

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 ± 0.02 cal./gram/°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 ΔH_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 (ΔH_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 ΔH_f and ΔH_v of naphthalene were found to be ± 1.5 cal./gram and ± 2.0 cal./gram, respectively.

CONCLUSIONS

The application of this type of system permits the determination of ΔH_f and 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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