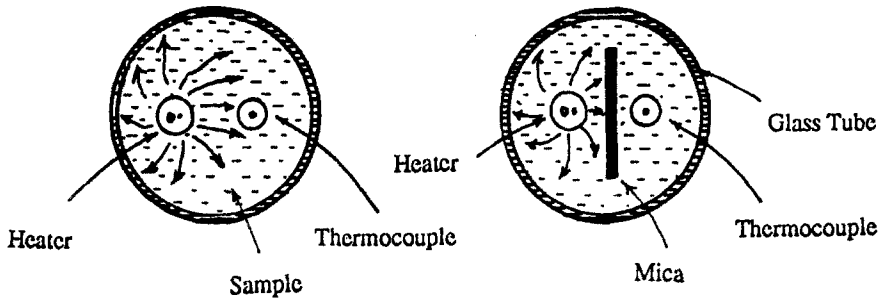

Fig. 2 Heater and Thermocouple position for different heaters. H: Heater, T: Thermocouple

The temperature difference (ΔT) between the sample and the metal block is recorded as a function of time (t). The peak area of the fusion and calibration pulses are determined by drawing a straight baseline through the two tails of the peak. The error in the peak area originating from the estimation of the base line is negligible. The calibration peaks are obtained on DTA curve before and after the transformation from the energy pulses withdrawn from the power supply. The calibration peaks are obtained at a temperature very close to that of the sample peak. The supplied energy (Q) is then calculated from the following equation,

$$Q = V I t \tag{2}$$

where V is the voltage in the volts read from the voltmeter, I is the current in amperes read from milliammeter, and t is the time period for energy supply in sec. The calibration constant (K) is the ratio between the heat (Q) supplied from the power supply and the average area (S) of the related calibration peaks, as seen in the following,

$$K = \frac{Q}{S} \tag{3}$$

As it is obvious K represents the heat of calibration per unit area. The heat of fusion (ΔH_f) of the sample can be calculated by the following equation,

$$\Delta H_f = K S_f \tag{4}$$

where S_f is the DTA peak area of the latent heat of fusion for the sample investigated. Peak areas are measured using planimeters. It is given in PU (Planimeter Unit, 1 PU = 0.106 cm^2) in the tables. Inherent variability of the technique, measurements are repeated several times, then, the measurements are averaged to obtain the mean.

Results and discussion

The effect of the barrier for heat transfer

Experiments have been carried out using In metal to see the influence of the barrier (mica) in determining the heat of fusion. In the apparatus used in this method, a cylindrical sample is utilized. A mica is placed between the thermocouple and the heater. The cross sectional figure of the cylindrical sample is shown in Fig. 3. For this arrangement of the sample, mica serves as thermal isolation, so the way heat transfer becomes longer. All other conditions are kept essentially constant.

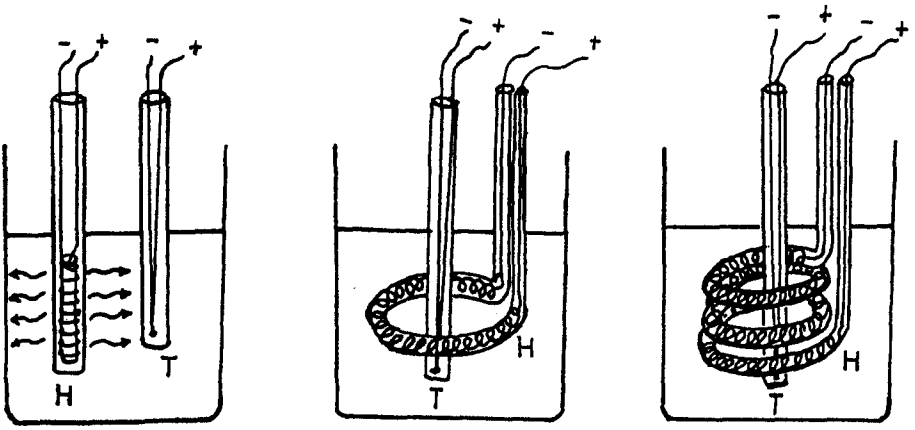

Fig. 3 Heat transfer pattern variation for heat transfer in the sample, according to isolator (mica).
a) Cross section of the pen heater and thermocouple in the sample; Sample without mica
b) Position of the mica with respect to heater and thermocouple in the sample

