

rect as far as it goes. The barrier theory, by contrast, is less concrete and has been responsible for a certain amount of confusion regarding mobility calculations. An interpretation of the barrier effect in which the cellulose fibers physically hinder the migration of charged species (8) has been shown as misleading by Edward (5). On the other hand a more general interpretation (9) of the barrier effect as that involving any hindrance to migration, whatever its source, is simply a definition of the phrase "barrier effect", and does not lead to a physical picture of the underlying processes. The nearest approach to the former definition is shown by impermeable migrants in the γ term, but, as just shown, this is usually negligible in paper electrophoresis. It is also possible to think of the barrier effect as that exhibited in the ion retardation factor, R . This is rather arbitrary, but at least one finds in R the most direct interaction of the migrant with the stabilizing material. This is also consistent with the point of view of Syge since R differs from unity only when the fibers are partially conducting. In view of the confusion existing over the barrier effect, however, it is probably best to divorce the terms developed in this paper from the terminology of the barrier theory. The terms developed here, while giving only approximate re-

sults, are nonetheless quantitatively defined, and this clarity should not be lost in an attempt to link them with past qualitative results. An exception, again occurs with tortuosity which is a clearly defined (although not easily calculated) concept.

NOMENCLATURE

A = cell area, excluding solid.
 a = shape factor in tortuosity expression (Eq. 22).
 A_e = effective area for conduction.
 A_0 = total cell area normal to x .
 b = conductance ratio, $(\sigma_0 - \sigma)/\sigma_0$.
 C = constrictive factor (Eq. 12).
 \bar{c}_i = average electrolyte concentration with solid.
 c_{i0} = average electrolyte concentration without solid.
 F = functional expression (Eq. 23 et seq.)
 f = conductance factor for cell with no lateral resistance (see Eq. 7).
 K = conductance of cell with solid.
 K_0 = conductance of cell without solid.
 ℓ = half of cell length along x .
 R = ion retardation factor (Eq. 13).
 r = fiber radius.
 T = tortuosity.
 w = cell length.
 x = coordinate in field direction.
 γ = diffusion-time factor (Eq. 27).
 θ = filled fraction.
 θ_i = pre-swelling value of θ .
 $\bar{\mu}_i$ = average mobility with solid.
 μ_{i0} = mobility without solid.
 ξ = obstructive factor, $\bar{\mu}_i/\mu_{i0}$.
 ξ' = obstructive factor for nonpenetrating migrants.

σ = intra-fiber conductivity.
 σ_0 = free solution conductivity.
 χ = fractional swelling of fiber.
 T' = absolute temperature.

LITERATURE CITED

- (1) Bailey, R. A., Yaffe, L., *Can. J. Chem.*, **37**, 1527 (1959).
- (2) Biefer, G. F., Mason, S. G., *Trans. Faraday Soc.* **55**, 1239 (1959).
- (3) Boyack, J. R., Giddings, J. C., *Arch. Biochem. Biophys.* **100**, 16 (1963).
- (4) Crawford, R., Edward, J. T., *ANAL. CHEM.* **29**, 1543 (1957).
- (5) Edward, J. T., ACS Symposium on Solution Chromatography, Cleveland, June 1961.
- (6) Giddings, J. C., Boyack, J. R., *J. Theoret. Biol.* **2**, 1 (1962).
- (7) Kunkel, H. G., Tiselius, A., *J. Gen. Physiol.* **35**, 89 (1951).
- (8) McDonald, H. J., "Ionography," Yearbook Publishers, New York, 1955.
- (9) McDonald, H. J., in "Chromatography," E. Heftmann, ed., Reinhold, New York, 1961.
- (10) O'Sullivan, J. B., *J. Textile Inst.* **38** T271 (1947).
- (11) Ott, E., Sparlin, H. M., Grafflin, M. W., "Cellulose and Cellulose Derivatives," p. 319, Interscience, New York, 1954.
- (12) *Ibid.*, p. 318.
- (13) *Ibid.*, p. 432.
- (14) Syge, R. L. M., *Biochem. J.* **65**, 266 (1957).

RECEIVED for review October 17, 1963.
 Accepted March 23, 1964. This investigation was supported by a research grant, GM 10851-07, from the National Institutes of Health, United States Public Health Service.

A Differential Scanning Calorimeter for Quantitative Differential Thermal Analysis

E. S. WATSON, M. J. O'NEILL, JOSHUA JUSTIN, and NATHANIEL BRENNER

The Perkin-Elmer Corporation, Norwalk, Conn.

