Journal of Thermal Analysis, Vol. 6 (1974) 335–343

A STUDY OF TRANSITION TEMPERATURE STANDARDS BY DTA

B. WUNDERLICH and R. C. BOPP

Department of Chemistry, Rensselaer Polytechnic Institute Troy, N.Y. USA

(Received November 3, 1972)

Thirteen reference standards (TherMetric melting point standards and NBS-ICTA standards) for temperature calibration of DTA in the range from 50 to 425° have been compared and found to be accurate to within ±0.5°. Most of these standards are shown to be usable to at least 100°/min heating rates.

A general review of differential thermal analysis carried out in this laboratory some three years ago [1] revealed that one of the essential shortcomings of modern DTA for application to polymer science is the non-existence of a reliable set of standards for temperature calibration. At this time an initial set of pure organic and inorganic substances of sharp melting temperature was suggested by us for the temperature range from 0 to 325° [1]. Standard deviations of as little as ±0.2° were achieved for 15 different reference substances. At the same time a set of eight provisional standards for DTA was recommended by ICTA [2] for the temperature region from 0 to 1000°. These standards are based on solid I ⇌ solid II transitions to eliminate problems such as atmospheric changes, sublimation, decomposition, and sample packing and shifting. Based on data from 25 workers using 18 different instruments, mean transition temperatures with standard deviations of ±4 to 7° were reported. Since Fall 1971 some of these standards have been distributed by the Bureau of Standards. We thought it of importance to analyze these standards with our equipment and compare them to the previously used standards. This paper reports on this comparison and provides a third generation of information on temperature standards for DTA. As first generation data one may want to use melting point tables of organic salts. Utermark and Schicke [3] list melting points for 3213 organic compounds in the temperature region from −190 to +500°; McCrone [4] has compiled lists of compounds suitable for melting point determinations by microscopy. More than 200 solid-solid transitions are listed by the U.S. Bureau of Standards Circular 500 and Supplements [5]. Additional literature values are available through standard reference works [6].

Experimental

A) Equipment used

All experimental work was performed on the duPont 900 differential thermal analyzer using standard glass capillary sample and reference holders (~ 1 mm inner diameter). The heating block (furnace) consists of a silver cylinder (2.2 cm diameter and 3.7 cm length) fitted with an axially-located, rod-shaped cartridge heater of 55 watt. Sample and reference capillaries are symmetrically placed between the heater and outer surface in tightly fitting holes. Chromel-alumel thermocouples were imbedded into the center of the sample and reference materials which filled about 4 mm of the capillary. Centering was accomplished by ceramic spacers. The sample and reference came to rest about midway down the silver block. Ice point reference voltages were supplied by a thermoelectrically heated and cooled automatic ice point bath manufactured by Joseph Kaye and Co., Cambridge, Massachusetts.

B) Mode of operation

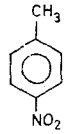
Most the measurements were carried out at a heating rate of 10°/min. For analysis of changes in melting points, heating rates as high as 96°/min were employed. Baselines were brought to approximately horizontal positions by using the proper amount of reference material rather than electric compensation. Recordings of ΔT versus sample temperature were made at sensitivities of $0.2-1.6\times10^{-2}$ mV/cm on the ΔT scale and 0.16–0.8 mV/cm on the temperature scale. The melting peak height of the different samples varied between 0.07 and 0.17 mV. The sample size was approximately 5–10 mg. To check on the reversibility of melting, samples were recrystallized in the DTA furnace at about 5–20°/min cooling rate and remelted once or several times. All measurements were carried out with the capillaries open to the atmosphere. The temperature range measured was normally from >30° below the melting temperature to 10–20° above the melting temperature.

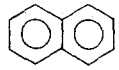
The temperatures of interest taken from the DTA-curves were: a) the first noticeable onset of the transition, b) the extrapolated onset of the transition obtained at the point of intersection of the extrapolated baseline and the linear portion of the transition peak, and c) the peak. The thermocouple EMF measured was corrected to temperature using the NBS Circular 561.

