Thermochimica Acta, 26 (1978) 27–37

NEW SETARAM CALVET DIFFERENTIAL SCANNING CALORIMETER*

ROSS T. MARANO
MARCHE Instruments, Inc., 1009 Southwood Drive, Waco, Texas 76710 (U.S.A.)

ABSTRACT

The new SETARAM Calvet DSC is the most recent of a long line of Calvet-type calorimeters manufactured over the past twenty years. It weds the classical Calvet theory detector with the most modern in digital microprocessor electronics.

The major features of the new SETARAM Calvet DSC are increased temperature range from −123 to 827°C, increased sample size up to 0.4 cc, scanning rates from 1°C h^{-1} to 30°C min^{-1}, sensitivity from 0.05 μW mm^{-3}, stepwise scanning for specific heat and purity measurements, horizontal or vertical operation of calorimeter detector, and operation at pressures up to 100 atm or more.

INTRODUCTION

The following is a description of a new DSC based on the Calvet heat-flow principal which has been designed and fabricated by SETARAM of Lyon, France. This paper will also describe the many new areas that this design opens up.

For many years, several rapid thermal analysis instruments have been available. These units have been differential scanning calorimeters based either on power compensation or instruments for exact differential thermal analysis. These instruments have been utilized in numerous areas, in particular the study and quality control of polymers or their components; to study the structure of solids and their changes of state; to study phase diagrams; purity control, etc. The value of this type of instrument is universally recognized, but it is apparent to many in the field of thermal analysis that these instruments do not encompass the total applications field for thermal analysis, due to two deficiencies which they share either alone or in combination. These deficiencies are (a) the thermal sensing units, either temperature sensing units or power compensating units, are too much of a point source detector and poorly encase the sample under investigation. (b) Contact between the sample and its environment is ill-defined and is therefore a function of secondary factors such as sample size and placement, type of holder, nature of gas present, temperature of interest, etc. In certain cases, this difficulty is accentuated by the manner in which the

---

* Presented at the 7th North American Thermal Analysis Society Conference, St. Louis, Missouri, September 25–28, 1977.

active parts of the system, the sample and the thermosensing units, are placed, following its own temperature, completely independent of the temperature of the surrounding block. Thus the primary thermal exchanges are difficult to control or to make symmetrical.

The point source detector, poor control of the thermal contact and the very small sample size usually utilized, practically prohibit the establishment of "connections" between the sample and the outside. In reality, the accuracy of the measurement is only satisfactory if one wishes to study an isolated sample, placed on the thermal detectors and most frequently held stationary in a sealed crucible (Fig. 1).

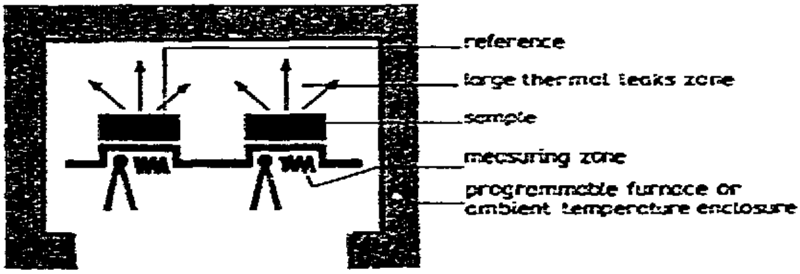


Fig. 1. Schematic of the point source detector.

In contrast to the foregoing, the practice SETARAM has used for many years in the heat-flow calorimeter based on the design of E. Calvet, has shown that experiments with "open" systems connected to the exterior are possible and compatible with very exact measurements.

The new SETARAM design provides for

(a) a thermostated block completely enveloping the experimental zone and the sensitive detectors; this block imposes an exact temperature to the system under study.

(b) a detector within the interior of the block and, at the same time, largely enveloping the experimental zone where the sample is placed. The detector thus controls the total heat exchange between the sample and the environment formed by the gas tight thermostat.

