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# Determination of Specific Heat and Heat of Fusion by Differential Thermal Analysis

## Study of Theory and Operating Parameters

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► Utilization of differential thermal analysis under nearly equilibrium conditions permits the determination of heat of fusion and specific heat on a variety of inorganic and organic compounds from a single calibration of an easily handled material like tin. Variables such as sample size, heating rate, and sample state were studied for their effect upon the heat of fusion. These variables did not exhibit effects upon the results within the limits of error of the determination. The theory and equations underlying the specific heat determination are discussed and a practical method is presented which is applicable to a wide range of materials. The standard deviation at the 95% confidence level for the heat of fusion and specific heat was found to be 1.5 cal./gram and 0.02 cal./gram/°C., respectively.

**D**IFFERENTIAL THERMAL ANALYSIS has been applied previously to a variety of both inorganic and organic materials. These applications were initially concerned with minerals and soils (3, 23), and subsequently with pure inorganic compounds (7, 15, 21). More recently, less well defined organic materials and compounds have been studied. The investigators have reported both qualitative and quantitative results (1, 2, 6, 11, 17, 22, 30, 31).

As a result of the gradual development of a variety of differential thermal analyzers, a re-evaluation of qualitative and quantitative variables has resulted in some duplication of effort (27).

The variation of peak temperature has been reported to be dependent upon sample size, size of the cylindrical holder, and heating rate (12, 24, 28).

The effects of diluent techniques have been covered in various papers. Particle size and packing were found to be important factors that affected the thermograms obtained (19). In addition, the formation of complexes with the inert diluent has also been reported (4, 18).

However, with the development of more sophisticated and sensitive instrumentation, the effect of sample size, diluent, size of sample holder, heating rate, and difference in heat capacities between reference and sample, and other parameters can be better evaluated.

Base line deviation, especially at the beginning of a run, is a common occurrence in differential thermal analysis. This is due to an imbalance in heat capacities between the sample and reference thermocouples and is affected by symmetry, sample loading, inert loading, and packing (3).

Many of the detrimental and non-uniform parameters that accompany the great variety of techniques common to each specific analyzer, may be turned to advantage when the proper technique is employed as in the present application.

The aspects of differential scanning calorimetry (DSC) and applications to quantitative measurements of transition energies have been reported recently by Watson, *et al.* and O'Neill (20, 29). DSC measures the transition energy

directly (29) while conventional DTA measures  $\Delta T$  vs. sample temperature. Thus, DTA must be calibrated before it can be utilized for quantitative transition energy measurements.

The present paper will show that when DTA is carried out under nearly equilibrium conditions, a single calibration can be performed which is applicable to the determination of the specific heat and heat of fusion of both organic and inorganic compounds.

### THEORY

The major factors affecting base line deviation (equilibrium conditions) are mismatched heat capacities, improper heat transfer, symmetry, packing, particle size (sample and diluent), dilution effects, inertness of diluent, and sample concentration.

When a sensitive system is employed in which the sample size is small (1 to 10 mg.), the sample does not have to be diluted, and the system contains fixed thermocouples allowing reproducible results; the disadvantage of base line deviation can be an asset by allowing the determination of the specific heat of the sample.

Assuming the above conditions exist, the deviation in base line would be greater for those materials with a high specific heat value. To obtain a mathematical expression for  $C_p$ , we must consider two factors: the effects of the system upon the differential thermocouple; and the effects of the system plus sample upon the differential thermocouple.

In considering heat effects upon the differential couple, the equations of heat balance employed by Borchardt and Daniels are used (5).

$$C_{p,s}dT_2 = dH + K_s(T_3 - T_2)dt \quad (1)$$

$$C_{p,r}dT_1 = K_r(T_3 - T_1)dt \quad (2)$$

$T_1$ ,  $T_2$ , and  $T_3$  are temperatures of the reference thermocouple, sample thermocouple, and air bath (furnace thermocouple), respectively (see Figure 1).  $C_{p,r}$  is the total heat capacity of the reference thermocouple (including cup) and  $C_{p,s}$  is the total heat capacity of the measuring thermocouple including cup. The absolute values which will be obtained are dependent upon the effects of thermocouple symmetry, size, and shape of sample containers and furnace, when these variables can be reduced to constants as in a fixed system.

Equation 1 shows that any increase in enthalpy of the sample side of the differential thermocouple is due to the total enthalpic effects of sample plus the heat transferred to the thermocouple by the surroundings. Equation 2 describes the enthalpic effects on the reference side except that the  $dH$  term is necessarily not present.  $K_s$  is the heat transfer coefficient for the sample (measuring) thermocouple and  $K_r$  is the heat transfer coefficient for the reference side.