► An instrument for differential thermal analysis has been developed which directly measures the transition energy of the sample analyzed. The instrument performs thermal analyses of milligram level samples at high speeds (scan rates up to 80° C. per minute) and in a temperature range of 173° to 773° K. (−100° to +500° C.). Analytical data are recorded in a fashion graphically similar to that of traditional DTA, but peak amplitude directly represents millicalories per second of transition energy and peak area directly represents total transition energy in millicalories. Direct temperature marking is also displayed. Atmosphere control and vacuum operation are also provided. Samples may be run in closed-cup or open-cup configurations and are conveniently handled in powder or

sheet form. Quantitative performance is independent of specific heat of sample, sample geometry, and temperature scanning rate. Qualitative information is equivalent or superior to conventional DTA in terms of speed, sensitivity, resolving power, and operational convenience. However, the principal innovation of the unit is the capability for direct, convenient, and precise quantitative measurement of transition energy.

THE EXAMINATION of the rate and temperature at which materials undergo physical and chemical transitions as they are heated and cooled and the energy changes involved has been the subject of investigations for almost a century.

Conventional differential thermal

analysis instruments subject a sample and an inert reference material to a controlled heating program and measure the differential temperature between sample and reference material. The appearance of an increase or decrease in the sample temperature with respect to the reference temperature is attributable to the energy-emitting (exothermic) or energy-absorbing (endothermic) transitions occurring in the sample. Systems of this type were developed by Roberts-Austen (9) and Saladin (10) over fifty years ago and have been improved over the years for mineralogical and inorganic chemical applications and, more recently, in the organic chemical field (13, 15). The desirability of direct calorimetric information rather than indirect thermometric data has been recognized by advanced workers in DTA for many years. Sykes (1935–36)

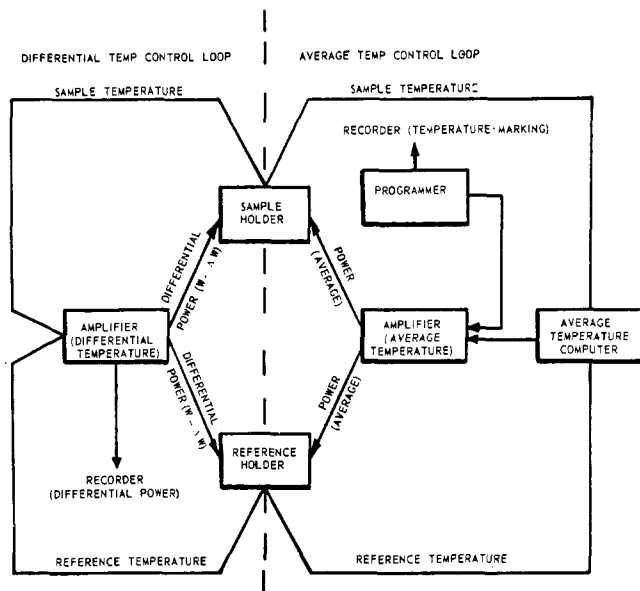


Figure 1. Block diagram, Perkin-Elmer differential scanning calorimeter

(14), Kumanin (1947) (8), and Eyraud (1954) (4) built and operated equipment in which this objective was indeed accomplished by various elegant means.

A new system for differential thermal analysis has been developed which offers direct calorimetric measurement of the energies of transition observable in the analysis and therefore improves the utility of the DTA technique for quantitative analysis. The system, called a Differential Scanning Calorimeter (DSC), differs from the conventional thermal analyzers in one fundamental respect. The conventional units measure and record the temperature difference between sample and reference channels. The DSC system measures the differential energy required to keep both sample and reference channels at the same temperature throughout the analysis. When an endothermic transition occurs, the energy absorbed by the sample is replenished by increased energy input to the sample to maintain the temperature balance. Because this energy input is precisely equivalent in magnitude to the energy absorbed in the transition, a recording of this balancing energy yields a direct calorimetric measurement of the energy of transition.

Figure 1 shows a schematic representation of the DSC system.

The schematic system may be most easily comprehended if we divide the system into two separate control loops, one for average temperature control, the second for differential temperature control. In the average temperature loop, a programmer provides an electrical output signal which is proportional to the desired temperature of the sample and reference holders. The programmer temperature information is also relayed

to the strip chart recorder and appears as the abscissa scale marking. The programmer signal, which reaches the average temperature amplifier, is compared with signals received from platinum resistance thermometers permanently embedded in the sample holder and reference holder via an average temperature computer. If the temperature called for by the programmer is greater than the average temperature of the sample and reference holders, more power will be fed to the heaters, which, like the thermometers, are embedded in the holders. If the average temperature demanded by the programmer is lower than the average of the two holders, the power to the heaters will be decreased.

