chapter**THIRTY-ONE**

Thermal Methods

Thermal analysis techniques are those in which a physical property of a substance or its reaction products is measured as a function of temperature. Usually, the substance is subjected to a controlled temperature program during the analysis. Although there are more than a dozen thermal analysis techniques, we confine our discussion in this chapter to four methods that provide primarily chemical rather than physical information about samples of matter. These methods include **thermogravimetric analysis, differential thermal analysis, differential scanning calorimetry,** and **microthermal analysis.**

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Thermal methods differ in the properties measured and the temperature programs applied.[1] The four methods discussed here find widespread use for both quality control and research applications on polymers, pharmaceutical preparations, clays, minerals, metals, and alloys.

31A THERMOGRAVIMETRIC ANALYSIS

In a thermogravimetric analysis (TGA) the mass of a sample in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample is increased (usually linearly with time). A plot of mass or mass percentage as a function of time is called a *thermogram* or a *thermal decomposition curve*.

31A-1 Instrumentation

Commercial instruments for TGA consist of (1) a sensitive microbalance, called a thermobalance; (2) a furnace; (3) a purge-gas system for providing an inert, or sometimes reactive, atmosphere; and (4) a computer system for instrument control, data acquisition, and data processing. A purge-gas switching system is a common option for applications in which the purge gas must be changed during an experiment.

The Thermobalance

A number of different thermobalance designs available commercially are capable of providing quantitative information about samples ranging in mass from less than 1 mg to 100 g. The usual range of thermobalances, however, is from 1 to 100 mg. Many of the balances can detect changes in mass as small as 0.1 μg. Although the sample holder must be housed in the furnace, the rest of the balance must be thermally isolated from the furnace. Figure 31-1 is a schematic diagram of one thermobalance design.

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[1] For a detailed description of thermal methods, see *Principles and Applications of Thermal Analysis*, P. Gabbott, ed., Oxford, UK: Wiley-Blackwell, 2008; *Principles of Thermal Analysis and Calorimetry*, P. J. Haines, ed., Cambridge, UK: Royal Society of Chemistry, 2002; P. J. Haines, *Thermal Methods of Analysis*, London: Blackie, 1995; B. Wunderlich, *Thermal Analysis*, Boston: Academic Press, 1990; W. W. Wendlandt, *Thermal Analysis*, 3rd ed., New York: Wiley, 1985. For reviews, see S. Vyazovkin, *Anal. Chem.*, **2010**, *82*, 4936, **DOI**: 10.1021/ac100859s; *Anal. Chem.*, **2008**, *80*, 4301, **DOI**: 10.1021/ac8005999; *Anal. Chem.*, **2006**, *78*, 3875, **DOI**: 10.1021/ac0605546.

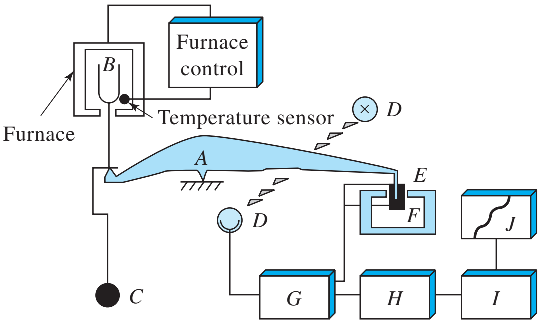

FIGURE 31-1 Thermobalance components. The balance beam is shown as *A*. The sample cup and holder are *B*; *C* is a counterweight. *D* is a lamp and photodiodes, *E* is a magnetic coil, and *F* is a permanent magnet. The computer data-acquisition, data-processing, and control systems are components *G*, *H*, and *I*. Component *J* is the printer and display unit. (Courtesy of Mettler-Toledo.)

A change in sample mass causes a deflection of the beam, which interposes a light shutter between a lamp and one of two photodiodes. The resulting imbalance in the photodiode current is amplified and fed into coil *E*, which is situated between the poles of a permanent magnet *F*. The magnetic field generated by the current in the coil restores the beam to its original position. The amplified photodiode current is monitored and transformed into mass or mass-loss information by the data-processing system. In most cases mass versus temperature data can either be plotted in real time or stored for further manipulation or display at a later time.