The assumptions governing the validity of these equations to the present system are: the differential thermocouples are fixed; a small sample size is employed; the sample does not have to be diluted; the sample holder is capable of maintaining even heat distribution consistent with the demands of the temperature programmer; and linear heating rates from one run to the next can be realized.

There are two situations which we must consider—the absence of a sample and the presence of a sample. Let us consider the first case where a sample is not present in the container. In this instance there can be no heat evolution or absorption except that due to slightly different heat capacities of the thermocouples and empty containers caused by symmetry and size considerations.

Then, any change in base line from the horizontal due to differences in heat capacity may be expressed as:

$$C_{p,s}dT_2 - C_{p,r}dT_1 = K_s(T_3 - T_2)dt - K_r(T_3 - T_1)dt \quad (3)$$

where  $C_{p,s}dT_2 - C_{p,r}dT_1 = C_p dT$  and  $C_p$  = heat capacity of the system.  $K_r$  and  $K_s$ , the heat transfer coefficients from  $T_3$  to  $T_2$  and  $T_3$  to  $T_1$ , should be equal even under dynamic conditions providing linear reproducible programming rates exist, thermal gradients within the holder are absent, and the total

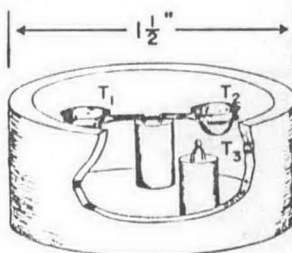


Figure 1. Sample holder

$T_1$  = Reference temperature  
 $T_2$  = Sample temperature  
 $T_3$  = Air bath temperature

heat capacity of the air bath is more than sufficient to provide the thermal energy required to maintain nearly equilibrium conditions within the system.

Rearranging Equation 3 gives

$$C_p dT = K(T_1 - T_2)dt \quad (4)$$

where  $K = K_r = K_s \neq 0$

This is true providing the previous assumptions are true and  $K_r$  and  $K_s$  are temperature independent over the temperature range of interest ( $dT$ ). This is indeed true as will be shown later.

Thus Equation 4 becomes

$$C_{p(w/o \text{ sample})} = \frac{K(T_1 - T_2)dt}{dT} = \text{cal./}^\circ\text{C.} \quad (5)$$

where

$K$  = heat transfer coefficient of system in cal./mm.<sup>2</sup>.

$C_p$  = heat capacity of system in cal./°C.

$dT$  = temperature range of interest

$(T_1 - T_2)dt = \Delta T dt$ ; and over a time interval, say  $t_0$

$\int_t^{t_0} \Delta T dt$  = area encompassed by base line curve and constructed horizontally, measured over temperature range of interest.

The  $K$  value does not incorporate a time-temperature function since the chart speed of the recorder and the response of the DC amplifier and recorder were considered fixed.

We now consider the second case where a sample has been placed in the proper container and the enthalpic effects will be registered on  $T_2$  which is one side of the differential couple.

We now choose a time (temperature) interval where  $dH = 0$ —i.e., the heat of transformation is 0 because the sample is not undergoing a chemical or physical transformation. Thus, the equation

describing the heat capacity due to the presence of a sample is identical to Equation 5. By evaluating Equation 5 without sample and subsequently with sample and subtracting, the heat capacity of the sample is

$$\bar{C}_p = C_{p(w/o \text{ sample})} - C_{p(w/sample)} = (\text{System effects}) - (\text{System} + \text{sample effects}) \quad (6)$$

$$= \frac{K \Delta T dt}{dT} (w/o \text{ sample}) - \frac{K \Delta T dt}{dT} (w/sample) \\ = \frac{K}{dT} (\Delta T dt)_{\text{area due to sample}} \quad (7)$$

But there are thermal effects within the sample. Through the sample itself a thermal lag occurs and the rate at which heat is received by the measuring side of the differential couple becomes highly dependent upon sample size, heating rate, and the thermal diffusivity ( $\alpha$ ) of the sample. The lag experienced is precisely why the specific heat can be measured since it is characteristic of each material.