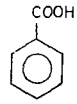
C) Description of samples

a) TherMetric standards

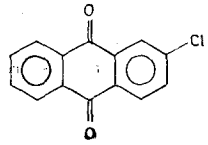
Eight highly-pure, homogeneous organic compounds supplied by Fisher Scientific Co. served as melting standards from 51.5° to 284.6° in 30°–40° intervals. These Fisher TherMetric standards are:

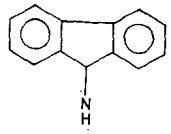
(1) *p*-nitrotoluene  51.54°

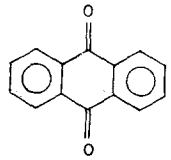
(2) naphthalene  80.27°

(3) benzoic acid  122.35°

(4) adipic acid $HOOC-(CH_2)_4-COOH$ 151.42°

(5) 2-chloroanthraquinone  209.06°

(6) carbazole  245.34°

(7) anthraquinone  284.59°

The temperatures listed above are triple-points which have been determined by the supplier for each sample lot using an evacuated, closed system and measured with a platinum resistance thermometer and Mueller bridge whose calibration is traceable to the U.S. National Bureau of Standards.

Organic compounds generally exhibit a 20° melting point elevation for each 1000 atmosphere external pressure. Since the vapor pressure for these compounds at their triple points is less than 150 mm Hg, differences in temperature between the triple point and the melting point (at 1 atmosphere) are very small. In addition, melting under normal atmosphere is accompanied by dissolution of some air into the molten phase which tends to lower the melting point and thereby counterbalance what little pressure effects exist. Each TherMetric standard is certified by its manufacturer to melt within $\pm 0.05°$ of the triple point measured. Standards were kept in a calcium chloride desiccator without further treatment.

b) ICTA samples

Eight inorganic substances exhibiting solid I $\rightleftharpoons$ solid II transitions and two low melting metals have been selected by the Committee on Standardization,

International Confederation for Thermal Analysis as suitable for DTA temperature standardization over the range 130–900°. As previously mentioned these materials have been tested in a "round robin" series by twenty-five laboratories throughout the world using some eighteen different commercial and laboratory instruments. The participating laboratories were instructed to use the samples (1) as received, (2) without dilution, (3) with nitrogen atmosphere, (4) at heating rates of 3°/min and 10°/min, and (5) with maximum sample size of 300 mg; for further details see reference [2]. The National Bureau of Standards in conjunction with ICTA has made available five of these substances as NBS–ICTA reference material #758 for DTA standardization over the temperature range 125–435°. These materials are collectively listed as highly purified, but without further description. Each substance carries a mean extrapolated onset of melting and melting peak temperature value as determined by DTA the "round robin" series. The five substances included in the reference material #758 are:

		T_0	T_s	T_p, °C
(1) potassium nitrate (KNO_3) [5, 7, 8]	ortho ⇌ rhomboic	129.5	129.9	131.8
(2) indium (In) [5]	solid ⇌ liquid	157	157.6	158.2
(3) tin (Sn) [5]	solid ⇌ liquid	231.9	232.1	234.1
(4) potassium perchlorate ($KClO_4$) [5, 9, 10]	cubic ⇌ rhombic	299.5	299.9	301.4
(5) silver sulfate (Ag_2SO_4)		424	423.1	426.4

The first column of temperatures are the literature values. The second and third columns of temperatures are their extrapolated onset (T_s) and peak temperatures (T_p) as determined by this investigation.

Results

Table 1 lists for all analyzed reference materials the best transition temperature T_0 as proposed presently in the literature, the number of experiments n, the average extrapolated onset of the transition $\bar{T}_s$ and the average peak temperature $\bar{T}_p$ as well as the respective standard deviations of a single measurement. In addition, the temperature differences ΔT which are to be added to the measured temperatures to correct the temperature to T_0 are listed.

Besides analyzing the reference materials as received with the pretreatment given above, most samples were cooled through the transition in the DTA cell at 5–20°/min. This was followed by reheating under standard conditions. The results of reheating the reference materials are listed in Table 2.