The Furnace

Furnaces for TGA typically cover the range from ambient temperature to 1000°C, although some can be used for temperatures up to 1600°C. Heating rates can often be selected from 0.1°C/min to 100°C/min. Some units can heat as rapidly as 200°C/min. Insulation and cooling of the exterior of the furnace is required to avoid heat transfer to the balance. Nitrogen or argon is usually used to purge the furnace and prevent oxidation of the sample. For some analyses, it is desirable to switch purge gases as the analysis proceeds. Figure 31-2 provides an example in which the purge gas was automatically switched from nitrogen to oxygen and then back to nitrogen. The sample in this case was a bituminous coal. The purge gas was nitrogen during the first 18 min, while the moisture content and the percentage of volatiles were recorded. The gas was then switched to oxygen for 4–5 min, which caused oxidation of carbon to carbon dioxide. Finally, the experiment was concluded with a nitrogen purge to give a measure of the ash content. Most newer TGA instruments use digital flow controllers for the purge gas flow monitoring.

The temperature axis is usually calibrated by using a material of known Curie point or sometimes a melting point standard. The *Curie point* is the temperature at which a ferromagnetic material becomes paramagnetic. The ferromagnetic material is suspended in a magnetic field oriented such that a vertical component of magnetic force acts on the sample. The magnetic force acts as an equivalent magnetic mass on the TGA balance beam to indicate an apparent sample mass. When the sample is heated through its Curie point, the magnetic mass is lost, and the balance indicates an apparent loss in mass. Temperature accuracy is better than 1°C with most furnaces, and temperature precision is typically ±0.1°C. Furnaces are usually cooled by forced air. Many furnaces can be cooled from 1000°C to 50°C in less than 15 minutes.

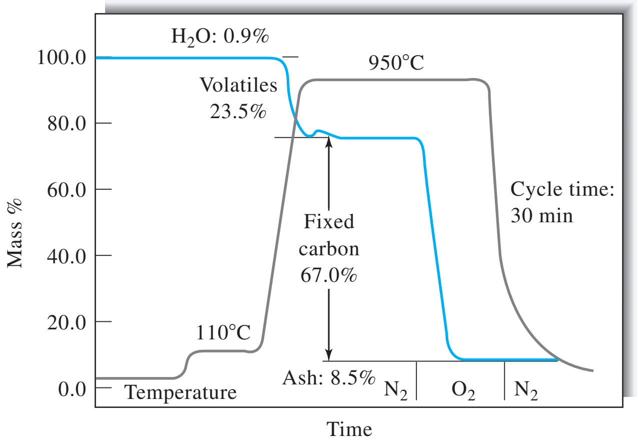

FIGURE 31-2 Controlled atmospheric thermogram for a bituminous coal sample. A nitrogen atmosphere was used for about 18 min followed by an oxygen atmosphere for 4–5 min. The experiment was then completed in nitrogen. (Reprinted with permission from C. M. Earnest, *Anal. Chem.*, **1984**, *56*, 1471A, **DOI:** 10.1021/ac00277a786.)

Sample Holders

Samples are typically contained in sample pans made of platinum, aluminum, or a ceramic such as alumina. Platinum is most often used because of its inertness and ease of cleaning. The volumes of sample pans range from 40 μL to more than 500 μL. Ceramic pans are best for high-volume, low-density samples (e.g., foams) and for materials that react with platinum. Aluminum pans are inexpensive substitutes, but cannot be used for temperatures exceeding 600°C. Autosamplers are available as attachments for most TGA systems. With the majority of these units, all aspects are automated under software control. The sample-pan taring, loading, and mass measurement; the furnace heating and cooling; and the pan unloading are totally automatic.

Temperature Control and Data Processing

The temperature recorded in a thermogram is ideally the actual temperature of the sample. This temperature can, in principle, be obtained by immersing a small thermocouple directly in the sample. Such a procedure is seldom followed, however, because of possible catalytic decomposition of samples, potential contamination of samples, and mass measurement errors resulting from the thermocouple leads. Because of these problems, recorded temperatures are generally measured with a small thermocouple located as close as possible to the sample container. The recorded temperatures then generally lag or lead the actual sample temperature. In some cases, dual thermocouples are used in a control/feedback mode.

