DIFFERENTIAL CALORIMETER BASED ON THE HEAT LEAK PRINCIPLE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a differential scanning calorimeter based on the heat leak principle, i.e., to a calorimeter which measures the heat capacity of a sample relative to an appropriate reference as the temperature of the environment surrounding the reference and the sample is scanned through a desired range.

2. Description of the Prior Art

In the past, two basic designs for scanning calorimeters have been used with successful results. These designs represent different philosophies on how to measure heat capacity as a continuous function of temperature. However, both designs depend on the fact that two materials, at the same initial temperature, will have the same final temperature after absorbing identical quantities of heat, if and only if their heat capacities are identical. Thus, when a sample and a reference material, initially at the same temperature, are both heated with the same power to increase the temperature thereof, any difference in heat capacity is expressed as a difference in temperature between the sample and the reference materials. This temperature difference is conveniently measured by a thermocouple, or several thermocouples connected in series (called a thermopile), which generates an easily measured electrical voltage, which in accordance with the Seebeck effect, is directly proportional to the temperature gradient existing across the planar surfaces of the thermopile.

In one basic differential scanning calorimeter (DSC) design, a thermal null is maintained between a reference and a sample as the environmental containing the two is temperature scanned. Generally, DSC's of this type employ electronic circuitry to supply power to a sample heater (or a separate reference heater) as necessary to prevent temperature differences between the reference and the sample. The amount of this power delivered is then directly related to the difference between the heat capacities of the sample and reference materials.

The constraints on this thermal null design are severe, both electronically and thermally. Since it is based upon the principle of maintaining an ideal adiabatic barrier between the calorimeter and the environment, an extensive adiabatic shielding arrangement is required. Furthermore, an extremely sensitive feedback heating system is required to maintain the temperature null between the reference and sample cells.

The other basic DSC design, known as the heat conduction design, dispenses with the active feedback network and simply records thermopiles voltage as a function of temperature as temperature is scanned through a specific range. Such a DSC has been described by Ross et al., Thermochimica Acta, 10 (1974) pages 143–151. While scanning calorimeters of the prior art have demonstrated considerable utility in measuring the energies of transition in solutions, they have for the most part provided only qualitative data with respect to the temperature dependent heat capacities of the samples under test. Furthermore, heat conduction calorimeters found in the prior art have to some extent suffered in sensitivity and accuracy because of thermal gradients existing within the calorimetric equipment.

In addition, the scanning calorimeters found in the prior art are generally designed to operate at only atmospheric pressure, since the introduction of pressure as a calorimetric variable potentially complicates the calorimetric calibration and corrupts the environment of the substances under test. More recently, however, applications have arisen where it is desirable to obtain calorimetric data as a function of pressure. As a result, the need for a sensitive, accurate, and reliable calorimeter which is simple to operate and yet provides calorimetric data at various pressure levels, has arisen.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide a novel differential scanning calorimeter which is simple to operate and inexpensive to construct.

Another object of this invention is to provide a novel differential scanning calorimeter for measuring the absolute heat capacity of a sample substance.

Yet another object of this invention is to provide a novel differential scanning calorimeter with improved sensitivity and accuracy.

A further object of this invention is to provide a novel differential scanning calorimeter in which sensitivity and accuracy is enhanced as a result of the minimization of thermal gradients existing within the calorimeter.

Yet another object of this invention is to provide a novel differential scanning calorimeter which provides calorimetric data as a function of pressure.

A further object of this invention is to provide a novel differential scanning calorimeter which provides calorimetric data as a function of pressure without requiring recalibration of the calorimeter at the different pressure levels.

Another object of the invention is to provide a novel differential scanning calorimeter wherein positive and negative temperature scanning rates are precisely controlled.

Another object of this invention is to provide a novel method for controlled-temperature scanning a differential scanning calorimeter.

A further object of this invention is to provide a novel method for obtaining calorimetric data as a function of pressure.

A further object of this invention is to provide a novel method for deriving the absolute heat capacity of a substance as a function of temperature.

These and other objects of the present invention are achieved by providing a novel differential scanning calorimeter having a reference measuring cell and a sample measuring cell symmetrically seated within a copper heat sink. Each measuring cell includes a cylindrical stainless steel ampoule which contains a test substance, an aluminum cell frame which supports the ampoule, and a pair of thermopiles which are placed between the aluminum cell frame and the copper heat sink and which measure the temperature difference between the two. The aluminum cell frame is honeycombed to reduce the heat capacity thereof, thereby improving system sensitivity.

The copper heat sink which has end plates connected to conical end sections flanking a middle section is surrounded by a cylindrically copper isothermal shield. A plurality of resistive heating elements are applied to the end plates and conical end sections of the heat sink and the isothermal shield. Each heating element has a resistance proportional to the heat capacity of a respective end plate, conical end middle section or shield, and are