Thermochimica Acta, 5 (1973) 377–389
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

PRECISE DETERMINATION OF MELTING AND BOILING POINTS BY DIFFERENTIAL THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY*

EDWARD M. BARRALL II
IBM Research Laboratory, San Jose, Calif. 95114 (U. S. A.)

(Received 25 June 1972)

ABSTRACT

The theory, operation and instrumentation of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are sufficiently well developed to determine melting and boiling points with a high degree of certainty and reproducibility. However, certain precautions must be taken if data of maximum value are to be obtained. Sampling techniques, encapsulation, instrumental parameters and theoretical considerations will be treated in detail.

In addition to the very small amount of material required for a melting or boiling point determination, DTA and DSC have other advantages. If certain precautions are observed it is possible to use several equations from classical thermodynamics to obtain absolute purity. A complete Cox Chart of a pure liquid can be obtained and the heat of vaporization determined in a few hours. Complex solid phase diagrams are easily studied. The success or failure of fractionation techniques can be predicted from single thermograms if several phase transitions are present.

INTRODUCTION

The most frequently reported properties of matter are the melting point and boiling point. These properties have been assigned importance since the earliest days of chemistry. Various methods of determination have been employed from hot stage microscopy to melting point capillary. Wide differences in results on essentially identical material have been reported between laboratories, methods, workers, and as a function of time. These differences are due in part to the actual complexity of the apparently simple determinations. This complexity arises from the nature of the thermodynamics which are in operation when a less than 100% pure material undergoes a phase transition. It is quite safe to assume that any material is impure from the thermodynamic viewpoint unless *very* special precautions are taken. Therefore, the determination of a "precise" melting point is somewhat complicated by the fact that melting of an impure material is a temperature distributed property. No single number

---

*Presented at the "Thermal Analysis Methods Symposium", A. B. Wist, Chairman, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 6–10, 1972.

will describe that whole process. The temperature at maximum rate of melting is considered useful by most authorities[1,2], but is subject to procedural variations by the very fact of being a rate measurement.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) offer a method for the determination of phase transition temperatures which is more closely related to the thermodynamic considerations than a visual melting point or boiling point measurement. However, these methods, DSC and DTA, have their own peculiarities which must be recognized if accurate and reproducible results are to be obtained. A consideration of the thermodynamic and instrumental parameters which must be known for the precise determination of these "simple" phase transitions will be the subject of this discussion.

GENERAL CONSIDERATIONS

The boiling point of a material is a better "defined" transition than the melting point. It is simply the temperature at which the liquid vapor pressure equals the atmosphere pressure. Given a single plate of reflux (saturated vapor) over the liquid, the event is easy to detect if the heat flow is measured. Barring singular surface tension effects and given a sufficiency of liquid phase, the onset of boiling is noted as a sharp endothermal dip in the DTA or DSC base line[3,4]. Traces of low boiling components and changes in the composition of the liquid during heating can cause some uncertainty in extreme cases.

The enthalpy, *H*, versus temperature curve for a simple phase transition is shown in Fig. 1 for a 100% pure material under ideal conditions. The transition is truly isothermal. For most materials normally encountered, Fig. 1 does not describe

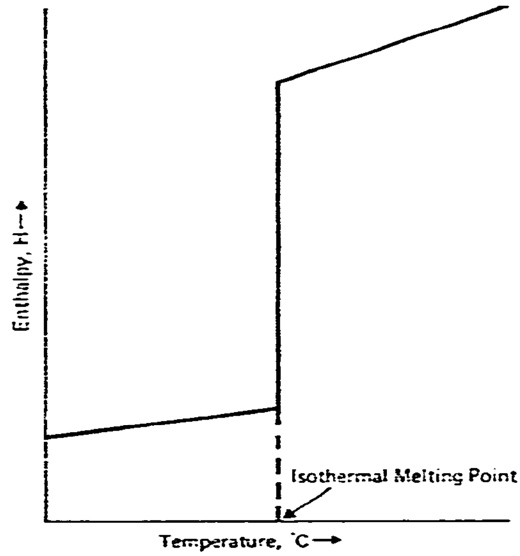


Fig. 1. Enthalpy of a simple phase transition in a 100% pure material.

melting. Indeed, Fig. 1 does not describe melting for many ultra pure organic compounds. According to Westrum and McCullough many organic materials do not melt isothermally[1]. Thus, it is necessary to define what we shall call the melting point for less than 99.999% pure materials and many organic compounds. Such a definition should also apply to polymeric materials.