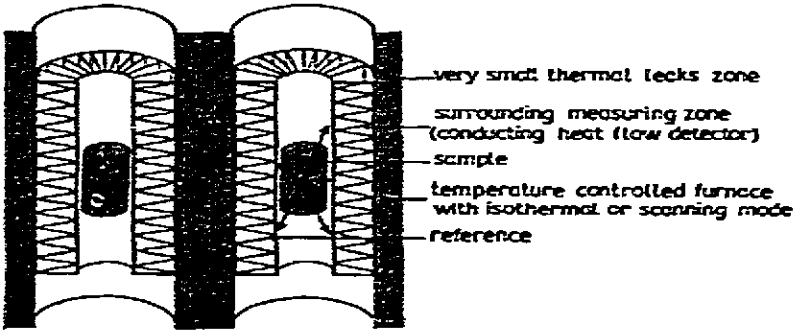


Fig. 2. Schematic of the heat-flow detector.

One can thus see that the calorimeter — this name is truly justified due to its intrinsic measuring performance — is able to utilize independently an isolated sample like those previously described or, as part of a "system" in the true chemical sense, a system opened or closed and easily modified from the exterior during the experiment (Fig. 2).

The construction of a miniature heat-flow calorimeter represents a major technical advance which gives high sensitivity, great accuracy, and variable operating conditions including indifference to studying open or closed systems, i.e. thermal analysis performed hand-in-hand with thermo chemistry.

DESCRIPTION

The new SETARAM DSC is shown in Fig. 3. The calorimeter itself is contained in a rectangular box attached to the movable arm on the work station. The outer rectangular box is closed; access to the active zone of the calorimeter is made by two conduits that traverse the calorimeter from end to end: one can see on the left side of the figure the holes which lead to these conduits.

Because of its movable arm, the calorimeter may be used horizontally, as shown, or vertically, supported by the arm to which it is attached and through which the fluids flow and the signal wire is carried. Sufficient space is supplied under the calorimeter for placement of auxiliary equipment, for example, to introduce or remove samples. The choice of calorimeter disposition is a novel operating convenience.

