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TECHNIQUES FOR IMPROVING THE PERFORMANCE OF THE PERKIN–ELMER SCANNING CALORIMETER*

EDWARD M. BARRALL, II AND BARBARA DAWSON
IBM Research Laboratory, San José, California (U.S.A.)
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ABSTRACT

The Perkin–Elmer DSC-1B differential scanning calorimeter is now a relatively standard laboratory instrument. Although reasonably well designed, it is possible to improve the operation significantly with a few simple modifications. The most major of these is thermostating the cell compartment. Using a dry nitrogen atmosphere outside as well as inside the thermostated cell greatly reduces noise and decreases drift. Sub-ambient operation under these conditions becomes relatively simple. The baseline drift becomes very reproducible—a significant aid in heat capacity measurement. Simple electronic modifications in the control potentiometers also bring about significant improvements. Directions with drawings and sample runs contrasting operation are given for the optimization of this instrument.

INTRODUCTION

Differential scanning calorimetry (DSC) is an outgrowth of the general improvement in dynamic thermal techniques experienced during the past decade. By using platinum resistance thermometers as temperature sensors and individual sample and reference heaters a close approach has been made to the more classical technique of adiabatic calorimetry. The operation of the apparatus and its theory were adequately described prior to the commercialization of the apparatus[1].

The instruments, Perkin–Elmer DSC-1 and DSC-1B have found broad application throughout the world. It is possible that no one specific instrument for calorimetric measurement has found broader currency than this particular instrument. However, with application the equipment has been found to have several inherent problems which in extreme cases can lead to results of questionable accuracy. This paper will describe techniques developed in this laboratory for removing some of the more troublesome problems encountered in temperature and endothermal transition measurements.

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EXPERIMENTAL

Instrumentation

The equipment used in this study is a standard Perkin–Elmer DSC-1B attached to a Servowriter recorder. The equipment was purchased as a package along with a Cahn microbalance in 1969. Although the DSC is now connected to an IBM System 7 data acquisition system, the points to be discussed here shall apply in any case. The samples and standards employed were semiconductor grade metals (99.999%) and optical grade sapphire blanks.

Electronic modifications to the instrument

A steady, non-shifting baseline is the foundation of all differential and absolute techniques. Vibration sensitivity is a serious problem in some examples of the DSC-1 and DSC-1B. In our particular instrument the temperature average (R801, Fig. 1*) and differential potentiometers (R802) were found to be both vibration sensitive and too coarse. Both were replaced with two (each) Beckman precision ten-turn helical potentiometers of the same value wired in series. As it later developed, a fixed resistor plus the precision helical potentiometer on each circuit would have been adequate. Low noise solder was used throughout.

The replacement of the coarse helical potentiometers conferred two significant improvements: the instrument became essentially vibration insensitive and it became possible to exactly reset individual cell requirements, thus reproducing the calibration to ±0.08 K. Being able to exactly reset these two controls makes it possible to use several DSC cell heads interchangeably without recalibrating.

The high and low range switch (S4, Fig. 1), located on the back of the DSC-1B is both inconvenient to use and a source of electrical noise and drift. This switch was replaced with a silver contact, twelve position, three sector, ceramic element switch. The switch was mounted in an aluminum sub-assembly box. The whole assembly was brought around to the front of the machine through a ten conductor steel shielded cable. Care must be taken in soldering with low noise solder and completely grounding the cable shield. The authors used several switches before a satisfactory system was found. The reproducible contact resistance obtained with a silver/ceramic switch made it unnecessary to recalibrate each time the switch was moved for maximum temperature precision. This had been necessary in the past.

The mechanical chopper system used both to chop the d.c. signals prior to amplification as well as to determine the reading function of the amplifiers and controls is prone to degradation. Mechanical chopping was the best that the state of the art could offer when the DSC-1B was introduced. The newer DSC-2 has a potentially much more reliable solid state chopper. At present, little can be done to improve the mechanical chopper. However, it is essential that the wave forms be

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*Due to technical problems Fig. 1 (Schematic diagram of the Perkin–Elmer DSC-1B electronics showing alterations to decrease mechanical noise) was impossible to include, but it will be gladly furnished by the authors upon application.

checked at the test points with a small oscilloscope. As the chopper ages the phasing of the critical T average and T differential signals can change. This alters the whole electrical system which results in a shift of the calibration curve for temperature and the calorie calibration factor. In extreme cases the shape of the endotherm is altered. The authors have replaced choppers after two weeks and two years. The performance is highly individual. A weekly check is recommended. Replacement is the only solution to erratic operation. Malfunction is indicated by the appearance of signals other than a true square wave—spikes, rounded edges, irregular intervals, lack of positive or negative side of the wave. The test points are described by the manufacturer on page 50 of the instruction manual.