Therefore, we must take into account, thermal effects within the sample and consider the diffusion effects by means of the following equation (10, 16, 32).

$$\frac{dT}{dt} = \frac{k}{\rho C_p} \frac{d^2T}{dx^2} \quad (8)$$

where

$\frac{dT}{dt}$  = change of temperature of sample with respect to time

$k$  = thermal conductivity of sample

$\rho$  = density of sample

$C_p$  = specific heat of sample

$\frac{d^2T}{dx^2}$  = rate of change of the temperature through the sample

The average heat capacity of the sample can now be defined by solving for  $C_p$  in Equation 8 and adding to Equation 7.

$$\bar{C}_p = K \Delta T \frac{dt}{dT} + \frac{k}{\rho} \left( \frac{d^2T}{dx^2} \right) \frac{dt}{dT} \quad (9)$$

= (sample effects) + (sample thermal diffusivity effects)

$$= \left( \rho + \frac{k}{\Delta T K} \frac{d^2T}{dx^2} \right) \Delta T dt \frac{K}{\rho dT} \quad (10)$$

Allowing for sample size Equation 10 becomes

$$\bar{C}_p = \frac{K' K (\Delta T dt)_{\text{area due to sample}}}{\rho g dT} \quad (11)$$

which describes the average specific heat of the sample.

Where

$$K' = \left( \rho + \frac{k}{K\Delta T} \frac{d^2T}{dX^2} \right) = 1.68 \text{ (experimentally determined)}$$

$g$  = sample size in grams

$\bar{C}_p$  = average specific heat of sample in cal./gram/°C.

The other terms in Equation 11 have been defined previously. The term  $k/\rho C_p$  in Equation 8 is  $\alpha$  which is a measure of the thermal inertia or diffusivity of the sample. Although the individual terms in Equation 10 comprising  $K'$  cannot be evaluated,  $K'$  itself can be.

All determinations of specific heat should be performed using the same heating rate—that is, the rate at which heat is received by the differential couple is a constant. In cases where  $dH \neq 0$ , the total heat of transformation (solving for  $dH$ ) is the area generated by the transformation (cal./gram) plus the heat due to the change in specific heat of the sample. The specific heat of the sample is generally not included because of suitable base line construction.

#### EXPERIMENTAL

**Apparatus.** The apparatus consists of a controlled pressure and controlled atmosphere differential thermal analyzer Model 12BC2, recorder-controller assembly Model JAC, and furnace platform assembly Model GS-2 manufactured by the Robert L. Stone Co. This instrumentation has been described by Stone (25, 26).

The apparatus is equipped with an L & N Spedomax G dual pen recorder and two ARA Model 4A-DC amplifiers. The highest sensitivity of the amplifiers is 0.5  $\mu$ volt/inch. Normal operating sensitivity is from 1  $\mu$ volt to 50  $\mu$ volt/inch depending upon the type of sample and the purpose of the analysis.

The sample holder and recorder system permit the recording of two thermograms simultaneously. The recorder is linear in time only and has a chart speed of 0.1 inch/minute. A separate recorder in conjunction with an L & N Series 60 linear temperature recorder-programmer is an integral part of the instrument.

The sample holder assembly, Model SH-M4CL, consists of two separate Chromel-Alumel differential thermocouples and a Chromel-Alumel furnace couple which is utilized for programming as well as recording the temperature of the furnace. A quick cool furnace, Model F-1-F, which is positioned over the sample holder by two guide pins was utilized throughout the experiments.

The differential couples are circular in shape and hold aluminum pans in which the samples are placed (see Figure 1). For demonstration purposes, only one of the differential couples has been shown. A top which fits over the Inconel sample holder

in Figure 1 is not shown. In addition, a furnace cover was placed over the furnace to render the system insensitive to room air currents.

**Thermocouple and Sample Parameters.** Since the thermocouples are relatively fixed in this type of sample holder, once the system has been balanced to provide an acceptable base line, thermal asymmetry will not be an important factor because the base line will remain reproducible.

The initial base line may be adjusted by decreasing or enlarging the size of the loop as well as by movement in a horizontal or vertical direction. A base line is then run using semispherical aluminum pans which vary in weight from 1.75 to 1.80 mg. Evaluation of this base line permits subsequent adjustment of the differential couples to provide a more horizontal base line.

The sample size required in this type of system is generally from 0.1 to 10.0 mg. depending upon whether or not the thermograms are to be used for qualitative or quantitative purposes. Obviously, the nature of the transition is an important factor since first order transitions will require generally less sample and a lower sensitivity than the determination of second order transitions.

A decided advantage of this technique is that the sample pans may be discarded after each run and replaced with new ones. Also, when polymers are run the carbonization of these materials does not contaminate the thermocouples since the sample is not in actual physical contact with the thermocouples. This system provides excellent base line stability from one run to the next.