For the study of metastable states, faster heating rates are frequently needed. For this reason we checked the superheating behavior of the transition temperatures. This information is of importance for the use of the references at different heating rates. Typical data for the change in melting temperature with heating

Table 1

Transition temperatures in °C of reference materials heated at 10°/min as delivered

Sample	T_0	n	$\bar{T}_s$	σ	$\Delta\bar{T}_s$	$\bar{T}_p$	σ	$\Delta\bar{T}_p$
p-nitrotoluene	51.5a	6	51.5	0.2	0.0	52.0	0.1	−0.5
naphthalene	80.3a	4	80.4	0.1	−0.1	81.4	0.5	−1.1
benzoic acid	122.4a	6	122.1	0.4	+0.3	123.1	0.3	−0.7
adipic acid	151.4a	5	151.0	0.5	+0.4	152.8	0.9	−1.4
anisic acid	183.0a	6	183.1	0.5	−0.1	184.5	0.2	−1.5
2-chloroanthra-quinone	209.1a	6	209.4	0.3	−0.3	210.7	0.1	−1.6
carbazole	245.3a	4	245.2	0.3	+0.1	246.3	0.4	−1.0
anthraquinone	284.6a	8	283.9	0.6	+0.7	284.6	0.4	0.0
potassium nitrate	129.5b	4	129.9	0.3	−0.4	131.8	0.6	−2.3
indium	157c	4	157.6	0.3	−0.6	158.2	0.3	−1.2
tin	231.9c	4	232.1	0.7	−0.2	234.1	0.7	−2.2
potassium perchlo-rate	299.5c	4	299.9	0.7	−0.4	301.4	0.7	−1.9
silver sulfate	424d	4	423.1	1.0	+0.9	426.4	0.5	−2.4

a. TherMetric standard as measured for the lot used.
b. NBS-ICTA standard as listed in second NBS study, reference [7].
c. NBS-ICTA standard as listed in reference [5].
d. NBS-ICTA standard as listed with the sample bottle; reference [2] lists 426°.

Table 2

Transition temperatures in °C of reference materials heated at 10°/min after cooling to 5—20°/min

Sample	T_0	n	$\bar{T}_s$	σ	$\Delta\bar{T}_s$	$\bar{T}_p$	σ	$\Delta\bar{T}_p$
p-nitrotoluene	51.5a	3	51.3	0.2	+0.2	52.3	0.3	−0.8
naphthalene	80.3a	4	80.3	0.1	0.0	81.5	—	−1.2
adipic acid	151.4a	6	150.9	0.4	+0.5	153.1	0.7	−1.7
anisic acid	183.0a	7	182.5	0.4	+0.5	185.4	0.5	−2.4
2-chloroanthra-quinone	209.1a	5	208.5	0.1	+0.6	210.4	0.7	−1.3
carbazole	245.3a	8	244.5	0.3	+0.8	246.3	0.3	−1.0
anthraquinone	284.6a	5	283.5	0.3	+1.1	284.4	0.4	+0.2
potassium nitrate	129.5b	6	130.1	0.5	−0.6	131.8	0.7	−2.3
indium	157c	4	157.4	0.1	−0.4	157.9	0.1	−0.9
tin	231.9c	7	231.5	0.5	+0.4	233.5	0.6	−1.6
potassium perchlo-rate	299.5c	7	299.5	0.8	0.0	300.6	0.7	−1.1
silver sulfate	424d	6	423.2	0.9	+0.8	425.5	0.6	−1.5

a—d, see footnotes of Table 1.

Table 3

Transition temperatures in °C for reference materials heated at 95°/min as delivered

Sample	T_0	T_s	T_0-T_s	$T_s-\bar{T}_s$	$\bar{T}_p$	T_0-T_p	$T_p-\bar{T}_p$
p-nitrotoluene	51.5a	52.2	−0.7	0.7	54.7	−3.2	2.7
naphthalene	80.3a	81.6	−1.3	1.2	84.2	−3.9	2.8
benzoic acid	122.4a	122.8	−0.4	0.7	124.8	−2.4	1.7
adipic acid	151.4a	150.5	+0.9	−0.5	154.5	−3.1	1.7
anisic acid	183.0a	183.5	−0.5	0.4	186.7	−3.7	2.2
2-chloroanthra-quinone	209.1a	209.7	−0.6	0.3	212.1	−3.0	1.4
carbazole	245.3a	245.7	−0.4	0.4	246.9	−1.6	0.6
anthraquinone	284.6a	284.3	+0.3	0.4	286.2	−1.6	1.6
potassium nitrate	129.5b	132.5	−3.0	2.6	136.4	−6.9	4.6
indium	157c	157.2	−0.2	−0.4	160.9	−3.9	2.7
tin	231.9c	232.4	−0.5	0.3	235.7	−3.8	1.6
potassium perchlo-rate	299.5c	302.0	−2.5	2.1	303.7	−4.2	2.3
silver sulfate	424d	424.4	−0.4	1.3	431.5	−7.5	5.1