It is absolutely necessary to use stabilized voltage for the DSC-1 and DSC-1B. The internal reference voltage is drawn from the mains. It is not uncommon to experience a 20 V swing in the building power depending on the season of the year and time of day. This swing will be registered as a displacement in the temperature calibration curve.

Cell isolation and thermostating

The DSC, in common with other calorimeters, is coupled to its environment. Goldberg and Prosen have recently commented on this coupling from a general viewpoint[2]. Rogers and Morris have used this external coupling effect to measure thermal emissivity with a DSC-1B[3]. External coupling makes itself felt in the DSC record in the slope of the program baseline and the location on the y-axis of the beginning and ending levels of the program. Operation with the usual room temperature cap for several hours will usually show some baseline drift as the cap warms up

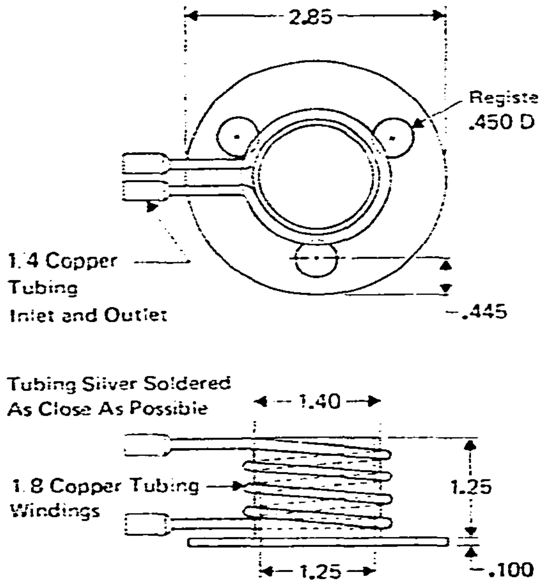
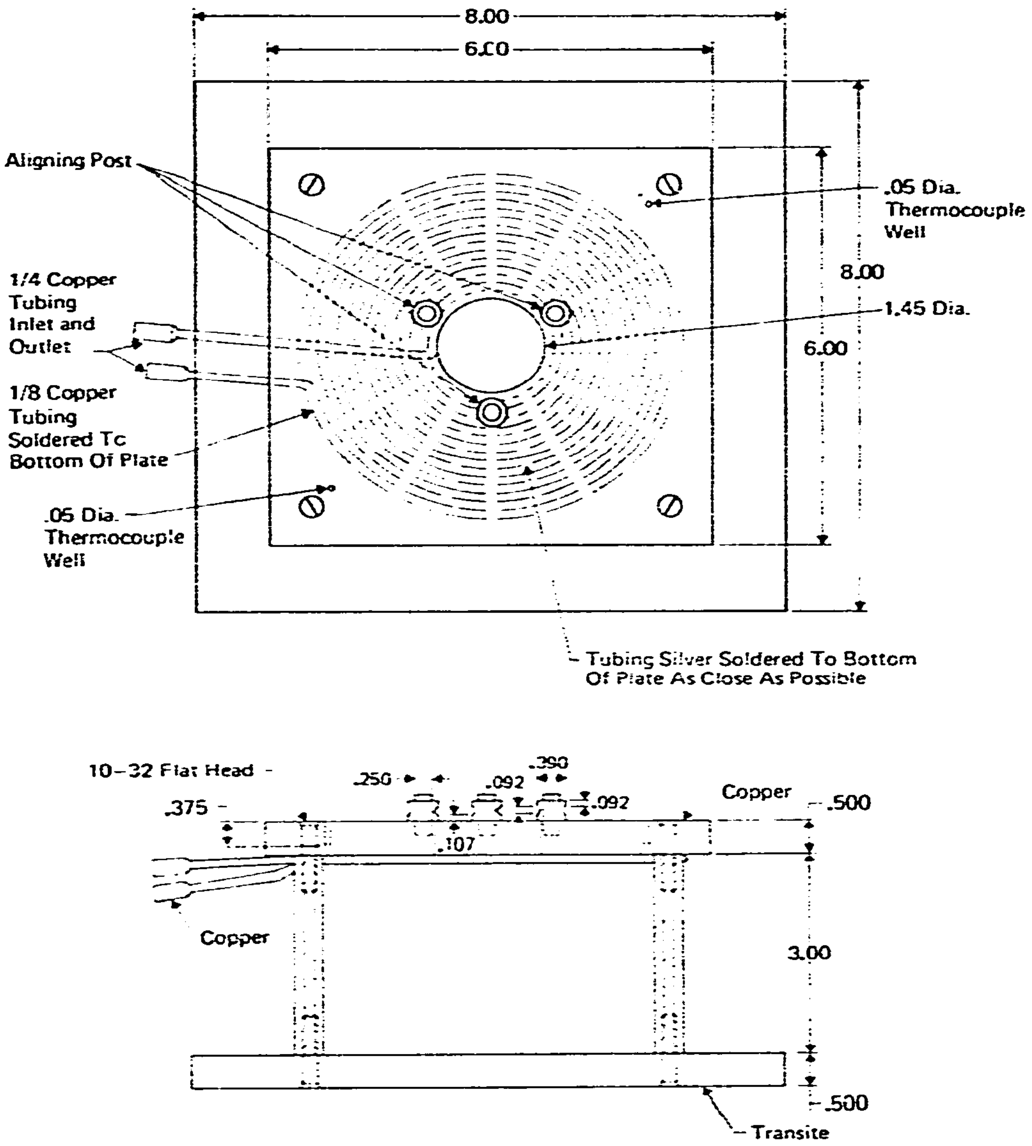


