

A STUDY OF DIFFERENT ASPECTS OF DTA CALIBRATION

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ABSTRACT

In this work, an attempt is made to establish the relation of proportionality between the heat of transition inside the sample and the corresponding area on the DTA peak vs. temperature curve. The influence of the particle size in this relation of proportionality is demonstrated. Finally, a theoretical model of DTA is discussed.

INTRODUCTION

While the temperature calibration of an instrument of differential thermal analysis does not present specific problems, the calorimetric calibration is more complex. The calibration coefficient, C , of DTA is determined by use of compounds having known heats of transition. The heat of transition, Q , inside the sample is then related to the peak area by

$$Q = 1/C \int_{t_i}^{t_f} \theta dt \quad (1)$$

where C is the empirical proportionality between the heat of transition inside the sample and the corresponding peak area, and θ is a linear function of the EMF generated by the differential temperature. The limits of integration, t_i and t_f , are the initial and final times of the detectable differential temperature. The latter are generally taken to be equivalent to the limits of the thermogram peak [1].

The numerous parameters which influence DTA and the difficulty of controlling some of them make DTA a semi-quantitative technique for measuring transition enthalpies. Nevertheless, many attempts have been directed towards finding a quantitative or improved semi-quantitative technique. There are studies dealing with the influence of instrumental factors [2], thermal conductivity of the sample [3], grade of contact between sample and crucible [4], the possibility of giving off a gas with a thermal conductivity different from the existing atmosphere—as happens in some chemical reactions and dehydrations [5],— and the kinetics of transformation [6].

In this paper, the variation of the calibration coefficient, C , vs. temperature in an atmosphere of air using a fixed heating rate is studied. Also the influence of the particle size on the value of C is proved. A systematic study of the influence of the atmosphere on the value of C will be dealt with at a later date. A theoretical model and its concordance with experimental reality is also analyzed.

DISCUSSION

The experimental work was carried out with standard M-4H Setaram equipment, its main characteristic being a semi-micro DTA device such as described by Mazières [7]. Its originality consists in the use of the specimen holder assembly according to transversal and vertical plans (Fig. 1).

A heating rate of $3^{\circ}\text{C min}^{-1}$ was used. Higher heating rates can produce a superposition of phenomena. However, if the heating rate is too low, the apparatus, due to its own design (the programming of temperature, volume of gas, signal amplification, etc.) can simulate non-existent thermal phenomena. The linearity between the sample mass and the peak area demonstrated by Sturm [8] permitted a choice of the sample mass according to its density, transition enthalpy, etc. The diameter of the particle was $\phi < 0.3$ mm. Only air atmosphere was used. An empty crucible was used as reference.

Calorimetric calibration of the DTA thermocouples

The influence of the particle size in the determination of C was proved as follows. Three sizes of particles were selected, one inferior to $300 \mu\text{m}$, one between 400 and $600 \mu\text{m}$ and one with a diameter between 1200 and $2500 \mu\text{m}$. A DTA was then made for the particles of a different size until the

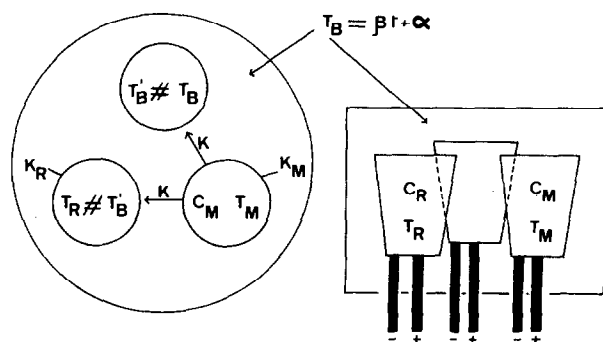


Fig. 1. A vertical and horizontal view of the specimen holder assembly showing the temperature in the different parts. The thermal interchanges are regulated by the K , K_M and K_R coefficients.

TABLE 1

Values of C for different diameters of particles obtained from two consecutive heatings on the sample showing the influence of recrystallization (analyses have been made with KNO_3 , KClO_4 and $\text{C}_{18}\text{H}_{36}\text{O}_2$)

	C ($\mu\text{V min cal}^{-1}$)	
	First heating	Second heating
$\text{C}_{18}\text{H}_{36}\text{O}_2$		
$\phi < 0.3$ mm	448.52	453.68
0.4 mm $< \phi < 0.6$ mm	444.33	442.05
1.2 mm $< \phi < 2.5$ mm	431.78	393.78
KNO_3		
$\phi < 0.3$ mm	444.87	401.40
0.4 mm $< \phi < 0.6$ mm	429.43	399.66
1.2 mm $< \phi < 2.5$ mm	401.21	388.91
KClO_4		
$\phi < 0.3$ mm	372.04	356.41
0.4 mm $< \phi < 0.6$ mm	369.01	336.06
1.2 mm $< \phi < 2.5$ mm	358.28	331.63

transition temperature was reached. This was followed by cooling to produce recrystallization. A new DTA was made later.

