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REFERENCE MATERIALS FOR ENERGY AND TEMPERATURE CALIBRATIONS OF DTA AND DSC INSTRUMENTATION IN THE RANGE 100–300 K

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Abstract

Fourteen organic compounds, 1-pentene, 2-methylbutane, 2-methyl-1,3-butadiene (isoprene), *n*-pentane, 2-chloropropane, ethyl alcohol, 2,2,4-trimethylpentane, *n*-hexane, *n*-heptane, 1,3-difluorobenzene, 1,2-dichloroethane, hexafluorobenzene, cyclohexane and diphenyl ether, as new reference materials for energy and temperature calibrations of differential thermal analysers (DTA) and differential scanning calorimeters (DSC) in the temperature range 100–300 K, were investigated. The purities, triple point and transition temperatures, fusion and transition enthalpies of these compounds were measured using a low-temperature DTA apparatus developed by the CTM of the CNRS in Marseille. The results obtained were compared with those produced by adiabatic precision calorimetry. Our data are in good agreement with literature values. Enthalpies of fusion and transition, triple point and transition temperatures are reproduced within ±1% and ±0.1 K, respectively.

Keywords: DSC, DTA, low-temperature, reference materials

Introduction

Differential thermal analysis is one of the useful techniques for investigating the thermal behaviour of materials and for determination of sample purity. Improvements in instrumentation and productivity have increased the popularity of thermal analysers in both basic and applied research. In order to make good use of the quantitative aspect of this technique to obtain reliable results with good reproducibility and accuracy, it is necessary to carefully calibrate the apparatuses using standard reference materials.

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In the temperature interval 100–300 K and especially below 200 K, reference materials proposed by ICTA, IUPAC and ICWM [1–3] for energy and temperature calibrations of DTA and DSC apparatuses are scarce. For this reason and to satisfy the needs of the scientific community, we have carefully studied a series of organic compounds by using the low temperature differential thermal analyser developed by the CTM of the CNRS in Marseille [4].

Experimental

Substances

The majority of the substances investigated in this work are alkanes and alkenes. These compounds include: 1-pentene (Fluka, purity >99%), 2-methylbutane (Fluka, purity >99.7%), 2-methyl-1,3-butadiene (isoprene) (Fluka, purity >99.5%), *n*-pentane (Fluka, purity >99.8%), 2-chloropropane (Fluka, purity >99.5%), ethyl alcohol (Fluka, purity >99.8%), 2,2,4-trimethylpentane (Fluka, purity >99.7%), *n*-hexane (Fluka, purity >99.7%), *n*-heptane (Aldrich, Gold Label, purity >99%), 1,3-difluorobenzene (Fluka, purity >99%), 1,2-dichloroethane (Aldrich, purity 99.8%), hexafluorobenzene (Aldrich, purity 99%), cyclohexane (Aldrich, Gold Label, purity >99.9%), diphenyl ether (Aldrich, Gold Label, purity >99%). All the substances listed above were purchased at the highest purity available and used directly for the DTA measurements without further purification with the exception of ethyl alcohol. Commercial ethyl alcohol was purified further by fractional distillation using a spinning-band column under vacuum (70 Torr [1 Torr = 133.322 Pa], 303 K). Traces of water remaining in the distilled ethanol were finally removed by using molecular sieves 5A.

Apparatus

The low-temperature differential thermal analyser used in this work has previously been described in detail in [4]. The main features and some recent improvements are briefly described in this paper. The apparatus, which is housed in a metallic Dewar vessel, consists of a cylindrical aluminium alloy (Al-96%, Cu-4%) furnace with two wells, each containing a chromel-alumel thermocouple for temperature and temperature difference measurements. Heating of the furnace was achieved through a resistance band wound around the cylinder. An iridium resistance thermometer placed between the cylinder and the heating-band is used for temperature regulation of the furnace. The furnace is mounted on a massive aluminium pedestal above a layer of liquid nitrogen. The aluminium pedestal serves as the major conduit for heat transfer from liquid nitrogen to the furnace.

The liquid nitrogen in the DTA Dewar vessel was manually maintained at a constant level during the experimental runs. Liquid levels were monitored by means of a float to which a thin metal rod was attached. The rod was maintained in a vertical position and extended outside the apparatus. Liquid nitrogen was transferred from an external metallic Dewar vessel by using the pressure from a compressed nitrogen gas cylinder. The height of the rod could be kept constant (±5 mm) by controlling the pressure. A valve at the external Dewar flask allowed for bleed of nitrogen gas when liquid was not being transferred.