Fig. 2A.



2B

Fig. 2A and B. Thermostated cell isolation cap and platform.

with respect to the sample and reference cells. It is very important in any system of calorimetry to keep the coupling factor either constant or changing in some uniform and reproducible rate. Isolation of the cell in a controlled and thermostated environment is the simplest and most direct answer to this problem.

Isolation is easily effected by construction of an extension cord for the cell. This consists of a nine-pin ceramic miniature tube socket, a nine-pin tube plug and a ten-wire shielded cable. Leads are soldered with a minimum of flux and low noise solder. After cleaning all soldered areas the exposed metal areas are potted with RTV silicone rubber potting compound. With such an extension the calorimeter cell may be placed in any convenient location where a stable thermal and atmospheric environment can be obtained. A copper thermostat housing was constructed to hold the cell. The details are shown in Figs. 2A and B. This jacket is thermostated with silicone fluid circulated in a Lauda WB/20R thermostatic bath. The thermostated cell is placed in a plastic nitrogen dry box along with the microbalance, samples and encapsulation equipment. This treatment prevents the condensation of water during sub-ambient work as well as furnishing a good inert atmosphere.

Variations in humidity can significantly alter the resistance and leakage of current in the cell, plug and lines. Since resistance change is the measured quantity, it is important to assure that all electrical components are exposed to a relatively uniform humidity. Between the dry box and the use of silicone potting agents this condition may be fulfilled.

Sample encapsulation

Good thermal contact between the sample pan and the sample are essential. As shown previously, every effort must be made to reduce the thermal resistance of the system[4]. The sample must be immobilized so that displacement does not occur during melting or freezing. Most organic materials have finite vapor pressures near and above the melting point. It is essential that no vapor be lost. All of the above conditions may be satisfied by using the volatile sample incapsulation with a metal plate insert as shown in Fig. 3 (ref. 5). In practice, the degassed sample is weighed into the bottom of the sealer, the insert pressed firmly down on the sample and the lid cold welded in position. All of the above operations are done under nitrogen. Given reasonable stability the sample can be scanned a number of times with only its physical properties affecting the thermogram. It is essential that the sample encapsulation be placed reproducibly on the cell if accurate temperature measurements are required. This is necessary since the thermal resistance of the system has a first order effect on the location and shape of the endotherm. The authors have found that the most reproducible place to locate the sample is in the center of the cell with none of the edges touching the walls of the cell[5]. Careful positioning of the cell covers and the thermostat lid are required in order to avoid jarring the encapsulation out of place.

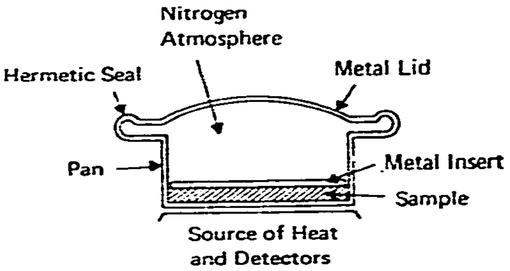


Fig. 3. Sample encapsulation.