Since no single temperature is adequate for a complete description of a non-isothermal process, we must consider the temperatures which are operationally important. The temperature at which the first detectable liquid phase appears is one such term. For relatively pure materials this term can be obtained with an accuracy of 1 to 2°C. For polymeric materials the transition may be so subtle as to be imponerable. Polypropylene is a good example[5]. Measurements done by careful calorimetry have not been able to determine a clear cut onset of melting temperature. The thermal properties of the amorphous but "solid" phase grade continuously into the amorphous liquid phase. The temperature at the disappearance of the last trace of the solid phase is another often quoted value. Given reasonably rapid melting this term is identical with the temperature at the maximum rate of melting. Many workers have attempted to show that the final solid melting is identical to the vertex of the DTA or DSC endotherm. Depending on instrumental design and sample size this is probably true for most classes of compounds. The best evidence for coincidence of these two events has been obtained by simultaneous or consecutive DTA-optical microscope studies[6,7]. The last trace of solid anisotropy coincides to ±0.05°C with the endothermal minimum. Very small samples were employed in these studies. Thus, if a single temperature must be given, the temperature at the endothermal minimum is probably the most significant. This discussion will revolve around a consideration of variable control and measurement which will insure reproducible measurement of the endothermal minimum.

The van't Hoff equation provides a satisfactory definition for materials which have impurities which are insoluble in the solid phase and completely soluble in the melt

$$T_0 - T_m = \frac{RT_0^2 X_2}{\Delta H_f} \tag{1}$$

where T_0 = the melting temperature of the 100% pure material in °K
T_m = the melting temperature of the impure material in °K
R = the gas constant, 1.9865 cal/°K/mole
ΔH_f = heat of fusion in cal/mole
X_2 = mole fraction of impurity.

This equation states that all temperatures beyond the onset of melting are important. As we shall see DTA and DSC can provide sufficient information to use this equation to obtain a precise melting point as well as purity.

In almost all equipment for the measurement of temperature where a net heat flow occurs, some thermal lag is present. This lag arises from the thermal conductivity of the sample and various parts of the apparatus[3,8]. It is necessary to measure the thermal lag for each piece of equipment as a part of the calibration procedure. Depending on instrument design the lag can be a more or less important term. In all cases it is necessary to bear in mind that lag is a proportional or exponential term and the correction depends on the magnitude of the thermal transition involved and the temperature of the system.

Because of lag and thermal conductivity effects, it is important to use the smallest sample consistent with instrument sensitivity and the statistics of sampling. This is particularly important in the measurement of melting points. Sizable and non-reproducible thermal gradients can accumulate in large samples between the heat source and temperature detectors.

INSTRUMENTATION

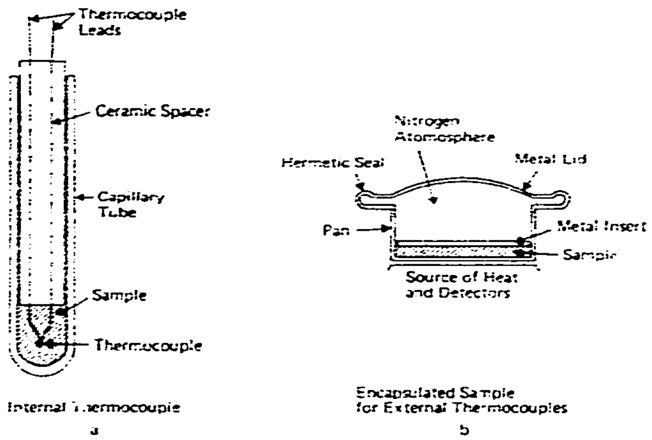
Excellent commercial DTA and DSC equipment is now available. Unless the conditions of the experiment are very unusual, neither economics nor accuracy can recommend construction of one's own equipment. Companies such as duPont Instrument Products, Perkin–Elmer Corp., and Mettler have developed equipment suitable for the measurement of organic and inorganic melting and boiling points.

