Thermochimica Acta, 94 (1985) 17–31
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALIBRATION OF DIFFERENTIAL SCANNING CALORIMETERS USING ΔH-/T- AND C_p-STANDARDS: EXTENDED APPLICATION TO TWO INSTRUMENTS

S. SARGE and H. K. CAMMENGA
Institut für Physikalische und Theoretische Chemie,
Technische Universität Braunschweig, Hans-Sommer-Straße 10,
D-3300 Braunschweig, Bundesrepublik Deutschland

ABSTRACT

This paper introduces some organic substances which might be suitable for simultaneous temperature and enthalpic calibration of differential heat-flux-calorimeters. The results are compared with values obtained with other well-accepted reference materials and methods. The influences of sample and instrumental properties are discussed.

INTRODUCTION

Since many years enthalpic and temperature calibration of DTA and DSC equipments is a widely discussed theme in this field of thermal analysis (see ref. 1...3, for example). The ICTA Standardization Committee recommends only a few certified reference materials for calibration of temperature scales (ref. 4) but until now there are no equivalent sets of reference materials for enthalpic calibration available.

Thus different workers use different calibration procedures which lowers the comparability of the obtained values.

Generally, the calibration of a calorimeter needs the consumption or production of an exactly known amount of heat in its interior. This heat can be latent, sensible, electically or radioactively generated. The fundamental requirement of any exact calibration is that calibration procedure and measurement procedure differ as little as possible. For determining the enthalpies of phase transitions or chemical reactions it is recommended to calibrate with the respective enthalpies of standard materials.

In our work we use some organic materials (newly selected for this purpose), metallic materials (well-accepted for this purpose) and a standard for heat capacity measurements.

0040-6031/85/$03.30 © 1985 Elsevier Science Publishers B.V.

BASIC EXPRESSIONS

The thermal analogon of OHMs electric law applied to a differential heat-flux-calorimeter gives (ref. 5):

$$\dot{Q} = \frac{dQ}{dt} = \frac{\Delta T}{R_{th}} = \frac{\Delta U}{E} \quad , \qquad (1)$$

with Q = heat, t = time, T = temperature, R_{th} = thermal resistance, U = electric potential, E = calibration factor.

For instance, by melting of a sample of a standard material of mass m, molar mass M and molar enthalpy of fusion $\Delta_{fus}H$ integration over the measured peak leads to expression (2):

$$E = \frac{M}{m\,\Delta_{fus}H} \int_{t_0}^{t_\infty} \Delta U(t)dt \quad . \qquad (2)$$

The thermal resistance can be determined approximately by means of the slope tg(α) of a fusion peak of a highly pure substance:

$$R_{th} = \frac{1}{tg(\alpha)} \left(\frac{dT}{dt}\right)_{ref} \quad . \qquad (3)$$

From measurements of the heat capacities C_p of standard materials the calibration factor is obtained by:

$$E(T) = \frac{\Delta U(T)\ M}{C_p(T)\ dT/dt\ m} \quad . \qquad (4)$$

For temperature calibration the extrapolated peak onset temperature is used.

REFERENCE MATERIALS

Suitable materials for temperature and enthalpic calibration must simultaneously fulfil several criteria.

They must:
- allow easy purification
- be chemically stable in the solid and liquid phase
- be non-toxic
- be non-hygroscopic
- have only one phase transition in the temperature range of interest
- have transitions with exactly determined enthalpy and temperature
- be inert against the container materials used
- have small vapour pressures.

In accord with these criteria we selected thirteen organic and metallic substances. The metals were purchased as pure as possible whereas the organic substances were purified by zone refining and vacuum sublimation.

TABLE 1

Materials selected for calibration

Material	ϑ_{fus}/°C	$\Delta_{fus}H$/kJmol^{-1}	Ref.
Carbon tetrachloride	-22.80	2.52	6,7
Water	0	6.008	6,8
Diphenyl ether	26.869	17.216	6,9
Gallium	29.772	5.586	6,10
Biphenyl	69.2	18.58	6,11
Naphthalene	80.25	18.79	12,11
Benzoic acid	122.4	18.00	13
Indium	156.634	3.283	6,14
Anthracene	215.82	29.37	15
Tin	231.968	7.195	6,16
Bismuth	271.442	11.131	6,17
Lead	327.502	4.77	6,18
Zinc	419.58	7.28	6,19

For heat capacity measurements a synthetic monocrystalline sapphire was used (ref. 20).