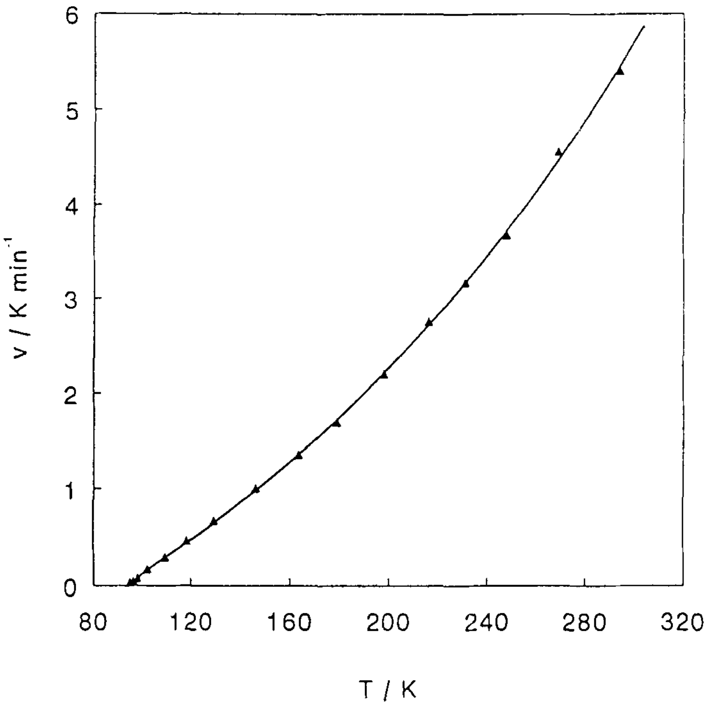

Fig. 1 Intrinsic cooling rate of the low-temperature differential thermal analyser

Our DTA apparatus can also be utilized in the cooling mode. The intrinsic cooling rate of the calorimeter is affected by the vertical distance between the thermocouples in the furnace and the liquid nitrogen level. The maximum cooling rate of our apparatus, as estimated from Fig. 1, is approximately 5 deg·min^{-1} when the temperature of the furnace is at 300 K and a level of liquid nitrogen is maintained to achieve a minimum temperature of 90 K. As shown in the cooling curve, approximately 6 hours were needed to reach the lowest temperature from the ambient (Fig. 2).