RESULTS

The isolation of the cell and the stabilization of the thermal environment at 0°C produced the greatest effect in the sub-ambient and room temperature ranges, see Fig. 4. The upward baseline drift was greatly reduced for the melting of gallium when the thermostated cap was used. In addition, the melting temperature was moved downwards by 3°C. This is an indication of the absolute effect of the external environment on the accuracy of the temperature measurement. The melting of indium, Fig. 5, is less effected by thermostating. The baseline drift is some better. The authors are unable to account for the 1.4°C increment in melting temperature with the thermostat. However, in ten runs the variation in melting temperature with thermostating was ±0.12°C. Whereas the melting temperature without thermostating showed a variation of ±2°C. It is obvious that for each isothermal range the thermostat is to operate a temperature calibration must be constructed. The present workers have chosen −40, 0 and 80°C as convenient ranges with the 0°C range most frequently used.

Drifting baselines and irreproducible power differentials cause the most trouble in the measurement of heat capacity with the DSC-1B. The usual technique of running the empty pan, sapphire standard plus pan and sample plus pan requires that all instrumental parameters be reproducible at least three times. Any departure from reproducibility will be counted as a change in heat capacity of the sample.

The heat capacity of one sapphire standard was compared to that of a similar sapphire standard which weighed half again as much as the first standard. The results of this comparison, thermostated and unthermostated, are shown in terms of percent

TABLE 1

HEAT CAPACITY RUNS ON SAPPHIRE 30°C INCREMENTS

Temp. (K)	*Percent error*							
	Without thermostat				*With thermostat*			
	Run 1	*Run 2*	*Run 3*	*Run 4*	*Run 1*	*Run 2*	*Run 3*	*Run 4*
325	1.85	4.71	2.41	1.81	3.29	2.81	0.09	0.32
330	3.50	4.49	3.19	3.14	2.88	2.93	0.51	0.89
340	5.25	5.03	5.80	5.28	4.92	2.52	1.58	0.78
350	6.70	7.18	7.77	7.33	3.05	0.70	2.97	0.31
360	2.83	4.74	2.61	1.69	0.19	0.89	1.04	0.061
370	3.79	4.99	3.79	4.05	1.76	2.03	0.035	0.53
380	4.64	4.21	5.44	4.64	2.35	2.72	2.43	0.70
390	5.82	4.73	5.02	7.54	0.10	0.0097	0.14	0.42
400	7.13	5.17	5.78	7.73	0.40	0.70	0.17	0.23
410	6.80	7.28	6.59	8.25	1.43	0.20	0.14	0.65
	Average							
	4.82	5.25	4.84	5.15	2.04	1.55	0.91	0.49

error between measured and calculated heat capacity of the larger standard in Table 1. The results obtained with the thermostat cap are remarkably good. At worst the error is half the unthermostated value and at best it is one tenth as much. The decrease in error with successive runs under the thermostat is thought to be due to the removal of water from the system with successive runs. The effect is not noticeable in the unthermostated runs since baseline drift overpowers the small drift due to loss of water.

From a simple calculation involving the statistics of three runs (pan, standard, sample) at least a 200-fold reduction in baseline random drift would be required to produce the reduced error figures given in Table 1. From the melting studies it is probable that this reduction will be larger near room temperature and smaller further away from room temperature. However, it is obvious that thermostating does have a real effect.

In all thermal measurements with the DSC-1B it is necessary to reduce the internal resistance of the system to heat flow between the sample and the heater-temperature sensor. This thermal lag causes the sample to follow behind the heating program by some fixed amount and has been described in detail[3,6]. The net result of the thermal lag is not inherently harmful to the thermogram while the sample is