a—d, see footnotes of Table 1.

Table 4

Summary of data on precision of reference samples in °C

Samples	$<\Delta\bar{T}_s>$[a]	$\sigma(\Delta\bar{T}_s)$	$<\Delta\bar{T}_p>$[b]	$\sigma(\Delta\bar{T}_p)$
(1) All standards (50°—425°)				
As received	0.0	0.5	−1.4	0.7
Reheated	+0.3	0.5	−1.3	0.7
(2) Fisher TherMetric Standards (50°—285°)				
As received	+0.1	0.4	−1.0	0.6
Reheated	+0.5	0.4	−1.2	0.8
(3) NBS-ICTA Standards (130°—425°)				
As received	−0.1	0.6	−2.0	0.5
Reheated	0.0	0.6	−1.5	0.5

[a] Average of all $\Delta\bar{T}_s$ values measured (see Tables 1 and 2).

[b] Average of all $\Delta\bar{T}_p$ values measured (see Tables 1 and 2).

rate for indium, a substance which superheats only little or not at all, and for trigonal selenium, a substance which shows considerable superheating are shown in Fig. 1. Table 3 summarizes data obtained at 95°/min heating rates. Listed

are values for the extrapolated onset of the transition and the peak temperature along with the degrees of superheating over the temperatures in Table 1.

A summary of the overall precision of the data presented here is listed in Table 4.

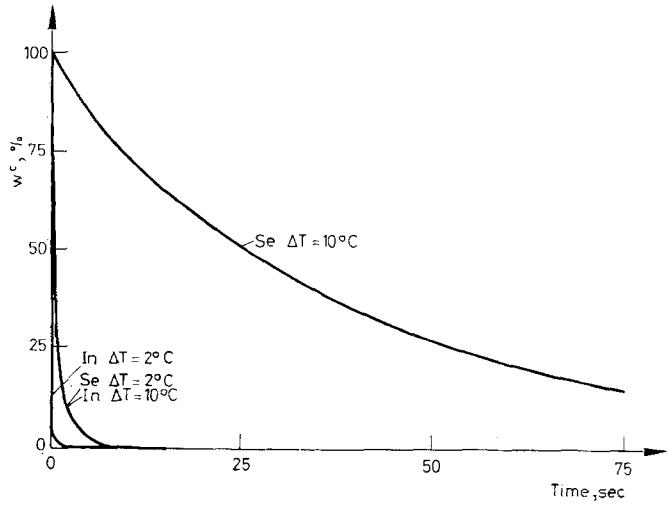


Fig. 1. Relative rates of melting for polymeric selenium and indium; crystalline weight fraction vs. melting time

Discussion

Tables 1 and 4 show that both the TherMetric melting point standards and the ICTA standards can be used as received for the calibration of the temperature scale of a DTA apparatus with an accuracy of about $\pm 0.5°$ when using 10°/min heating rate and calibrating at the back-extrapolated onset of the transition. This accuracy is considerably higher than reported by the ICTA Committee on Standardization [2] and indicates that the larger error limit was instrument caused.

The values for T_0 chosen represent in our judgement the best presently available and most consistent transition temperatures. Some discrepancies exist between the different literature sources [2, 5, 12].

The peak temperatures are somewhat less accurate (see Table 4), despite an effort to adjust the weights analyzed to achieve relatively similar heats of transition in this investigation. The peak temperatures occur one to two degrees higher than T_0.

Reheating the standards after cooling from 10 to 20° above the transition

leads to only slightly different average values (see Table 4). The extrapolated onset of melting is in most cases the same or slightly lower.

