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Note

CALIBRANTS FOR THERMAL ANALYSIS. MEASUREMENT OF THEIR ENTHALPIES OF FUSION BY ADIABATIC CALORIMETRY

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A programme for the provision of a series of energy- and temperature-certified reference materials (CRMs) has recently been completed. These materials, which are, with one exception, organic substances, are intended as calibrants for thermal analysis equipment, especially differential scanning calorimeters. The measurements leading to the certification of the organic substances are described in this note. The certification of indium has been described elsewhere [1].

EXPERIMENTAL

Samples of the materials were purified in the Division of Chemical Standards, NPL, usually by zone refining. Thermal measurements on 4-nitrotoluene, naphthalene, benzil, acetanilide, and benzoic acid were made in a low-temperature calorimeter [2] and measurements on diphenylacetic acid were made in a medium-temperature calorimeter [3]. Two samples of both naphthalene and benzil were available and independent measurements were made on each sample.

The data-collection system has been modified since the last published description [2]. The sample temperature is measured by a platinum resistance thermometer whose resistance is compared with that of a standard 25 ohm resistor by an automatic a.c. bridge. The energy input to the sample is measured by a digital voltmeter connected alternately across the sample heater and a standard resistor in series with the heater. The duration of energy inputs and equilibration periods, the frequency of readings of voltage and thermometer resistance, the switching of the DVM to record heater voltage or heater current, and the format of the printed record of measurements, are all controlled by a logic system constructed largely from TTL integrated circuits. The multiplexer, data serializer, and Teletype driver used to route the DVM and bridge outputs to the Teletype, are circuit modules designed and in general use at NPL. The operation of the logic system is best understood by reference to Fig. 1.

The basic timing interval is a 1 Hz pulse derived from a commercial counter-timer incorporating a 10 MHz crystal. The accuracy of this source has

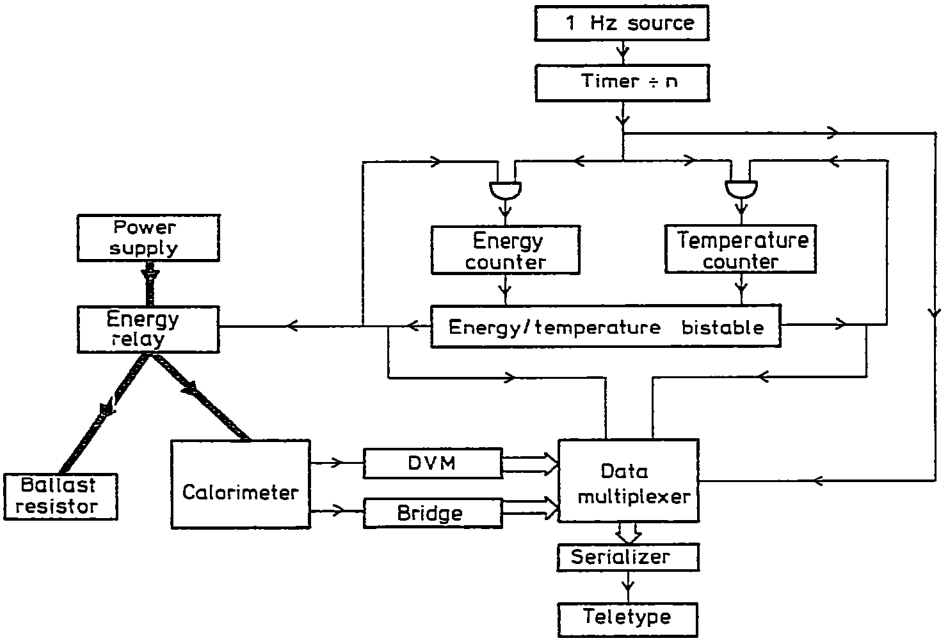

Fig. 1. Measurement and data collection system.

been shown to be better than 0.001%. The 1 Hz pulses are counted by a divider circuit (timer) which produces a "read" pulse at intervals which can be varied from 1 to 99 s. The setting of the timer determines the frequency with which readings are taken. The "read" pulse is gated to either the energy counter or the temperature counter, depending upon the state of the energy/temperature bistable. Both of these counters can be preset to produce an output pulse after any number of "read" pulses from 1 to 99, and this output is used to change the state of the bistable. Therefore these settings determine the number of energy and temperature readings, respectively, in any one cycle and hence, in combination with the setting of the timer, the length of the energy and equilibration periods. The bistable controls a relay which determines whether current from a stabilized power supply passes through the calorimeter heater (energy period) or through a ballast resistor (equilibration period); the use of a ballast resistor ensures that a constant load is presented to the power supply.