In the differential temperature control loop, the major distinction between the DSC-1 and traditional DTA devices is most marked. Signals representing the sample and reference temperatures, measured by the platinum thermometers, are fed to the differential temperature amplifier via a comparator circuit which determines whether the reference or the sample signal (temperature) is greater. The differential temperature amplifier output will then adjust the differential power increment fed to the reference and sample heaters in the direction and magnitude necessary to correct any temperature difference between them. A signal proportional to the differential power is also transmitted to the pen of the galvanometer recorder. The direction of the pen excursion will depend upon the direction of excess power input (sample or reference heater).

The instrumental system may be broken down into the following subgroups for analysis:

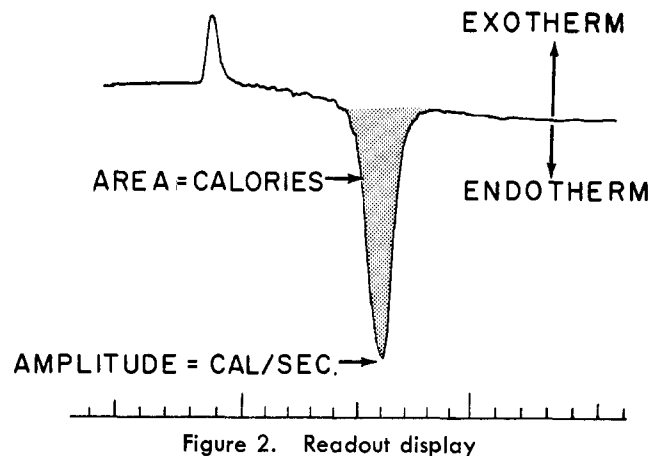


Figure 2. Readout display

A pair of platinum resistance thermometers, the associated circuitry, a double-pole, double-throw mechanical chopper, and two input transformers. Also, a program potentiometer and associated circuitry. This group of components measures sample and reference temperatures and generates a ΔT error signal at 60 c.p.s. A summing network provides the average temperature T_{AV} , which is compared with the set-point temperature T_P generated by the program potentiometer, to generate a second error signal at 60 c.p.s.

A ΔT signal amplifier, an output transformer, and a half-wave balanced output circuit. The output of this amplifier is connected differentially to the two heater elements in the sample holders. Every half-cycle, therefore, the differential temperature loop is closed, and ΔT is nulled. An a.c. voltage proportional to differential power is generated and fed to...

...the readout system, which includes a demodulator, range and zero controls, and a closed-loop d.c. amplifier. This system drives a 5-ma. Texas Instruments Recti/Riter Recorder. Outputs suitable for a Perkin-Elmer Model 194 Integrator and a 10-mv. recorder are also provided.

A T_{AV} signal amplifier, which supplies power to the sample and reference heaters, to close the loop around T_{AV} . This amplifier and the ΔT amplifier are operated on a time-sharing basis, each connected to the heaters for half of the time. A secondary circuit controls a pilot light which allows the operator to monitor the operation of this loop. (See discussion below.)

A scaling circuit which provides line-synchronized pulse trains at eight pulse repetition frequencies, one of which is selected by the Speed Selector switch and fed to...

...the motor drive circuit. This is a flip-flop circuit, driving the field windings of a stepping motor in the temperature programmer. In addition, there is a pulse generator, triggered by signals from the programmer, which drives a ballistic marker pen mounted on the Texas Instruments Recti/Riter Recorder. This action is inhibited by a signal from the T_{AV} amplifier when that loop loses control. This will