There are at least one dozen ways of recording the DTA differential temperature as some function of time or temperature[9,10]. Although each method has specific points to recommend it, we shall consider but one system. The differential temperature will be measured between the sample and an inert reference of equal heat capacity at the transition temperature. The differential temperature is recorded as a function of the sample temperature. This is most conveniently done with an x–y recorder, but a cross plot of two records of differential temperature versus time and sample temperature versus time will serve.

In DSC the differential power is recorded as a function of time. Because of the way DSC operates, if temperatures are related to a given sample compartment by calibration, the recording will be versus the sample temperature. In the DSC system, if time and temperature are not interrelated directly, the machine is not working properly.

Melting points

In DTA there are essentially two ways to handle the sample. These are shown in Fig. 2. In the case where the thermocouple is located in the sample, a diluting agent may be employed. This serves to equalize the heat capacity and thermal conductivity of the sample and reference cells. Good results have been obtained using either this method or by melting a few crystals of the compound onto the sample thermocouple directly. In any case, it is important to insure good thermal contact between detector and sample. In this particular discussion, the author recommends the use of the melting point capillary method for melting point determination with a centrally located thermocouple.



Internal Thermocouple
a

Encapsulated Sample for External Thermocouples
b

Fig. 2. (a) DTA and (b) DSC cell designs.

In DSC as well as in certain DTA instrumentation, the sample must be encapsulated since the detectors are external to the sample. These encapsulations are usually a tightly sealed metal container of high thermal conductivity. Encapsulation results in the formation of several thermal barriers between the sample and the detector. Since these barriers are unavoidable, it is essential that they be reproducible. It is necessary to accurately evaluate the thermal lag.

A satisfactory encapsulation is shown in Fig. 2b. The addition of the metal plate to the usual encapsulation is necessary to keep the sample from detaching from the encapsulation while in the melt[11]. For example, a flat sheet of tin melts to form an almost perfect sphere against a single aluminum surface. On second melting, the thermal barrier between the encapsulation and the spherical sample is orders of magnitude greater than on first melting. Double sheets prevent the formation of a sphere with point contact. The added plate also discourages the breakup of the sample melt into separate pockets. Because of small variations in local thermal conductivity, a divided sample may display a set of melting endotherms when only one exists.

Boiling points

The statements applied to melting points also pertain to boiling points with the addition of two more factors: (1) Provisions must be made for the equilibration of liquid and vapor; and (2) instrument atmospheric pressure must be controlled. Both of these considerations arise from the thermodynamic laws surrounding boiling.

In order to obtain a meaningful boiling point, one plate of equilibration is necessary. This can be provided by several means, two of which are shown in Figs. 3 and 4 for encapsulated and internal thermocouple instruments. A single plate of reflux is easily provided in encapsulated samples by drilling a small hole in the lid[3]. This permits the sample to assume the pressure of the instrument while not losing a significant amount of material due to vaporization below the boiling point. The few tenths of a degree difference between the liquid at the bottom of the cell (warmer) and

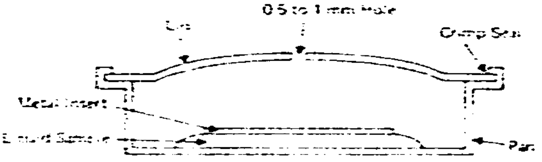


Fig. 3. Boiling point cell for an encapsulated sample.