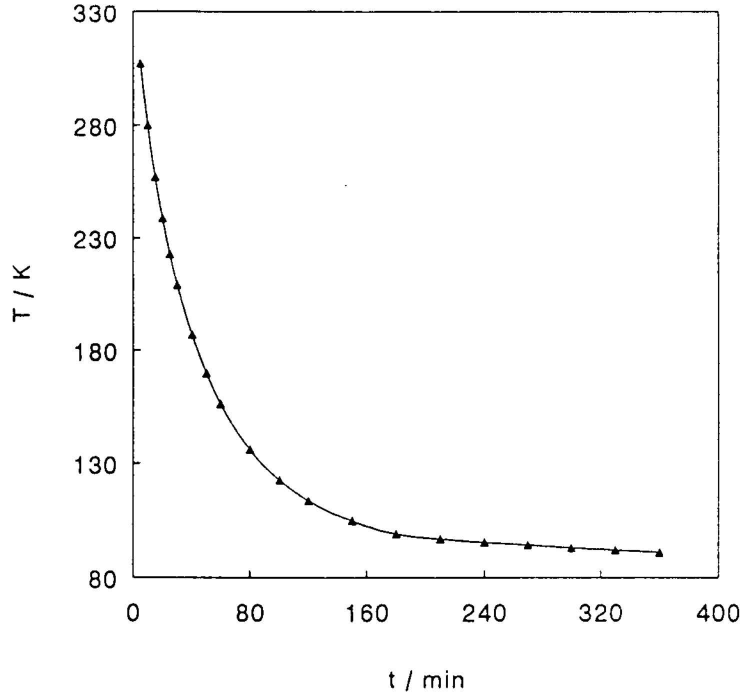

Fig. 2 Cooling curve of the low-temperature differential thermal analyser

The temperature of the sample, as mentioned in [4], was measured by using a Keithley 196 digital multimeter at a sensitivity range of 300 mV and a resolution of ±0.1 μV. The sensitivities of the thermocouple used are 40 $\mu V\ K^{-1}$ at 300 K and 18 $\mu V\ K^{-1}$ at 100 K, respectively. The temperature of the sample, correspondingly, could be measured to 0.0025 K at 300 K and 0.0056 K at 100 K, respectively, by the digital multimeter. The e.m.f. difference between the sample and reference (an identical ampoule loaded with α-alumina) was measured and amplified by a DC-microvoltmeter (AOIP type EVA, see Fig. 3) using a sensitivity range of 100 μV. The amplified signal was then digitalized by a Keithley 175 multimeter and both temperature and temperature differences were continuously monitored and stored on a computer through a IEEE488 interface. For experiments performed at smaller cooling rates than is intrinsic to the thermal analyser, heat input to the apparatus was controlled by a progammable device of the furnace temperature. Data processing was also performed automatically and enthalpies of fusion (or transition), purity of the substance and the triple point (or transition) temperature were calculated.

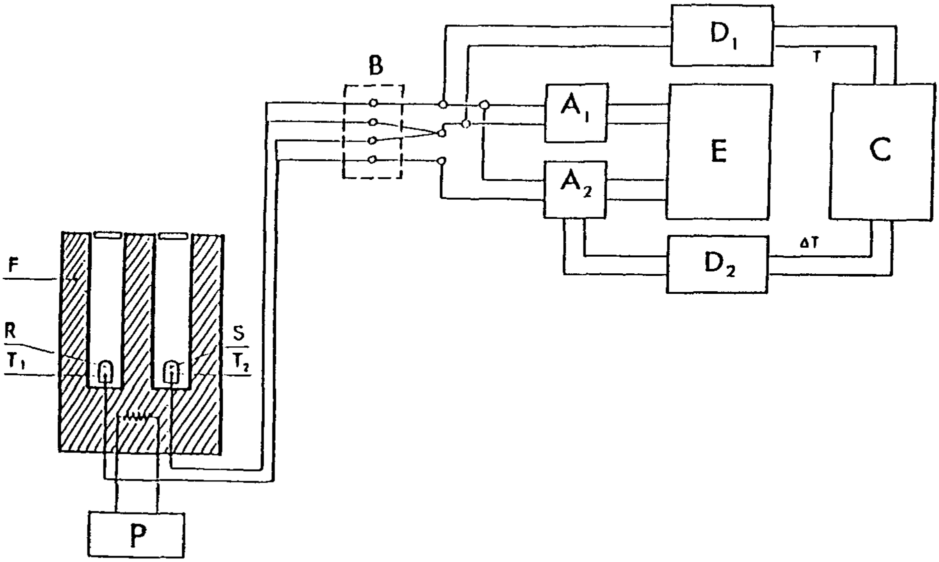

Fig. 3 Schematic diagram of the DTA measurements.
A_1 and A_2: amplifiers; B: reference junctions; C: computer; D_1 and D_2: digital voltmeters (Keithley 196 and 175 respectively); E: recorder; F: furnace; P: programmable control device of the furnace temperature; R: reference (α-alumina); S: sample; T_1 and T_2: thermocouples (chromel-alumel)

The thermocouple signals corresponding to the temperature and temperature difference were also sent to a recorder (SEFRAM type Gépérac). The block diagram of temperature measurements and record system is shown in Fig. 3.

Mode of operation

About 0.1 ml liquid sample of the investigated substance was carefully injected by a long needle syringe into the bulb of the pyrex glass ampoule [4] and connected to a vacuum line (10^{-2} Torr). Air was removed by pumping at ambient temperature until bubbling ceased. The sample was frozen in liquid nitrogen and quickly sealed under evacuating conditions by means of a miniature welding torch (gas and oxygen flame welder). So, the pressure inside the ampoule is approximately equal to the saturated vapour pressure of the substance. The mass of the sample in the ampoule was determined by differential weighings of the empty ampoule and the sealed ampoule plus sample together with the remaining glass neck of the ampoule. Control experiments using empty ampoules demonstrated that determination of the mass of both sealed and unsealed ampoules was reproducible using this technique to within ±5 μg. All weighings were performed on a Mettler M5 microbalance sensitive to 1 μg with an accuracy of ±2 μg.