CALORIMETERS

The experiments were carried out using two differential heat-flux-calorimeters:

1) Mettler FP 800/84: This instrument allows the simultaneous examination of heat effects (DSC) and optical effects by light microscopy (TOA). The differential temperature is measured by a fivefold Au/Ni-thermopile. Temperature range: -60...+300°C.
2) Heraeus TA 500: Two Pt-resistors deposited on a rectangular ceramic plate are used as differential temperature sensors. The sample temperature is measured by the resistor under the sample pan. Temperature range: -100...+500°C.

EXPERIMENTAL

All samples were weighed on a microbalance into sealed aluminium pans (ca. 40 µl volume). Each sample was melted and recrystallized several times except those which obviously changed their properties during melting (anthracene, bismuth, lead, zinc). After each experiment the sample was removed from the calorimeter and allowed to recrystallize before the following experiment was started. Therefore, the reported values include the influences of weighing error, sample mass, position of sample pan relative to the temperature sensor, values of absolute and specific enthalpy and heat conductivity. Reference was an empty pan.

Evaluation was done by a personal computer on line and self-developed programs. Starting and ending point for peak integration were set by eye. In all cases the straight line between these two points was assumed to be the baseline.

RESULTS (METTLER FP 84)

Calibration factor

Table 2 shows the calibration factor as determined by means of the reference materials of Table 1. In each case three samples were prepared. The sample weight was 0.7 to 14 mg, the absolute enthalpy varied from $1.9 \cdot 10^{-2}$ J to 2.1 J and the heating rate was 3 K/min.

TABLE 2

Mean calibration factors $\bar{E}$ from fusion experiments (Mettler FP 84)

Material	ϑ_{fus}/°C	$\bar{E}$/µVmW^{-1}	σ/%	ΔE_{max}/%	n
Water	0	6.28	0.66	+1.41	9
Diphenyl ether	26.869	6.83	1.73	-4.03	9
Gallium	29.772	6.89	1.62	+2.74	12
Biphenyl	69.2	7.63	1.20	+1.94	10
Naphthalene	80.25	7.84	0.81	-1.10	9
Benzoic acid	122.4	8.19	1.75	-2.83	9
Indium	156.634	8.32	1.46	+3.37	16
Anthracene	215.82	8.22	1.22	+1.36	3
Tin	231.968	7.95	1.45	+2.12	12
Bismuth	271.442	7.47	2.83	+3.14	3

(σ = percental standard deviation, ΔE_{max} = maximum deviation from mean value, n = number of experiments)

These data were fitted by a second order orthogonal polynomial (Figure 1).

Another widely used method for calibration is the measurement of the heat capacity of a standard. Three experiments were done with a sapphire of 60.219 mg weight and a heating rate of 10 K/min. Figure 2 shows the results graphically. In Table 3 the data are compared with the fitted results of the fusion experiments.

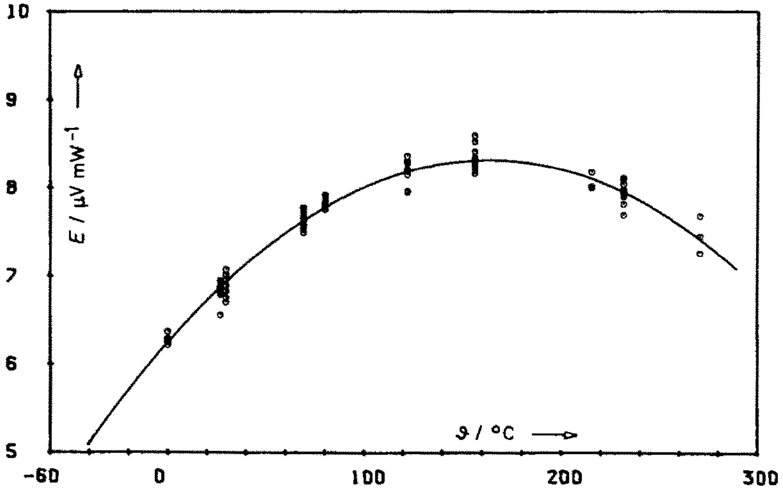

Fig. 1: Calibration factor E determined by fusion experiments (Mettler FP 84)

