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USE OF A PROGRAMMABLE CALCULATOR FOR ON-LINE INTERACTION WITH A DIFFERENTIAL THERMAL ANALYSIS SYSTEM*

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ABSTRACT

A differential thermal analysis (DTA) system containing a microcomputer is discussed. The microcomputer performs instrument control, data collection, data processing, and x–y plotting of the data. The introduction of a low-cost microcomputer and plotter to a DTA system can add a new dimension to this technique. A true interaction between the system and the microcomputer can result not only in convenience of data reduction, but also in some areas, a significant improvement in the quality of the data collected.

Although the system described here is based on DTA, it can easily and conveniently be applied to other thermal analysis techniques as well. For DTA, it can be used to integrate the curve peak areas directly in calories. To compare the ΔH values for various reactions at different temperatures, the constant sensitivity mode can be employed.

INTRODUCTION

The rather heavy demands on the thermal analysis investigator for more types of data, better data, and faster response on the data requested have increased yearly. In an attempt to be responsive to these demands, the investigator simply increases the human effort to meet the demand. Either fortunately, or unfortunately depending on one's perspective, this demand soon begins to exceed the capacity of the human effort available at this point, and the investigator begins to search for other solutions to the problem. In many cases, one solution lies in the area of turning much of the redundant work over to a digital computer or controller. Only ten years ago, this solution was available only to the most demanding situation where the data processing problems were virtually insoluable and the investigator had access to a rather large supply of funds, not only for the purchase or lease of equipment, but a contin-

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uing source of revenue for data processing personnel and the upkeep on the system. As a consequence, the nature of the thermal analysis technique, along with the comparative simplicity of data reduction relegated the computer controlled thermal analysis system to the category of a laboratory novelty rather than a viable system.

The availability of the microcomputer or programmable calculator is a rather ideal solution for the thermal analyst who requires a processor of sufficient capacity to meet his needs, and yet has limited funds. The simplicity of operation and programming obviates the need of onsite data processing personnel, since the system can now be operated and maintained by rather low skilled personnel. Another attractive feature of the microcomputer is that it can be taken off-line from the thermal analysis system at any time and be made available for other instruments or data processing problems. Transfer of the system from instrument to instrument to data processing problem and back is a matter of altering software codes and requires no more than the time it takes to load a program, which is a matter of seconds.

EQUIPMENT CONFIGURATION

The DTA system described here is based on a Hewlett-Packard Model 9810 Programmable Calculator. It performs instrument control, data collection and processing, and x–y plotting of the data. Although the system at the present can only be used for differential thermal analysis, it has the capacity for use with thermogravimetry, heat capacity measurements, dilatometry, evolved gas detection, and other thermal analysis techniques.

A block diagram of the differential thermal analysis system is shown in Fig. 1.

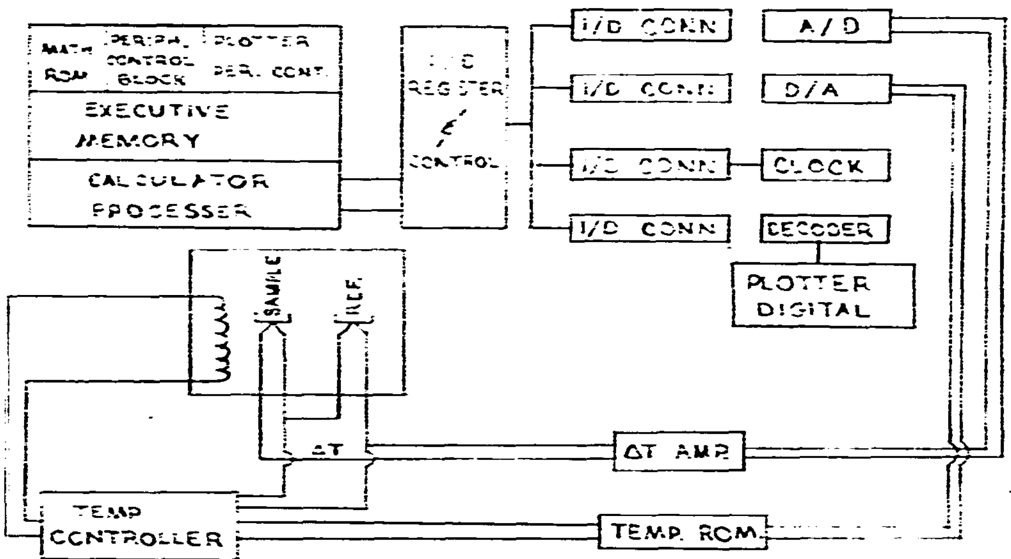

Fig. 1. Block diagram of DTA–computer system.