**Calibration.** The calibrations were performed utilizing a linear programming rate of 10° C./minute and helium as the dynamic gas to prevent any oxidative effects. The instrument was calibrated, and the  $K$  values were determined by utilizing the heat of fusion of tin, 14.0 cal./gram (9). The material under study was placed in the sample container and no reference material was used.  $K$  was determined for each differential thermocouple by means of the following equations which describe the response of the system.

$$\frac{\text{Area}}{\text{gram}} = \frac{\text{Area of sample transition} \times \text{range setting of interest } (\mu\text{volt})}{\text{Sample wt. (grams)}} \quad (12)$$

$$\frac{\Delta H_f \text{ of standard (cal./gram)}}{\text{Area/gram}} = \frac{\text{Cal.}}{\text{Area}} = \frac{\text{Cal.}}{\text{mm.}^2} = K \quad (13)$$

$$\bar{C}_p = \frac{KX(\text{Area under base line w/o sample} - \text{area under base line w/sample}) \times 1.68}{g \times \rho \times dT} \quad (14)$$

The  $K$  values determined were  $2.80 \times 10^{-6}$  cal./mm.<sup>2</sup> for differential couple 1 and  $2.65 \times 10^{-6}$  cal./mm.<sup>2</sup> for differential couple 2. Various range settings of the d.c. amplifiers provided identical  $K$  values from Equations 12 and 13.

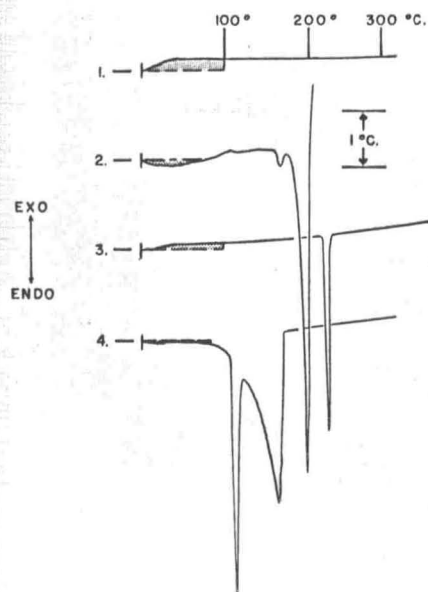


Figure 2. Thermograms showing areas used for  $C_p$  determinations

(Sensitivity, 50  $\mu$ volt/inch)

1. Thermogram of base line with empty pans
2. Thermogram of 7.55 mg. of dicyandiamide
3. Thermogram of 10.0 mg. of tin
4. Thermogram of 7.66 mg. of benzoic acid

#### Determination of Specific Heat.

To test the validity of the preceding equations governing specific heat, a base line, in duplicate, was run with empty sample pans. The area (b) encompassed between the base line and a line extended horizontally from ambient to the desired upper temperature was measured. (See Figure 2.)

The (a) area, as shown in Figure 2, was measured on a series of samples to the desired upper temperature. When a transition occurred below 100° C., only the area below this transition was usable and the same area measurement to this transition temperature must be carried out on a blank run.

Those areas above the constructed horizontal were considered positive and those areas below it negative. All measured areas due to sample effects were subtracted from the area of the blank base line. This area was then treated according to Equation 11.

From an initial run of benzoic acid, the net correction resulted in a multiplication factor of 1.68 ( $K'$ ). The equation utilized for all subsequent specific heat determinations reduced to,

The terms in Equation 14 have been defined previously.

The specific heat of a series of samples was determined. These results are shown in Table I.

**Determination of Heat of Fusion.** The variation of heating rate, sample

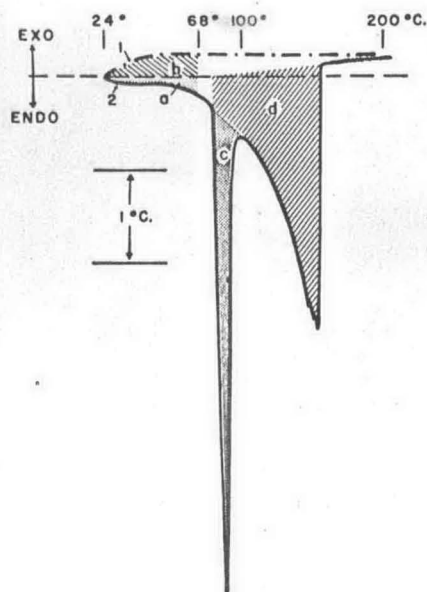


Figure 3. Thermogram of naphthalene showing areas used for  $\Delta H_f$  and  $\Delta H_v$  and  $C_p$  determinations

