

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 Speedomax 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.

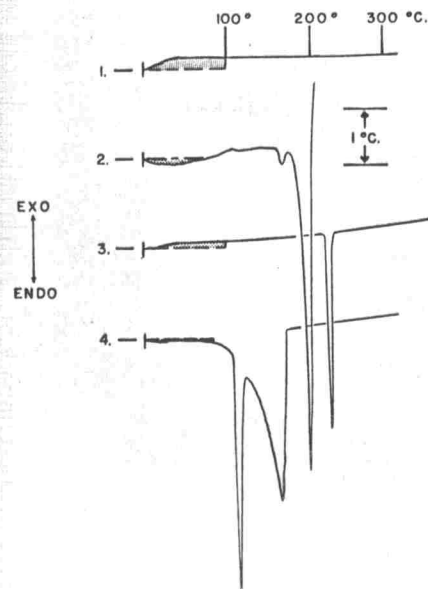


Figure 2. Thermograms showing areas used for  $C_p$  determinations

(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