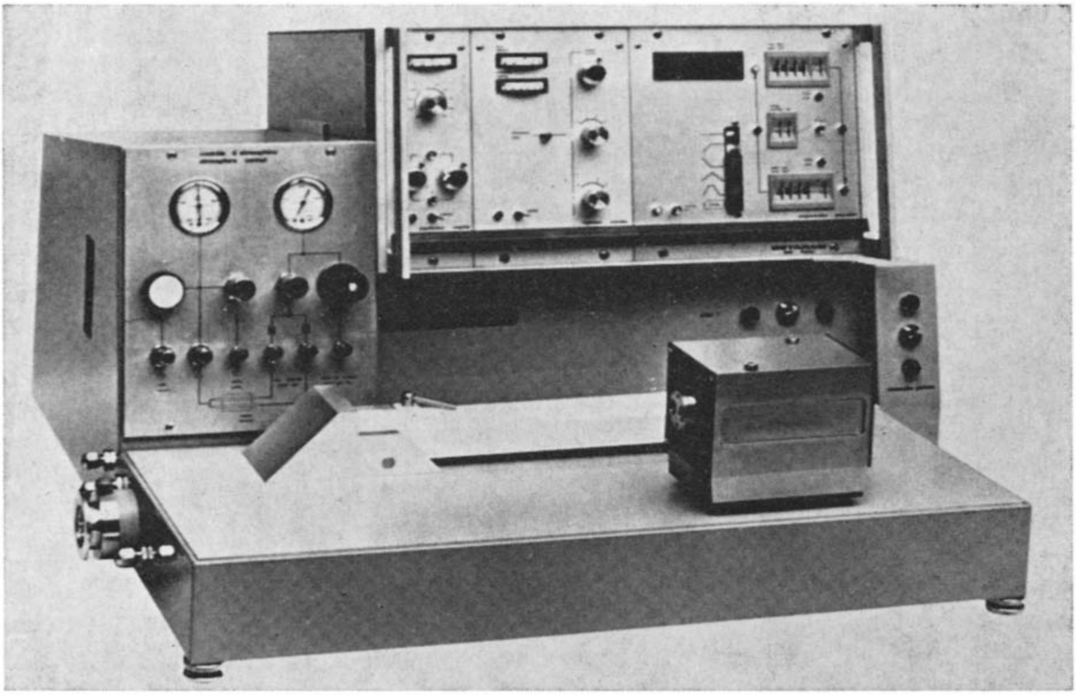


Fig. 3. SETARAM DSC.

At the rear of the work table, one finds the digital electronic temperature programmer and regulator, and the calorimetric signal amplifier. At the left is placed a gas supply system utilized to control the atmosphere within the calorimeter, i.e. vacuum, inert or reactive gas atmosphere at controlled flow and pressure. This gas control system utilizes external systems to aid in its function.

The electronic temperature programmer is especially well designed: entirely digital microprocessor controlled and has excellent precision and large useful range due to its varied programming. A new original programming mode allows one to conduct rapid measurement of the specific heat of samples.

Figure 4 is a schematic drawing of the calorimeter's internals. The vapor tight resistance heated block occupies the major portion of the calorimeter. The enclosed space is almost totally useful as a sample holder. The block is enveloped by a vapor tight jacket held at ambient temperature by a small flow of water. For sub-ambient operation, a cryogenic fluid is circulated in a special system surrounding the block. One sample cell which traverses the calorimeter and gives access to the useful zone is shown. One can see that the tube is completely open, permitting sample introduction or allowing passage of the sample and is free to allow the passage of gas through the sample. These tubes are both cylindrical.

This is only a partial figure. There are two identical tubes placed side by side,