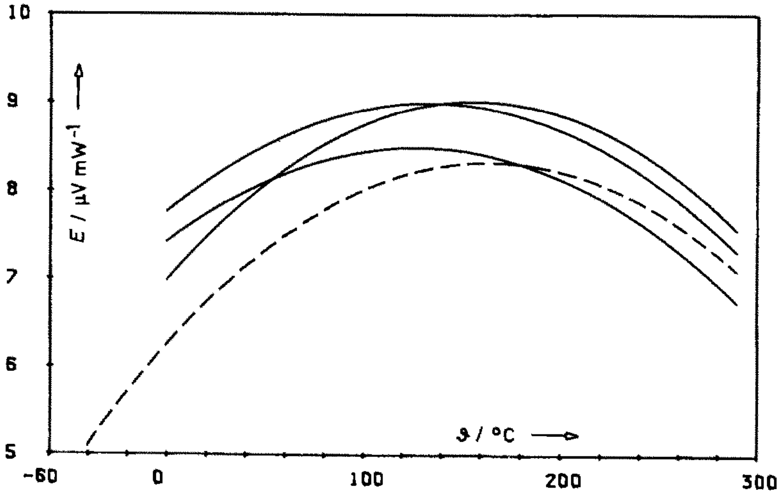

Fig. 2: Calibration factor E determined by heat capacity experiments (——) and by fusion experiments (---) (Mettler FP 84)

TABLE 3

Mean calibration factor $\bar{E}$ from heat capacity experiments compared with fitted results from fusion experiments (Mettler FP 84)

$\vartheta/^{\circ}C$	$\bar{E}/\mu V mW^{-1}$	$\sigma/\%$	$\Delta E/\%$
0	7.38	5.31	+18.35
50	8.22	3.01	+12.36
100	8.70	2.77	+8.65
150	8.81	3.54	+6.02
200	8.56	4.43	+4.10
250	7.95	5.26	+2.61
300	6.97	6.05	+1.25

The above decribed experiments were made between January and May 1984. A test of the calibration factor in March 1985 led to the results shown in Figure 3. During this year the calibration factor decreased slightly (-2.0 % at indium fusion temperature) and also changed its temperature dependence.

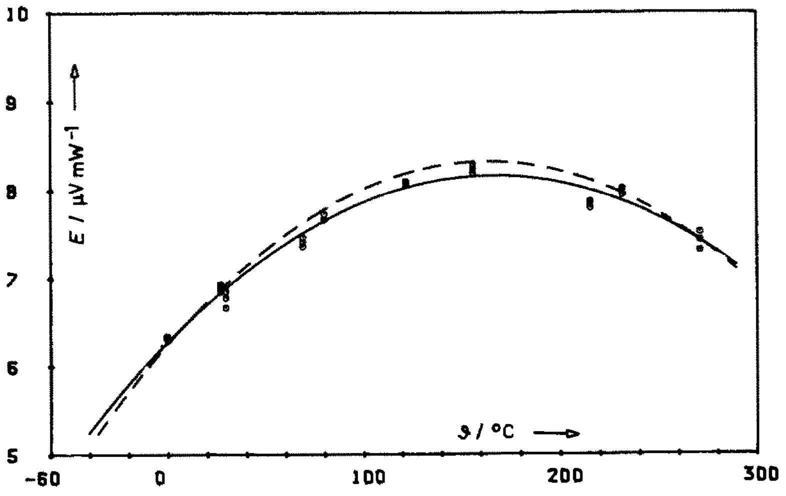

Fig. 3: Calibration factor E in March 1985 (——) and May 1984 (---) (Mettler FP 84)

Following theoretical considerations the calibration factor should decrease with increasing heating rate (ref. 21). Our experiments on indium show a slight decrease of the calibration factor by increasing the heating rate from 0.1 to 20 K/min, but this effect is of the same order as the reproducibility of the instrument (Figure 4).