The calculator portion of the system includes a calculator with a math ROM, a peripheral ROM, a plotter-printer alpha ROM, a printer, an executive memory package, a processor package, an I/O buss, a digital plotter, and an interface of BCD decoding of input and output information. It operates either as a stand-alone unit or as a controller–data processor part of the thermal analysis system. It is fully programmable; its memory enables both program steps and data to be stored and manipulated. The memory can store up to 500 program steps with up to 51 data numbers per step. Programming is simple because the various keyboard operations become the programmed instructions; as a consequence, no special language need be learned. Programming features include separate data and program memories, conditional and unconditional branching, direct and indirect data storage, register arithmetic, relocatable programs, subroutines and the ability to automatically load magnetic cards containing either program steps or data.

Due to the rather limited memory, extensive use is made of *read-only-memory* modules, ROM. A ROM is a cluster of back reversed diodes which are selectively burned out in such a manner so as to output a given sequence code, (ASCII code in this case). In this manner, many operations can be executed with a single instruction rather than four or five instructions that would be necessary to accomplish the functions without the ROM. In other words, selected repetitive functions are hand wired into the system rather than executed through the use of software.

The following is a description of the various ROM's used in the system.

The temperature read-only memory

The ROM has stored in it a plot of temperature versus EMF (microvolts) for various types of thermocouples. In this case, Chromel–Alumel thermocouples were used. The nonlinearity of Chromel–Alumel thermocouples at higher temperatures has been well documented. Since the curve is nonlinear it is necessary to store a reference table so that the calculator can have access to the exact temperature. If this information were stored in main memory, it alone would use up all of the locations. The ROM simply supplies the BCD output to the calculator, thus presenting the temperature in the x-register with a single instruction.

The printer alpha read-only memory

This ROM enables the printer and the plotter to print alphabetic characters and messages and to insert mnemonics into program listings. In this way, alpha characters can be printed on the printer or the plotter with a single instruction.

The mathematics of the read-only memory

This ROM adds twenty six mathematical functions and additional programming features to the calculator. These include logarithms, exponential functions, trigonometric function (in degrees, radians, or grads), coordinate transformations, vector arithmetic, manipulation of complex numbers, automatic scaling for x–y plotting, and a user definable function.

The calculator uses five working registers:

1. The x-register—All data input from peripherals enter the calculator through the x-register.

2. The y-register—The results of mathematical operations accumulate in the y-register.

3. The z-register—Numbers can be temporarily held while arithmetic operations are being performed in the x-register and y-register.

4. The a-register—The a-register is a temporary storage register much like the z-register.

5. The b-register—The b-register is a temporary storage register much like the z-register.

The z-register is used for serial transfers from the x-registers to the y-register. Data must always be transferred through the y-register. The a- and b-registers can be operated with parallel transfers from the x-register and the y-register.

DTA apparatus

The DTA apparatus consists of the Deltatherm IIIB, which is illustrated in Fig. 2. It is a prototype system designed from the start with the idea of being capable of being interfaced with a digital processing system. As a consequence, the ΔT and T