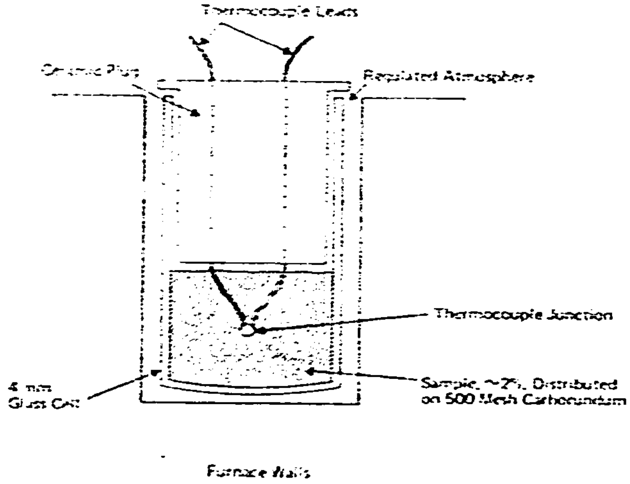


Fig. 4. Boiling point cell for a solid supported liquid sample with internal thermocouples.

the vapor against the lid at the top of the cell (cooler) provides almost ideal reflux. At the boiling point the rapid conversion of liquid to vapor and the lack of condensation at the lid results in a sudden escape of vapor through the vent hole. This produces a sharp endotherm.

When internal thermocouples are used it is necessary to distribute the liquid on an inert support. It is important that the liquid not be chemisorbed on the support. The present author has found that calcined 200 mesh carborundum is very satisfactory to support the liquid[4]. At most, 2% of the solid by weight should be coated with liquid. Diffusion, evaporation, and recondensation of the adsorbed liquid provides the necessary refluxing.

Few commercial DTA or DSC machines have adequate atmosphere regulation for boiling point determination. A manometer, barometer, vacuum pump, needle valve, nitrogen tank, and assorted tubing are necessary. These are arranged as shown in Fig. 5. Since the heating rate is relatively rapid and run times are short, great stability is not necessary in the system. It is necessary to know the pressure precisely only during the boiling endotherm. For reasonable precision, the boiling point should be determined at three pressures or more between 5 and 760 torr.

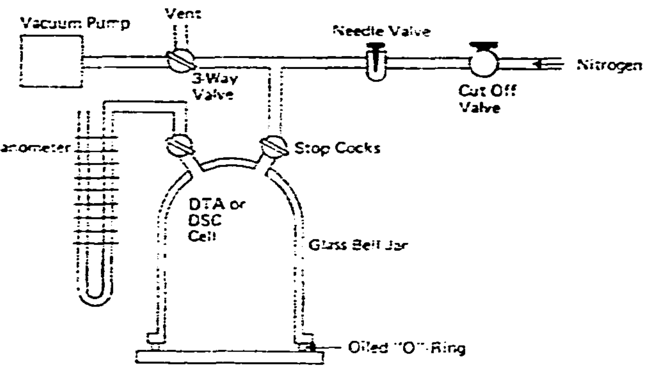


Fig. 5. Atmosphere-pressure control for boiling point determinations.

Standardization

Both melting point and boiling point techniques should be standardized by the melting of solids if the temperature range permits. Suitable standards are shown in Table I. Most of the metals listed may be obtained in semiconductor grades (99.999 to 99.9999% pure) from Research Organic/Inorganic Chemical Corp., 11686 Sheldon St., Sun Valley, Calif. 91352.

TABLE I

MELTING POINT STANDARDS FOR THE CALIBRATION OF DTA AND DSC

Temperature °C	*Material*	*Melting* (M) *or inversion* (I)	*Enthalpy change cal/g*
−38.9	mercury	M	2.74
29.8	gallium	M	19.9
69.4	stearic acid	M	47.6
125.2	ammonium nitrate	I	12.6
169.6	ammonium nitrate	M	16.2
122.4	benzoic acid	M	33.9
156.6	indium	M	6.79
231.9	tin	M	14.2
264	lithium nitrate[a]	M	88.4
273	sodium nitrate	I	9.5
327.4	lead	M	5.89
419.5	zinc[a]	M	27.0
588	potassium sulfate	I	12.3

[a] Place between mica strips prior to encapsulation.