The bridge is permanently connected to the platinum resistance thermometer in the sample container and the DVM is connected to a relay, not shown in the diagram, but also controlled by the logic, which ensures that measurements of heater voltage and heater current are made alternately. The outputs from both bridge and DVM are taken to a data multiplexer, which accepts DVM readings when the bistable is in the energy mode and bridge readings when it is in the temperature mode. Upon receipt of a "read" pulse, these readings are transferred in parallel to a data serializer and thence to a Teletype, which produces both printed and punched-tape records.

Facilities are incorporated in the logic circuit to enable sample-temperature readings to be made by a thermocouple if so desired, using the same DVM as for the energy measurements and for the data system to close down in an orderly fashion after a preset number of measurement cycles.

For each sample, measurements of the temperature rises (ΔT) corresponding to the introduction of measured amounts of electrical energy (ΔH) were made from about 20 K below the melting point to about 20 K above it. Since ΔT was small, the heat capacity at the mid-point of the temperature rise was taken to be equal to $\Delta H/\Delta T$. The experimental technique and calculation of heat capacities are described in detail elsewhere [1]. The enthalpy of fusion of each sample was calculated from the heat capacities, the total energy supplied, and the temperature rise. The triple-point temperature of a completely pure sample and the mole fraction, x, of impurity actually present were obtained by application of the van't Hoff equation assuming that the impurity was insoluble in the solid bulk material and dissolved to form an ideal solution in the melt [4].

RESULTS

The results of the measurements are given in Table 1. For each substance, several replicate measurements were made on the same sample. The values of

TABLE 1

Molar enthalpies of fusion and impurity contents of actual samples and triple-point temperature of pure samples *

Substance	Run	ΔH_{fus} (J mole^{-1})	10^2x	T_{TP} (K)
4-Nitrotoluene	1	16812	0.011	324.789
	2	16820	0.011	324.787
	3	16800	0.011	324.786
	4	16789	0.011	324.784
	5	16829	0.012	324.791
	6	16796	0.011	324.789
	7	16821		
Mean		16810	0.011	324.788
Standard error of mean		5.6	0.0002	0.0010
95% confidence limits		±14	±0.0004	±0.003
Naphthalene (sample 1)	1	19053	0.014	353.377
	2	19072	0.015	353.378
	3	19031	0.017	353.378
	4	19024	0.012	353.369
Mean		19045	0.0146	353.376
Standard error of mean		10.9	0.0073	0.0022
95% confidence limits		±35	±0.023	±0.007
Naphthalene (sample 2)	1	19001	0.004	353.416
	2	19101	<0.001	353.410
	3	19116	<0.001	353.413
	4	19047	<0.001	353.410
	5	19103	<0.001	353.414
Mean		19074		353.413
Standard error of mean		21.7		0.0012
95% confidence limits		±60		±0.003

TABLE 1 (continued)

Substance	Run	ΔH_{fus} (J mole^{-1})	10^2x	T_{TP} (K)
Benzil (sample 1)	1	23488	<0.001	368.021
	2	23605	<0.001	368.024
	3	23658	<0.001	368.019
	4	23428	<0.001	368.021
	5	23591	<0.001	368.026
Mean		23554	<0.001	368.022
Standard error of mean		41.8		0.0012
95% confidence limits		±116		±0.003
Benzil (sample 2)	1	23486	0.004	368.002
	2	23551	0.004	368.003
	3	23542	0.005	368.003
	4	23566	0.005	368.003
Mean		23536	0.005	368.003
Standard error of mean		17.5		0.0003
95% confidence limits		±56		±0.001
Acetanilide	1	21636	0.021	387.532
	2	21695	0.023	387.526
	3	21646	0.032	387.523
	4	21637	0.034	387.521
	5	21652	0.036	387.522
Mean		21653	0.029	387.525
Standard error of mean		10.9	0.0030	0.0020
95% confidence limits		±30	±0.008	±0.006
Benzoic acid	1	17993	0.008	395.536
	2	18108	0.007	395.525
	3	18046	0.008	395.527
	4	18031	0.008	395.527
	5	17950	0.008	395.526
	6	18098	0.008	395.525
	7	18130	0.009	395.527
	8	18106	0.007	395.524
	9	18109	0.008	395.526
Mean		18063	0.008	395.527
Standard error of mean		20.6	0.0002	0.0012
95% confidence limits		±48	±0.0005	±0.003
Diphenylacetic acid	1	31289	0.060	420.444
	2	31235	0.061	420.441
	3	31228	0.063	420.441
	4	31325	0.066	420.441
	5	31276	0.071	420.441
Mean		31271	0.064	420.441
Standard error of mean		17.9	0.0020	0.0007
95% confidence limits		±50	±0.006	±0.002

* See discussion section for estimate of systematic errors.