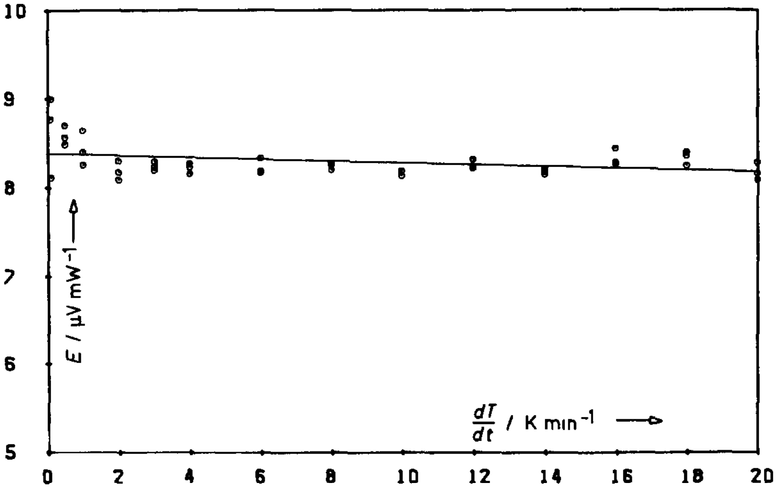

Fig. 4: Calibration factor E for indium as a function of the heating rate (Mettler FP 84)

Thermal resistance

Considering equations (1) and (2) the measured peak area depends strongly on the thermal resistance between sample and temperature sensor. Because of the very different heat conductivities of metals and molecular crystals and with respect to differences in heat transfer between aluminium pan and powdery or premelted samples Figure 5 shows the thermal resistance of each sample as a function of the number of experiments on this sample.

Only gallium and tin samples change the thermal resistance significantly. (Anthracene and bismuth are not stable in the liquid phase, their influence on the thermal resistance is a consequence of their melting point depression). This variation in R does not affect the calibration factor.

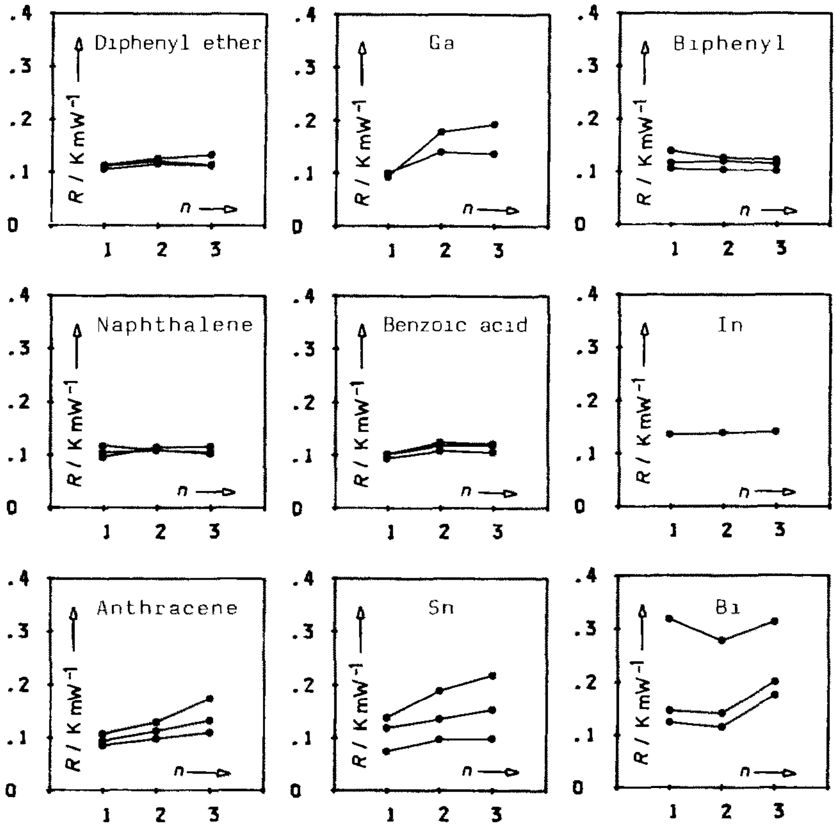

Fig. 5: Thermal resistance R of the different samples (Mettler FP 84)

Figure 6 shows the influence of sample weight on the thermal resistance at the second run of each sample. Small weights of gallium, indium and bismuth cause great thermal resistances. Optical examinations prove that because of their high surface tension, these molten samples lie like sessile drops in the aluminium pan. Therefore, the contact area between sample and pan is small. Organic materials like anthracene do not show this behaviour.

But all these differences and variations in thermal resistivity do not influence the calibration factor significantly.