The author recommends neither water nor benzoic acid as standards. Water has a very high heat of fusion so that problems with micro manipulation of a volatile liquid are encountered. For example, if organic samples of about 2 mg are being studied, a water temperature standard could weigh only 0.6 mg. This assumes that the same instrumental sensitivity is used on both (desirable). In addition, a water standard can recondense any place in the cell on standing at room temperature. This produces erratic results. Benzoic acid sublimes below the melting point. This makes it usable only in encapsulated cells of robust design. Even under these conditions a drift-free base line is difficult to obtain.

A series of standards bracketing the sample should be run. The calibration curve should be good for sometime barring changes in the instrument. Heating rates greater than 10°C/min should not be used. A heating rate of 5°C/min is a good compromise between the demands of time and thermodynamic equilibrium. Whatever heating rate is chosen, it is important that it be used for both the standardization and the sample run.

The mechanics of the DTA scan are determined by the type of sample encapsulation employed. For DSC there is currently only one encapsulation available—thus, no choice. If a metal encapsulated sample is used with external detectors, the following run should be followed. An empty cell is used as reference.

1. Balance the instrument and obtain the zero heating scan at some temperature below the melting (or boiling) point.
2. Start the program and heat through the transition.
3. Turn off the program and obtain the zero heating scan at some known temperature above the transition.

These run operations are shown in Fig. 6.

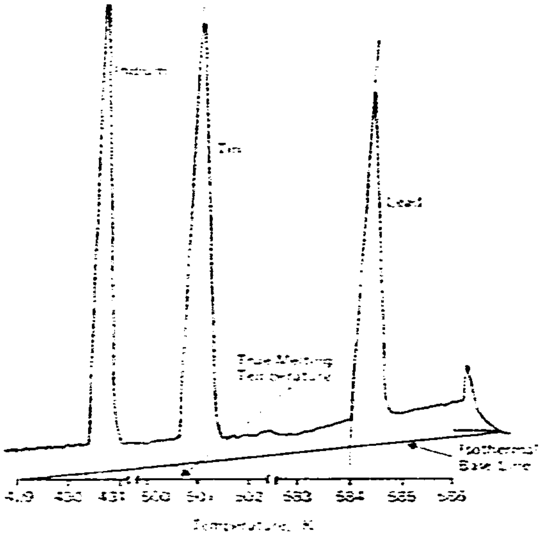


Fig. 6. Variation of a sharp-melting peak slope with transition temperature. All samples 99.99999 mole % pure 1.25°/min at 2.00 mcal/inch.

The temperature of the standard melt is read as shown in Fig. 6. This extrapolation reflects the thermal lag in the system as well as the melting point of the standard[11]. A calibration curve for a commercial DTA using encapsulated samples is contrasted with a commercial DSC in Figs. 7a and 7b. The parabolic shape of DSC calibration is due to electronic parameters of the system. In the latest model of this machine, the calibration is reported to be more nearly linear.

