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Heat Calibration for an Apparatus of Thermoanalytical Microscopy

Kazuko S. Kunihisa*

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A method of heat calibration is given for the previous apparatus of thermoanalytical microscopy and the heat of fusion of stearic acid was measured, which was used as the standard substance in the previous papers. The experimental result agrees with the most reliable value in the published references.

Several apparatuses for TAM (thermoanalytical microscopy) have been constructed and applied to study the phase transitions of some aliphatic esters of cholesterol by the author and co-workers.[1–4),19)] In the last two papers, stearic acid was used as the standard to estimate the heat quantity and some discrepancies between the values of the heat of fusion in the published references were found. In this paper, a method of heat calibration by electric energy will be given for the previous apparatus and mainly the result of the measurement of the heat of fusion of stearic acid will be discussed.

EXPERIMENTAL AND THEORETICAL

A heating cell is located at the position 'h' in Fig. 1 to calibrate the heat generated in a sample. Fig. 1 shows only the mutual positions of sample cells in the interior of the copper block. 's' and 'r' express the sample and reference cells respectively. The lined part expresses the rods of thermoelement as the heat sensitive material and the connecting parts equalizing the potential differences which rise from the junctions between thermoelements and the block wall. The heating cell 'h' involves a small coil of constantan wire (60 ohms) and some machine oil.

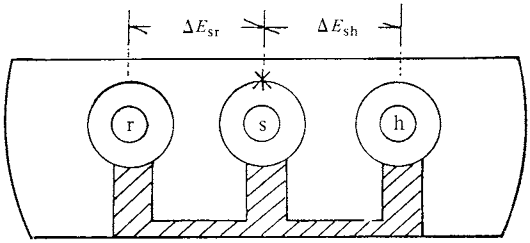

Fig. 1. The relative positions of the cells in the intiorior of the copper block. r: reference (Al_2O_3), s: sample, h: heater for calibration. *: position of thermocouple for temperature measurement.

The TAM apparatus is special mainly in the following points:

(I) The cell holders are suspended in the air except the junction parts with the respective thermoelements.

(II) Only the center cell receives some energy of the light for microscopy. These points should be discussed:

(I) Heat Transfer in the Air.

The heat transfer by the air convection is practically proportional to the temperature difference, when the air flow is not turbulent and the temperature difference is small.[5,6)] Therefore, the air contribution may be included effectively into the heat transfer in solids where Newton's cooling law holds. Heat conductivities of copper and air are 400 and 0.03 $J\ m^{-1}\ s^{-1}\ K^{-1}$ respectively. The thermal contact between the cell and the copper holder is very tight by applying silicone grease. On the other hand, the space between a cell and the block wall is minimum at the gap between the cover glass of the cell and the cover plate of the copper block, which is 1 mm. The ratio of the speed of heat transfer in the copper holder to that in the air space is more than 4×10^4, since the thickness of the copper holder is 0.3 mm. Then the dispersion of the heat to measure into the air is negligibly small.

(II) The Influence of the Light for Microscopy.

The heat flows into the sample cells may be estimated by the following equations according to the reason discussed in (I).

$$C_s \frac{dT_s}{dt} = k_s (T_w - T_s) + \frac{dQ}{dt} + q_0 \qquad (1)$$

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* National Chemical Laboratory for Industry,
Shibuya-ku, Tokyo 151

$$C_r \frac{dT_r}{dt} = k_r (T_w - T_r) \tag{2}$$

$$C_h \frac{dT_h}{dt} = k_h (T_w - T_h) \tag{3}$$

where C, k, T, and t express heat capacity, effective heat conductivity, temperature, and time, respectively. Subscripts s, r, h, and w express the sample part, reference part, the heating cell part, and the wall which has the junctions between thermoelements and itself. The quantity dQ/dt expresses the rate of heat generation (positive or negative either) in the sample and q_0 denotes the effective power of the light for microscopy. In eq. (3), it is assumed that any electric energies are not supplied into the heating cell. Then the next equation can be obtained from eq. (1) and eq. (3).

$$C_s \frac{d\theta}{dt} + (C_s - C_h) \frac{dT_h}{dt} = -k_s \theta + (k_s - k_h)(T_w - T_h) + \frac{dQ}{dt} + q_0 \tag{4}$$

where, $\theta = T_s - T_h$.

In stationary state, dQ/dt and $d\theta/dt$ vanish. Therefore if θ^* is defined as θ in the stationary state, the heat Q generated during the time from t_1 to t_2 will be given by eq. (5).

$$Q = k_s \int_{t_1}^{t_2} (\theta - \theta^*)\, dt \tag{5}$$

here,

$$\theta^* = \frac{1}{k_s} \left\{ (C_h - C_s) \frac{dT_h}{dt} + (k_s - k_h)(T_w - T_h) + q_0 \right\} \tag{6}$$

So that q_0 is included in θ^* which corresponds to the base line on the thermogram.[7] In the optimum condition, only q_0/k_s may be left as the base line. Practically the deviation of the base line corresponding to q_0/k_s is 25 μV. Therefore it is impossible to detect a small heat quantity to be measured in the range of 25 μV of the amplifier. It is usual, however, to use the range of 250 μV. It is sufficient even to measure a mesophase-mesophase transition. For example, cholesteryl myristate of 66 mg gives the peak height of 25 μV to the smectic-cholesteric transition in the range of 250 μV. Practically, the range of 100 μV is the minimum which can suppress the noise levels. Therefore, 25 μV due to the light for microscopy does not affect the experimental results.