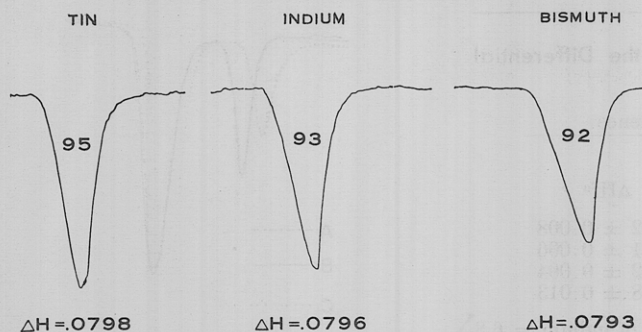


Figure 3. Energies of fusion

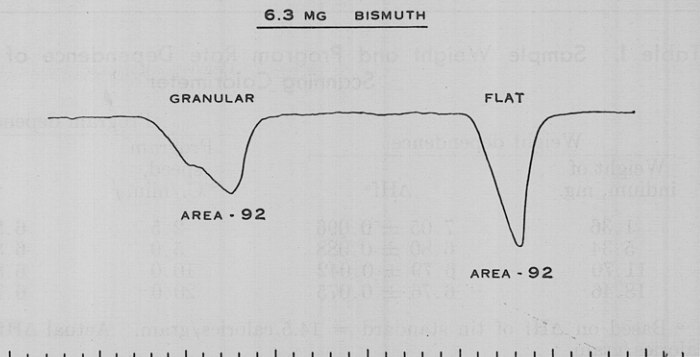


Figure 4. Effect of sample geometry on peak shape and area

happen if the operator attempts to set the temperature below, or only slightly above the ambient temperature, or if the operator attempts to program the temperature down too fast. In either case, the heater power will be turned off, and the true sample temperature will be somewhere above the indicated (dial) temperature. The pilot light monitors this situation visually; the absence of a temperature scale on the chart provides a *post facto* record.

The calorimeter part of the instrument; namely, the ΔT loop and ΔW readout, operates continuously, entirely unaffected by the situation in the T_{AV} loop.

The thermal conductivity effluent monitor cell and its associated circuitry, plus a proportional temperature controller for the detector block.

The power supply which provides plus and minus voltages for all parts of the instrument.

The programmer unit which includes the stepping motor, gear train, clutch, counting dial, commutator, and program potentiometer.

The graphic data obtained from the calorimeter superficially resemble those obtained from a traditional DTA. Figure 2 illustrates the display as seen on a galvanometer recorder equipped with an auxiliary pen for temperature marking. As in DTA, the abscissa represents temperature and each mark equals one degree C. or K. Larger marks are inscribed each 5 and 10 degrees. The second pen draws the thermogram itself and, as in DTA, a flat baseline indicates ranges in which

no transition occurs, while excursions (peaks) above and below the baseline represent exothermic and endothermic transitions, respectively.

The distinction between calorimetric and traditional DTA lies in the fact that the amplitude of the pen from the baseline position is directly measurable as a rate of energy output or input (millicalories per second) and the area under a peak equals total transition energy (calories).

The validity of this distinction is illustrated in Figure 3. Here three samples of pure metal were weighed out in quantities calculated to yield, upon melting, approximately equal energies of fusion. The heat capacities and thermal conductivities of two of the metals (Sn and In) are very similar, but that of the third (Bi) is very much different. (The thermal conductivities of the materials also vary considerably: Sn, 0.150 cal. cm.⁻¹ sec.⁻¹ deg.⁻¹; In, 0.059 cal. cm.⁻¹ sec.⁻¹ deg.⁻¹; Bi, 0.020 cal. cm.⁻¹ sec.⁻¹ deg.⁻¹) Figure 3 shows that the areas of the

fusion peaks are essentially equal ($A_{Sn} = 95$, $A_{In} = 93$, $A_{Bi} = 92$) and that the measurement made is of the fundamental energy value undistorted by other sample properties.

In conventional DTA, the thermal conductivity of the sample will markedly influence the area obtained per unit of energy input or output. In practice, this problem is handled by diluting the sample with a large volume of the reference material so that the resultant conductivity is essentially equal to that of the pure reference (1). In this way, dissimilar compounds may be quantitatively compared. Naturally, the dilution takes its toll in terms of sensitivity, and runs the risk of possible interaction between diluent and sample.

The freedom from effects of sample geometry is illustrated in Figure 4. Here a sample of bismuth in the form of large lumps was melted and the heat of fusion recorded. Because of poor heat transfer, an irregular peak shape results.

The second record is of the same sample run in a thin layer form. A

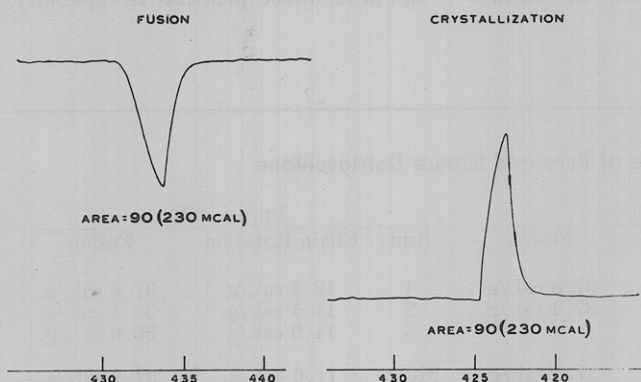


Figure 5. Fusion and crystallization transitions of indium



Figure 6. Operating head, open view

Table I. Sample Weight and Program Rate Dependence of the Differential Scanning Calorimeter