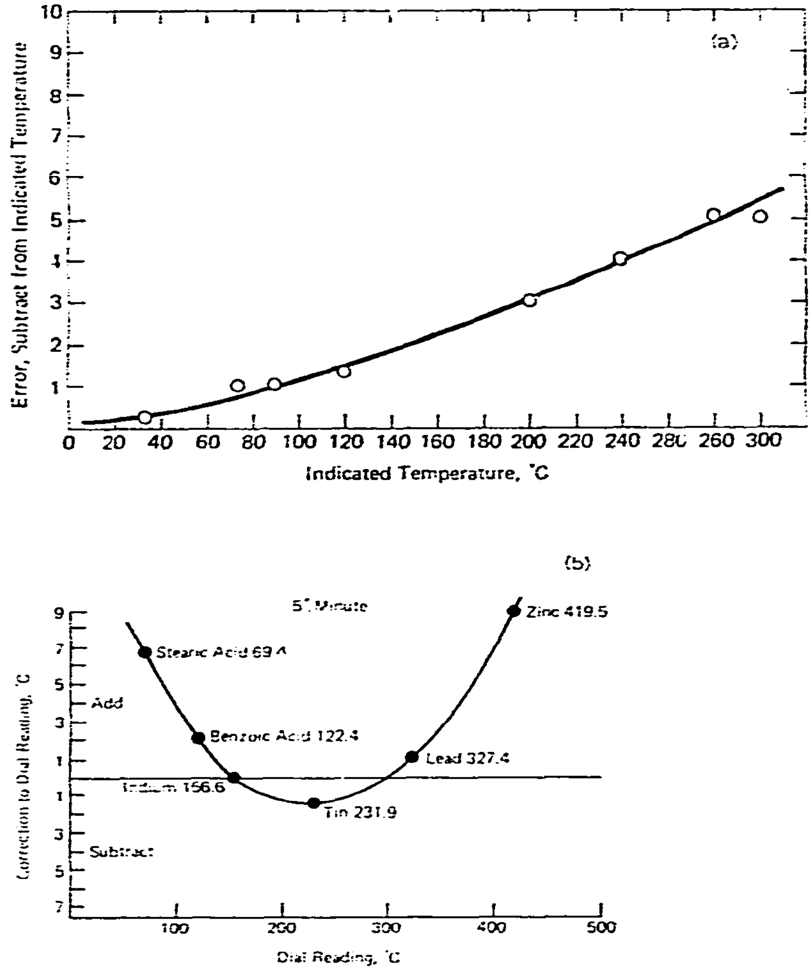


Fig. 7. Temperature calibration curves for (a) an internal thermocouple DTA, and (b) a Perkin–Elmer DSC–1B calorimeter.

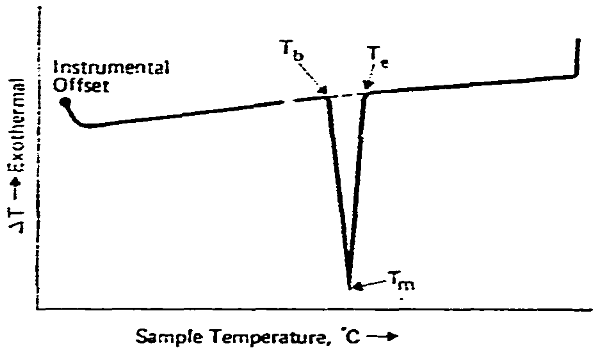


Fig. 8. Thermogram made with an internal thermocouple.

If the internal thermocouple system is used, no thermal lag correction is possible or really necessary. The sample is in direct contact with the thermocouple and given a small sample the shape of the endotherm is an accurate reflection of the process. A curve is shown in Fig. 8.

APPLICATIONS

Melting point determination

The sample size is chosen so as to give an endotherm of nearly the same height as the standard in that temperature range. This is usually 1 to 5 mg. The sample should be encapsulated under nitrogen to avoid oxidation. Steps 1 to 3 are followed as given above and the record shown in Fig. 9 is obtained. The isothermal base line is constructed. The melting standard is applied as shown in Fig. 9 and the onset of melting, T_b, maximum of the endotherm, T_m, and the end of the endotherm, T_e, are located, extrapolated, and corrected using the calibration curve. If internal thermocouples are used, the temperatures are only corrected for thermocouple error.

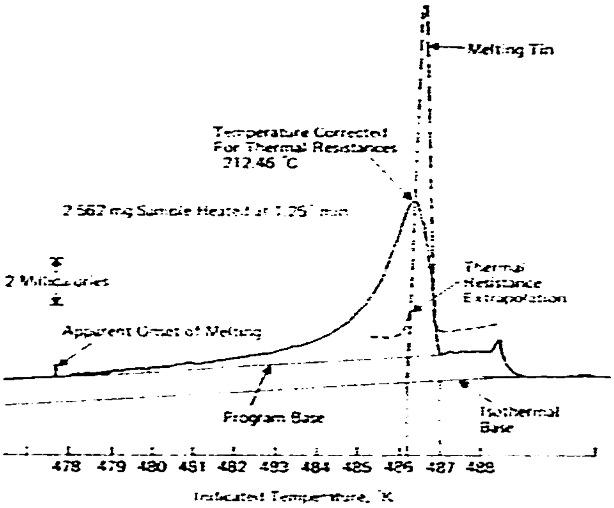
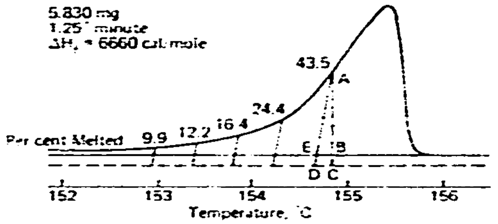