(III) Heat Calibration

In the temperature range where any heat anomalies do not occur in the sample, a definite quantity of electric energy can be supplied to the heating cell. In this case, the following equations hold:

$$C_s \frac{dT_s}{dt} = k_s (T_w - T_s) + q_0 \tag{7}$$

$$C_h \frac{dT_h}{dt} = k_h (T_w - T_h) + Q_e \tag{8}$$

here, Q_e is the supplied power. If Q_e is supplied during the time from t_1' to t_2', eq. (9) will be obtained similarly to the preceding paragraph.

$$Q_e (t_1' - t_2') = -k_s \int_{t_1'}^{t_2'} (\theta - \theta^*)\, dt \tag{9}$$

The integration can be obtained graphically. Since Q_e and t_1', t_2' are known, k_s is obtained from eq. (9). Plotting the values of k_s to the corresponding temperatures, k_s to the temperature at which the heat anomaly occurs in the sample will be obtained by interpolation. Using the k_s and the graphical integration of the right hand of eq. (5), the value of Q will be obtained.

RESULTS AND DISCUSSIONS

(I) Characterization of Apparatus.

Figure 2 shows the plot of the thermoelectric potential, ΔE_{sh}, plotted against temperatures, when Al_2O_3 is stuffed into the cells, s and r. The ordinate corresponds to the inverse of k_s. The result shows that the thermoelectric potential between the thermoelement (p-type) and copper decreases with temperature. The depression of the potential at 100°C amounts to 10% of that at room temperatures. The sensitivity of the apparatus decreases proportionally to the decrement of the thermoelectric potential.

ΔE_{rh} was found to be similar to ΔE_{sh} but 2% more than ΔE_{sh}. It is preferable, however, to take ΔE_{sh} rather than ΔE_{rh} in spite of the symmetrical positions of r and h. Because the heating cell is located at the position

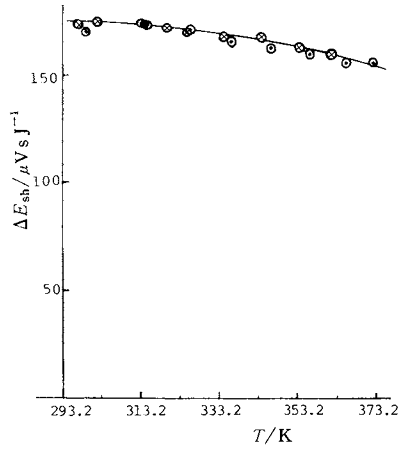

Fig. 2. Temperature dependence of thermoelectric power of thermoelement.
○ : heating, ⊗ : cooling.

based on the general principle of contact potential difference, $\pi_{ab}(T) = -\pi_{ba}(T)$, here a and b denote different metals or semiconductors. The reversibility can be carried out only by selecting the couple of the cells, s and h. Besides, it has been clear that the light for microscopy is not effective as described above.

The sensitivity of the apparatus was constant against the supplied power in the range of 2–20 mW. The time constant of the apparatus was 90 s.

(II) Heat of Fusion of Stearic Acid.

Table 1 shows the result of the measurements of the temperature and the heat of fusion of stearic acid. The standard deviation is 0.7%. The values of the heat of fusion in the published references appear very scattered as shown in Table 2 in which the data are arranged in the order of published years. At first, Garner *et al.* gave the empirical formula, $\Delta H = 1.03n - 3.61$ (n: carbon numbers in the acid), for the even-number carbon acids

Table 1. The temperature and the heat of fusion of stearic acid.

Sample wt.	Run	Rate	Fusion		Crystzn.	
mg		K min^{-1}	T/K	ΔH/kJ mol^{-1}	T/K	$-\Delta H$/kJ mol^{-1}
11.42	1	0.63	343.8	66.2	343.8	62.0
	2	″	343.2	63.6	342.8	63.3
	3	″	342.8	61.0	342.6	63.0
37.22	1	″	342.6	63.8	342.5	61.8
	2	″	342.8	60.8	342.5	62.0
17.05	1	1.25	342.4	62.4	342.1	64.0
	2	″	342.4	62.6	342.1	63.1
	3	2.5	342.7	64.4	341.9	64.8
	4	5(3.5)	343.2	63.0	(341.7	63.5)
mean			342.9	63.1	342.4	63.1

The values in parentheses refer to the cooling rate.

Table 2. Values of the temperature and the heat of fusion of stearic acid in references.