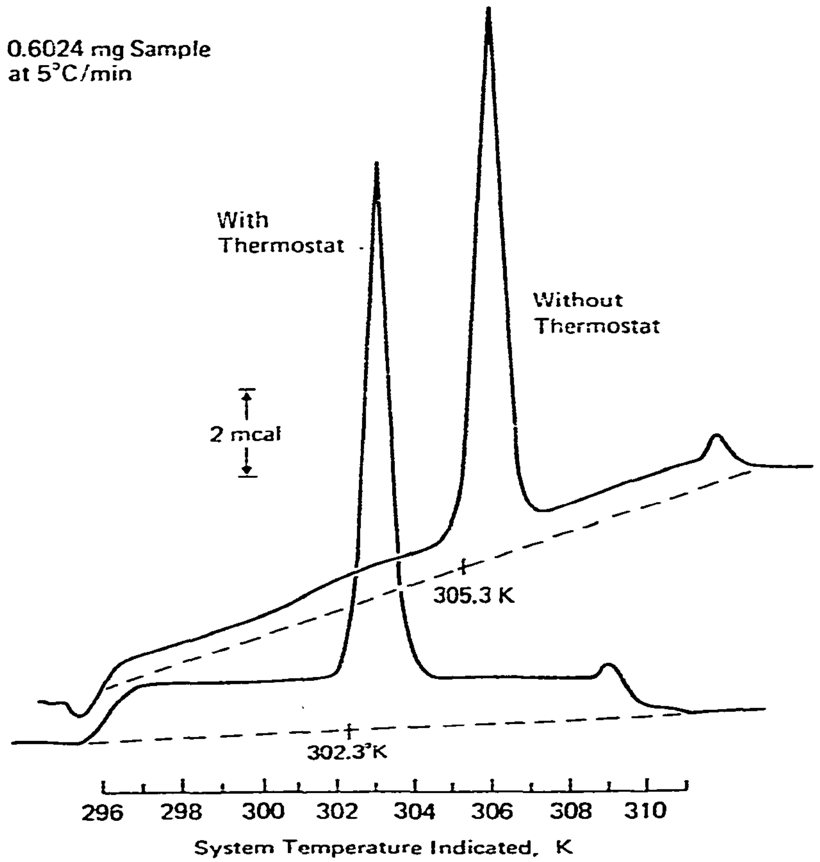


Fig. 4. Thermograms of gallium with and without thermostating.

undergoing linear heating or cooling. However, if some isothermal event occurs in the sample the amount of lag is proportional to an instrument constant multiplied by the magnitude of the event. Should the lag become very large it is impossible for a nulling instrument such as the DSC-1B to function.

If there were no thermal lag in the DSC-1B system, a very pure metal sample would melt to give a sharp vertical "line" during the isothermal region. The line would not be of infinite height since the rate of melting inherent in the relaxation time of the crystal lattice cannot become infinite for a real material. Thus, the height of the line would be proportional to the heat of transition and lattice constants.

Examination of Figs. 4 and 5 indicates that there is appreciable thermal lag in the DSC-1B irrespective of thermostating. Most of the lag exists across the metal, air, cell boundary provided the sample is encapsulated as shown in Fig. 3. This encapsulation mitigates the metal, air, sample boundary as well as the sample bottom to top boundary. It is possible to sharply decrease the metal, air, cell boundary resistance by several methods. In thermal conductivity measurements the sample container is pressed firmly against the heater and sensors. With the present DSC-1B cell configuration this is not easily accomplished. A thin layer of non-volatile liquid can be placed on the bottom of the encapsulation so that when it is placed in the DSC-1B cell no air gap exists. To a first approximation this should remove much of the thermal lag, and the operation is simply carried out without cell modification. Figure 6 was obtained by placing a single microsyringe drop of silicone oil on the DSC-1B cell and setting the encapsulated sample down on it firmly. This resulted in a much sharpened

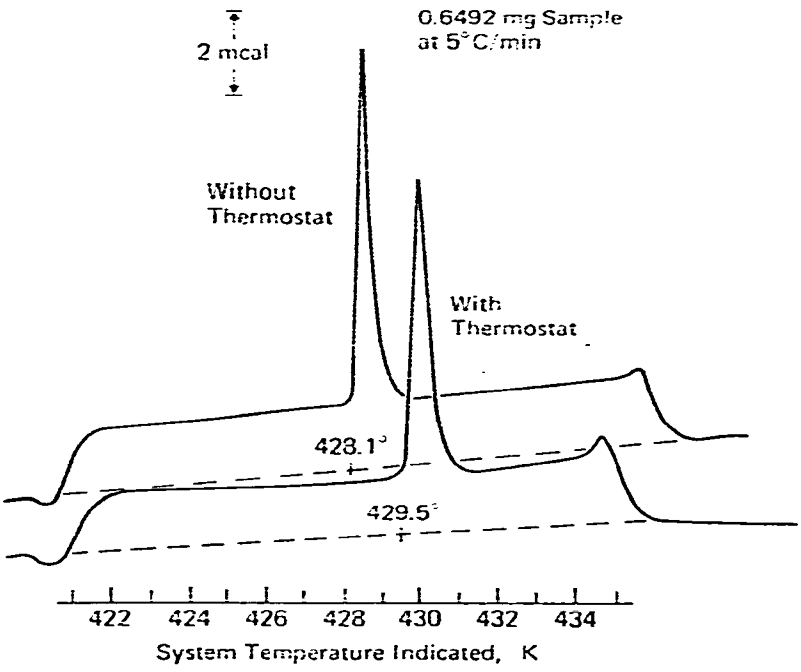


Fig. 5. Thermograms of indium with and without thermostating.

