DEVELOPMENT AND APPLICATIONS OF A LOW-TEMPERATURE DIFFERENTIAL THERMAL ANALYZER (77 < T, K < 330)

P. Knauth and *R. Sabbah**

CENTRE DE THERMODYNAMIQUE ET DE MICROCALORIMÉTRIE DU C. N. R. S., 26, RUE DU 141E R. I. A., F-13003 MARSEILLE, FRANCE

A differential thermal analyzer for the temperature range 77 to 330 K is described and some applications, determination of the impurity content, the triple point temperature and the enthalpy of fusion of a substance, are given. The temperature and energy calibration of the apparatus are done with diphenyloxide, hexafluorobenzene and 1,3-difluorobenzene. The energy calibration coefficient can be expressed as a linear relation of T^3. *n*-Heptane, cyclohexane and 1,2-dichloroethane are investigated.

Differential thermal analysis is a powerful tool for the determination of the purity of substances and for the investigation of their phase transitions. The total impurity content of a substance sample can be readily determined from its melting curve. The temperatures and energies of phase transitions may be determined with good accuracy, if the apparatus is previously carefully calibrated, using standard reference substances.

In the following, a new differential thermal analyzer for the low-temperature region is described, which was built and tested in our laboratory, completing the previously described mean-temperature version (300-600 K [1]). The apparatus has been conceived to use glass ampoules, which do not react with the investigated substances and can be sealed under vacuum. No contamination or reaction with air of the substance under investigation can thus occur, and work can be carried out under the saturated vapour pressure of the substance.

---

*To whom reprint requests should be addressed.

An important requirement has been the possibility to work on small quantities of substance ($m < 0.1$ g). Furthermore, the form of the glass ampoules permits to avoid thermal disturbances and to allow a more accurate measurement of the temperature.

Experimental

Apparatus

The differential thermal analyzer (Fig. 1) was installed inside a metallic Dewar vessel (D) of 90 l volume (purchased from "Cryo diffusion"). The apparatus consists of a cylindrical furnace made of an aluminium alloy (AU4G) of 65 mm diameter and 205 mm height, with two wells (K) of 10 mm diameter and 120 mm depth, each containing a chromel-alumel thermocouple ("Thermocoax" type 2ABI15). The other extremity of the thermocouple is held at (292.5 + 0.01 K) during an experiment. A heating resistance band (N) ("Silisol", 64 Ω at 298.15 K) is wound round the AU4G cylinder. The furnace stands on a massive aluminum pedestal (E), which is, at its lower part, immersed in the liquid nitrogen reserve (F). An iridium resistance thermometer (M) (100 Ω at 273.15 K) is placed between the AU4G cylinder and the resistance band; its signal is used for temperature regulation. An aluminium shield (O) prevents condensation of water on the resistance band. The temperature (77-330 K) and the rate of temperature variation (0.1-2.5 deg/min in the heating mode) are selected with a control device built in our laboratory. Our differential thermal analyzer can also be used in the cooling mode; the intrinsic cooling rate of the apparatus fixes the upper limit of the rate of temperature decrease.