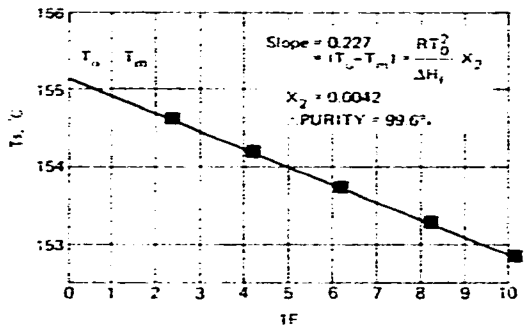
Fig. 9. DSC scan showing correction for thermal log using the melting endotherm of a pure metal. Correction of a DSC curve for thermal resistance 9,10-dichloroanthracene containing 1.10 mole % anthracene (2.562 mg sample heated at 1.25°/min).

The range between T_b and T_m is a function of purity of the sample. T_b is occasionally difficult to locate in impure samples due to base line drift. T_m corresponds to the temperature at the maximum rate of melting and should be closest to equilibrium freezing measurements of a more classical design.

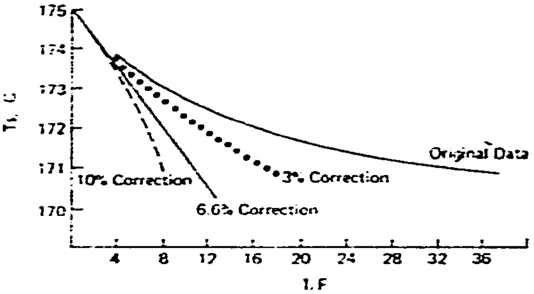
If the data has been obtained using a DSC, it is possible to determine the impurity as well as the melting point of the "hypothetical" 100% pure material. This assumes that the laws of ideal solution are followed and Eqn. (1) is obeyed. The method involves the calculation of the fraction of the sample melted at various temperatures (including the fraction which melted before the instrument detected an endothermal event). A plot is made of the reciprocal of the fraction melted (x-axis) as a function of the temperature. The y-intercept is the 100% melting point and the slope is a function of the purity. The method as well as several variations have been discussed in detail elsewhere[11–13]. A summary of the operations involved is given in Fig. 10.



Testosterone purity run.



Testosterone purity determination.



Graphical linearization of 1/F plot, phenobarbitol 99.4% (60).

Fig. 10. Steps involved in the determination of theoretical melting point, to, and purity from a DSC scan.

Boiling point

The heat of vaporization of most materials is several orders of magnitude greater than the heat of fusion. Thus, smaller samples and less sensitive instrumental parameters are used. The vertex of the boiling endotherm, T_m, if measured has little significance. It is a function only of various instrumental parameters, rate of vapor diffusion, and the amount of sample present at the onset of boiling. The onset of boiling is the temperature measured and the extrapolated temperature used for calculation after correction for instrumental lag (if applicable) and temperature calibration. A boiling curve is shown in Fig. 11. The same three steps given in the melting point measurement are followed for boiling point. In addition, the manometer and barometric pressure are read at the start of the inflex.