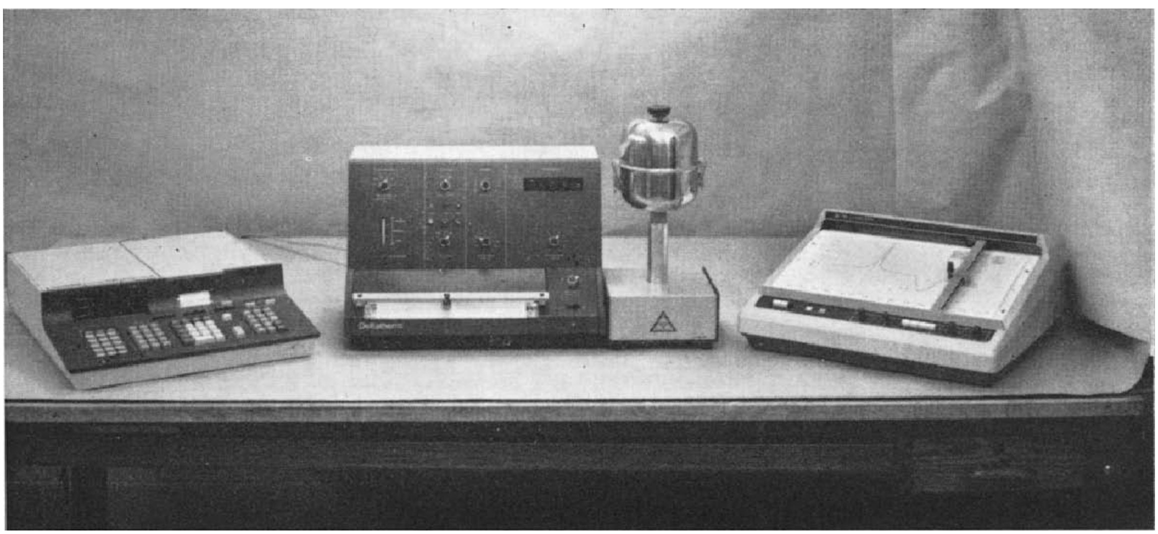

Fig. 2. The Deltatherm IIIB with a Hewlett–Packard minicomputer.

outputs are available in digital format, either BCD or binary, with the analog signals available at various test points. The ΔT amplifier receives its analog signal from the differential thermocouples, amplifies the signal, and gates the signal into a 10-bit analog-to-digital converter. From this point on, the data is gated into the calculator at a rate of 10 readings per second. The software "scales" this ΔT value and finds an average value for plotting once each six seconds. This means that as far as ΔT is concerned, each point plotted is in reality an average of 60 measurements. This has significant advantages from a statistical point of view as well as a diminution of the time constant problems so inherent in this type of analysis.

The temperature programmer operates on a stepper-driver arrangement; the furnace heating rate is driven by a pulse train, either from a built-in oscillator or from the calculator pulse output. This arrangement allows the calculator to have supervisory control over the heating rate while the temperature programmer itself maintains the short term temperature programmed changes. This feature would allow software controlled "slowing" of the temperature just prior to the data collection temperature range, then returning the heating rate duties to the temperature programmer for incrementing the temperature at the standard scanning rate. Subroutines in the software are such that the heating rate is checked each 10 degrees. Should the heating rate fall out of tolerance, an indication is output on the printer. This feature would be of great use in an automated thermal analysis system with an automatic sample changer. It should be noted that there is a rather basic difference between the temperature axis on this system and conventional DTA system. In most DTA systems, the recorder chart drive is driven by a synchronous motor moving that axis at a selected rate of speed. By design, this rate of speed is coincident with, or is some coincident multiple of the heating rate. Thus, one unit of length on this axis is equivalent to some span of temperature. In this system, the temperature is measured and plotted each time with the complimenting ΔT measurements on the coordinate axis of the chart.

The software

The following software has been developed to use with the system.

a. DTA x-axis generation routine. This program causes the plotter to plot the x-axis for differential thermal analysis. It can easily be modified to plot variations on this axis in any parameters needed. The convenience of plotting the x-axis for different types of DTA experiments is easily seen.

b. Routine for calculation of ΔT sensitivity as a function of temperature. This routine measures the number of millicalories needed for each 1 square millimeter of peak area between the two temperature limits. Constants needed for this program are temperature limits, heat of transition of the sample, sample mass, and sample mass of one mole. Program outputs on printer the number of millicalories per square millimeter and the constants entered.

c. Program for plotting the data points found in (b) as a function of temperature. This program plots the millicalories per square millimeter (see Fig. 4). Constants needed are: various data points with appropriate transition temperatures.

