DETERMINATION OF SMALL THERMAL EFFECTS BY A THERMOGRAPHIC METHOD AT TEMPERATURES BELOW 0°

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Abstract

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DETERMINATION OF SMALL THERMAL EFFECTS BY A THERMOGRAPHIC METHOD AT TEMPERATURES BELOW 0°

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Two methods are known for the quantitative determination of thermal effects: calorimetric and thermographic. The calorimetric method is structurally more complicated and requires a longer time for carrying out the experiment, but it has high accuracy. The thermographic method is simpler and considerably faster, but less accurate.

The studies available in the literature on the determination by the thermographic method of heats of fusion ([1], [2]), heats of recombination of frozen radicals ([3]), thermal effects of transformation in hydrogen peroxide in the frozen state ([4]), etc., are not limited in the amount of substance. For many purposes, however, it is possible to work only with small weighed portions. Work in microcalorimetry, although possessing a high degree of accuracy, is also complex and requires a long time ([5]). The complexity of these procedures increases, and the accuracy decreases, if the investigations are conducted in the region of negative temperatures. Recently a number of attempts have been made to bring the accuracy of the thermographic method closer to that of calorimetry, while retaining the speed and simplicity of the former method. The work described here is one such attempt as applied to small weighed portions (hundredths of a gram) and temperatures below 0° (down to the temperature of liquid nitrogen*).

The thermometric part of the apparatus consisted of a copper-constantan thermocouple, a low-resistance PMS-48 potentiometer, and an electronic recording potentiometer EPP-09, reconstructed to a sensitivity of ±0.07°/mm, which was used as a null instrument. On the chart tape of the recorder there was recorded a segment of the time-heating-temperature curve in which heat evolution or absorption occurs.

The thermocouple was welded by the method of a short current pulse ([6]) or simply soldered with tin. The diameter of the wires forming the junction was 0.1 mm; at a distance of approximately 5 cm from the junction, thicker wires, each 0.25 mm in diameter, were soldered on. Reducing the thickness of the wires at the junction is necessary in order to decrease the inertia of the thermocouple**.

To obtain a temperature interval from −190° to −70° and above, a small cryostat was constructed. The cryostat made it possible to record heating curves of samples at a definite and adjustable rate. For this purpose, so-called radiant heating of the substance was used. The design of this apparatus was as follows: a glass vessel in the form of a test tube was closed with a ground-glass stopper, into the head of which two copper wires (about 0.6 mm in diameter) were sealed (Fig. 1, I).

Inside the test tube, a glass tube with a heater wound on it was fastened to the stopper; the heater was connected to the wires sealed into the head to the ground-glass-joint wires. The heater consisted of nichrome wire 0.2 mm in diameter, the turns of which were separated from one another by a glass-fiber thread, and the whole was impregnated with bakelite varnish. The resistance of the heater was about 50 ohms.

In the center of the ground-glass-joint head there was another ground-glass joint, into which copper and constantan wires forming a thermocouple were sealed. The thermocouple junction was located inside the glass frame of the heater, so that above and below it there was approximately the same number of turns. The wires forming the thermocouple were fixed in three stoppers. The diameter of the stoppers was 1 mm smaller than the inner diameter of the tube with the heater. All three stoppers were inside the tube and did not allow the thermocouple to touch its walls.

In studying processes in the solid phase accompanied by the evolution or absorption of heat, the substances were frozen directly onto the thermocouple junction. The junction was at the center of the resulting ball of substance. The charge of substance was 0.005–0.05 g. To determine heats of fusion, when studying substances taken directly in the form of powders, for compounds that decompose on melting, and in other analogous cases, we used a cup made of copper foil (Fig. 1, *II*). The thermocouple junction was soldered to the bottom of the cup, so that the thermocouple and the cup formed a single whole. The presence of the cup increased the inertia of the thermocouple and, consequently, somewhat reduced its sensitivity. A substance in the liquid state was poured into the cup by means of a pipette graduated to 0.005 ml. Knowing the density of the substance, it was not difficult to calculate its weight, which is necessary for calculating thermal effects per unit weight.

Fig. 1. Vessel with heater for thermal analysis (*I*) and cup for determining heats of fusion (*II*): *T*—thermocouple, *H*—heater, —cup made of copper foil.

The weight of the substance frozen onto the junction was determined by weigh-

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* The method is not limited to this temperature interval. Very slight modifications permit recording curves at positive temperatures.

** The thermocouple was not made entirely of thin wires because in that case its resistance would have increased considerably.

Fig. 1. Vessel with heater for thermal analysis (I) and cup for determining heats of fusion (II): T—thermocouple, H—heater, —cup made of copper foil.