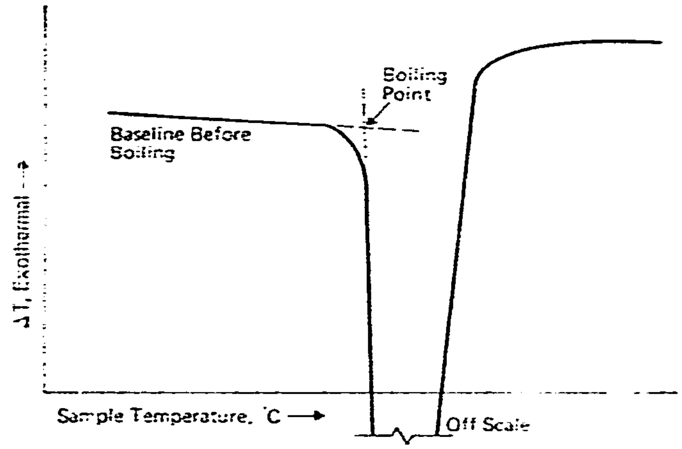


Fig. 11. Boiling point thermogram.

It is possible to measure the boiling point more accurately as well as measure the heat of vaporization if thermograms are run at several pressures. A plot of ln P is made versus $1/T$. The pressure, P, should be in atmospheres and the boiling point should be in °K. A good straight line plot should be obtained between ~5 and 760 torr. The slope of this line will be $-E/R$ where R is the gas constant and E will be ΔH_v in cal/mole. The plot serves to average out experimental error as well as obtain ΔH_v. In addition, the boiling point can be stated at 760 torr and not at whatever the local barometric pressure indicates.

CONCLUSION

The methods given in this discussion certainly are not intended as the *only* way possible to obtain good melting and boiling data by DTA and DSC. Many other schemes are possible and have been given in detail in the literature[9,14]. However, the techniques given here are consistent, readily adaptable to commercial instruments, and will cover a wide range of organic and inorganic materials. Improvements will be obvious to most serious investigators. These techniques are generally applicable as they stand. The data obtained should be much more consistent than that measured with the hot stage, oil bath, or capillary tube techniques. A closer comparison exists between routine melting data obtained by DTA and DSC and adiabatic calorimetric results than that obtained from visual methods. Boiling data obtained by DTA and DSC are far more reproducible and usually more closely comparable to equilibrium still results than data from micro ebulliometry. It is certain that DTA and DSC are more rapid. Between operator variations are minimized by DTA and DSC. After the developmental period of the last two decades, the differential techniques are now at the point that they need no longer be justified—only to be applied.

REFERENCES

1 E. F. Westrum Jr. and J. P. McCullough, *Thermodynamics of Crystals*, in D. Fox *et al.* (Eds.), *Physics and Chemistry of the Organic Solid State*, Interscience, New York, 1963, pp. 67–73.
2 M. J. Vold, *Anal. Chem.*, 21 (1949) 683.
3 *Thermal Analysis Newsletter*, Perkin–Elmer Corp., Norwalk, Conn., 1967, No. 7, pp. 4–8.
4 E. M. Barrall, R. S. Porter and J. F. Johnson, *Anal. Chem.*, 37 (1965) 1053.
5 R. W. Wilkinson and M. Dole, *J. Polym. Sci.*, 58 (1962) 1089.
6 E. M. Barrall and E. J. Gallegos, *J. Polym. Sci.*, *A-2*, 5 (1967) 113.
7 G. W. Miller, *S.P.E. Annual Technical Conference*, *No. 29*, Washington, D. C., May 10–13, 1971, p. 290.
8 M. J. O'Neill, *Anal. Chem.*, 36 (1964) 1238.
9 P. D. Garn, *Thermoanalytical Methods of Investigation*, Academic Press, New York, 1965.
10 E. M. Barrall and J. F. Johnson, in P. E. Salde and L. T. Jenkins (Eds.), *Techniques and Methods of Polymer Evaluation*, M. Dekker, New York, 1966, p. 10.
11 E. M. Barrall and R. D. Diller, *Thermochim. Acta*, 1 (1970) 509.
12 *Thermal Analysis Newsletter*, Perkin–Elmer Corp., Norwalk, Conn., 1965, No. 4, p. 14.
13 C. Plato and A. R. Glasgow Jr., *Anal. Chem.*, 41 (1969) 330.
14 W. W. Wendlandt, *Thermal Methods of Analysis*, Interscience, New York, 1964.