d. Program for data fetch from thermal analysis system, sensitivity correction as a function of temperature, and plot of ΔT as a function of temperature. Various constants are used.

e. Program for calculation of ΔH between two temperature limits. This program integrates the thermal transition between the two temperature limits and adjusts for constant sensitivity; it also calculates the ΔH value after passing the second limit and outputs ΔH on the printer. Constants needed are as follows: sample mass, mass of one mole of sample, temperature limits, and constant sensitivity curve.

f. Programs for manipulation of ΔT baseline level. The conventional method for presentation of the plot of ΔT as a function of temperature is with zero ΔT at or near the central axis of the chart with endothermic peaks going in one direction and exothermic peaks going in the opposite direction. As a consequence, at a given sensitivity, half of the span of the chart is allocated to endothermic transitions, and half of the span to exothermic transitions. With digital plotting techniques, this mode of plotting is still available to the investigator, along with at least two others, such as:

1) If the baseline or zero ΔT is located at either the bottom or top of the chart, the full span of the amplification system and recorder are available. If the ΔT data are plotted without regard for polarity, the series of peaks would all be in the same direction. With this mode, the system has the ability to discriminate between endothermic and exothermic peaks and also twice the dynamic range of the system has been gained. It is possible to discriminate between the two types of peaks, by allocating solid-line curves to one and point plotting to the other.

2) Operation in the mode that would allow log plots on the ΔT axis, which is not presently possible; this program is currently being developed.

APPLICATION OF THE DTA SYSTEM

Constant sensitivity differential thermal analysis

It has long been known in DTA that an increase in temperature results in a diminution in the ΔT sensitivity. The change in the sensitivity precludes the direct correlation of ΔH values at different temperatures on the same curve. Thus, it is not possible to make qualitative or quantitative predictions on the heat of transition or reaction. Williams and Wendlandt[1] have described a simple, constant sensitivity DTA system for use below 300 °C. Their approach was to use an analog, $y = mx + b$, device to alter the ΔT amplifier gain as a function of temperature. Unfortunately, such a system fails when applied to a nonlinear situation. The introduction of a microcomputer provides a convenient solution to the problem of nonlinearity of the ΔT sensitivity. The following demonstrates the calibration procedure and other details of the system.

Instrument calibration

The ΔT sensitivity as a function of temperature was determined by measuring the area under a transition peak for various materials of known ΔH values. These materials covered the temperature range from 125 °C to 960 °C, which is a convenient range for most DTA studies. The ΔT sensitivity was expressed in calories per square millimeter.

A typical DTA curve, using the printer output from program (b), is shown in

Fig. 3. The sample is indium metal and the curve represents the fusion transition. In the center of the figure, data pertaining to the computer program are given. Similar data for the other compounds used are given in Table 1. The key to the data is found in Fig. 3.