The temperature of the sample is determined from the thermo-e.m.f. using a Keithley 196 digital multimeter; the difference between the thermo-e.m.f. of the sample and the reference (normally an identical ampoule filled with α-alumina) is measured with an analogic voltmeter (AOIP type EVA, sensitivity ranges: 100 or 300 μV). The signal is then digitalized by a Keithley 175 multimeter. Data acquisition and treatment are performed with a personal computer. Temperature and temperature difference curves can also be registered with an analogic recorder (SEFRAM type Gépérac).
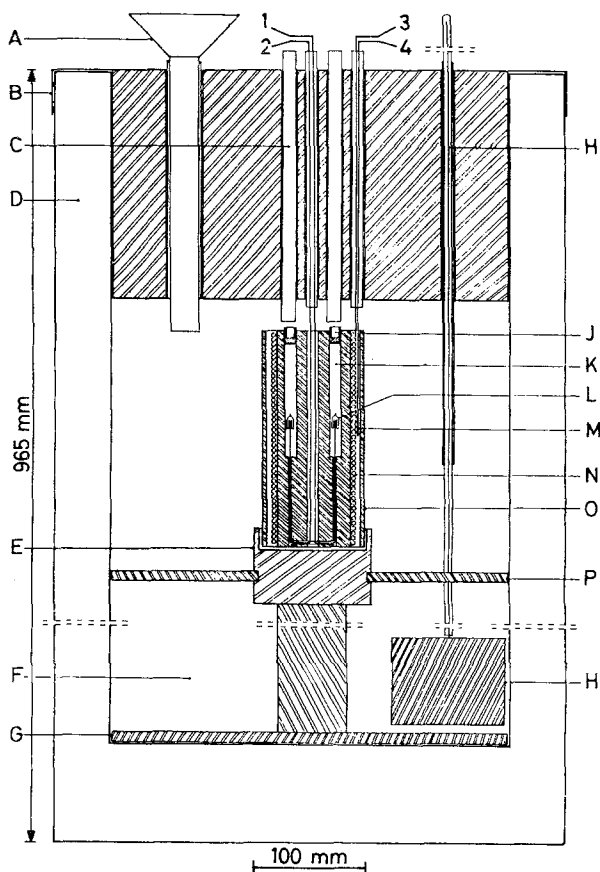
Fig. 1 Low-temperature differential thermal analyzer. A: funnel for filling with liquid nitrogen; B: cover; C: opening; D: metallic Dewar vessel; E: aluminium pedestal; F: liquid nitrogen reserve; G: metal base; H: float for observing liquid nitrogen level from outside; J: metalic plug; K: well; L: glass ampoule; M: iridium resistance thermometer; N: heating resistance band; O: aluminium shield; P: centering-screw

Substances

The following substances, which were proposed as standard reference materials [2], are used for temperature and energy calibration: 1,3-difluorobenzene (> 99 %, Fluka), hexafluorobenzene (99 %, aldrich), diphenyloxide (99 + %, Gold Label, Aldrich). Moreover, *n*-heptane (99 + %, Gold Label, Aldrich), cyclohexane (99 + %, Gold Label, Aldrich) and 1,2-dichloroethane (99.8 %, Aldrich), which were previously investigated [3-

7], are also studied. The commercial 1,2-dichloroethane has been further purified by fractional distillation over a rotating-band column.

Mode of operation

About 100 mg of substance are introduced into a pyrex glass ampoule shown on Fig. 2. After evacuating, the glass ampoule is quickly sealed, the pressure inside the ampoule consists then on saturated vapour pressure of the substance. The mass of substance is determined by difference weighings using a microbalance, sensitive to 1 μg (Mettler M5).
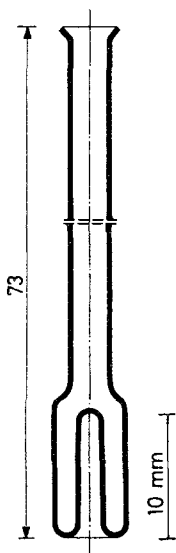
Fig. 2 Glass ampoule

The ampoule is brought to a temperature approximately 15 K below the triple point temperature; the stabilization of temperature takes approximately 20 minutes. The temperature is then increased with a rate of about 0.2 deg/min, which is sufficiently small to present, in the sensitivity range used, only slight base line deviations before and after the melting peak, and to allow to determine accurately triple point temperatures.

Results and discussion

The uncertainties associated, in the following, to the experimental results are in all cases standard deviations of the mean of six experiments. The temperatures are related to IPTS-68.

Purity of the investigated substances

As stated in detail in ref. [1], Clausius-Clapeyron's law applied to melting equilibrium and Raoult's law are used for purity determination and the following hypotheses are made: first, impurities are only soluble in the liquid phase, and, second, the impurity content is low enough to consider the liquid phase as an ideal one. Under these conditions, it has been shown [1] that a relation:

$$T = T_0 - (N_B / K) \ 1 / F \ \text{ with } \ K = \Delta_{fus} H / R T_0^2 \tag{1}$$

exists between the temperature T and $1/F$, F being the fraction of the product melted at temperature T. The triple point temperature T_0 of the pure substance may be determined by extrapolation to $1/F = 0$. The total impurity content N_B can be determined from the slope (N_B/K), if the molar enthalpy of melting $(\Delta_{fus} H)$ is previously calculated from the peak area (see Energy calibration). For the heating rate used, the curve $T = f(1/F)$ is linear in a range of about $3 < 1/F < 8$.