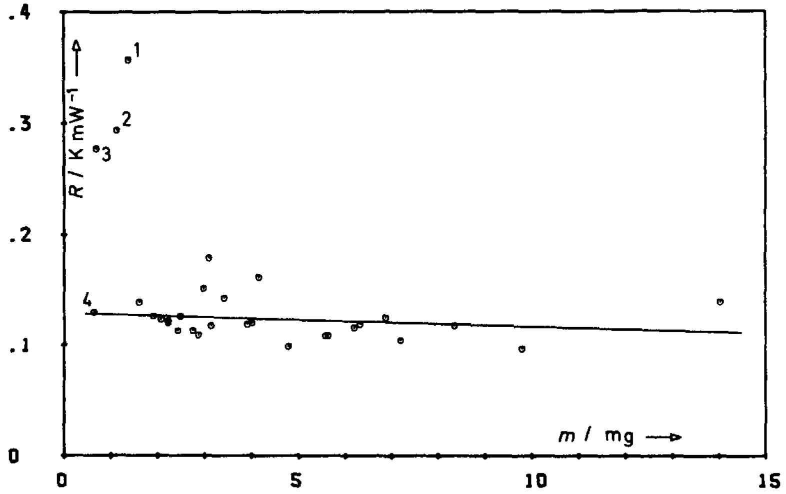

Fig. 6: Thermal resistance R as a function of sample mass m
(Mettler FP 84)
1: 1.409 mg Ga
2: 1.141 mg In
3: 0.703 mg Bi
4: 0.659 mg anthracene
(Points 1...3 were not used for linear regression)

Temperature calibration

The differences between measured peak onset temperature and true melting point of the samples were used for constructing temperature calibration curve (Figure 7). The kind of the reference material (resp. its thermal resistance) does not affect the calibration factor but influences the temperature calibration: Metals give always smaller values for the correction term ΔT than organic substances melting at comparable temperatures.

RESULTS (HERAEUS TA 500)

Calibration factor

The calibration factor of the Heraeus TA 500 calorimeter was determined by the same procedure as described above. Sample mass was 0.6 to 6.8 mg, absolute enthalpy varied from $1.1 \cdot 10^{-2}$ J to 1.8 J, heating rate was 5 K/min. Table 4 and Figure 8 show the results. The data were fitted by a third-order orthogonal polynomial.

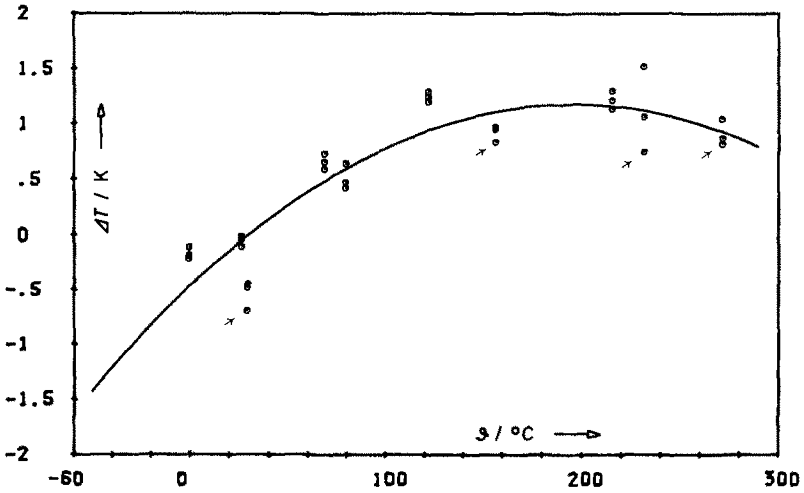

Fig. 7: Temperature calibration curve. Metals are marked with an arrow. ϑ_{fus}(true) = ϑ_{fus}(onset) + ΔT (Mettler FP 84)