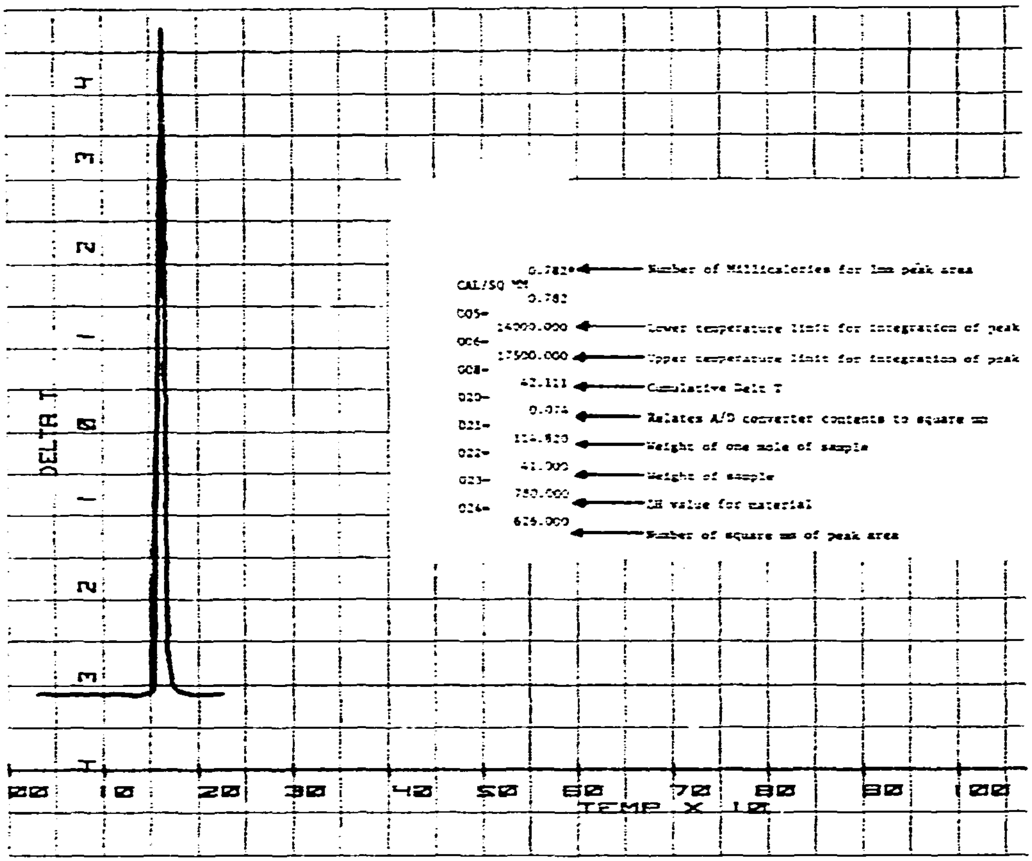

Fig. 3. DTA curve of indium and the pertinent program data. $\Delta T = 0.5$; heating rate $= 10\,^{\circ}C/min$; sample weight = 41. mg; reference used = Al_2O_3; reference weight = 35 mg.

The ΔT sensitivity curve obtained for the DTA apparatus is shown in Fig. 4. It is of inetrest to note that the sensitivity is about 0.1 as great at 1000 °C as that at 25 °C. The ΔT sensitivity given in most DTA curves in the literature is that measured at 25 °C. A DTA curve peak for a transition of equal ΔH would have an area ten times larger at 25 °C than at 1000 °C; this type of a display can, at times, be quite misleading. From the measured ΔT sensitivity curve, a corrected curve can be constructed which displays a constant ΔT sensitivity throughout the temperature range of interest.

Introduction of the constant sensitivity correction into the microcomputer program can be accomplished in at least three ways:

a. The expression can be segmented into a number of $y = mx + b$ expressions. When ΔT and T are read into the x-register the subroutine can look at the temperature,

TABLE I

DTA DATA FOR OTHER CALIBRATION COMPOUNDS

Key in Fig. 3.

Potassium nitrate *5 °C/min* $\Delta T = 1.0$	*Tin* *10 °C/min* $\Delta T = 1.0$	*Potassium perchlorate* *5 °C/min*
cal mm^{-2} = 0.707	cal mm^{-2} = 0.939	cal mm^{-2} = 1.121
0.707	0.939	1.121
005 = 10000.000	005 = 21000.000	005 = 34300.000
006 = 15000.000	006 = 26000.000	006 = 34300.000
008 = 41.902	008 = 0.000	008 = 50.938
020 = 0.074	020 = 0.074	020 = 0.074
021 = 101.110	021 = 118.700	021 = 138.560
022 = 29.000	022 = 52.000	022 = 32.500
023 = 1300.000	023 = 1720.000	023 = 3290.000
024 = 555.321	024 = 411.782	024 = 688.351

Lead *10 °C/min* $\Delta T = 1.0$	*Silver* *10 °C/min* $\Delta T = 0.2$	*Potassium sulfate* *5 °C/min* $\Delta T = 1.8$
cal mm^{-2} = 1.322	cal mm^{-2} = 10.311	cal mm^{-2} = 3.361
1.322	10.311	3.361
005 = 25000.000	005 = 93000.000	005 = 55500.000
006 = 30000.000	006 = 97500.000	006 = 61600.000
008 = 0.000	008 = 12.565	008 = 10.416
020 = 0.074	020 = 0.074	020 = 0.074
021 = 207.210	021 = 107.880	021 = 174.270
022 = 96.000	022 = 130.000	022 = 39.200
023 = 1140.000	023 = 2855.000	023 = 1940.000
024 = 214.800	024 = 194.322	024 = 129.830