Table 1 Purity, experimental (T_{exp}) and recommended (T_{rec}) triple point temperature of 1,3-difluorobenzene (DFB), hexafluorobenzene (HFB), diphenyloxide (DPO) and temperature calibration coefficient α

| Substance | Purity, mol % | Triple point temperature | | α |
		T_{exp}, K	T_{rec}, K	
DFB	99.91±0.02	205.03±0.05	204.06 [2, 8]	0.9953
HFB	99.95±0.01	278.21±0.01	278.30 [2, 8]	1.0003
DPO	99.95±0.01	299.72±0.03	300.02 [2]	1.0010

Purities of the investigated samples are summarized in Tables 1 and 3. The impurity content is in all cases lower than 0.1 per cent. As previously noted [1], the reproducibility depends on the purity of the studied sample: the higher the purity is, the lower the uncertainty of the impurity content, because the melting peak is sharper.

Table 2 Energy calibration coefficients k

Substance	T_{rec}, K	$\Delta_{fus}H$, J mol^{-1}	$k \times 10^4$, J μV^{-1} s^{-1}
1,3-difluorobenzene	204.06	8581±2 [2, 8]	1.510±0.004
hexafluorobenzene	278.30	11590±13 [2, 12]	1.684±0.007
diphenyloxide	300.02	17216±17 [2, 13]	1.757±0.010

Temperature calibration

Generally, a differential thermal analyzer should be calibrated as near as possible to the experimental conditions, especially concerning heat transfer. For this reason, we have calibrated our apparatus with standard reference substances [2]. In Table 1, recommended triple point temperatures T_{rec} of 1,3-difluorobenzene, hexafluorobenzene and diphenyloxide are summarized, together with our experimental values T_{exp}. A temperature calibration coefficient $\alpha = T_{rec}/T_{exp}$ is calculated (Table 1). In lack of other internationally admitted reference substances for low temperatures, we adopted α values calculated by interpolation between two consecutive values.

The transition temperature of 1,3-difluorobenzene was not included, since our corrected peak onset temperature (191.3 ± 0.2) K is very different from the value of Messerly and Finke (186.77 K [8]) (*).

Energy calibration

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

$$k = \Delta_{fus}H / S \; (m / M) \qquad (2)$$

where S is the area under the peak of melting, $\Delta_{fus}H$ the molar enthalpy of fusion, m the mass and M the molar mass of the substance [9].

The calibration coefficient depends in a complex manner on the heat transfer mechanisms and varies with temperature. In Table 2, the energy calibration coefficients obtained with our standard reference substances are given. With these results and those obtained with the mean-temperature version for naphthalene, fluorene, benzoic acid and diphenylacetic acid [1, 10], the following relation can be written, for temperatures between 200 and 600 K:

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

An analogous linear relation of T^3 is obtained by Heide [11].

n-Heptane, cyclohexane and 1,2-dichloroethane

The enthalpies of fusion, triple point temperatures and purities of the investigated samples of n-heptane, cyclohexane and 1,2-dichloroethane are given in Table 3, together with some values taken from literature [3-7]. For n-heptane, our corrected triple point temperature is slightly higher than the value reported by McCullough and Messerly [3], whereas for 1,2-dichloroethane, our value is inside the error limits indicated for the extrapolated onset temperature of fusion by Garn and Menis [5]. The triple point temperature of cyclohexane is nearly identical to the temperature of fusion mentioned by Ruehrwein and Huffman [4]. Our peak onset temperature for the transition of cyclohexane (186.9 ± 0.)1 K is slightly different from the value of Ruehrwein and Hoffman [4] (186.10 ± 0.05) K (*) and within the error limits for the extrapolated onset temperature (187.1 ± 3.5) K (*) given by Garn and Menis [5].

