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NEW REFERENCE MATERIALS FOR THE CALIBRATION (TEMPERATURE AND ENERGY) OF DIFFERENTIAL THERMAL ANALYSERS AND SCANNING CALORIMETERS

R. Sabbah and L. El Watik

CENTRE DE THERMODYNAMIQUE ET DE MICROCALORIMETRIE DU CNRS. 26, RUE DU
141EME RIA-13003 MARSEILLE, FRANCE

Several organic compounds like phenanthrene, benzanilide, anisic acid, triphenylene, 2-chloroanthraquinone, hexachlorobenzene, carbazole, 4-iodobenzoic acid, perylene, anthraquinone, as new reference materials for temperature and energy calibration of DTA and DSC apparatuses were studied in the range 300–600 K.

Keywords: calibration materials, DSC, DTA

Introduction

Differential thermal analysis is a powerful tool for the determination of the purity of substances and for the investigation of their phase transitions and thermal behaviour.

The temperatures and energies of phase transitions can be determined with good accuracy if the apparatus is previously carefully calibrated using standard reference substances.

In the range 300 –600 K where are generally studied organic compounds, the reference materials proposed by international organizations like IUPAC, ICTA and ICWM [1, 2, 3] for the calibration of differential thermal analysers and scanning calorimeters are few and irregularly distributed inside this range.

Experimental

Substances

Excepted naphthalene (99.96%) and benzoic acid (99.997%), all the substances had an initial purity of 97–99%. We have purified the majority of them

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by crystallization in absolute ethanol or in a mixture containing 50% water. All the substances were then sublimated sometimes twice or three times under a residual pressure of 10^{-2} Torr at a temperature depending on the nature of the compound in the range 50°–180°C. The coloured substances were always handled screened from light. More details concerning the preparation of pure samples are given in Ref. [5].

Apparatus

The differential thermal analyser used is described in Refs [4, 5] (Fig. 1). The temperature of the sample and the difference of temperature between the sample and the reference (here α-alumina) are determined by chromel-alumel thermocouples (Thermocoax, type 2ABI15) (Fig. 2).

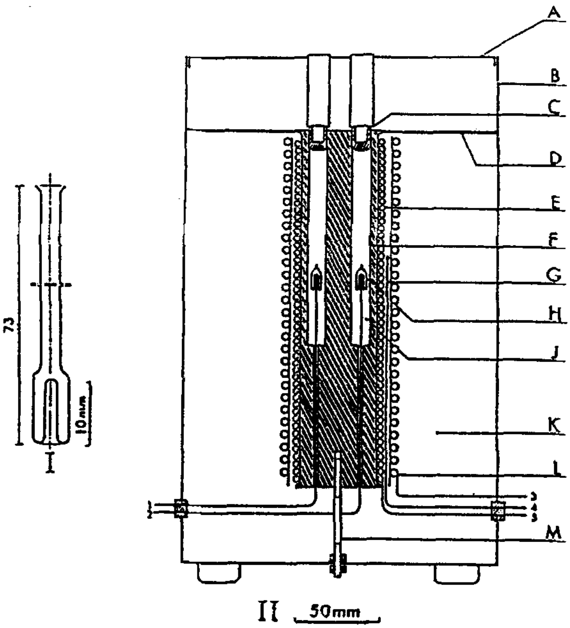

Fig. 1 Differential thermal analyser. I – Glass ampoule used as cell. II – Differential thermal analyser section. A: cover, B: external metallic vessel, C: metallic plug, D: centering screw, E: heating resistance, F: furnace, G: platinum resistance thermometer, H: glass ampoule, J: well, K: isolating material (Kwool), L: cooling circuit, M: fixing screw, 1, 2: thermocouple terminals, 3: compressed air arrival and departure, 4: resistance thermometer terminals, 5: heating resistance terminals