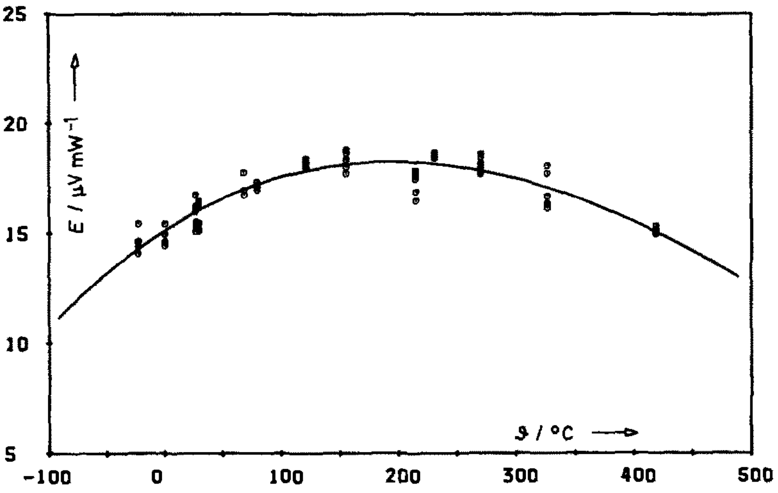

Fig. 8: Calibration factor E from fusion experiments (Heraeus TA 500)

TABLE 4

Mean calibration factors $\bar{E}$ from fusion experiments (Heraeus TA 500)

Material	ϑ_{fus}/°C	$\bar{E}/\mu V mW^{-1}$	σ/%	ΔE_{max}/%	n
Carbon tetrachloride	-22.80	14.64	3.03	+5.43	6
Water	0	14.90	2.54	+3.61	5
Diphenyl ether	26.869	15.83	3.41	+5.91	9
Gallium	29.772	15.83	3.96	-4.49	6
Biphenyl	69.2	17.18	3.13	+3.51	3
Naphthalene	80.25	17.15	0.60	+1.27	8
Benzoic acid	122.4	18.25	0.86	-1.27	7
Indium	156.634	18.43	2.06	-3.55	8
Anthracene	215.82	17.37	3.12	-4.95	6
Tin	231.968	18.53	0.52	+0.92	7
Bismuth	271.442	18.09	1.85	+3.07	8
Lead	327.502	16.92	4.85	+7.09	6
Zinc	419.58	15.14	0.89	+1.51	6

The standard deviation is of the same order as for the Mettler FP 84 calorimeter, though significantly higher for the Heraeus TA 500 calorimeter.

Three experiments on the heat capacity of sapphire gave the following results (sample mass: 202.774 mg, heating rate: 10 K/min):

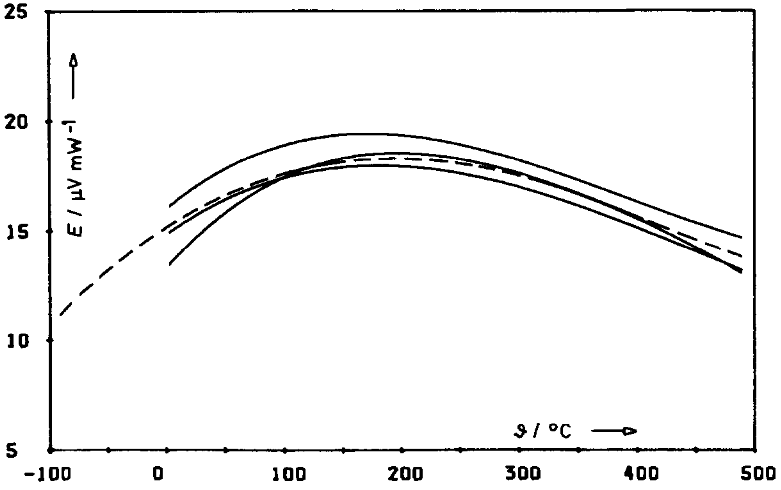

Fig. 9: Calibration factor E determined by means of three heat capacity experiments (——) and same fusion experiments as shown in Figure 8 (---) (Heraeus TA 500)

TABLE 5

Mean calibration factors $\bar{E}$ from heat capacity experiments compared with fitted results from fusion experiments (Heraeus TA 500)

ϑ/°C	$\bar{E}/\mu V mW^{-1}$	σ/%	ΔE/%
0	14.66	9.28	-3.05
50	16.65	6.20	+0.33
100	17.90	4.78	+1.80
150	18.53	4.14	+2.13
200	18.63	3.81	+1.80
250	18.30	3.58	+1.16
300	17.64	3.44	+0.54
350	16.75	3.45	+0.30
400	15.73	3.72	+0.92
450	14.68	4.42	+3.06
500	13.70	5.69	+7.85

The heating rate has no obvious influence on the calibration factor. Figure 10 and 11 show the calibration factor as a function of the heating rate determined by fusion experiments and heat capacity measurements.