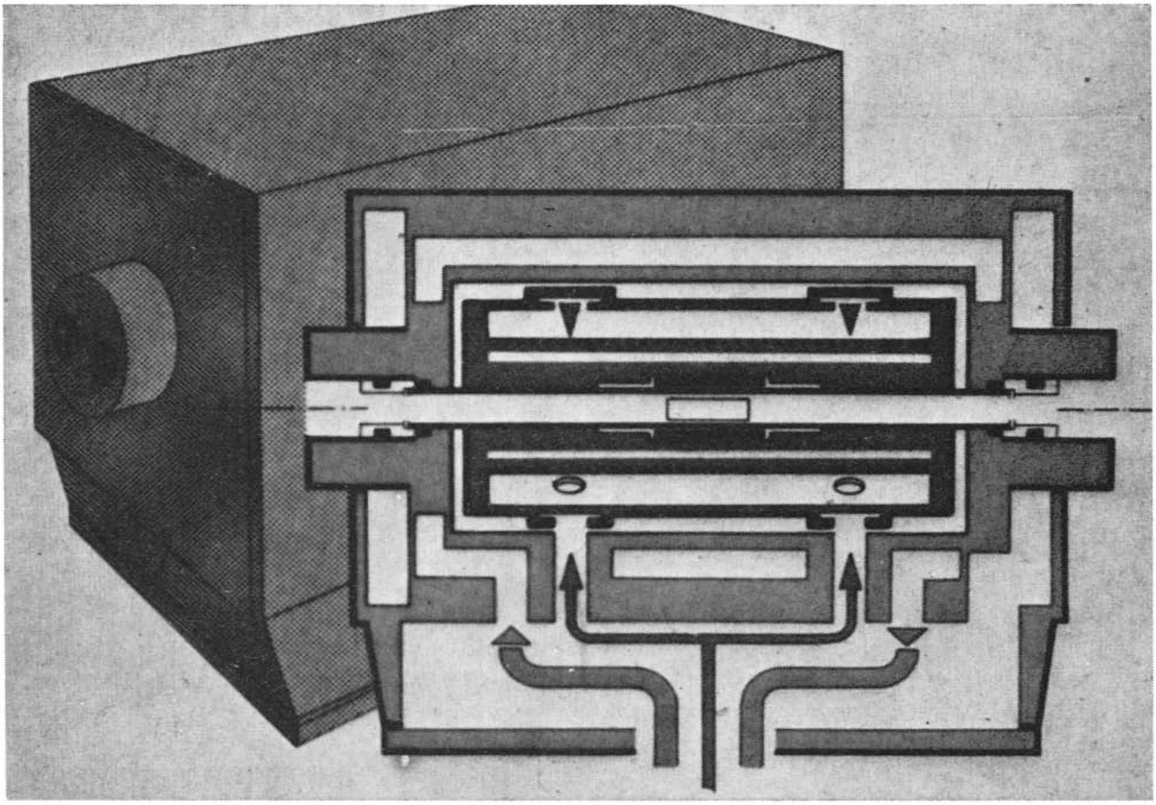


Fig. 4. Schematic of the calorimeter.

one holding the sample as indicated by the small rectangle in the center of the tube, and the other holding an inert reference material. The output signal is the differential signal from the detector with the sample opposed to the signal from the detector with the reference material. The detectors are collections of thermocouple conductors radially fixed in the middle zone of the thermostated block around the tubes forming the experimental area. The detectors extend beyond the experimental zone and are tightly bound to their tubes in such a manner that the lateral heat exchanges are suitably specific and total such that any thermal transformation in the sample is exactly shown. It is this total envelopment which gives the instrument its precise calorimetric quality.

Increased sensitivity is easily obtained by the large number of thermoelectric elements forming the enveloping heat flux detectors. It is necessary to say at this point that the dimensions chosen (7 mm useful diameter and 10 mm useful length) allow for the utilization of samples much longer than those used in the usual micro sample operations. It follows that the "specific" sensitivity, that is to say sensitivity reduced to the same "unit" quantity of sample, reached with this unit is unequalled when considering a completely filled cell.

Measurement stability is a function of the excellent thermal homogenity obtained in the large thermostated block. Due to this stability, and the high calorimetric sensitivity, the calorimeter lends itself not only to the small energies observed in isothermal operation, or to those thermal effects developing during pseudo-isothermal (very slow temperature programming) conditions, but also to those thermal effects developing during rapid programming. This property is very important in order to allow one to study any system exactly. During such a study, it is necessary to maintain its thermodynamic equilibrium state precisely for as more research is done on equilibrium, less deviation will be allowed in the control parameters (temperature, pressure, etc.). One also needs high stability at slow heating rates. The SETARAM digital programmer has such a high stability that rates as low as 1 °C h^{-1} have excellent precision.

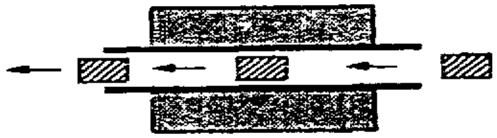
The SETARAM design allows one to introduce samples directly into the detector during the experimental process or during the course of a particular measurement. It also allows the use of open or closed crucibles.

OPEN SYSTEM

At this point, it is important to discuss the term "open" calorimeter. There are two principle aspects in effect.

(a) "*Mechanically*" *open*, that is to say that the operator has access to the detector area during the course of a calorimetric experiment as shown in Figs. 5 and 6. In Fig. 5, the sample is instantaneously positioned by simply sliding it along the tube. It may be removed just as easily and, in fact, can pass directly through the detector. It is useful for isothermal treatment or automatic transfer of samples. In Fig. 6, the calorimeter is vertical and sample introduction can be accomplished by gravity feed.

It is used, for example, during rapid exit and tempering of a sample after treatment in the calorimeter, or as a drop calorimeter in which one phase is placed in the calorimeter and a small sample is dropped into it in order to measure heats of mixing or dissolution etc.



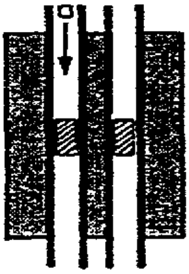


Fig. 5. Schematic of the "mechanically" open calorimeter.