Authors or Editors	Publication Form	Year	Method or Source	T/K	ΔH/kJ mol^{-1}
Garner *et al.*[9)	Original	1926	Empirical formula	343.75	62.5
Vold[5)	″	1949	DTA	342.2	58.6
Singleton *et al.*[10)	″	1950	Calc. from fusion data	342.7	68.4
Mod *et al.*[11)	″	1953	Calc. from solubility data	–	70.3
Adriaanse *et al.*[12)	″	1964	Calorimetry	342.62	63.0
Lebeder[13)	″	1964	Calorimetry	–	45.2
Freeberg *et al.*[14)	″	1966	P. E. DSC	342.8	57.9
Lutton[15)	Monograph	1967	Interpolated	342.8 (342.6)*	63.2
Barrall & Guffy[16)	″	1970	DTA	342.6	56.7
Assoc. Oil-Chem.[17)	Handbook	1971	from Garner	342.5	62.5
Perry-Chilton[18)	″	1973	from NBS	342.02	56.6
I. Tanaka	(Private commun.)		DSC	343.6	54.6
This paper			TAM	342.9 (342.4)*	63.1
″			P. E. DSC1B	336.8**	61.4

* temperature of crystallization

** The apparatus of Perkin-Elmer DSC1B employed indicates considerably lower temperature than the actual temperature only below 373.2 K.[19) in the C-form. This formula has been quoted by a number of authors and interpolated for stearic acid, namely, by Lutton, Japanese association of oil chemistry, Vold, and Barrall II *et al.* The last two groups, however, obtain a different value, 56.7 kJ mol^{-1} (47.6 cal g^{-1} in the texts), from those of the first two groups, 62.5 or 63.2 kJ mol^{-1}. Two other calculated values[10,11] seem to be too high.

The value of Adriaanse *et al.* using a microcalorimeter appears to be the most reliable because the authors refer to the sample purity (99.8 mol%) and limit to the errors of the temperature measurement (± 0.1 K). Another calorimetric value of Lebeder is considered to be too low. Chemical Engineer's Handbook refers to another accurate temperature measurement authorized by National Bureau of Standard Project but the source is unclear.

The data above may be separated into two groups, one in the neighborhood of 62.5 kJ mol^{-1} and another in the neighborhood of 56.7 kJ mol^{-1}. If the difference were related to the irreversible transition from the polymorph B to the polymorph C at around 327K, there should be two melting points. The data of the transition temperature, however, can not be separated into the corresponding groups.

After all, the value obtained in this work is very close to that obtained by Adriaanse *et al.* The purity of the sample used, was determined to be 99.56% by a gaschromatograph.

The same sample was tested by a Perkin-Elmer DSCIB and 61.4 kJ mol^{-1} was obtained for the heat of fusion as the mean of five experiments. The difference between the values obtained from the two apparatuses is 2.7%. The fluctuations appeared in both of the experiments are overlapped partially. The difference is very small in contrast with differences between the values appeared in Table 2.

(III) The Temperatures and the Heats of Transition of Two Cholesteryl Esters.

The transition temperatures and the heats of transition of cholesteryl nonanoate and myristate were measured as shown in Table 3. The values of the previous papers were obtained by applying the value of the heat of fusion of stearic acid given by Garner *et al.*, that is 62.5 kJ mol^{-1}. If the value, 56.7 kJ mol^{-1} [20] were applied, those data would be 10% less than those appeared in Table 3. Some discrepancies between the values in the mesophase-mesophase transitions are inevitable since the area of a small peak is considerably dependent on the way of taking the base line.

CONCLUSION

The reasonable results have been obtained by the above calibration method. Regarding the heat of fusion of stearic acid, 62.5 kJ mol^{-1} is more probable than

Table 3. Transition temperatures and heats of cholesteryl nonanoate and myristate.

Substance	Authors	Course	Cryst. – Chol. T_1 / K	Cryst. – Chol. Q_1 / kJ mol^{-1}	Smec. – Chol. T_2 / K	Smec. – Chol. Q_2 / kJ mol^{-1}	Chol. – Iso. T_3 / K	Chol. – Iso. Q_3 / kJ mol^{-1}
Ch. nonanoate	This work	H*	351.5	23.8			364.5	0.44
		C			345.8	0.40	364.6	0.59
	Previous Paper[4]	H	351.0	23.4			363.2	0.53
		C			345.7	0.42	365.2	0.59
	Davis *et al.*	H	350.4	25.1			364.9	0.55
		C			347.8	0.31		
	Barrall *et al.*	H	354.0	22.5			366.2	0.48
		C			339.2	0.24	359.2	0.51
Ch. myristate	This work	H	344.0	45.7	351.8	1.12	356.9	0.77
		C	327.8	43.2	351.6	1.25	356.9	1.00
	Previous Paper[4]	H	343.8	47.2	351.6	1.37	356.7	0.92
		C		43.5	351.6	1.60	356.8	1.29
	Previous Paper[3]	H	343.8	45.5	351.6	1.3	356.7	0.7
		C		40.7	351.7	1.5	356.7	1.2
	Davis *et al.*		343.7	46.5	351.0	1.40	356.4	1.02
	Barrall *et al.*		346.8	46.7	352.9	1.30	358.7	1.02

* H and C express heating and cooling, respectively.

56.7 kJ mol^{-1}.

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