Zinc *10 °C/min* $\Delta T = 1.0$	*Aluminium* *10 °C/min* $\Delta T = 0.5$	*Barium carbonate* $\alpha \rightarrow \beta$ *10 °C/min* $\Delta T = 0.2$
cal mm^{-2} = 1.504	cal mm^{-2} = 3.611	cal mm^{-2} = 5.850
1.504	3.611	5.850
005 = 38000.000	005 = 60000.000	005 = 78000.000
006 = 45000.000	006 = 70000.000	006 = 83000.000
008 = 49.201	008 = 31.476	008 = 13.910
020 = 0.074	020 = 0.074	020 = 0.074
021 = 65.380	021 = 26.900	021 = 197.300
022 = 44.500	022 = 25.000	022 = 47.000
023 = 1765.000	023 = 2570.000	023 = 3550.000
024 = 791.820	024 = 802.213	024 = 189.216

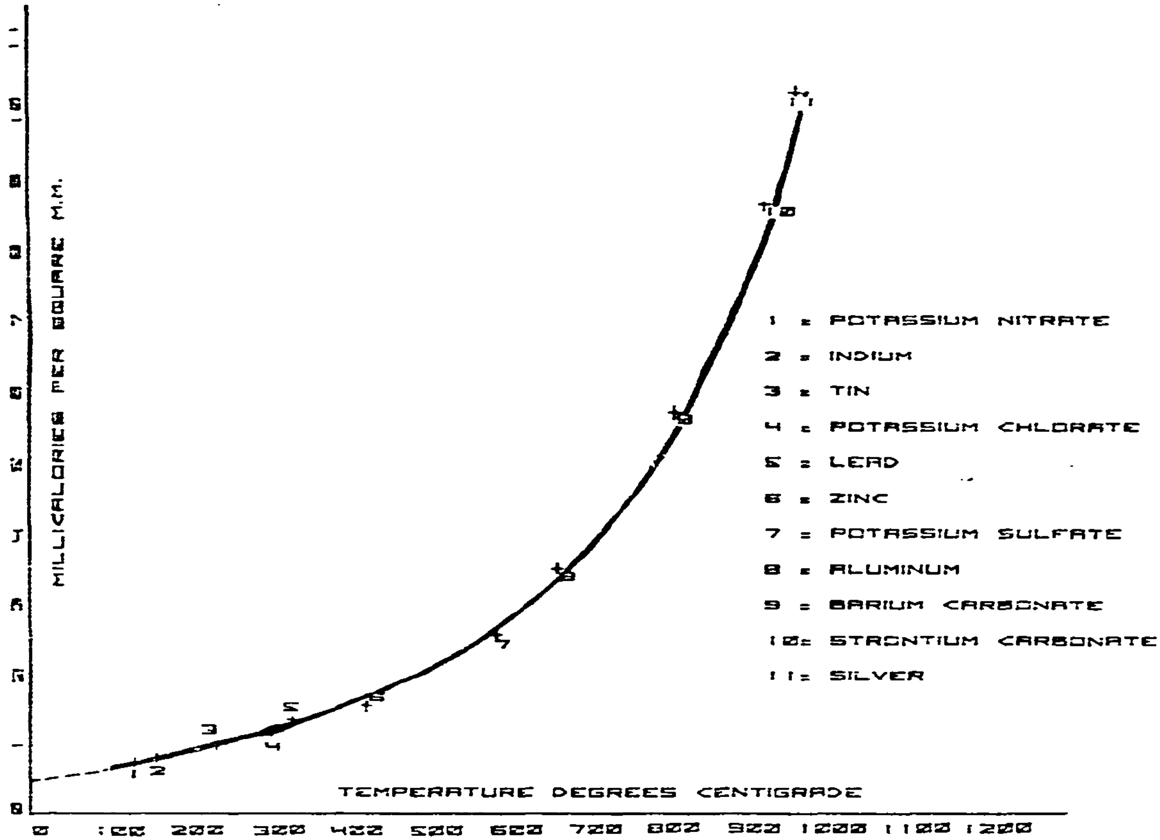

Fig. 4. The ΔT sensitivity curve determined on this apparatus.