The enthalpies of fusion (Table 3) and of phase transition (6.64 ± 0.04) kJ/mol of cyclohexane are in good agreement with the values reported by Ruehrwein and Huffman [4] mean of their two experiments for the enthalpy of phase transition: (6740 ± 2) J/mol, whereas for n-heptane and 1,2-dichloroethane, our enthalpies of fusion are slightly lower than the literature values (Table 3).

Conclusion

The low-temperature differential thermal analyzer presented in this work allows us to work now in a temperature range between 77 and 600 K and to investigate the purity of all substances melting without decomposition in this temperature range. Furthermore, temperatures and enthalpies of phase transitions can be determined using the temperature and energy calibration coefficients presented here, for the low-temperature and, in the near future, for the mean-temperature version [10]. The energy calibration coefficient can be described by one linear equation in T^3 over the whole temperature range.

Table 3 Purity, triple point temperature T_{tp} and molar enthalpy of fusion $\Delta_{fus}H$ of n-heptane, cyclohexane and 1,2-dichloroethane and comparison with literature values

Substance	Purity mol %	T_{tp}, K exp.	T_{tp} or T_{fus} K lit.	$\Delta_{fus}H_m$, kJ mol^{-1} exp.	$\Delta_{fus}H_m$, kJ mol^{-1} lit.
n-heptane	99.94±0.01	183.2±0.1	182.58 [3]	13.20±0.09	14037±9 [3]
cyclohexane	99.98±0.01	279.7±0.1	279.82±0.05 [4]* 278.0±1.1 [5, 6] *	2.70±0.02	2677±2 [4]
1,2-dichloroethane	99.91±0.01	237.6±0.3	237.2±0.1 [7]* 237.3±2.0 [5, 6]*	7.95±0.06	8837±9 [7]

* Authors did not clearly mention the IPTS used. Consequently, temperatures could not be converted to IPTS-68

Note

The temperatures given with an asterisk (*) in the text do not relate to the IPTS-68.

* * *

References

1 R. Sabbah and I. Antipine, J. Thermal Anal., 32 (1987) 1929.
2 A. J. Head and R. Sabbah, Recommended Reference Materials for the Realization of Physicochemical properties, K. N. Marsh, Ed., Blackwell, Oxford, 1987.
3 J. P. McCullough and J. F. Messerly, The Chemical Thermodynamic Properties of Hydrocarbons and Related Substances. The Use of n-Heptane as a Reference Substance for Low Temperature Calorimetry, Bull. N° 596 Bureau of Mines, U.S. Government Print. Off., Washington, 1961.
4 R. A. Ruehrwein and H. M. Huffman, J. Am. Chem. Soc., 65 (1943) 1620.
5 P. D. Garn and O. Menis, Thermochim. Acta, 42 (1980) 125.
6 A. Langier-Kuzniarowa, J. Thermal Anal., 29 (1984) 913.
7 K. S. Pitzer, J. Am. Chem. Soc., 62 (1940) 331.
8 J. F. Messerly and H. L. Finke, J. Chem. Thermodyn., 2 (1970) 867.
9 Atomic masses of the elements 1987, Pure and Applied Chem., 60 (1988) 841.
10 R. Sabbah and L. El Watik, J. Thermal Anal., in press.
11 K. Heide, Dynamische thermische Analysenmethoden, 2. Auflage, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1982.
12 J. F. Counsell, J. H. S. Green, J. L. Hales and J. F. Martin, Trans. Faraday Soc., 61 (1965) 212.
13 G. T. Furukawa, D. C. Ginnings, R. E. McCoskey, R. A. Nelson, J. Res. Nat. Bur. Stand., 46 (1951) 195.

Zusammenfassung — Es wird eine DTA-Apparatur für den Temperaturbereich 77-330 K beschrieben und einige Anwendungen gegeben, z. B. die Bestimmung des Verschmutzungsgrades, des Tripelpunktes oder der Schmelzwärme einer Substanz. Die Kalibrierung der Apparatur auf Temperatur und Energie erfolgte mit Diphenyloxid, Hexafluorbenzol und 1,3-Difluorbenzol. Der Kalibrationskoeffizient für die Energie kann als eine lineare Funktion von T^3 beschrieben werden. n-Heptan, Cyclohexan und 1,2-Dichlorethan wurden untersucht.