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.

DIFFERENTIAL THERMAL ANALYSIS has been applied previously to a variety of both inorganic and organic materials. These applications were initially concerned with minerals and soils (8, 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 nonuniform 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 ΔT *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.