then decide which $y = mx + b$ expression is indicated, solve that expression for ΔT correction factor and correct the ΔT value. This corrected ΔT value is then plotted with the temperature as a data point on the constant sensitivity DTA curve. The disadvantage of this approach is that it requires a large amount of memory space to get enough segments for a true fit to the curve. This was the method that was used here.

b. A better method would be to write a nonlinear expression for the curve. At present, this seems to be a quadratic expression. This technique, although more difficult to accomplish, requires only six memory locations and approximately five program steps, hence would be an ideal approach.

c. Perhaps the best method would be the incorporation of a table consisting of a data point for each degree of temperature in the range considered. For the temperature range between 0 and 1000°C, this would require one thousand data points to be stored. If the data points were stored in the active memory, it follows that 1000 active memory locations would be required. This far exceeds the capacity of the computer system, and as a consequence is not possible. A possible solution to this problem would lie in the use of a ROM which has been explained earlier in this paper. In this manner, an exact fit to the sensitivity curve can be obtained which would use a minimum active memory and instructions. Prior to implementing the ROM table, the exact curve must be specific for the system. This is necessary because while ROM's are relatively inexpensive when compared to memory, the first ROM is expensive to configure.

Conversion of ΔT values to calories

With the introduction of the sensitivity correction factor to accomplish constant sensitivity through the temperature range, the ΔT values must now be related to ΔH values (or calories per mole or calories per unit volume). This step involves developing a relationship between the area under the curve to calories which is linear. The factor, 0.074, which is stored in memory location number 020 (see Fig. 3) is the slope of this linear relationship. As a result, the integration between the two temperature limits can be converted to calories per mole. A slight modification of the program allows data presentation in other formats.

Application of ΔT constant sensitivity system

Since the ΔT sensitivity correction is greatest at higher temperatures, the system chosen to illustrate this approach was the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transitions in barium carbonate. The uncorrected DTA curve for these transitions is given in Fig. 5. As can be seen, the $\alpha \rightarrow \beta$ transition occurs at 806°C while the $\beta \rightarrow \gamma$ transition takes place about 965°C.

The ΔT constant sensitivity DTA curve is illustrated in Fig. 6. The sample is the same one as was used in obtaining the uncorrected DTA curve but the curve was