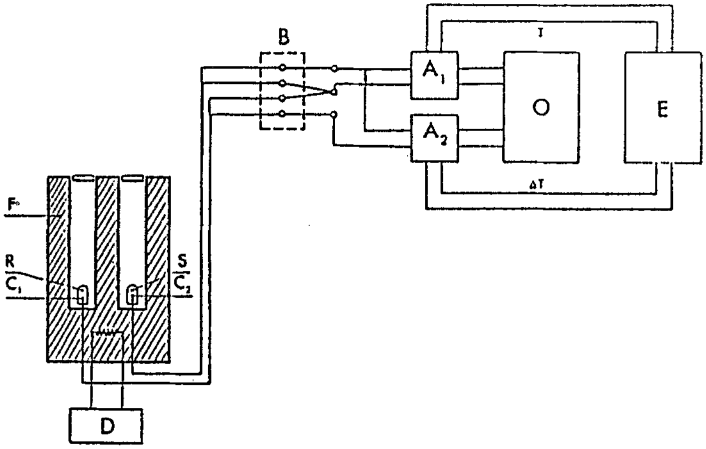

Fig. 2 Wiring diagram. A_1 and A_2: amplifiers, B: cold junction, C_1 and C_2: thermocouples, D: control device or furnace heataing, E: recorder, F: furnace, O: computer, R: reference (in our case: α-alumina), S: substance

Mode of operation

The triple point temperature (T_o) and the total impurity content (N) of a substance sample are readily determined from its melting curve using Raoult law and Clausius-Clapeyron equation.

If the following hypotheses are made:

– impurities are only soluble in the liquid phase;

– the impurity content is low enough to consider the liquid phase as an ideal one;

in has been shown (4) that a relation:

$$T=T_o-N/KF \tag{1}$$

with

$$K=\Delta_{\rm fus}H_{\rm m}/RT_o^2 \tag{2}$$

exists between T and $1/F$
F being the product fraction melted at temperature T; R, the gas constant.

The triple point temperature (T_o) of the pure substance can be determined by extrapolation to $1/F=0$. The total impurity content (N) can be calculated from the slope (N/K) if the molar enthalpy of melting of the pure substance ($\Delta_{\rm fus}H_{\rm m}$) is previously determined from the peak area. For the heating rate used (0.2 deg·min^{-1}), the curve $T=f(1/F)$ is linear in a range of about $3<1/F<8$.

Table 1 Temperature calibration of the differential thermal analyser

Substance	Purity/mol%	Triple point temperature*/K		α
		our value	literature	
Naphthalene	99.978±0.001	353.73±0.02	353.39±0.02 [2b]	0.9990
Fluorene	99.958±0.001	387.85±0.01	387.94[8]	1.0002
Benzoic acid	99.993±0.001	396.18±0.02	395.52±0.02 [2b]	0.9983
Diphenylacetic acid	99.950±0.002	421.04±0.04	420.44±0.02 [2b]	0.9986
Anisic acid	99.813±0.002	456.70±0.02	456.70±0.02 [1]	0.9988
Carbazole	99.911±0.003	518.33±0.01	518.49±0.02 [1]	1.0003
Anthraquinone	99.790±0.020	557.53±0.02	557.74±0.01 [1]	1.0004

*Related to IPTS-68

Table 2 Energy calibration of the differential thermal analyser

Substance	M^*/g·mol^{-1}	m/g	$\Delta_{fus}H_m$ /kJ·mol^{-1}	$\frac{RT_o^2/\Delta_{fus}H_m}{K}$	S /μV s	Q /J	$k\cdot10^4 = Q/S$ / J μV^{-1}s^{-1}
Naphthalene	128.1735	0.090610	19.060±0.016 [2b, 9]	54.51	67880±461	13.474132	1.985±0.002
Fluorene	166.2224	0.103079	19.578±0.003 [8]	63.96	55271±478	12.140847	2.197±0.019
Banzoic acid	122.1234	0.108568	18.063±0.021 [2b, 9]	72.06	71617±611	16.058051	2.242±0.019
DAA**	212.2481	0.095888	31.271±0.018 [2b, 9]	47.03	59000±276	14.127399	2.395±0.011

* The molar masses are calculated using standard atomic masses 1987 [10]