The average values of heat of fusion for two samples (238 and 298 J, first sample without mica, second sample with mica) give an answer to the question whether the heat transfer pattern in the sample between the heater and thermocouple must be taken into account. We could not find any papers concerned with the particular problem: how this relation should be taken into account in thermal analysis. This difference in the heat of fusion for two samples arises from

the mica placed between the thermocouple and the heater. The thermal effect of the heater on the thermocouple appears to be lower when the mica is present. Therefore calibration peak area (S) has been small when the same heat (Q) is injected into the sample with mica for calibration. The amount of heat per unit area, ($K = Q/S$) will be large in the case of the sample with mica, at the same time peak areas of the samples with and without mica are nearly the same but you can observe variation in the calibration constant as seen in

$$K_{\text{sample with mica}} > K_{\text{sample without mica}}$$

t-test for two independent samples has been applied (Table 1). The value of the calculated test statistic [18] is bigger than the critical value at the 1% significance level. We are able to conclude that there is a significant difference between the means of heat of fusion of the two samples.

Table 1 The effect of barrier. Sample mass; 9.5254 g. Heater type; Ring, Sample diameter: 1.27 cm

Sample	Number of experiments / n	Calibration constant $K \pm SD^*$ / J/PU	Peak area $S \pm SD$ / PU	Heat of fusion $Q \pm SD$ / J
Sample without mica	12	1.80 ± 0.05	158 ± 6	283 ± 5
Sample with mica	10	1.90 ± 0.09	160 ± 9	299 ± 9

SD^*: Standard deviation

At this point it may be concluded that the heat transfer pattern and the distance between the heater and the thermocouple are important in determination of K. In the light of this result, the effect of the different types of heaters on the calibration was studied.

The influence of the types of heaters

In this study, three types of electrical heater pen, ring and spiral, are used to observe the influence of their geometry on heat of fusion. They are illustrated in Fig. 2. Having a pictorial way of looking at Fig. 2, we are able to see different geometries for heat transfer between the heater and the thermocouples. The results of the experiments obtained by using three types of heaters are given in Table 2. The heat of fusion values of In have been found by using three different types of heaters in the following order:

$$\Delta H_f(\text{Pen}) > \Delta H_f(\text{Ring}) > \Delta H_f(\text{Spiral})$$

To explain the above order, it is necessary to look at the Fig. 2 which shows the position of the heater and the thermocouple in the sample. The flow of heat from pen type heater to the thermocouple advances in the large angle, differential effect (ΔT) on the thermocouple will be small, consequently the calibration peak will be small too. Therefore Q/S ratio increases and thus the calculated value of ΔH_f have been greater than the expected one.

Table 2 Variation heat of fusion values using three types of heaters. Sample mass: 9.5254 g. Sample diameter: 1.32 cm

Type of heater	Experiment number	$K \pm SD^*$ / J/PU	$S \pm SD$ / PU	$Q \pm SD$ J
Pen	11	1.77 ± 0.10	161 ± 7	283 ± 6
Ring	13	1.42 ± 0.04	191 ± 4	272 ± 6
Spiral	12	1.45 ± 0.05	188 ± 5	265 ± 3

At a spiral heater the flow of heat to the thermocouple would be larger than the pen type heater. Consequently differential effect (ΔT) on the thermocouple would be greater. The peak area (S) of the calibration due to fixed amount of heat have been larger and Q/S ratio will decrease. The heat of fusion calculated by the Eq. (1) should be smaller than the expected one. At a ring heater, the flow of heat to the thermocouple has been larger than the heat flux in the pen heater, however smaller than the one in the spiral heater. Therefore the differential effect falls between these values. At the same time, the heat of fusion experimentally found also remains between the values obtained from the other two heaters.

Three groups were tested by using Kruskall-Wallis k sample test [19], as the test statistic is more than critical values from the χ^2-Table. We can say that the type of the heater has an effect on calibration peaks, in other words, geometry of the heaters has large effect on the calibration peak. These differences were ascribed to the differences in geometry of the three heaters and the resulting heat transfer pattern.