Fig. 6. Schematic of the gravity sample feed.

Fig. 7. Schematic of the "chemically" open calorimeter.

Accessory measuring systems may be attached in the vertical mode for additional information on samples, i.e. TG, dilatometer, and is limited only by the researchers resourcefulness.

(b) *Chemically open*, used essentially to control the gas phase. In Fig. 7, simple control of the gas phase is immediate. One can also work under inert atmosphere by flowing gas in one end while the other is left open. At this point, it is necessary to note that the sensitivity is unaffected by the type of gas utilized.

A more fundamental method of use with a small dead space, allows one to work with a flowing gas and the calorimeter insensitive to the nature of the gas used, permitting one to study thermal decompositions. Furthermore, the calorimeter may be attached to a gas analyzer such as a gas chromatograph, a mass spectrograph or both (Fig. 8).

The calorimeter as easily adapted to function as a solid–gas reactor, the sample normally being a reactive solid, with a small continuous gas flow. The temperature is either fixed or scanning for kinetic studies. One can also program the gas composition or make additions of a reactive gas to a carrier gas, oxidation reactions by small additions of oxygen to argon or helium.

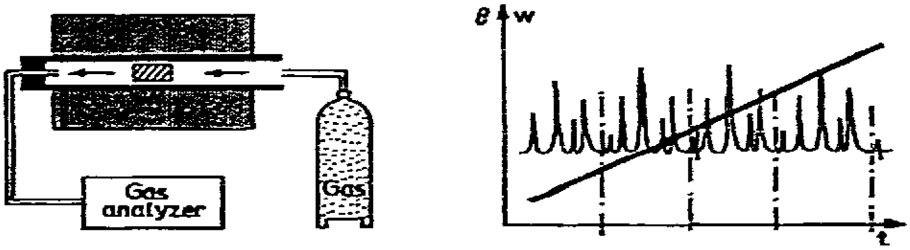


Fig. 8. Schematic of the calorimeter and gas analyzer.

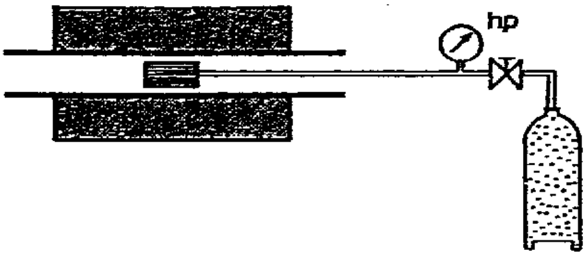


Fig. 9. Schematic of the high pressure system.

One very interesting use is that for heterogenous catalysis. The sample placed in the calorimeter is the catalyst. As before, the reactive gas is introduced in a continuous fashion, but the temperature and/or the pressure is controlled, which in turn changes the reaction kinetics, or the respective concentration of one to the other modifies the equilibrium. If one wishes, one can also introduce one of the reactants in a slug form while the other flows in a continuous mode. The ease of temperature control allows one to study systems under slowly variable temperature or via stepwise scanning: at each temperature, a series of studies changing composition or flow can thus be made very rapidly.

One special possibility, half way between the "mechanically" open and "chemically" open is the DSC study under controlled high pressure, up to 100 bars or more (Fig. 9). A high pressure cell is placed in the calorimeter. The cell is connected by a metal capillary connector to a continuous pressure source (gas or liquid). The fundamental difference from the simple gas-tight cell is that the pressure is controlled by the operator and is independent of the vapor pressure of the sample.

EXAMPLES OF THE DSC OPERATION AND APPLICATION

Fusion of tin

Figure 10 was obtained from the fusion of 51.4 mg of tin with a heating rate of 2 K min^{-1}. One observes the classical triangular form followed by an exponential return to equilibrium, corresponding to transformation effected at constant temperature.

The return to "base line" is excellent and allows utilization of this fusion as an internal method of standardizing the calorimeter, concurrent with the available Joule effect system.