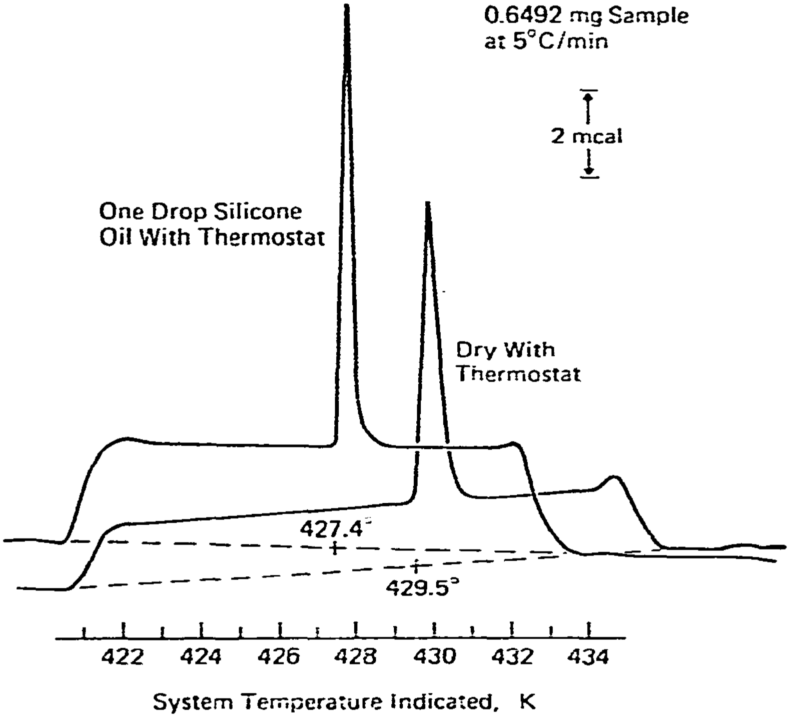


Fig. 6. Thermograms of indium with and without thermally conductive fluid.

thermogram and caused a translation of the peak to lower temperatures by 2.1 °C. From this it is possible to judge both the absolute lag (2.1 °C) and the thermal resistance in terms of rate of heat transfer (about 6 mcal/sec). The slope of the thermogram with oil was too great to measure. This would make the coefficient greater than 20 mcal/sec. The slope on the high temperature side is due to the rate at which the system can null electrically as well as the rate at which the sample reattains thermal equilibrium as the liquid rather than a solid.

The silicone oil treatment appears to be fairly universal in application so long as the temperature range does not intrude into the range of appreciable vaporization of the oil or grease. We have, using high molecular weight silicone greases, gone up to 320 °C and with low molecular weight silicone fluids down to −40 °C. It is important that the silicone material not turn into a glass for low temperature work. In that case thermal expansion differences tear the bond apart. The technique, although desirable for heat capacity measurements, is not applicable since the amount of silicone oil added is not sufficiently reproducible by the methods suggested here. The thermogram obtained with oil in Fig. 6 has a noticeably higher heat capacity deflection than the dry sample. It is interesting to note that the thermogram obtained with the silicone oil has a flatter baseline than the dry material. Part of the endothermal drift of the isothermal start and stop lines must be due to a systematic change of the heat transfer coefficient with increased temperature. This agrees well with what is known about heat transfer coefficients.

CONCLUSIONS

It is possible to significantly improve the performance of the DSC-1B calorimeter by making a few elementary changes in the electronic circuit and insuring that isothermal conditions and heat flow are both reproducible and optimized. With these changes both the convenience of use and the accuracy are significantly improved. Nothing simple can be done about the non-linear calibration curve for temperature or the weakness in the chopping system. These must be monitored closely if optimum results are to be obtained. However, excellent results, approaching those obtained by classical calorimetry, can be produced with care.

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