The ampoule filled with sample was dropped into the sample well and cooled down to a temperature approximately 10 K below the triple point temperature of the substance. It took about 30 minutes to reach thermal equilibrium. The temperature was then increased at a rate sufficiently small to maintain thermal equilibrium, 0.2 deg·min^{-1}. In the sensitivity range used (100 μV), only slight base line deviations were observed before and after melting. This enabled us to accurately evaluate the area of the peak corresponding to the fusion or transition observed, the triple point or transition temperature and the purity of the substance under investigation.

In order to prevent the condensation of water on the walls of the sample and reference wells, we designed a moisture shielding system in which dry nitrogen gas was continuously introduced into the sample and reference compartments by means of tubes inserted into each well The compartments were flushed with nitrogen until the furnace was cooled down to the lowest temperature required by the experiment. Condensation of water in the sample and reference compartments seriously affected the accuracy and reproducibility of the peak area.

Results and discussion

The uncertainties associated with the experimental results in this work are reported as standard deviations of the mean, usually, of ten experimental runs. The temperatures reported in this work are in terms of the ITS-90 [5]. The molar masses of the substances are calculated in terms of the standard atomic masses of the elements of 1989 [6] and the value of the gas constant, R = 8.314510 J·K^{-1}·mol^{-1}, adopted by IUPAC [7], is used.

Purity of the investigated substances

The determination of purity of a solid by thermal analysis is based on measurements of the melting point depression of a substance in the presence of impurities. A plot of melting temperature against the reciprocal of the fraction of melted usually results in a straight line. The concentration of the impurity in the substance can be calculated from the slope of this line.

As stated in detail in [8], the Clausius-Clapeyron equation and Raoult's law are used for the determination of purity and the following is assumed: impurities are only soluble in the liquid phase (i.e. the impurity does not form a solid solution with the solvent) and the impurity content is low enough to consider the liquid phase as an ideal solution. Under these conditions, it was shown [8] that the following relationship exists between the melting temperature , T, and the fraction melted, F:

$$T = T_o - (N/K)1/F \tag{1}$$

where

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

R is gas constant, T_o is the triple point temperature of the pure substance and $\Delta_{\mathrm{fus}} H_{\mathrm{m}}$ is its molar enthalpy of fusion.

The triple point temperature of the pure substance can be determined by extrapolation to $1/F = 0$. The impurity content (N) can be calculated from the slope (N/K) by using the molar enthalpy of fusion ($\Delta_{\mathrm{fus}} H_{\mathrm{m}}$) previously calculated 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 $3<1/F<8$.

Purities of the investigated samples are summarized in Tables 1 to 4. The impurity content is, in most cases, lower than 0.2 mol%. As previously noted [8], the accuracy of the method depends to a certain extent on the purity of the samples studied: the higher the purity is, the smaller the uncertainty associated with the content of the impurity is.

Temperature and energy calibrations

A differential thermal analyser is a dynamic measurement apparatus, and it is generally used to make relative rather than absolute measurements. The instrument should be calibrated as near as possible to the experimental conditions used to measure the samples, especially with regards to the temperature range studied. Very few standards are available in the temperature range 100–300 K. We have selected only three substances: diphenyl ether, *n*-heptane and 2-methylbutane as reference materials to perform the temperature and energy calibrations of our low-temperature differential thermal analyser. The thermal data of these three substances, reported in the literature and including triple point temperature and enthalpy of fusion, were determined by adiabatic precision calorimetry and hence are assumed known to a high level of accuracy. Diphenyl ether is a standard reference material recommended by IUPAC for the determination of enthalpies of fusion [2b, 9]. *n*-Heptane is a reference substance recommended for low temperature heat capacity measurements [10]; the high accuracy data of enthalpy of fusion of this compound were reported by Huffman *et al.* [11], Douglas *et al.* [12] and Van Miltenburg [13]. The thermal behaviour of 2-methylbutane was investigated in detail earlier by Guthrie and Huffman

[14] and later by Sugisaki *et al.* [15]; the enthalpy of fusion and the melting point temperature data obtained by them are in fair agreement with each other.