(Sensitivity, 50  $\mu$ volt/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  $\Delta H_f$
- d = Area due to  $\Delta H_v$

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:

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

Table I. Results of Determination of Specific Heat

Sample	Cal. 15°/gram/°C. $C_p$ , determined	Cal. 15°/gram/°C. $C_p$ , known <sup>a</sup>
<i>p</i> -Dinitrobenzene <sup>b</sup>	0.25	0.259 at 119° C.
<i>p</i> -Dinitrobenzene <sup>b</sup>	0.23	0.259 at 119° C.
2,4-Dinitrotoluene <sup>b</sup>	0.34	0.350 at 100° C.
2,4-Dinitrotoluene <sup>b</sup>	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

<sup>a</sup> All known  $C_p$  values were obtained from References 9, 13, and 14.

<sup>b</sup> 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  $\Delta H_f$  Determinations

Sample	Sample size, mg.	Heating rate	Sample state	Cal. 15°/gram determined $\Delta H_f$	Cal. 15°/gram known <sup>a</sup> $\Delta H_f$
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 <sup>b</sup>	8.80	4° C./min.	Normal	27.9	26.4
Tin	5.31	4° C./min.	Normal	13.3	14.0

<sup>a</sup> All  $\Delta H_f$  values were obtained from reference 9.

<sup>b</sup> Eastman White Label, all other reagents are c.p. grade or better.

#### 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

were averaged. Greater error was experienced for the inorganic samples examined. This may be due in part to the lower specific heat values of silver nitrate and tin in particular, or perhaps differences in the thermal conductivity of these materials as compared to organics.

Many known specific heat values are available only at certain temperatures, while all values reported in this paper are average values. Whenever possible the temperature region used for an area measurement was ambient to 100° C., which made  $dT = 76^\circ \text{C}$ . If a smaller  $dT$  must be used, due to transitions below 100° C., the area measured will be smaller and greater error will be introduced.

The specific heat was determined on 10 separate samples of naphthalene. The standard deviation at the 95% confidence level was found to be  $\pm 0.02 \text{ cal./gram/}^\circ\text{C}$ .

Sample size, heating rate, and sample state did not affect the accuracy of the heat of fusion measurement for this system. These results substantiate Vold's equations (28) and show that nearly equilibrium conditions exist for this system. The depth of the differential temperature and the width of the transition peak vary with heating rate; but the total area does not change within the error of the measurement itself for identical size samples.

These results also show that  $K$  is a constant and temperature independent over the temperature ranges investigated and that the physical shape of the samples does not affect the results within the precision of the determination. The fact that accurate  $\Delta H_f$  values were obtained for a variety of substances over extended temperature ranges shows that any one material could have been used for calibration. Tin was chosen as the calibration standard because of the comparative ease in handling this material and also for determining whether or not the calibration value could subsequently be applied to other materials which manifest transitions at widely divergent temperatures.

The theoretical discussions assume  $K_r = K_s = K$ . Although it has been shown that  $K$  is invariant, in practice it is difficult to achieve the condition that  $K_r = K_s$ ; however, it is possible, but

time consuming, to do so. This does not invalidate the theoretical treatment since  $K_r$  can be made equal to  $K_s$  by thermocouple adjustment (synthetically), or by quantitative measurement from known materials, such as tin or benzoic acid and then adjusting one by a suitable factor. However, the experimental treatment takes into account slight differences between  $K_r$  and  $K_s$  by considering the system effects and system plus sample effects, separately.

The calibration was repeated weekly to provide accurate results and establish any indeterminate instrument changes. Slight variations in  $K$  were experienced over a 7-day period. The calibration factor,  $K$ , from an easily handled material like tin, was applicable for all heats of fusion of those compounds investigated.

In addition, a value of 77.2 cal./gram for the heat of vaporization of naphthalene ( $\Delta H_v$ ) was obtained. This compares favorably with the literature value of 75.5 cal./gram. Figure 3 shows the area utilized for this measurement.

The standard deviation at the 95% confidence level for  $\Delta H_f$  and  $\Delta H_v$  of naphthalene were found to be  $\pm 1.5 \text{ cal./gram}$  and  $\pm 2.0 \text{ cal./gram}$ , respectively.

#### CONCLUSIONS

The application of this type of system permits the determination of  $\Delta H_f$  and  $\bar{C}_p$  on a variety of inorganic and organic compounds from a single calibration of an easily handled material—e.g., tin.

Although every effort must be extended to maintain a constant effect of parameters that cannot be numerically evaluated, variables such as sample size (within limits), heating rate, and sample state did not have deleterious effects upon the results.

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