Modern TGA systems use a computerized temperature control routine that automatically compares the voltage output of the thermocouple with a voltage-versus-temperature table stored in computer memory. The computer uses the difference between the temperature of the thermocouple and the temperature specified to adjust the voltage to the heater. In some systems the same thermocouple behaves as the heating element and the temperature sensor. With modern control systems, it is possible to achieve excellent agreement between the specified temperature program and the temperature of the sample. Typical run-to-run reproducibility for a particular program falls within 2°C throughout an instrument's entire operating range.

Combined Thermal Instruments

Several manufacturers offer systems that provide simultaneous measurement of heat flow (see Section 31C for differential scanning calorimetry) and mass change (TGA) or of energy change (see Section 31B for differential thermal analysis) and mass change. Such instruments can not only track the loss of material or a vaporization phenomenon with temperature but also reveal transitions associated with these processes. These combination units can eliminate the effects of changes in sample size, homogeneity, and geometry. Many TGA systems produce the derivative of the thermogram as well as the thermogram itself. Such derivative plots are not true differential thermograms as produced in differential thermal analysis, but they provide similar qualitative information. They are often called single differential thermal analysis (SDTA) plots.

TGA/MS and TGA/FTIR

TGA is used to determine the loss in mass at particular temperatures, but TGA cannot identify the species responsible. To obtain this type of information, the output of a thermogravimetric analyzer is often connected to a Fourier transform infrared (FTIR) or a mass spectrometer (MS). Several instrument companies offer devices to interface the TGA unit to a spectrometer. Some even claim true integration of the software and hardware of the TGA/MS or TGA/FTIR systems.

High-Resolution TGA

In high-resolution TGA, the sample heating rate fluctuates so that the sample is heated more rapidly during periods of constant mass than during periods when mass changes occur. This allows higher resolution to be obtained during the interesting periods and reduces the time of inactivity.

31A-2 Applications

Because TGA monitors the mass of the analyte with temperature, the information provided is quantitative, but limited to decomposition and oxidation reactions and to such physical processes as vaporization, sublimation, and desorption. Among the most important applications of TGA[2] are compositional analysis and decomposition profiles of multicomponent systems.

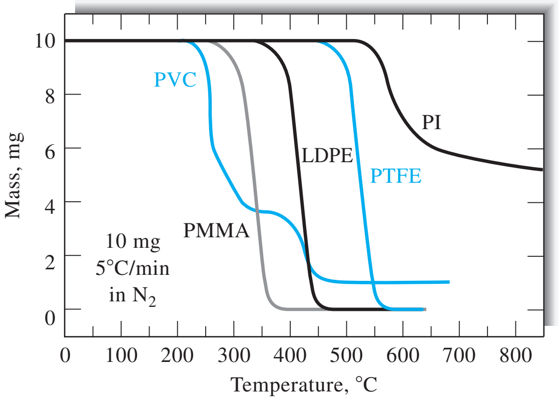

FIGURE 31-3 Thermograms for some common polymeric materials. PVC = polyvinyl chloride; PMMA = polymethylmethacrylate; LDPE = low-density polyethylene; PTFE = polytetrafluoroethylene; PI = aromatic polypyromelitimide. (From J. Chiu, in *Thermoanalysis of Fiber-Forming Polymers*, R. F. Schwenker, ed., New York: Wiley, 1966.)

In polymer studies, thermograms provide information about decomposition mechanisms for various polymeric preparations. In addition, the decomposition patterns are characteristic for each kind of polymer and can sometimes be used for identification purposes. Figure 31-3 shows decomposition patterns for five polymers obtained by thermogravimetry.