Figure 11 was obtained by heating poly(methyl methacrylate) from 313.9 to 443.2 K (40 to 170°C). The calorimeter is loaded with two crucibles, one empty and the other containing the sample. When the run is started, with programmed temperature, an initial baseline deviation is observed which is proportional to the specific heat of the sample. At the end of the program, a return to the base line is observed whose deviation is proportional to the final specific heat. One can calculate the amount of variation in the specific heat between these two extreme values as

$C_p\,(313.9) = 0.391\ \text{cal g}^{-1}\ \text{K}^{-1}$

$C_p\,(443.2) = 0.553\ \text{cal g}^{-1}\ \text{K}^{-1}$

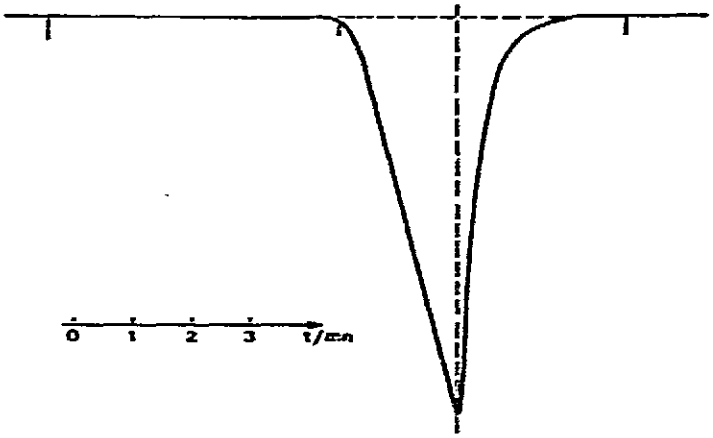


Fig. 10. Fusion of tin. Sample weight 51.4 mg; scanning rate 2 K min^{-1}; inert atmosphere; open crucible; time to regain equilibrium 20 sec.

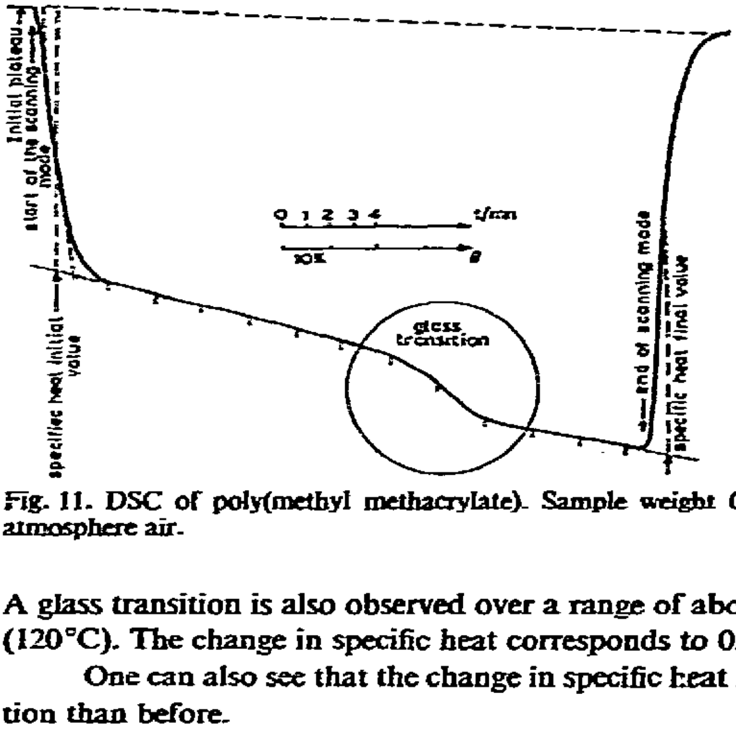


Fig. 11. DSC of poly(methyl methacrylate). Sample weight 0.215 g; scanning rate 5 K min^{-1}; atmosphere air.