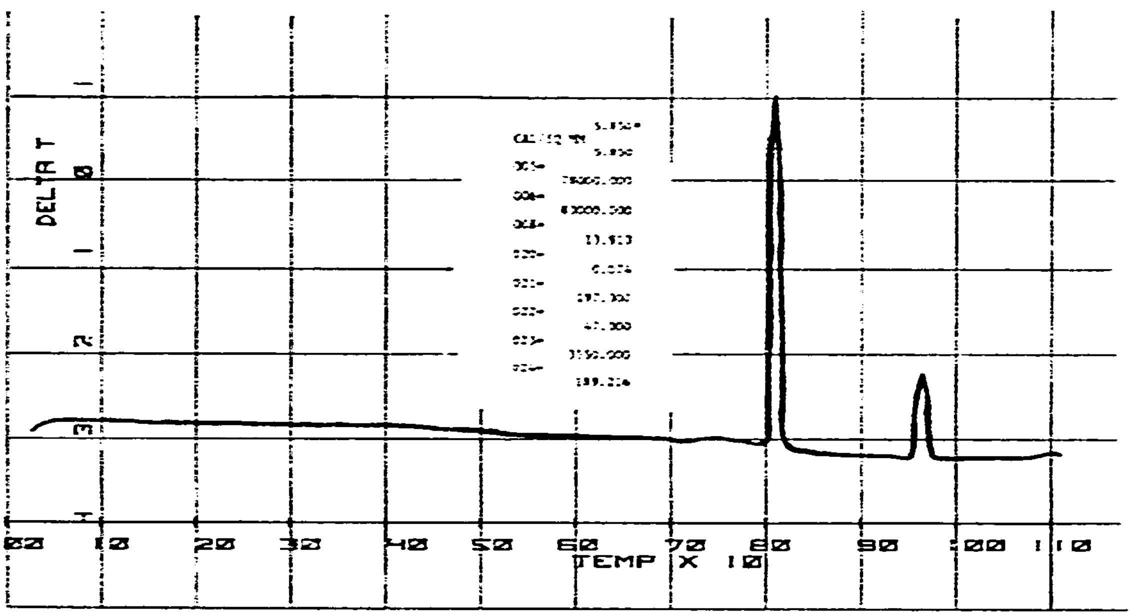

Fig. 5. Uncorrected DTA curve for $BaCO_3$ showing the $\alpha \rightarrow \beta$ transition. $\Delta T = 0.2$; heating rate = 10°C/min; sample weight = 47 mg; reference used = Al_2O_3; reference weight = 30 mg.

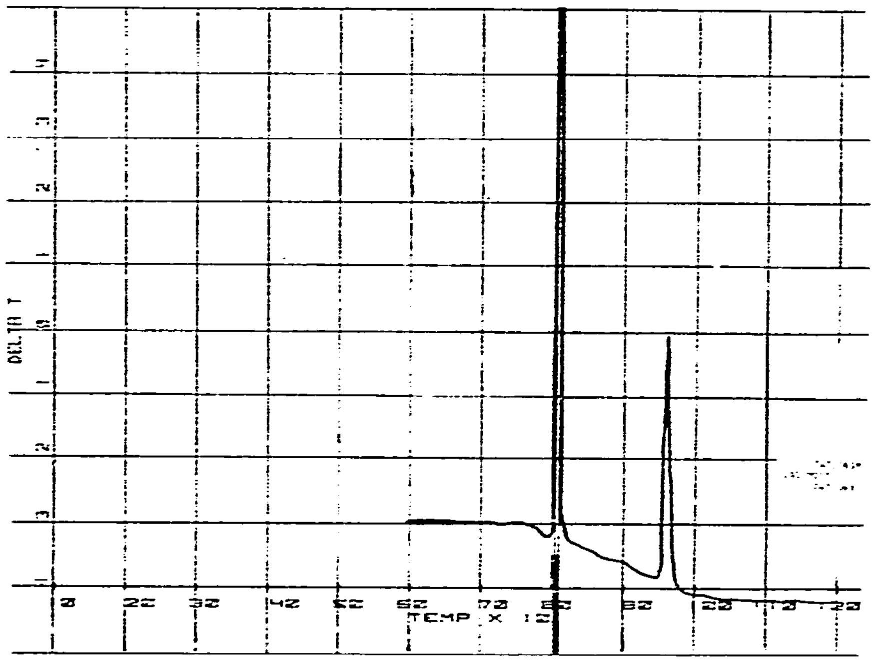

Fig. 6. The ΔT constant sensitivity DTA curve for $BaCO_3$ showing the β to γ transition. $\Delta T = 0.5$; heating rate = 10°C/min; sample weight = 47 mg; reference used = Al_2O_3; reference weight = 30 mg.

corrected using program (e). This program introduces both the constant sensitivity parameter and the calculation of ΔH values between two temperature limits. With the introduction of the constant sensitivity factor, the correction increases the measured ΔT by a factor of approximately ten. As a consequence, the ΔT amplifier sensitivity was adjusted from a setting of 0.2 microvolts per inch for the uncorrected curve, to a setting of 0.5 microvolts per inch for the constant sensitivity curve. This change of amplifier gain is a factor of 2.5 and not the factor of ten anticipated by the introduction of the constant sensitivity program. As expected, the transition is considerably larger than the similar transition in Fig. 4. To test the ΔH calculation subroutine and the constant sensitivity subroutine in the program, the heat of transition for the $\beta \rightarrow \gamma$ transition was calculated. The value found was 747 cal mole^{-1} which is in reasonable agreement with the value of 730 cal mole^{-1} previously reported.

REFERENCES

1 J. R. Williams and W. W. Wendlandt, in H. G. Wiedeman (editor), *Thermal Analysis*, Birkhäuser Verlag, Basel, Vol. ', 1972, p. 75.