Figure 1: Fig. 1. Vessel with heater for thermal analysis (I) and cup for determining heats of fusion (II): T—thermocouple, H—heater, —cup made of copper foil.

ing, after thawing it, in a previously weighed box, with an accuracy of up to $±$0.001 g. The error in weighing samples of 0.05-0.01 g amounts to 2-10% of the charge taken. When working with the cup, charges are taken with an accuracy of $±$0.0005 g. Since in these cases larger charges are used (0.01-0.15 g), the relative errors are correspondingly reduced to 2-0.3%.

After the substance had been frozen on, or after the cup had been filled with it, the entire vessel, with the heater disconnected from the circuit, assumed the temperature of liquid nitrogen and was evacuated to a rarefaction of $(1—5)\cdot 10^{-2}$ mm Hg. At such a vacuum, the thermal conductivity of the air inside the test tube was somewhat reduced, and therefore so were the rate of heat influx from the liquid nitrogen to the sample and the heat losses of the substance during the evolution or absorption of heat. Then a current of 0.15 A was passed through the heater. Under our conditions this current provided smooth heating at a slowly varying rate over a temperature interval of about 100°. Heating was carried out by radiation, without any contact of the heater with the substance. This also reduced heat losses during its evolution or absorption. Thus, at the moment of evolution or absorption, almost all the heat, with small losses, went to the thermocouple and was recorded by the self-recording instrument.

Calibration of the instrument under identical conditions (heater current, degree of vacuum, temperature and amount of refrigerant, etc.) can

carry out calibration with substances with known values of thermal effects, occurring in different portions of the temperature scale. Having determined the ratio of the amount of heat evolved or absorbed to the length of the plateau on the heating curve of known substances, one can construct a curve in the coordinates temperature—calories per millimeter. Using this curve and knowing from experiment the length of the plateau on the heating curve of the substance under investigation, and the weighed portion taken, one can calculate the desired thermal effect:

Table 1

Experimental data obtained from the heating curve of cyclohexane in a drop in the region of a transformation in the solid phase
$(t_{\mathrm{tr}}, {}^\circ\mathrm{C})(^7);\ \Delta H_{\mathrm{tr}},\ \mathrm{cal/g}\ (^7))$

Nos. of experiments	g, g	L, mm	$\Delta H_{\text{tr}} \cdot g$, cal	A, cal/mm
1	0.009	18	0.17	0.0095
2	0.019	41	0.36	0.009
3	0.022	43	0.42	0.010
4	0.027	51	0.52	0.010
5	0.045	110	0.86	0.008

$$\Delta H_x = AL_x \frac{1}{g_x}, \tag{1}$$

where g_x is the weighed portion of the substance under investigation (in g); ΔH_x is the desired thermal effect (in cal/g); L_x is the length of the plateau (in mm); A is the quantity found from the calibration curve (in cal/mm) at the required temperature, corresponding to the evolution or absorption of heat.

The value A can also be determined without a calibration curve. If the desired thermal effect takes place at a temperature t, it is sufficient to record the melting curve of some compound a, which melts at a temperature close to t, and whose $\Delta H_{\text{m},a}$ is known. Then

$$A = \frac{\Delta H_{\text{m},a} g_a}{L_a}, \tag{2}$$

where $\Delta H_{\text{m},a}$ is the heat of fusion of compound a (in cal/g), g_a is its weight (in g), and L_a is the length of the plateau on its melting curve (in mm).

Table 2

Experimental data obtained from heating curves of substances in a cup

Substance	Nos. of experiments	g, g	$\Delta H_{\text{tr}} \cdot g$, cal	L, mm	A, cal/mm
Cyclohexane ($\Delta H_{\text{tr}} =$ 19.14 cal/g at −87.06° ([7]))	1	0.0325	0.62	32	0.020
Cyclohexane ($\Delta H_{\text{tr}} =$ 19.14 cal/g at −87.06° ([7]))	2	0.0450	0.86	41	0.021

Substance	Nos. of experiments	g, g	$\Delta H_{tr} \cdot g$, cal	L, mm	A, cal/mm
Cyclohexane (ΔH_{tr} = 19.14 cal/g at − 87.06° (7))					$0.020_5 \pm 0.0005$
n-Hexane (ΔH_m = 36.1 cal/g at − 95.35° (8))	1	0.0149	0.54	27	0.020
n-Hexane (ΔH_m = 36.1 cal/g at − 95.35° (8))	2	0.0321	1.16	52	0.022
n-Hexane (ΔH_m = 36.1 cal/g at − 95.35° (8))	3	0.0380	1.37	63	0.022
n-Hexane (ΔH_m = 36.1 cal/g at − 95.35° (8))	4	0.0487	1.76	78	0.022
n-Hexane (ΔH_m = 36.1 cal/g at − 95.35° (8))					$0.021_5 \pm 0.0015$
n-Heptane (ΔH_m = 33.5 cal/g at − 90.6° (8))	1	0.0194	0.65	32.5	0.020
n-Heptane (ΔH_m = 33.5 cal/g at − 90.6° (8))	2	0.0278	0.94	48	0.020