Influence of the sample size

In order to investigate the influence of amount of sample in quantitative determinations, experiments are carried out in two groups. When the tube is 0.81 cm in diameter, 1.4254 and 2.8505 g of sample were used. Findings are illustrated in Table 3 as group 1. In the same table, results of 4.344 and 8.688 g of samples are shown as group 2. Groups 1 and 2 are different from the standpoint of diameter. 4.344 g of In sample have a peak area of 161 PU and 8.688 g of In sample have a peak area of 205 PU. When the sample size is increased twofold (Table 3) we

would expect that the peak area of the sample should be increased two times according to the theories. But changing the sample size will result in variation in the heat transfer area in the tube as the sample size increases. The peak area does not increase linearly with the sample amount.

Table 3 Influence of amount of sample (In) on the heat of fusion

	Sample mass / g	S / PU	K / J/PU	q / J/g	Experiment number / n	Type of heater	Sample diameter / cm
Group 1	1.4254	70±5	0.56±0.02	27.6±0.4	10	spring	0.81
	2.8505	100±4	0.80±0.4	28.0±0.04	10	spring	0.81
Group 2	4.3440	161±11	0.78±0.05	28.83±0.54	11	spring	1.32
	8.6880	205±7	1.25±0.05	29.42±0.62	9	spring	1.32

In the present study, applied calibration compensates the disadvantages to a certain extent, resulted from the variation of the heat transfer area of the sample. However, K values for the sample of 4.344 g is approximately 0.78 J/PU. On the other hand, for the sample of 8.6880 g it is 1.25 J/PU. These two values show that the amount of the heat required per unit area in the calibration peaks increases with increasing sample size; in other words, K depends on the sample amount. Fusion peak area per gram of sample has decreased with increasing sample size. According to Eq. (1) decrease in S_{fusion} for large samples (according to the expected value) is compensated with the increase in K. In spite of this compensation, the larger the sample is the larger the value of heat of fusion obtained by this technique. The relationship between the heat injected into the sample and the area of calibration peak will depend on the sample size which affects the heat flow inside the samples by virtue of the basic geometric arrangement, not any other factor variation.

According to various theories of DTA for quantitative studies, the peak area should be directly proportional to the quantity of the sample and the amount of the heat transferred [20]. This is the basis of the practical quantitative evaluations. However in these theories, the experimental conditions for the proportionality constant between the heat and the area is not shown to be independent of the geometry of the samples and other experimental factors because the effects of the volume and the shape of the sample are neglected in the theories. A number of papers have been published investigating this relationship in detail [21–24], which conclude that the relationship is only valid in certain amount of sample ranges. However, the results cannot be generalized. Because they are dependent on the apparatus used.

Influence of the sample diameter

Samples with different diameters (0.31, 1.05 and 1.32 cm) are used in order to investigate the effect of the sample diameter on the heat of fusion which is found experimentally through electrical calibration. Results are shown in Table 4. In this study, by changing the sample diameter, the amount of the material, the size of the heater and the geometry of the heat transfer are also changed. The heat of fusion value decreases with the decreased sample diameter. Thermal effect of the ring type heater on the thermocouple has been increased with decreasing sample diameter, due to decrease in distance between the heater and the thermocouple. The increasing rate of heat supply to the thermocouple causes an increase in ΔT signal; consequently, calibration peak becomes larger too. The increase in calibration will cause the decrease in $(Q/S)_{\text{calibration}}$ at the same time we obtain heat of fusion smaller than the expected value. As the sample diameter increases, K and q values increase too. During the calibration, a known quantity of heat gives small peaks as the sample diameter increases. The calibration peak areas do vary considerably, but it is said to be due to changes in the heat transfer geometry resulting from the sample diameter.

Table 4 Influence of the sample diameter. Sample; In, Heater type; spring

Diameter / cm	Sample mass / cm	Sample height / cm	Experiment number / n	$K \pm SD$ / J/PU	$S \pm SD$ / PU	$Q \pm SD$ / J	$q \pm SD$ / J/g
0.85	1.4254	0.5	10	0.56±0.02	70± 2	39.3 ±0.6	27.6±0.4
1.05	2.5800	0.5	10	0.67±0.02	110± 3	73.77±0.86	28.6±0.3
1.32	4.344	0.5	11	0.78±0.05	161±11	124.5 ±1.9	28.8±0.5

Using Kuruskall-Wallis k sample test three groups were tested [19]. Three sets of measurements lead us to the conclusion that the mean values are significantly different. In other words, we can conclude that the sample diameter has an effect on the determination of the heat of fusion.