Weight dependence		Program dependence	
Weight of indium, mg.	ΔH_f^a	Program speed, °C./min.	ΔH_f^a
1.36	7.05 ± 0.096	2.5	6.82 ± 0.008
5.34	6.80 ± 0.088	5.0	6.81 ± 0.006
11.70	6.79 ± 0.042	10.0	6.82 ± 0.004
18.46	6.76 ± 0.075	20.0	6.78 ± 0.013

^a Based on ΔH_f of tin standard = 14.5 calories/gram. Actual ΔH_f of indium = 6.8 calories/gram.

well shaped peak results, which, while esthetically superior, is quantitatively identical to the first run since both areas are equivalent.

A similar example is shown in Figure 5 where the fast exothermic transition of crystallization of the indium yields a peak identical in area to that of the much slower endotherm of fusion of the same sample.

The temperature scanning rate of the calorimeter may be varied from as low as 0.6° to as high as 80° per minute. Output sensitivity may also be varied from levels corresponding to 0.002 calory per second half scale recorder reading to as low as 0.032 calory per second for a half scale deflection on the galvanometer recorder. Changes in scan rate produce no change in total area under a peak, though the peak shape (height-to-width ratio) will be altered. [In traditional DTA devices, scan rate changes may be accompanied by area, as well as peak shape changes, further complicating quantification of data (11).]

Changes in sensitivity range (signal attenuation) result in changes in area and peak amplitude in precise ratio to the ranges selected. The results of such changes are shown in Table I, along with results of changes in sample weight. (In the weight dependence determinations, all runs were made at a scanning rate of 10° C. per minute. In the program dependence determinations, sample weight in each case was 5.3 mg. All figures represent the mean

of three single determinations.) In all cases, the true energy of transition is accurately derived.

The calorimeter operates in the range 173° to 773° K. (-100° to $+500^\circ$ C.). Cooling below ambient temperature is accomplished by substituting an enclosure cover containing a liquid nitrogen well and Dewar Jacket for the standard enclosure cover. A small volume (200 cc.) of liquid nitrogen, poured into the well, will cool the sample enclosure to 173° K. in about 5 minutes.

The analyzer section of the calorimeter includes the operating head which is seen in exposed view in Figure 6. Samples in the usual range of 0.1 to 10 mg. are placed in small aluminum or gold pans and are set in either of the sample wells shown in Figure 6. Samples may be in powder or sheet form and may be run either encapsulated or open to the ambient atmosphere. Encapsulation of samples is accomplished with a sample pan sealer accessory designed for this purpose. A standard sample pan containing the sample and covered with a metal disk is placed into the sealer. Depression of the sealer handle causes a folding inward of the sample pan rim, creating a tight enclosure resembling a flat-bottomed metal aspirin. Samples may be visually observed during a run. In this case, the sample well cover (usually metal) is replaced by a mica disk and an inverted glass beaker is used in place of the stainless steel enclosure cover. In contrast

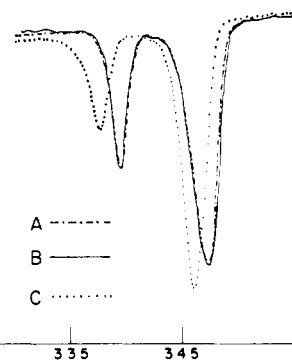


Figure 7. Chain rotation and fusion transitions

to most traditional DTA, no actual reference material is required. An empty sample pan is usually placed in the reference well, however.

Quantitative performance is illustrated by the measurement of the transition energies associated with the chain rotation and fusion of dotriacontane. These transitions have been previously investigated by Hoffman and Decker (5) and Ke (6).

Figure 7 shows three superimposed thermograms of dotriacontane. Two of the runs (A and B) were made from a sample shown to be 98% pure by gas chromatographic assay; the third (C) was an 80% pure material obtained from a second supplier. The transition temperatures of the impure material are shifted to lower temperatures and the band width of the chain rotation peaks broadened.

Table II shows the energy measurements obtained from these samples. Note that the fusion energy is essentially identical in both pure and impure materials, but that the chain rotation energy is considerably lower in the impure material.

The actual analyses were performed using an external standard method. A 12.1-mg. sample of pure indium served as the standard and the heat of fusion of indium was used to calibrate the area response of the calorimeter. Area measurements were made with a planimeter.