A glass transition is also observed over a range of about 20 K central around 393 K (120°C). The change in specific heat corresponds to 0.069 cal g^{-1} K^{-1}.

One can also see that the change in specific heat is greater after the glass transition than before.

"*Rilsan*" *transformation* (Fig. 12)

This is the comparison of three industrial products with different densities. One can see that the sample with the highest density (2) has a transformation temperature much lower, but with a heat absorption considerably higher, than the samples of lower densities (1 and 3).

A comparison of samples 2 and 3 shows that the "doped" sample transforms at a higher temperature than the "undoped" sample (approx. 120°C), with almost

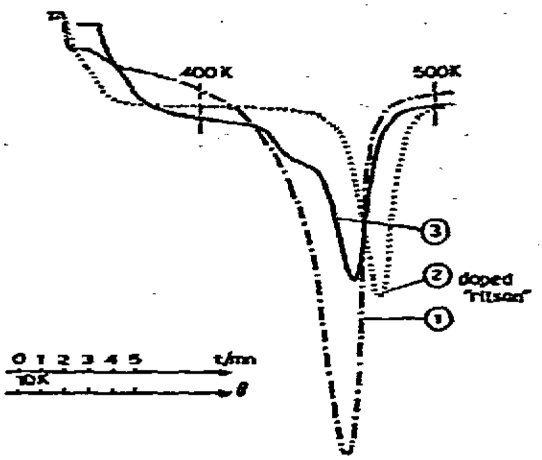


Fig. 12. "Rilsan" transformation. Sample 1, density 1.38 g cm^3; weight 73.3 mg; Q_m 37.9 cal g^{-1}. Sample 2, density 1.01 g cm^3; weight 466.7 mg; Q_m 13.0 cal g^{-1}. Sample 3, density 0.99 g cm^3; weight 67.3 mg; Q_m 16.5 cal g^{-1}.

the same absorption of heat. The respective heats of polymerization are 37.9, 13.0, and 16.5 cal. g^{-1} K^{-1}.

Polycondensation of a phenolic resin and a furanic resin

Figure 13 represents two recordings of two different types of resin which have completely different profiles.

This study shows the ease with which the calorimeter can indicate particular characteristics of the products being investigated. In this study, welded cylindrical crucibles were used. This system allows an excellent operation in spite of the high pressure developed by the water in the sample. (Saturation Pressure at 525 K = 40 bars.)

As in the other determinations, curves 1 and 2 in this study were made without a reference material. When the unit is started, an endothermic signal is generated

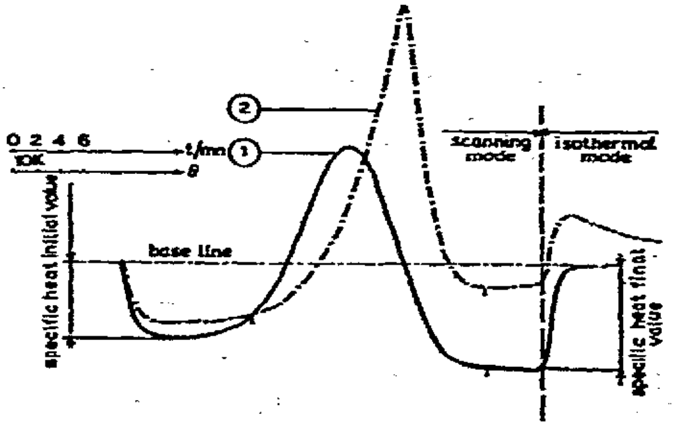


Fig. 13. High pressure polycondensation of 1, a phenolic resin (69.6 mg) and 2, a furanic resin (57.2 mg). Scanning rate 5 K min^{-1}.

which is proportional to the specific heat of the sample. On curve 1, one observes, after the initial deviation from base line, a large exothermic peak corresponding to the polycondensation. The signal that returns to a new value which is stable and lower than the previous base line. This new value corresponds to the new specific heat value. When the experiment is ended, the signal returns to the original base line. In the case of sample 2, the general outline of the curve is the same except that the polycondensation peak is different in profile indicating a rapid acceleration of the reaction and a rapid end point when reactants are consumed. One can also see that a new base line is established that is only slightly below the original, which leads one to believe it has only a small specific heat change. When the scan is stopped, the base line adjusts to a point higher than the original. This is most probably due, not to a change in specific heat but to isothermal degradation of the formed product.