**Diphenylacetic acid

Table 3 Triple point temperature for the proposed reference materials

Substance	$T_{\text{triple point}}$ (exp.)* /K	$T_{\text{triple point or fusion}}$ (literature) /K
Phenanthrene	373.81±0.01	371.35±0.5 [12] 371.97 [13] 372.39 [8]**
Benzanilide	436.49±0.01	436.72 [13]
Triphenylene	471.06±0.03	473.6±0.4 [12] 471.01 [15]
2-Chloroanthraquinone	483.02±0.03	482.58 [13] 482.18±0.01 [14] 482.75 [17] 482.73 [11]** 483.55 [2a]
Hexachlorobenzene	501.87±0.01	505 [19]
4-iodobenzoic acid	544.74±0.10	
Perylene	551.29±0.01	553.9 ±0.3 [12] 550.95 [16]

*Related to IPTS-68

Note: Underlined values correspond to triple point temperatures. Only values with two stars relate to IPTS-68

Table 4 Enthalpy of fusion for the proposed reference materials

Substance	M^* /g·mol^{-1}	purity /mol%	λ/K	$\Delta_{\text{fus}}H_{\text{m}}$ /kJ·mol^{-1}	
				our value	literature
Phenanthrene	178.2334	99.74 ±0.01	73.95	15.72±0.10	16.74±0.29 [12] 16.46±0.02 [8]
Benzanilide	197.2365	99.933±0.002	53.53	29.61±0.12	
Anisic acid	152.1497	99.813±0.002	61.10	28.33±0.14	29.72±0.23 [18] 28.43 [11]
Triphenylene	228.2933	99.85 ±0.01	76.34	24.19±0.09	25.10±0.46 [12] 24.74±0.01 [15]
2-chloroanthraquinone	242.6611	99.895±0.007	49.82	38.96±0.52	35.63±0.29 [18] 34.67 [11]
Hexachlorobenzene	284.7822	99.969±0.002	83.97	24.96±0.40	23.85 [19]
Carbazole	167.2102	99.911±0.003	82.61	27.08±0.48	26.41 [11]
4-iodobenzoic acid	248.0200	99.80 ±0.04	72.74	33.94±0.83	
Perylene	252.3153	99.889±0.002	77.61	32.58±0.14	31.76±0.59 [12] 31.87 [16]
Anthraquinone	208.2163	99.79 ±0.02	75.54	34.26±0.55	33.97 [11]

*Molar masses are calculated using standard atomic masses 1987 [10].

Note: Underlined values are obtained from adiabatic calorimetric measurements; other values from DTA or DSC measurements.

Temperature calibration

The f.e.m. were converted to temperatures using the NBS-thermocouple reference table [6].

The apparatus was calibrated with standard reference substances. A temperature calibration coefficient $\alpha = T_o(\text{literature})/T_o(\text{experimental})$ was determined (Table 1).

Energy calibration

An energy calibration coefficient (k) is determined with standard reference substances using the relation:

$$k = (\Delta_{\text{fus}} H_{\text{m}} / S)\ (m/M) \tag{3}$$

where S is the area under the peak of melting; m, the mass and M, the molar mass of the substance (Table 2).

The calibration coefficient varies with temperature:

$$(k / \text{J}\mu\text{V}^{-1}\text{s}^{-1}) = 1.392 \cdot 10^{-4} + 1.362 \cdot 10^{-12} (T/K)^3 \tag{4}$$

An analogous linear relation was obtained by Heide [7].

The substances proposed as reference materials for the calibration of differential thermal analysers and scanning calorimeters are listed in Tables 3 and 4. They well complete the few reference materials indicated by the international organizations in the range 300–600 K. They also satisfy the following criteria:

- their molar purity is at least 99.8 mol.%;
- they are thermally stable up to and above their melting temperature;
- absence of polymorphism particularly near their melting zone;
- they possess a suitable cryoscopic constant:

$$\lambda = RT_o^2 / \Delta_{\text{fus}} H_{\text{m}} < 100\ \text{K}$$

- they have a low vapour pressure:

P (298.15K)<14 Pa (about0.1 Torr);P (T_{fus} K)≤ 1.6 kPa (about 12 Torr).

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Zusammenfassung — Als neue Referenzsubstanzen für Temperatur- und Energiekalibrierung von DTA- und DSC-Geräten wurden im Temperaturbereich 300-600 K einige organische Verbindungen, wie z.B. Phenanthren, Benzanilid, Anissäure, Triphenylen, 2-Chloranthrachinon, Hexachlorbenzol, Karbazol, 4-Jodbenzoesäure, Perylen und Anthrachinon untersucht.