While the fundamental contribution of the calorimeter to thermal analysis lies in its direct quantitative capability,

Table II. Comparison of Transition Energies of Pure and Impure Dotriacontane

Pure (A)			Pure (B)			Impure (C)		
Run	Chain Rotation	Fusion	Run	Chain Rotation	Fusion	Run	Chain Rotation	Fusion
1	13.6 cal./g.	37.9 cal./g.	1	13.4 cal./g.	37.8 cal./g.	1	12.3 cal./g.	37.4 cal./g.
2	13.3 cal./g.	38.1 cal./g.	2	13.6 cal./g.	37.4 cal./g.	2	11.5 cal./g.	38.1 cal./g.
3	13.7 cal./g.	37.8 cal./g.				3	11.0 cal./g.	36.6 cal./g.
4	14.0 cal./g.	38.1 cal./g.						
Mean	13.7 cal./g.	38.0 cal./g.	Mean	13.5 cal./g.	37.6 cal./g.	Mean	11.6 cal./g.	37.4 cal./g.

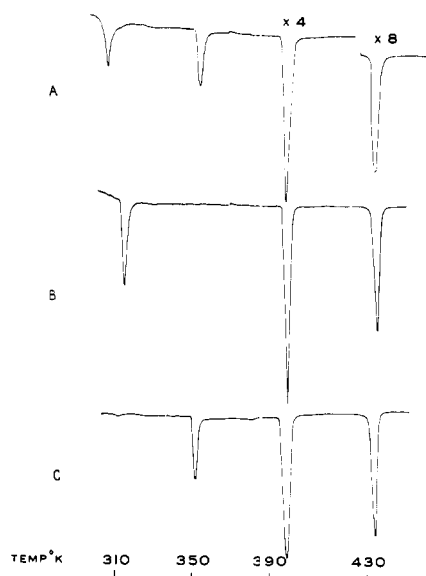


Figure 8. Ammonium nitrate transitions

the qualitative performance of the device is equivalent to that of the best conventional DTA equipment.

Barshad (2) suggested the use of NH_4NO_3 as a calibration standard for the temperature scale of conventional DTA units. The material undergoes four transitions between room temperature and decomposition, which have been carefully reported (3). It has been commonly used to illustrate the qualitative performance of thermal analyzers.

Figure 8 shows a series of heating curve analyses of ammonium nitrate from room temperature to 180°C . (553°K). Four transition points have been identified in Figure 8a—at 315°K . (32°C), 353°K . (80°C), 398°K . (125°C), and 443°K . (170°C). These transitions have been ascribed in the literature (3) to the following transitions:

- 315°K . (32°C) β rhombic to α rhombic
- 353°K . (80°C) α rhombic to rhombohedral
- 398°K . (125°C) rhombohedral to cubic
- 443°K . (170°C) cubic to liquid (fusion)

20mg, RANGE 2 40 °/MIN

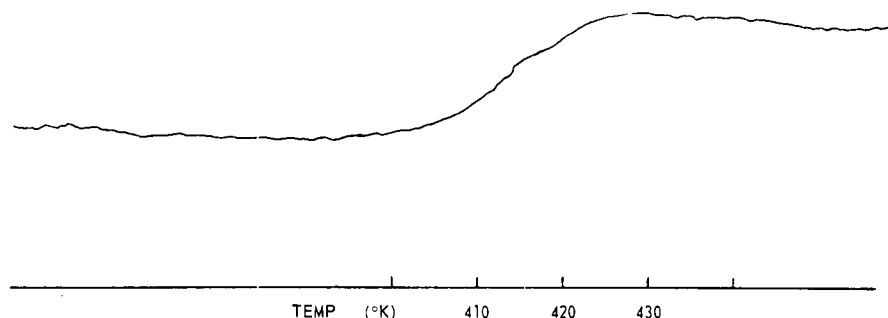


Figure 10. Glass transition of polycarbonate resin

The clear sharp peaks obtained using only 3 mg. of sample make the identification of the transition temperature unequivocal. Figures 8b and 8c illustrate the effect of prior cooling conditions on the transitions observed upon subsequent heating of the samples. Figure 8b shows the disappearance of the peak at 353°K , indicating that the sample went directly from the β rhombic to rhombohedral configuration. This sample had been previously melted and rapidly cooled with liquid nitrogen. Figure 8c shows the result when the molten sample was cooled to just below room temperature. Here the β to α transition is missing, indicating that the sample did not revert to the β state.