Isothermal polymerization of styrene at 140°C (Fig. 14)

This experiment also indicates the ease and versatility of the new DSC. In this experiment, the monomer was placed in the same cells as in the previous example, i.e. a closed "high pressure"-type crucible, while the calorimeter was stabilized at 140°C. Simultaneously, both an empty and a filled crucible were introduced into the calorimeter. This was instantaneously accomplished and without perturbing the calorimeter.

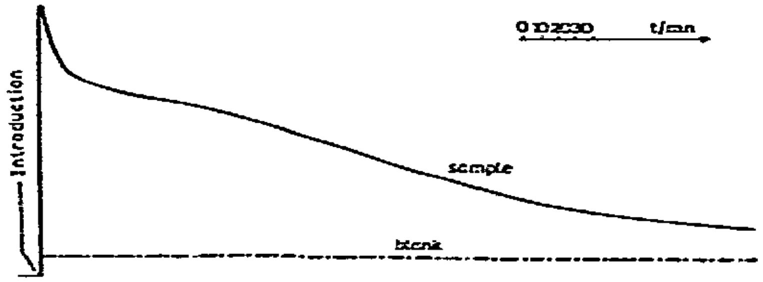


Fig. 14. Isothermal polymerization of styrene. 140°C, 106 mg.

In this example, the transitory range is very short. The reaction begins very rapidly and then continues for several hours with decreasing energy. If one superimposes a "blank" run of an empty crucible on the DSC curve, one can see the exact stability of the calorimeter. The energy measured has been calculated at 16.4 cal g^{-1}.

Glass transition and heat of recrystallization of a Cd Ge 0.5 Sb 0.5 glass

Grouped together in Fig. 15 are three different scans obtained under different conditions. Curves 1 and 2 show the exothermic heat of recrystallization and the accompanying change in specific heat.

Curve 1 was performed using 10.7 mg of sample. Curve 2 was obtained at maximum instrument sensitivity and used only 1.56 mg of sample. It is important to note the smallness of this sample compared with the total capacity of the calorimeter which holds 500 mg or approximately 300 times larger than the sample used. In-

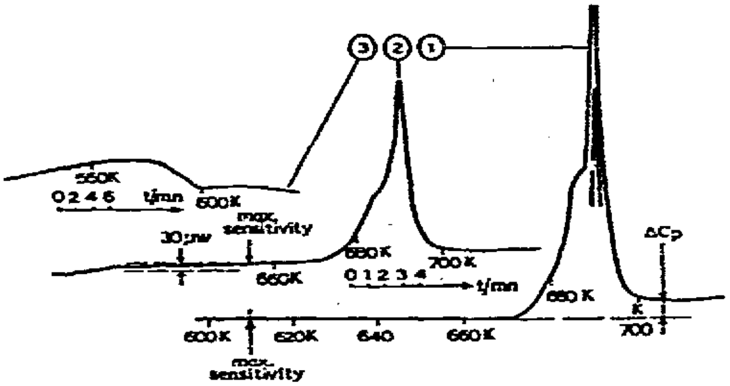


Fig. 15. Glass transition and heat of recrystallization of Cd Ge 0.5 Sb 0.5 glass.

dicated on the curve is an interval corresponding to the detector value at a nominal 30 μW. One can see the stable quality of the calorimeter over an interval of 50°C which still permits one to show the change in heat capacity on such a small sample.

Curve (3) represents the glass transition observed between 540 K and 600 K on 28.1 mg of sample. The change in specific heat corresponds to 0.106 cal g^{-1} K^{-1}.