The results obtained by this procedure are presented in Table 1. Examining the results, we may conclude that the smaller the particle, the bigger the peak area. This can be explained considering that with a smaller particle size, the thermal contact among the different particles is improved. The contact between the particles and the crucible also improves. This provides a better detection of the emitted heat. In the second heating, a larger area for a smaller size of departure can be observed. This is due to the fact that when the particle size is smaller, the crystallization is more compressed.

In order to study the variation of the calibration coefficient, C , vs. temperature, the values of transition enthalpies have been taken in accordance with Harmelin [9]. The chart speed (in cm min^{-1}) is v_r , the differential temperature sensitivity (in $\mu\text{V cm}^{-1}$) is ΔT , the transition enthalpy (in cal g^{-1}) is ΔH , and the peak area (in cm^2) is S . Therefore, $C = \Delta T S v_r^{-1} \Delta H^{-1}$ (in $\mu\text{V min cal}^{-1}$).

Table 2 lists the chosen substances together with their transition temperatures, transition enthalpies and the measured values of C . The results obtained are represented in Fig. 2. These results have been fitted to a third order curve

$$C = 449.55 + 0.11505 T - 1.2500 \times 10^{-3} T^2 + 7.5790 \times 10^{-7} T^3 \quad (2)$$

where T is expressed in $^{\circ}\text{C}$.

TABLE 2

Calorimetric calibration

	T_{tr} ($^{\circ}\text{C}$)	ΔH (cal g^{-1})	C ($\mu\text{V min cal}^{-1}$)
$\text{C}_{18}\text{H}_{36}\text{O}_2$	68	47.5	450.95 ± 12.60
KNO_3	127.7	13.2	449.18 ± 7.72
KClO_4	299.5	24.2	374.68 ± 3.64
K_2CrO_7	398	29.81	369.29 ± 14.01
K_2SO_4	583	11.13	224.32 ± 10.93
K_2CrO_4	665	8.52	202.88 ± 7.10
BaCO_3	810	22.65	128.11 ± 5.04
SrCO_3	925	31.84	85.10 ± 2.60

Figure 3 shows the calibration made by Harmelin [10] with an atmosphere of helium, and the similarity between the two calibrations can be observed. The sensitivity reduction in the atmosphere of helium is due to the lower thermal conductivity of this gas.

Comments on a DTA theoretical model

The theoretical model devised by Kessis [11,12] is applicable to our DTA device. In fact, this theoretical model supposes a block of great heat capacity

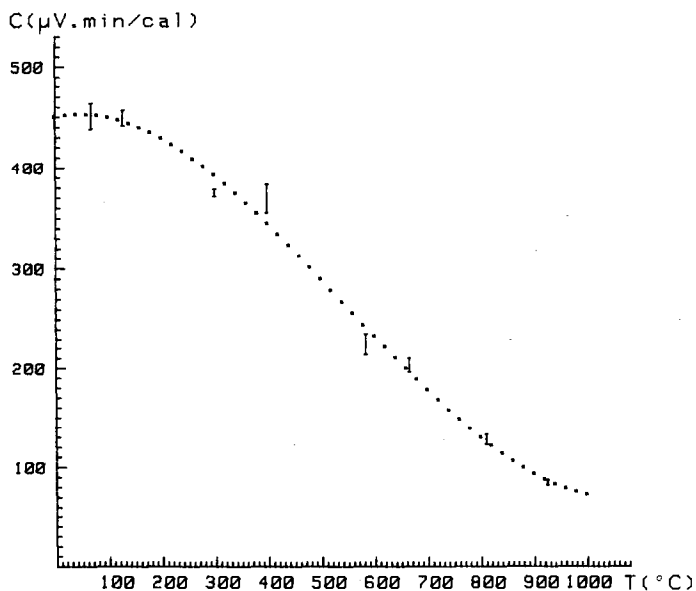


Fig. 2. Curve showing the variation of the coefficient of proportionality, C ($\mu\text{V min cal}^{-1}$), vs. temperature, T ($^{\circ}\text{C}$), between room temperature and 1000°C in an atmosphere of air.