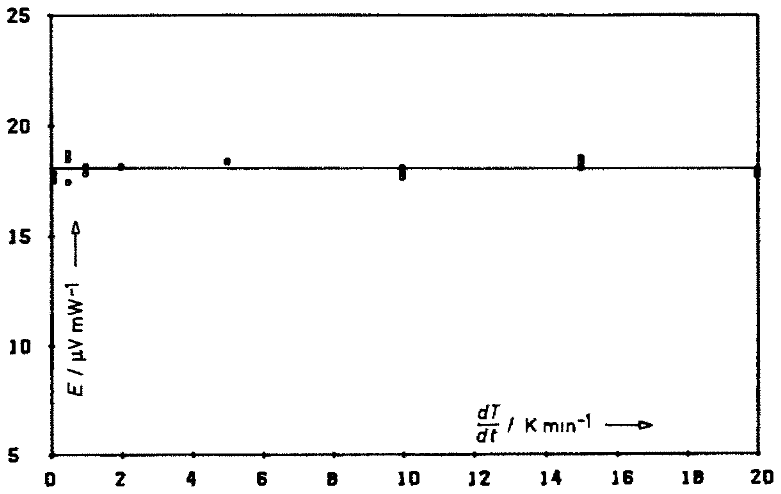

Fig. 10: Calibration factor E for indium as a function of the heating rate (Heraeus TA 500)

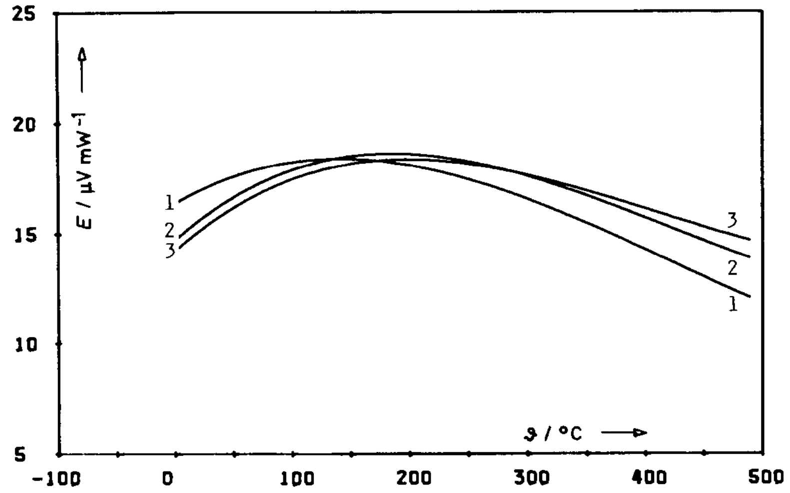

Fig. 11: Calibration factor E from heat capacity measurements at different heating rates (Heraeus TA 500)
1: heating rate 5 K/min
2: heating rate 10 K/min (mean value of three experiments)
3: heating rate 20 K/min

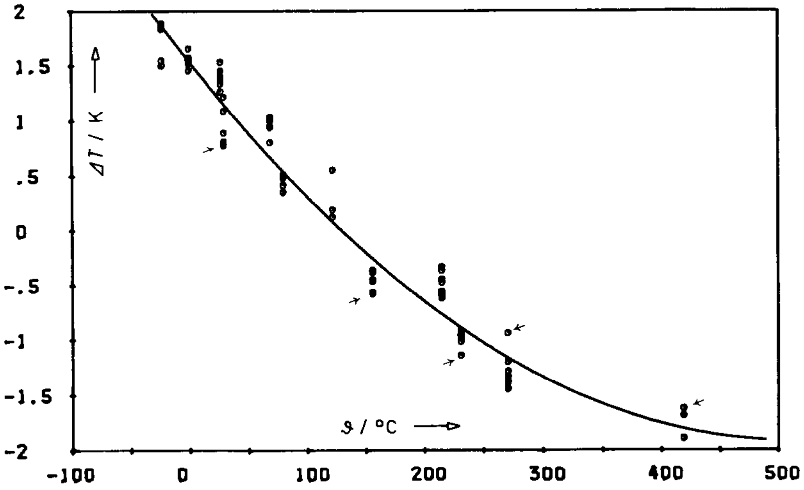

Fig. 12: Temperature calibration curve. Metals are marked with an arrow. ϑ_{fus}(true) = ϑ_{fus}(onset) + ΔT (Heraeus TA 500)

Temperature calibration

The temperature calibration curve of the Heraeus TA 500 calorimeter is shown in Figure 12. Obviously, there is a similar tendency in deviation of the measured fusion temperatures of the metallic samples from the non-metallic samples as shown in Figure 7 for the Mettler FP 84 calorimeter.