In Table 1, literature values of the triple point temperature ($T_{\mathrm{o\ lit}}$) of diphenyl ether, *n*-heptane and 2-methylbutane are summarized together with our values ($T_{\mathrm{o\ exp}}$) determined with the aid of Eq. (1). A temperature calibration coefficient, $\alpha = T_{\mathrm{o\ lit}}/T_{\mathrm{o\ exp}}$, is also listed in Table 1. The lack of other reference substances for low-temperature calibration prompted us to use values of α obtained both by interpolation and extrapolation of the values listed in Table 1 for the temperature range 100–300 K.

Energy calibration of our apparatus was also made with the same three substances (Table 2). An energy calibration coefficient (k) was determined using the following relationship:

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

where S is the area under the fusion peak, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ is the molar enthalpy of fusion of the sample under its saturated vapour pressure, and m and M are the mass and the molar mass of the substance, respectively.

The energy calibration coefficient (k) of our calorimeter depends in a complex manner on the heat transfer mechanisms. It has been found that for the temperature range 100–300 K, the energy calibration coefficient is related to a temperature by the following relation:

$$k / \mathrm{J\mu V^{-1}s^{-1}} = 1.479\cdot10^{-4} + 6.843\cdot10^{-8}(T / K) + 2.163\cdot10^{-10}(T / K)^2 \qquad (4)$$

The molar enthalpy of fusion of an investigated substance is then equal to:

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = S\cdot k\cdot M / m \qquad (5)$$

Triple point and transition temperatures, enthalpies of fusion and transition of the eleven investigated substances

The following eleven organic compounds are proposed as low-temperature reference materials: 1-pentene, 2-methyl-1,3-butadiene (isoprene), *n*-pentane, 2-chloropropane, ethyl alcohol, 2,2,4-trimethylpentane (isooctane), *n*-hexane, 1,3-difluorobenzene, 1,2-dichloroethane, hexafluorobenzene and cyclohexane. Triple point and transition temperatures, enthalpies of fusion and transition and purities of these substances are given in Tables 3 and 4, together with some values taken from literature [16–33].

From Table 3, it can be seen that for the triple point temperature, our values coincide within about ±0.1 K with literature data for all the substances studied.

Table 1 Temperature calibration of our DTA apparatus

Substance	Formula	Purity/ mol%	λ/ K	Triple point temperature (T_o)		$\alpha = T_{lit} / T_{exp}$
				T_{exp} /K	T_{lit} /K	
2–Methylbutane	C_5H_{12}	99.920±0.004	20.79	117.71±0.03	113.36±0.05 [15]	0.96304
n–Heptane	C_7H_{16}	99.896±0.003	19.74	184.30±0.02	182.55±0.05 [11]	0.99050
Diphenyl ether	$C_{12}H_{10}O$	99.963±0.006	43.47	299.71±0.01	300.02 [2b, 9]	1.0010

Table 2 Energy calibration of our DTA apparatus

Substance	Formula	Purity/ mol%	$\bar{M}$/ g·mol^{-1}	m/ g	$T_{o(exp)}$/ K	$\Delta_{fus}H_m$ / J·mol^{-1}	Q/ J	S/ μVs	$k10^{-4}$ / J·μV^{-1}·s^{-1}
2-Methylbutane	C_5H_{12}	99.920±0.004	72.1503	0.057740	117.71±0.03	5140±2 [15]* 5155±4 [14]	4.1134	25941±153	1.5857±0.0058
n-Heptane	C_7H_{16}	99.896±0.003	100.2040	0.043570	184.30±0.02	14037±8 [11]* 14022±9 [12]	6.1035	36783±166	1.6593±0.0045
Diphenyl ether	$C_{12}H_{10}O$	99.963±0.006	170.2109	0.110395	299.71±0.01	14061±25[13] 17216±17[2b,9]*	11.1659	59439±278	1.8786±0.0047

* adopted value for the determination of the calibration coefficient of our apparatus.

