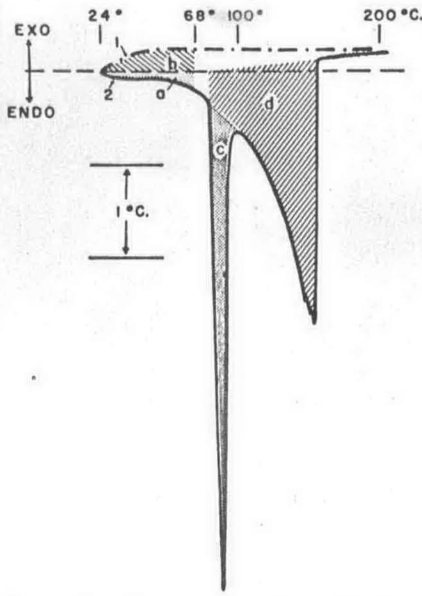

Figure 3. Thermogram of naphthalene showing areas used for ΔH_f and ΔH_v and C_p determinations

(Sensitivity, 50 μvolt/inch)
1. Thermogram of base line with empty pans
2. Thermogram of 8.34 mg. of naphthalene

Areas:
$b - (-a)$ = Area due to C_p
c = Area due to ΔH_f
d = Area due to ΔH_v

Table I. Results of Determination of Specific Heat

Sample	Cal. 15°/gram/°C. C_p, determined	Cal. 15°/gram/°C. C_p, known[a]
p-Dinitrobenzene[b]	0.25	0.259 at 119° C.
p-Dinitrobenzene[b]	0.23	0.259 at 119° C.
2,4-Dinitrotoluene[b]	0.34	0.350 at 100° C.
2,4-Dinitrotoluene[b]	0.35	0.350 at 100° C.
Silver nitrate	0.05	0.146 at 50° C.
Silver nitrate	0.09	0.146 at 50° C.
Benzoic acid	0.29	0.287 at 20° C.
Benzoic acid	0.22	0.287 at 20° C.
Tin	0.04	0.054 at 20° C.
Tin	0.04	0.054 at 20° C.
Oxalic acid	0.39	0.338 at −200° to +50° C.
Nickelous nitrate	0.47	0.473 at 80° C.
Dicyandiamide	0.40	0.456 at 0° to 204° C.
Naphthalene	0.40	0.402 at 87.5° C.
Polyethylene	0.56	0.55
Polystyrene	0.35	0.32–0.35

[a] All known C_p values were obtained from References *9*, *13*, and *14*.
[b] Eastman White Label, all other reagents are C.P. grade or better. Polyethylene and polystyrene were received through courtesy of Monsanto Chemical Co.

Table II. Parameters Studied and Results of ΔH_f Determinations

Sample	Sample size, mg.	Heating rate	Sample state	Cal. 15°/gram determined ΔH_f	Cal. 15°/gram known[a] ΔH_f
Tin	10.16	10° C./min.	Normal	13.8	14.0
Tin	10.70	10° C./min.	Flattened sheet	14.2	14.0
Benzoic acid	4.80	10° C./min.	Fused	34.6	33.9
Benzoic acid	6.16	10° C./min.	Normal	34.1	33.9
Benzoic acid	5.73	10° C./min.	Normal	33.6	33.9
Tin	2.45	10° C./min.	Normal	13.6	14.0
Indium	2.42	10° C./min.	Normal	6.9	6.8
Silver nitrate	10.00	10° C./min.	Normal	15.5	17.7
2,4-Dinitrotoluene	5.94	10° C./min.	Normal	28.2	26.4
Naphthalene	6.34	10° C./min.	Normal	36.0	35.6
Benzoic acid	6.67	4° C./min.	Normal	33.9	33.9
2,4-Dinitrotoluene[b]	8.80	4° C./min.	Normal	27.9	26.4
Tin	5.31	4° C./min.	Normal	13.3	14.0

[a] All ΔH_f values were obtained from reference *9*.
[b] Eastman White Label, all other reagents are C.P. grade or better.

size, and sample shape was evaluated since these factors have been known to have a major effect upon the results obtained (*3*, *12*, *28*).

The heats of fusion were determined on a series of compounds at a program rate of 10° C./minute. The heats of fusion of several compounds were then determined at a program rate of 4° C./minute. This rate was thought to be significantly different from the original to provide a basis for determining any effect upon area.

The sample size was varied from 2.0 to 11.0 mg. in order to determine this effect upon heat of fusion. Benzoic acid was utilized for this evaluation.

The effects of sample state upon benzoic acid were also determined. Benzoic acid is normally obtained as fine crystals. This compound was fused and a portion was utilized for the heat of fusion determination.

In a separate experiment, tin, which was in the physical state of small granules, was flattened into a thin sheet by pressure. The heat of fusion was then determined on an appropriate size sample of the tin sheet.

All heats of fusion are based on the calibration values reported previously. The results of these experiments are listed in Table II. The areas utilized for this measurement are shown in Figure 3, a thermogram of naphthalene. The heats of fusion and vaporization were calculated from the following equation:

$$\Delta H_f \text{ or } \Delta H_v = \frac{KX \text{ area in mm.}^2 \times \text{range setting of interest } (\mu\text{volt})}{g} \qquad (15)$$

DISCUSSION

The portion of the thermograms from ambient to 100° C., in Figure 2, show that the sample couple can lag the reference couple appreciably, depending upon the specific heat of the sample. Thermal diffusivity of the sample and heat transfer of the system are also important factors. The rate of transfer per unit time was considered a fixed value (constant), because the speed of response of the pen is fixed and an exact chart speed of 1 inch/10 minutes was used throughout.

Once this lag has been overcome by heat input to the system, the sample curve follows the base line curve closely and may render specific heat determinations in extended temperature regions inaccurate. However, when the specific heat value of a material changes abruptly due to a morphological transformation—e.g., glass transition—this change is readily detected and a reliable value of the change is possible even at elevated temperatures.

Equation 14 is valid only for a number of specific heat determinations in which the instrumental conditions are held constant. During any series of specific heat determinations, the thermocouples must not be moved and the same sets of semispherical sample and reference pans must be used. A change of sample pans, even though weight differences of the pans amounted to only 0.1 mg., affected the value of the result. Asymmetry of the pans which may vary slightly on forming may also be an important factor. Any adjustments of the recorder for sensitivity or dampening also affects this measurement. The furnace should also be covered to prevent drafts which will result in thermocouple drift and identical heating rates must be used.

Additional error may be introduced by the inability to measure accurately some of the small areas experienced. All areas were measured in triplicate with a plane planimeter and the results