Conclusion

This study has shown the importance of the heat transfer pattern, the type of heaters, sample size and the diameter of the sample for the internal calibration. According to the results we are able to conclude that there is significant difference between the heat of fusion of the sample with and without barrier. Heat transfer geometry has a pronounced effect on the DTA curve, especially for

calibration peaks necessary for quantitative studies. Types of heaters have also considerable effect on the differential signal, consequently calibration peaks are affected. Therefore it is essential to have good heater construction and positioning, otherwise inconvenient position of the heaters cause inaccuracy. This study shows a progressive dimunition in response of the differential signal to a given quantity of heat as the sample size increased. Sample diameter effect is said to be similar to that of sample size and could probably be explained in a similar manner.

From the results reported in this paper, it would appear that only under special circumstances peak-area measurement can be adopted in quantitative studies. MBDTA apparatus may be used to measure the heat of transformations after a suitable calibration. When the size of the pyrex tube and the heater can be improved, the accuracy will be considerably improved.

References

1 F. C. Kracek, J. Phys. Chem., 34 (1930) 225.
2 S. Speil, U.S. Bur. Mines Rept. Invest. No. 3764 (1944).
3 O. Alpaut and Th. Heuman, Acta Met., 13 (1965) 543.
4 G. Widmann, Thermochim. Acta, 11 (1975) 331.
5 J. W. Dodd and K. H. Tonge, Thermal Methods, John Wiley & Sons, London 1987, p. 145.
6 F. W. Wilburn, R. Melling and R. M. McIntosh, Anal. Chem., 41 (1969) 1275.
7 D. J. David, Anal. Chem., 36 (1964) 2162.
8 L. B. Rogers and E. M. Barral, Anal. Chem., 34 (1962) 1101.
9 L. Artus, Thermochim. Acta, 59 (1988) 133.
10 B. Predel and T. Neuman, Electrochem., 63 (1959) 988.
11 B. Kliburszky and Vogl-Földvári, Acta Geol., 5 (1958) 187.
12 Ozowa *et al.*, Bull. Chem. Soc. Japan, 40 (1967) 1583.
13 E. Dosch, Thermochim. Acta, 1 (1970) 367.
14 S. L. Boersma, J. Amer. Ceram. Soc., 38 (1955) 281.
15 Egunov *et al.*, Thermal Analysis Proc. 3rd ICTA, Davos (1971), Ed. H. G. Wiedmann, Birkhauser Verlog, Basel 1972, Vol. 1, p. 475.
16 M. Wittels, Am. Mineralogist, 36 (1951) 615.
17 Th. Heumann and B. Predel, Z. Metalkunde, 49 (1958) 90.
18 R. Caulcutt, Statistics in Research and Development, Chapmann and Hall, New York 1983, p. 66.
19 J. D. Gibbons, Nonparametric Statistical Inference, Mc Graw Hill, New York 1971, p. 198.
20 W. W. Wendlandt, Thermal methods of analysis, Interscience Publisher, New York 1964, p. 163.
21 E. M. Barral and L. B. Rogers, Anal. Chem., 34 (1962) 1101.
22 A. R. Carther, Am. Minerologist, 40 (1955).
23 V. P. J. Egunov and L. G. Berg, J. Thermal Anal., 2 (1970) 53.
24 P. D. Garn, Thermoanalytical methods of investigation, Academic Press, London 1965, p. 18.

Zusammenfassung — Vorliegende Arbeit stellt eine quantitative Anwendung der Metallblock-DTA (MBDTA) dar. Es wurden elektrisch Kalibrationen mit verschiedenen, innerhalb der Probe befindlichen Kalibrationserhitzern (Stift, Ring, Spirale) durchgeführt. Mit Hilfe dieser Anordnung wird die Auswertung der Ergebnisse durch die thermophysischen Eigenschaften der Probe erleich-

tert. Es wurde der Einfluß von Größe und Probendurchmesser, von Erhitzertyp, von Abstand zwischen Erhitzer und Thermoelement, mit anderen Worten von denjenigen Faktoren, die die Kalibration beeinflussen sowie der Einfluß der Wärmetransportgeometrie auf die Bestimmung der Schmelzwärme untersucht.