Table 3 Triple point temperature of the studied substances

Substance	Formula	Purity/ mol%	T_o/K this work	T/K* literature		
1–Pentene	C_5H_{10}	99.639±0.009	108.00±0.02	107.94 [16, 19]	108.016 [20]	
2–Methyl–1,3–butadiene	C_5H_8	99.759±0.004	127.23±0.01	127.27±0.05 [21]	127.20 [16, 22]	
n–Pentane	C_5H_{12}	99.858±0.003	143.46±0.01	143.43 [16]	143.46 [17, 18]	143.47±0.05 [23, 24]
2–Chloropropane	C_3H_7Cl	99.857±0.002	155.81±0.01	156.2 [16]	155.95 [17, 18]	
Ethyl alcohol	C_2H_6O	99.834±0.004	158.61±0.01	158.5 [16, 25]	158.65 [17, 18]	
2,2,4–Trimethylpentane	C_8H_{18}	99.875±0.004	165.80±0.01	165.77 [16]	165.85 [17, 18]	165.79 [27]
n–Hexane	C_6H_{14}	99.913±0.003	177.83±0.01	177.80 [16]	177.84±0.05 [26]	
1,3–Difluorobenzene	$C_6H_4F_2$	99.888±0.004	204.08±0.01	204.06 [2b, 28]		
			187.82±0.08**	186.80 [2b, 28]	191.3±0.2 [4]	
1,2–Dichloroethane	$C_2H_4Cl_2$	99.891±0.006	237.26±0.01	237.2±0.1 [29]	237.65 [17, 18]	237.6±0.3 [4]
Hexafluorobenzene	C_6F_6	99.861±0.005	278.20±0.01	278.30 [2b, 30]		
Cyclohexane	C_6H_{12}	99.979±0.003	279.80±0.02	279.82±0.05 [31]	279.83±0.01 [32]	279.7±0.1 [4]
			186.24±0.01**	186.10±0.05 [31]	186.9±0.1 [4]	187.1±3.5 [33]

* triple point or melting point temperature

** solid–solid phase transition temperature.

Table 4 Molar enthalpy of fusion $\Delta_{fus}H_m$ of the studied substances

Substance	Formula	Purity/ mol%	M / g·mol^{-1}	m / g	λ / K	$\Delta_{fus}H_m$ /J·mol^{-1} this work	literature	deviation /%
1-Pentene	C_5H_{10}	99.639±0.009	70.1344	0.072890	16.77	5783±27	5807±8 [16, 19]	−0.4
							5813 [17]	−0.5
							5810 [18]	−0.4
2-Methyl-1,3-butadiene	C_5H_8	99.759±0.004	68.1185	0.083963	27.67	4864±25	4925± 3 [21]	−1.2
							4830±15 [22]	0.7
n-Pentane	C_5H_{12}	99.858±0.003	72.1503	0.059550	20.34	8413±7	8393 [16]	0.2
							8420 [17, 18]	−0.1
							8415±4 [23]	−0.02
							8401±2 [24]	0.1
2-Chloropropane	C_3H_7Cl	99.857±0.002	78.5315	0.076485	27.33	7386±21	7387 [17]	−0.01
							7390 [18]	−0.05
Ethyl alcohol	C_2H_6O	99.834±0.004	46.0690	0.066210	41.18	5080±48	5021 [16, 17, 25]	1.2
2,2,4-Trimethylpentane	C_8H_{18}	99.875±0.004	114.2309	0.043570	25.16	9084±48	9213 [16]	−1.4
							9042 [17, 18]	0.5
							9211±8 [27]	−1.3

Table 4 Continued

Substance	Formula	Purity/ mol%	M/ g·mol^{-1}	m/ g	λ / K	$\Delta_{fus}H_m$ /J·mol^{-1} this work	literature	deviation /%
n–Hexane	C_6H_{14}	99.913±0.003	86.1772	0.059477	20.18	13030±22	13029 [16]	0.01
							13078 [17, 18]	–0.4
							13080±9 [26]	–0.4
1,3–Difluorobenzene	$C_6H_4F_2$	99.888±0.004	114.0946	0.109665	40.28	8597±21	8581±2 [2b, 28]	0.2
						829±2*	827.1 [2b, 28]	0.2
1,2–Dichloroethane	$C_2H_4Cl_2$	99.891±0.006	98.9592	0.144710	53.54	8742±30	8837±9 [16, 29]	–1.0
							8833 [17]	–1.0
Hexafluorobenzene	C_6F_6	99.861±0.005	186.0564	0.159925	55.44	11607±35	11590±13 [2b, 30]	0.1
							11585 [28]	0.2
Cyclohexane	C_6H_{12}	99.979±0.003	84.1613	0.079995	243.2	2677±25	2677±2 [31]	0
							2630 [17, 18]	1.7
							2732±2 [32]	–2.0
						6792±8*	6740±2 [31]	0.8

* enthapy of solid–solid phase transition.