The peak onset temperatures of lead scatter much more than the others and have therefore been omitted.

CONCLUSIONS

The reproducibility of enthalpy of fusion measurements varies for both calorimeters from 0.2 to 2 % (percental uncertainty of the mean). In one case out of 177 experiments the maximum deviation of a single experiment from the mean was 7 %.

Especially lead should not be used for temperature and enthalpy calibration measurements, because its values scatter significantly more than the others. In comparison with the enthalpies of indium, tin and bismuth the value for anthracene seems to be less certain, because the mean calibration factor obtained with anthracene is significantly lower.

The behaviour of metallic and molecular crystalline materials does not differ widely with respect to enthalpy calibration measurements, but concerning temperature calibration measurements they are not comparable.

The Mettler FP 84 is not suitable for calibration by or measurement of heat capacities. Admittedly, however, the instrument has not been designed for this special purpose. For the Heraeus TA 500 calorimeter the calibration curves $E = E(\vartheta)$ as determined by heat capacity and by fusion experiments are the same within error limits. Standard deviations are of the same order in both cases.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. H. Bothe for collaboration during the early stages of this work and Mrs. K. Haft for performing part of the measurements. One of the authors (S. S.) is indebted to Fonds der Chemischen Industrie, Frankfurt am Main, for financial support.

REFERENCES

1 A. P. Gray, in "Thermal Analyis", Proc. 4th ICTA, Budapest,1974, J. Buzas, ed., Akademiai Kiado, Budapest, 1975, Vol. 3, p. 991-1003

2 K.-H. Breuer and W. Eysel, Thermochim. Acta, 57 (1982) 317-329

3 W. Eysel and K.-H. Breuer, in "Analytical Calorimetry", Proc. Am. Chem. Soc. Symp. on Anal. Calorimetry, J. F. Johnson and P. S. Gill, eds., Plenum Press, New York, 1984, Vol. 5, p. 67-80

4 A. Langier-Kuźniarowa, J. Therm. Anal., 29 (1984) 913-918

5 R. Riesen and G. Widmann, "Thermoanalyse: Anwendungen, Begriffe, Methoden", Hüthig, Heidelberg, 1984

6 U. Schley, PTB-Mitt., 89 (1979) 13-21

7 L. A. K. Staveley and A. K. Gupta, Trans. Faraday Soc., 45 (1949) 50-61

8 F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Nat. Bur. Stand. (U. S.) Circ. No. 500 (1952) 539

9 G. T. Furukawa, D. C. Ginnings, R. E. McCoskey and R. A. Nelson, J. Res. Nat. Bur. Stand., 46 (1951) 195-206

10 G. B. Adams Jr., H. L. Johnston and E. C. Kerr, J. Am. Chem. Soc., 74 (1952) 4784-4787

11 K. Ueberreiter und H.-J. Orthmann, Z. Naturforsch. Teil A, 5 (1950) 101-108

12 L. H. Ward, J. Phys. Chem., 38 (1934) 761-769

13 G. T. Furukawa, R. E. McCoskey and G. J. King, J. Res. Nat. Bur. Stand., 47 (1951) 256-261

14 F. Grønvold, J. Therm. Anal., 13 (1978) 419-428

15 P. Goursot, H. L. Girdhar and E. F. Westrum Jr., J. Phys. Chem., 74 (1970) 2538-2541

16 F. Grønvold, Rev. Chim. Miner., 11 (1974) 568-584

17 F. Grønvold, Acta Chem. Scand. Ser. A, 29 (1975) 945-955

18 T. B. Douglas and J. L. Dever, J. Am. Chem. Soc., 76 (1954) 1824-1826

19 O. Kubaschewski, Z. Elektrochem., 54 (1950) 275-288

20 D. C. Ginnings and G. T. Furukawa, J. Am. Chem. Soc., 75 (1953) 522-527

21 G. W. H. Höhne, Thermochim. Acta, 69 (1983) 175-197