Quantitatively, the determination of transition energies were made by planimetric measurement of peak areas and comparison with a 6.47-mg. indium standard (44 millicalories). Values obtained for the NH_4NO_3 transitions were:

I Cubic to liquid (fusion)	19.0 cal./g.
II Rhombohedral to cubic	12.4 cal./g.
III α Rhombic to rhombohedral	4.0 cal./g.
IV β Rhombic to α rhombic	4.0 cal./g.

The literature value for transition I is 19.1 calories per gram (7), and for transition II, 12.3 calories per gram (12), as determined by conventional calorimetric procedures. Transitions III and IV are subject to wide variation with respect to sample history and cannot therefore, be compared with standard values.

It is interesting to note here the difference between the quantitative capabilities of the DSC and conventional DTA systems with respect to this problem. Figure 9 shows a comparison, with expanded ordinate and with no signal attenuation between peaks, of the two high temperature transitions of NH_4NO_3 (rhombohedral to cubic, cubic to liquid state). The energies of transition have been previously shown to be approximately 12 and 19 calories per gram, respectively

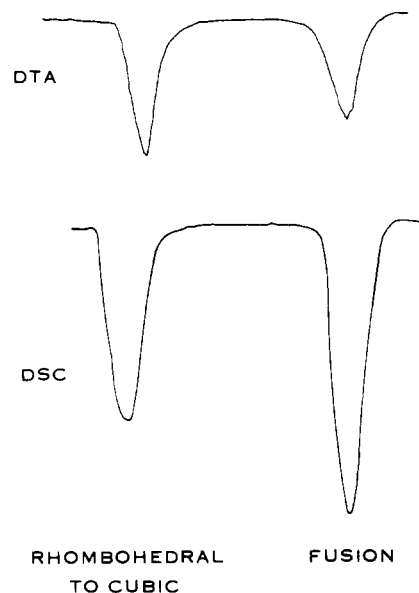


Figure 9. Comparison of conventional DTA and DSC records of NH_4NO_3 transitions

The DSC presentation obviously reflects this energy ratio, while the DTA areas, obtained on a well constructed system, are essentially equivalent.

Glass transitions are common phenomena in high polymer behavior. These transitions are changes in heat capacity resulting from relaxation of the chain segments in those portions of the polymer structure which are amorphous. It has been previously stated that when using the scanning calorimeter, sample heat capacity does not affect the measurement of transition energy. However, changes in heat capacity, such as those occurring in glass transitions, are observable with the calorimetric system. A change in heat capacity of a sample during a temperature scan will result in a change in the power necessary to keep the sample temperature tracking the temperature of the reference pan. This change in power will be reflected as a shift in the position of the baseline to a new level. While this display is graphically analogous to that shown on a conventional DTA system, the DSC baseline displacement may be interpreted quantitatively. In common with thermometric DTA, the DSC must be run at high sensitivity with high stability in order to observe the very small changes inherent in the glass transition. Figure 10 illustrates such a transition in a polycarbonate resin. The high scanning rate (40° per minute), large sample size (20 mg.), and high sensitivity (4 millicalories per second for full scale deflection) all help to magnify the observed transition. The direction of the transition is from lower heat capacity at a lower temperature to higher capacity at higher temperatures. In principle, the actual

values of the heat capacities may be determined with the calorimeter, but this has not been done in this instance.

LITERATURE CITED

- (1) Barrall, E. M., Rogers, L. B., *ANAL. CHEM.* **34**, 1101 (1962).
- (2) Barshad, I., *Am. Mineralogist* **37**, 667 (1952).
- (3) Early, R. G., Lowry, T. M., *J. Chem. Soc.* **115**, 1393 (1919).
- (4) Eyraud, C., *et al.*, *Compt. Rend.* **240**, 862 (1955).
- (5) Hoffman, J. D., Decker, B. F., *J. Phys. Chem.* **57**, 520 (1953).
- (6) Ke, Bacon, *J. Polymer Sci.* **62**, 15 (1960).
- (7) Keenan, A. G., *J. Phys. Chem.* **60**, 1356 (1956).
- (8) Kumanin, K. G., *Zh. Prikl. Khim.* **20**, 1242 (1947).
- (9) Roberts-Austen, W. C., *Proc. Inst. Mech. Engrs.* **1**, 35 (1899).
- (10) Saladin, E., *Iron and Steel Metallurgy and Metallography* **7**, 237 (1904).
- (11) Smothers, W. J., Chiang, Y., "Differential Thermal Analysis," pp. 120-1, Chemical Publishing Co., New York City, 1958.
- (12) Steiner, L. E., Johnston, J., *J. Phys. Chem.* **32**, 912 (1928).
- (13) Stone, R. L., *ANAL. CHEM.* **32**, 1582 (1960).
- (14) Sykes, C., *Proc. Roy. Soc.* **148**, 422 (1935).
- (15) Vassallo, D. A., Harden, J. C., *ANAL. CHEM.* **34**, 132 (1962).