TABLE 2

Specific enthalpies of fusion and calculated initial freezing temperatures of actual samples

Substance	Δh_{fus} (J g^{-1})	$t_{F.P.}$ (°C)
4-Nitrotoluene	122.6	51.63
Naphthalene	148.6	80.22
Benzil	112.0	94.87
Acetanilide	160.2	114.36
Benzoic acid	147.9	122.37
Diphenylacetic acid	147.3	147.26

TABLE 3

Triple-point temperatures

Substance	Triple point, T_{68} (K)	Ref.	Remarks
4-Nitrotoluene	324.677 ± 0.009 **	12	See footnote.
	324.788 ± 0.003 *		This work.
Naphthalene	353.414 ± 0.05 ***	8	See footnote.
	353.417 ± 0.005 **	12	See footnote.
	353.376 ± 0.007 *		This work (sample 1).
	353.413 ± 0.003 *		This work (sample 2).
Benzil	368.022 ± 0.003 *		This work (sample 1).
	368.003 ± 0.001 *		This work (sample 2).
Acetanilide	387.45	13	M.p. on heated plate.
	387.525 ± 0.006 *		This work.
Benzoic acid †	395.520 ± 0.002	14	Triple point cell; correction for impurity.
	395.509 ± 0.004 **	12	See footnote.
	395.520 ***	15	See footnote.
	393.527 ± 0.003 *		This work.
Diphenylacetic acid	420.244 ††	16	See footnote.
	420.442 ± 0.002 *		This work.

* Systematic errors in the triple point are estimated to amount to ±0.015 K in the present work.

** Measurements in a triple-point cell. No purity or correction for impurity quoted. No temperature scale given; IPTS-48 assumed.

*** Measurements by adiabatic calorimetry; value quoted corresponds to reciprocal fraction melted equals zero.

† The value 395.52 K is allotted to the triple point of benzoic acid as a secondary reference point on IPTS-68.

†† Measurement by DSC. Temperature scale not quoted; it depends upon temperature calibration by reference materials whose certified melting points are themselves on an unspecified scale.

the 95% confidence limits quoted are the products of the standard errors of the means and the appropriate Student's *t* factors. Temperatures are based on IPTS-68.

DISCUSSION

Samples of all the substances listed in Table 1 were certified as enthalpy-of-fusion CRMs with the exception of 4-nitrotoluene. This material was found to be unsuitable because measurements made by differential scanning calorimetry [5] showed that solidification of a small molten sample sometimes formed a metastable solid having a melting point lower than that of the stable solid. Depending upon whether a solid sample was in the stable or metastable state, measurements would yield different apparent values of the enthalpy of fusion. Table 2 gives mean values of the specific enthalpies of fusion of the samples and values of the initial freezing temperatures of the actual samples calculated from the triple points and the impurity contents given in Table 1. The freezing temperatures are not corrected for differences between atmospheric and triple-point pressures.

Only three reports of the measurement of the enthalpy of fusion of naphthalene have been published during the past 40 years. The latest of these [6] was based upon the depression of the freezing points of solutions of naphthalene in four different amines and is relatively imprecise, but values obtained from a study of the phase behaviour of the system naphthalene + methane at high pressures (19.00 kJ mole^{-1}) [7] and by adiabatic calorimetry (18.98 ± 0.004 kJ mole^{-1} [8], where the uncertainty interval is the maximum deviation from the mean of an unspecified number of observations) are close to the present value (19.05 ± 0.035 kJ mole^{-1}). ± Terms quoted for the present measurements, which are 95% confidence limits, relate to random errors. Systematic errors in the enthalpy-of-fusion and triple-point are estimated to amount to ±5 J mole^{-1} and ± 0.015 K, respectively.

Two precise measurements of the enthalpy of fusion of benzoic acid, both by adiabatic calorimetry, have been published. The first of these (18.00 kJ mole^{-1}) [9] was made at the National Bureau of Standards on a sample prepared for distribution by the Calorimetry Conference and is in agreement with the present value (18.06 ± 0.05 kJ mole^{-1}), while the second (17.798 ± 0.039 kJ mole^{-1}) [10] is significantly lower. Only one published measurement [11] of the enthalpy of fusion of benzil could be found. The accuracy claimed is relatively low and the value obtained (22.6 kJ mole^{-1}) is considerably below the present value (23.55 ± 0.12 kJ mole^{-1}). No report of measurements on acetanilide or diphenylacetic acid was found.

Precise measurements of the triple points of most of the substances studied have been published and these are quoted in Table 3. Comparison with the present results is hindered by a lack of information on the purity of the sample and the temperature scale used. Where information is not provided, the temperature scale most likely to have been used is inferred from the date of publication; published temperatures have been converted on this basis to IPTS-68, and where necessary, kelvin temperatures have been obtained by adding 273.15 to t_{68}. Agreement with the present values is, in most instances, good. Discrepancies can be attributed to the presence of impurities (where no correction for impurities is applied) or to the use of an inherently less accurate method, e.g. differential scanning calorimetry (DSC).

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