Substance	Nos. of experiments	g, g	$\Delta H_{\mathrm{tr}} \cdot g$, cal	L, mm	A, cal/mm
n-Heptane (ΔH_{m} = 33.5 cal/g at −90.6° (8))	3	0.0427	1.44	64	0.022
n-Heptane (ΔH_{m} = 33.5 cal/g at −90.6° (8))	4	0.0575	1.92	85	0.022
n-Heptane (ΔH_{m} = 33.5 cal/g at −90.6° (8))					0.021 ± 0.001
Toluene (ΔH_{m} = 17.2 cal/g at −94.99° (8))	1	0.0309	0.52	26	0.020
Toluene (ΔH_{m} = 17.2 cal/g at −94.99° (8))	2	0.0488	0.86	42	0.020_5
Toluene (ΔH_{m} = 17.2 cal/g at −94.99° (8))	3	0.0515	0.90	43	0.021
Toluene (ΔH_{m} = 17.2 cal/g at −94.99° (8))	4	0.0602	1.03	47	0.022
Toluene (ΔH_{m} = 17.2 cal/g at −94.99° (8))					0.021 ± 0.001

Having placed a drop of cyclohexane on the thermocouple junction, we investigated the thermal effect of the transformation in the solid phase (transformation temperature −87.06°) (7). The amounts of cyclohexane were from 0.009 to 0.045 g. Knowing the magnitude of the heat of transformation (19.14 cal/g) (7), it is not difficult to calculate that, in our weighed portions, we were dealing with effects from 0.2 to 0.9 cal (Table 1). The value A in all experiments with different weighed portions was the same and was 0.0095 ± 0.0015 cal/mm. Consequently, our instrument permits measurement of 0.1–0.2 cal with an accuracy of up to 10–15%.

All these data pertain to heating with a current of 0.15 A. When the magnitude of the current is changed, the rate of heating of the substance and the length of the area change.

With the cup we investigated the thermal effect of the transformation in the solid phase of the same cyclohexane, as well as the heats of fusion of *n*-hexane, *n*-heptane, and toluene. Samples ranged from 0.015 to 0.15 g. The results obtained are summarized in Table 2. The sensitivity for all substances was found to be 0.021 ± 0.001 cal/mm. For each sample, 2–3 experiments were performed, and the reproducibility of the areas in magnitude and temperature was taken into account.

We carried out a calculation by formula (1) of the heats of fusion of toluene, *n*-hexane, and *n*-heptane, which melt at similar temperatures. Toluene was taken as the known substance a with a known heat of fusion. The heat of fusion of toluene was calculated using *n*-hexane as substance a. Table 3 shows that the difference between the data obtained and

Table 3

Calculation of heats of fusion by the thermographic method

Substance	g_x, g	L_x, mm	$\Delta H_{\mathrm{m},a}$, cal/g [8]	$\Delta H_{\mathrm{m},a} \cdot g_a/L_a$, cal/mm (from Table 2)	ΔH_x, cal/g, from melting curves	ΔH_x, cal/g, from literature data [8]
Toluene (x) *n*-hexane (a)	0.0515	43	33.5	0.021	17.5	
Toluene (x) *n*-hexane (a)	0.049	42	33.5	0.021	18.0	
Toluene (x) *n*-hexane (a)	0.031	26	33.5	0.021	17.6	
Toluene (x) *n*-hexane (a)			33.5	0.021	17.7±0.3	17.2

Substance	g_x, g	L_x, mm	$\Delta H_{\mathrm{m},a}$, cal/g (8)	$\Delta H_{\mathrm{m},a} \cdot g_a/L_a$, cal/mm (from Table 2)	ΔH_x, cal/g, from melting curves	ΔH_x, cal/g, from literature data (8)
n-Hexane (x)toluene (a)	0.038	63	17.2	0.021	34.8	
n-Hexane (x)toluene (a)	0.032	52	17.2	0.021	34.1	
n-Hexane (x)toluene (a)	0.015	27	17.2	0.021	37.8	
n-Hexane (x)toluene (a)			17.2	0.021	35.6 ± 2	36.1
n-Heptane (x)toluene (a)	0.0575	85	17.2	0.021	35.2	
n-Heptane (x)toluene (a)	0.043	64	17.2	0.021	36.2	
n-Heptane (x)toluene (a)	0.028	48	17.2	0.021	31.5	
n-Heptane (x)toluene (a)	0.020	32.5	17.2	0.021	31.0	
n-Heptane (x)toluene (a)			17.2	0.021	33.5 ± 2.5	33.5

those taken from the literature lies within the experimental error. The experimental error in all cases is $\leq 10\%$. Thus, by the method described it is possible to estimate the thermal effects accompanying various physicochemical phenomena. In this case the substances under investigation are used in amounts of hundredths or tenths of a gram, and tenths of a small calorie are estimated with an accuracy of up to 10% of the quantity being determined.

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Note: Figure translations are in progress. See original paper for figures.

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