RECEIVED for review July 5, 1963.
Accepted December 11, 1963. Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., 1963.

The Analysis of a Temperature-Controlled Scanning Calorimeter

M. J. O'NEILL

The Perkin-Elmer Corp., Norwalk, Conn.

► The features of various types of scanning calorimeters are described and compared. It is shown that proportional temperature control of a sample-holding surface, with simultaneous measurement of the heat flow rate into or out of the sample, is a superior technique with respect to instrumental criteria such as analysis time and applicability to reversible and regenerative thermal phenomena. After an analysis of the performance of a temperature-controlled calorimeter with a sharp sample transition, such as fusion, it is further concluded that the small thermal source resistance inherent in such a system is ideally suited for the resolution of such phenomena. A figure of merit is derived, with which different instrument designs may be evaluated.

A FUNDAMENTAL CHARACTERISTIC of any substance is its enthalpy function, or the derivative of this function with respect to temperature, the specific heat function. These functions include intrinsic properties of materials, such as specific heat, heat of fusion, and solid-state transition energies. In addition, they characterize such phenomena as reaction, decomposition, and sorption, in which materials react with their environments.

Figure 1 is a representative enthalpy diagram and its derivative. The phenomena shown here are generally reversible, although there may be hysteresis associated with transitions such as fusion. In pure materials, fusion occurs in a very narrow temperature range; the specific heat in this temperature range may be orders of magnitude greater than the specific heat just outside it. In the limit, the dH/dT function is characterized by impulses of infinite

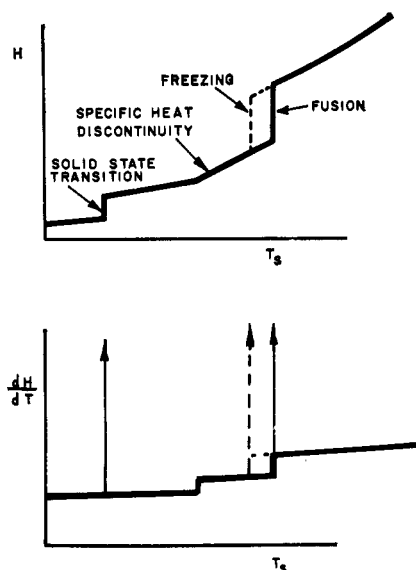


Figure 1. Enthalpy and specific heat functions

height and zero width at the melting and freezing points. The area of the impulse is the energy associated with the transition.

Many phenomena of more interest than the above are not reversible. Figure 2 shows the behavior of a fuel in a suitable atmosphere. In this case, the negative impulse in dH/dT at the combustion temperature represents the release of energy to the environment. In this hypothetical example, the combustion products are gaseous, and disappear from the measuring system; thus dH/dT is zero for all higher temperatures. Of practical importance in this sample is the comparison between ΔH , the total combustion energy, and ΔH_1 , the energy required to raise the fuel to the combustion temperature. This comparison is made between two ordinates in the enthalpy diagram, and between two areas in the specific heat diagram.

Frequently the characteristic transitions of a material are not sharply defined, but occur over a temperature range. In metal alloys, for example, the enthalpy in the vicinity of the freezing point is not uniquely determined by the temperature unless the transition proceeds slowly enough to maintain thermal equilibrium between the phases.

Temperature-Controlled and Enthalpy-Controlled Calorimetry. There are two basic approaches to the extraction of enthalpy data from a sample. (1) In adiabatic or enthalpy-controlled calorimetry, the enthalpy of the sample is a predetermined and reproducible function of time, while the sample temperature is the dependent, measured variable. This classic technique has much to recommend it, but it is fundamentally inferior to (2) isothermal or temperature-controlled calorimetry, in which the temperature of the sample is the independent, reproducible variable, while the enthalpy is the dependent, measured variable.

The obvious advantage of the latter technique is that the independent variable, the abscissa of the data presentation, is an intensive parameter, while the ordinate represents an extensive parameter. This is such a basic principle of scanning analytical instrumentation that the mere existence of the adiabatic calorimeter needs explanation. In fact, it is relatively simple to increase the enthalpy of a large thermal mass in a reproducible manner, while measuring its temperature. It is considerably more difficult to generate reproducible temperature programs, and to measure variable heat flow rates. However, if these problems can be solved, a number of instrumental advantages are immediately realized.

In Figure 3, the distinction between