Similarly for the solid-solid phase transition temperature of cyclohexane, our corrected peak onset temperature (186.25±0.01) K is nearly identical with the value reported by Ruehrwein and Huffman (186.10±0.05) K [31], and within the uncertainty limits of the extrapolated onset temperature (187.1±3.5) K given by Garn and Menis [33]. For 1,3-difluorobenzene, the value of our transition temperature (187.82±0.08) K is slightly higher than the value 186.80 K observed by Messerly and Finke [2b, 28]. Concerning the transition in 1,3-difluorobenzene, two crystalline forms were observed by Messerly and Finke [28]: crystals II stable from 11 K to the transition temperature and crystals I stable from this temperature to its triple point. We have further observed that the transition from crystal I to crystal II is initiated by a cooling rate of about 2 deg·min^{-1}; the sample invariably supercooled to some extent when cooled faster than this rate. Therefore, it is significant to carefully control the cooling rate in order to realize the transition from crystal I to II without supercooling in 1,3-difluorobenzene. Knauth and Sabbah also observed a higher transition temperature for 1,3-difluorobenzene (191.3±0.2) K [4].

The enthalpies of fusion (Table 4) of all the substances studied are in agreement within ±1% with literature values obtained by adiabatic precision calorimetry.

The enthalpy of transition of 1,3-difluorobenzene (829±2) J·mol^{-1} is in excellent agreement with the value 827.1 J·mol^{-1} reported by Messerly and Finke [28].

For cyclohexane, our values of the enthalpy of fusion (2677±25) J·mol^{-1} and transition (6792±8) J·mol^{-1} are identical with the values (2677±2) J·mol^{-1} and (6740±2) J·mol^{-1}, respectively, found by Ruehrwein and Huffman [31].

Among the substances studied in present work, 1,3-difluorobenzene and hexafluorobenzene are the standard reference materials for enthalpy measurements recommended by IUPAC [2b]. The enthalpies of fusion and transition of these two substances obtained in this work are in very good agreement with the recommended values. This confirms the reliability of our low-temperature DTA apparatus.

Conclusion

The fourteen substances proposed as reference materials for energy and temperature calibrations of DTA and DSC complement the few reference materials previously recommended as standards in the low-temperature range 100–300 K by IUPAC and ICTA. These substances satisfy the following criteria:

–they are available in high purity, at least 99.8 mol%;

–they are thermally stable up to and above their melting temperature;

–they are chemically inert;

–most of the compounds do not exhibit polymorphism particularly near the melting point;

–except for cyclohexane, they possess a suitable cryoscopic constant:

$$\lambda = RT_o^2 \,/\, \Delta_{\mathrm{fus}}H_{\mathrm{m}} < 100\ \mathrm{K} \tag{6}$$

Therefore, it can be concluded that the majority of the substances studied in this work would be acceptable as reference materials for energy and temperature calibrations of DTA and DSC apparatuses between 100–300 K.

* * *

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Zusammenfassung — Als neue Bezugssubstanzen für Energie- und Temperaturkalibrierung von DTA-Geräten und DSC-Kalorimetern im Temperaturbereich 100–300 K wurden vierzehn Verbindungen untersucht: 1-Penten, 2-Methylbutan, 2-Methyl-1,3-butadien (Isopropen), *n*-Pentan, 2-Chlorpropan, Ethylalkohol, 2,2,4-Trimethylpentan, *n*-Hexan, *n*-Heptan, 1,3-Difluorbenzol, 1,2-Dichlorethan, Hexafluorbenzol, Cyclohexan und Diphenylether. Mittels einer von CTM der CNRS in Marseille entwickelten Tieftemperatur DTA-Apparatur wurde die Reinheit, der Tripelpunkt und die Umwandlungstemperaturen sowie die Schmelz- und Umwandlungsenthalpien dieser Verbindungen gemessen. Die erhaltenen Ergebnisse wurden mit denen aus adiabatischer Präzisionskalorimetrie verglichen. Unsere Angaben stehen in guter Übereinstimmung mit den Literaturangaben. Schmelz- und Umwandlungsenthalpien, Tripelpunkt und Umwandlungstemperaturen wurden innerhalb 1% und 0.1K reproduziert.