None of the irregularities reported for potassium nitrate is observed on cycling below the melting point as reported earlier [12]. The reproducibility on reheating and repeated cycling was as good as for the "as received" samples.

The change of transition temperatures with heating rate can be judged using the Figure. Indium was shown previously to show only little superheating in its melting transition [13]; it was used to limit the apparatus lag. Selenium, in contrast, shows as a linear high polymer a slow melting such that the crystals can heat up faster than they melt, leading to superheating. Of all samples analyzed some signs of superheating occur for naphthalene, KNO_3, potassium perchlorate and Ag_2SO_4. The effect is small (see Fig. 1), but noticeably larger for all NBS-ICTA-samples. The largest lag occurs, as expected, in the peak temperatures. The extrapolated onset shows less effect. Checking the first noticeable onset of the transition of the DTA-curves shows no change within one standard deviation for all samples.

*

This work has been supported by Grant G. P. 17206 of the National Science Foundation. Help with instruments was provided by the Instrument Division of the duPont Co. An early set of the NBS-ICTA Standards was provided through the courtesy of Dr. O. Menis of the Bureau of Standards.

References

1. B. WUNDERLICH, Differential Thermal Analysis, Eds: A. WEISSBERGER and B. W. ROSSITER, Physical Methods of Chemistry, Volume 1, Part V, Chapter VIII. J. Wiley and Sons, New York, 1971.
2. H. G. MCADIE, Appendix 3, Eds: R. F. Schwenker, Jr. and P. D. Garn, Thermal Analysis, Academic Press, New York, London, 1969.
3. W. UTERMARK and W. SCHICKE, Melting Point Tables of Organic Compounds, Interscience Publishers, New York, 1963.
4. W. C. MCCRONE, Jr., Fusion Methods in Chemical Microscopy, Interscience Publishers, New York, 1957.
5. F. D. ROSSINI, Selected Values of Chemical Thermodynamic Properties, NBS Circular 500 (1952).
6. Handbook of Chemistry and Physics, The Chemical Rubber Co., Cleveland, Ohio, (Annual Editions).
7. F. C. KRACEK, Phys. Chem., 34 (1930) 225.
8. P. D. GARN, On the Dissimilarities in $Solid_I$–$Solid_{II}$ Phase Transformations, NBS Special Publication, 338 (1970) 447.
9. K. A. HOFMANN and P. H. MARIN, Sitzber. Preuss. Akad. Wiss. Physik-Math. Klasse (1932).
10. D. VORLANDER and E. KAASCHT, Ber., 56 (1923) 1157.
11. R. NACKEN, Neues Jahrb. Mineral Geol. Beilage Bd. 24, 1 (1907).
12. O. MENIS and J. T. STERLING, "Status of Thermal Analysis Temperature Scale Standards," NBS Special Publications, 338 (1970).
13. M. JAFFE and B. WUNDERLICH, Eds: R. F. Schwenker and P. D. Garn, Thermal Analysis, Vol. 1, Academic Press, New York, 1969.

RÉSUMÉ — On a comparé treize substances étalons pour l'échelle des températures en ATD entre 50 et 425° (étalons de points de fusion TherMetric et étalons NBS-ICTA) et l'on a trouvé que leur exactitude était de ± 0.5 °. On montre que la plupart de ces étalons peut être utilisée jusqu'aux vitesses de chauffage de 100 °C/min.

ZUSAMMENFASSUNG — Dreizehn Referenzstandarde (TherMetric Schmelzpunktstandarde und NBS-ICTA Standarde) zur Temperatur-Eichung von DTA zwischen 50 und 425° wurden verglichen und innerhalb von ± 0.5 ° für genau gefunden. Es erwies sich, daß die meisten dieser Standarde bis Aufheizungsgeschwindigkeiten von 100 °C/min verwendbar sind.

Резюме — Проведено сравнение 13 стандартных материалов (TherMetric melting point standards and NBS—ICTA standards) для калибровки температуры ДТА в области 50—425° и обнаружено, что разброс точек не превышает $\pm$ 0,5°. Показано, что большинство из этих стандартов можно использовать при скоростях нагрева до 100°/мин.