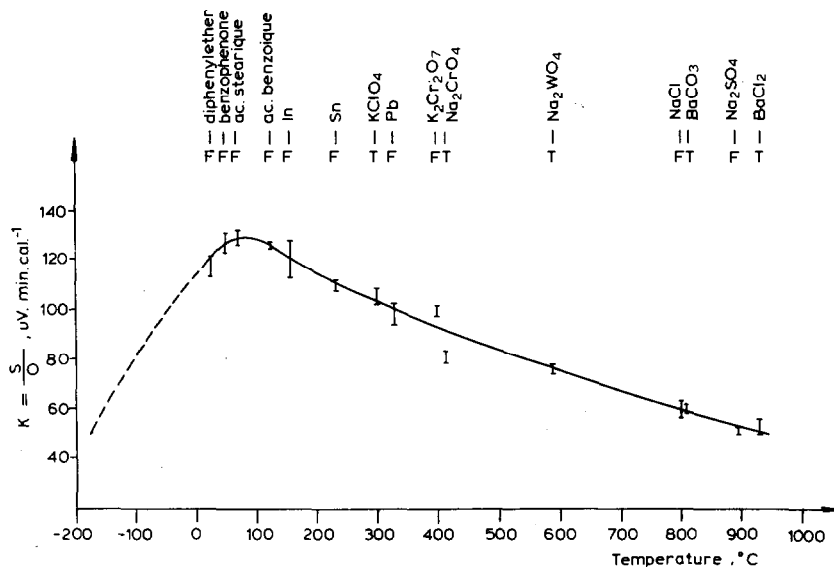


Fig. 3. Curve obtained from Harmelin [10] when studying the variation of C ($\mu\text{V min cal}^{-1}$) vs. T ($^{\circ}\text{C}$) in an atmosphere of helium.

whose temperature, T_B , changes vs. time in a linear way

$$T_B = \beta t + \alpha$$

This block contains the sample of specific heat C_M and temperature T_M and the reference of specific heat C_R and temperature T_R . The thermal interchanges are regulated by the superficial interchange coefficients K_M and K_R . The thermal coupling which exists between the sample cell and the reference cell is represented by coefficient K .

This theoretical model can be adjusted to this device by replacing temperature T_B of the heating block by the temperature of the atmosphere surrounding the thermocouples. The differences in temperature between atmosphere, sample, and reference are very weak due to the small sample mass and a low heating rate. To sum up, for the $3^{\circ}\text{C min}^{-1}$ heating rate used, the differences in temperature are less than 1°C . So, one may conclude that the thermal interchanges between the heating block, sample and reference are regulated by coefficients of superficial interchange K_M and K_R .

Although this model explains several DTA experimental phenomena, such as the existence of the derive in the base line, its dependence on the heating rate, the existence of a proportionality coefficient between the transition enthalpy and the peak area, etc., it is interesting to point out some of its limitations. In this model one supposes that the superficial interchange coefficients K_M and K_R , which have a closed dependence with the proportionality coefficient, C , are not functions of the temperature. On the other hand, in this paper the variation of the proportionality coefficient, C , vs.

temperature has been determined. Also, this model leads us to believe that the heat capacities of the sample and reference do not depend on temperature, which is quite acceptable for the reference but not for the sample. The influence of the particle size which has been demonstrated experimentally in this paper is not considered in this model, neither is the thermal resistance of the materials, which implies assigning them with infinite thermal conductivity.

CONCLUSION

The possibility of determining experimentally the variation of the proportionality coefficient between transition enthalpy and peak area vs. temperature permits the use of DTA to measure transition enthalpy. The semi-quantitative character of this measurement is due to the numerous, uncontrollable parameters that influence the DTA. The test performed with the particle size demonstrates that control of this parameter is of great importance. Even though the Kessiss' theoretical model explains some DTA experimental facts, the limitations found in this model lead us to believe that the superficial interchange model is too simple to provide a satisfactory explanation for all the DTA aspects.

REFERENCES

- 1 W.W. Wendlandt, *Thermal Methods of Analysis*, Wiley-Interscience, New York, 1964, p. 168.
- 2 Y. Chiang and W.J. Smothers, *Handbook of Differential Thermal Analysis*, Chemical Publishing Company, New York, 2nd edn., 1966.
- 3 G. Sabatier, *C.R.*, 235 (1952) 574.
- 4 H.G. Wiedemann and A. Van Tets, *Thermochim. Acta*, 1 (1970) 159.
- 5 W.W. Wendlandt, *Thermochim. Acta*, 9 (1974) 456.
- 6 P. Lehr and M. Harmelin, *C.R.*, 280 (1975) 1011.
- 7 C. Mazières, *Anal. Chem.*, 36 (1964) 602.
- 8 E. Sturm, *Thermochim. Acta*, 4 (1972) 461.
- 9 M. Harmelin, *Journées de Calorimétrie et d'Analyse Thermique de l'AFCAT*, Rennes, 1974, p. 14.
- 10 M. Harmelin, *First European Symposium on Thermal Analysis*, Salford, 20-24 September 1976.
- 11 J.J. Kessiss, Thesis No. A.O. 3995, Paris University, 1970.
- 12 J.J. Kessiss, *C.R. Acad. Sci., Ser. C*, 270 (1970) 1, 120, 265 and 1201.