Figure 31-4 illustrates how a thermogram is used for compositional analysis of a polymeric material. The sample is a

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[2] For discussions of applications of thermal methods, see K. S. Alexander, A. T. Riga, and P. J. Haines in *Analytical Instrumentation Handbook*, 3rd ed., J. Cazes, ed., Boca Raton, FL: CRC Press, 2005, Chap. 15; A. J. Pasztor, in *Handbook of Instrumental Techniques for Analytical Chemistry*, F. Settle, ed., Upper Saddle River, NJ: Prentice-Hall, 1997, Chap. 50.

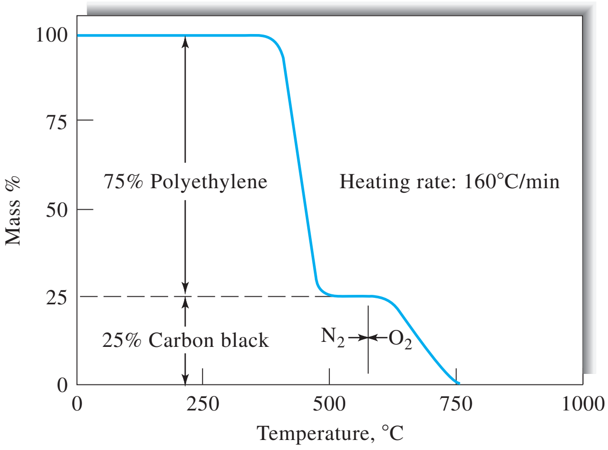

FIGURE 31-4 Thermogravimetric determination of carbon black in polyethylene. (From J. Gibbons, *Amer. Lab.*, **1981**, *13* (1), 33. Copyright 1981 by International Scientific Communications, Inc.)

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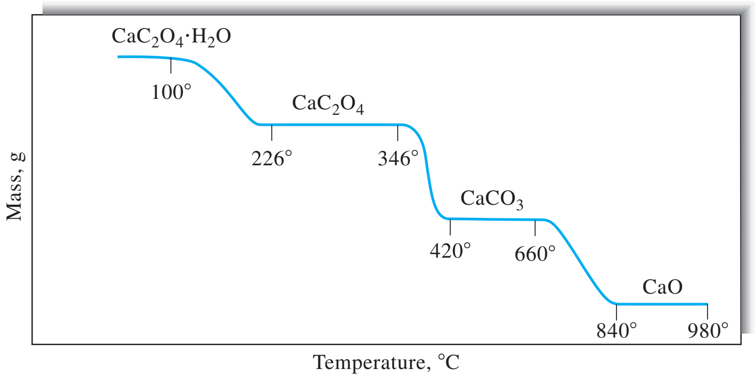


FIGURE 31-5 Thermogram for decomposition of $CaC_2O_4 \cdot H_2O$ in an inert atmosphere. (From S. Peltier and C. Duval, *Anal. Chim. Acta*, **1947**, *1*, 345, **DOI**: 10.1016/S0003-2670(00)89754-8. With permission.)

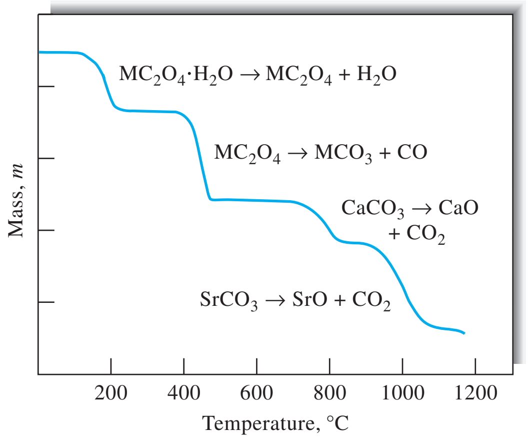
polyethylene that has been formulated with fine carbon-black particles to inhibit degradation from exposure to sunlight. This analysis would be difficult by most other analytical methods.

Figure 31-5 is a recorded thermogram obtained by increasing the temperature of pure $CaC_2O_4 \cdot H_2O$ at a rate of 5°C/min. The clearly defined horizontal regions correspond to temperature ranges in which the indicated calcium compounds are stable. This figure illustrates the use of TGA in defining the thermal conditions needed to produce a pure species.

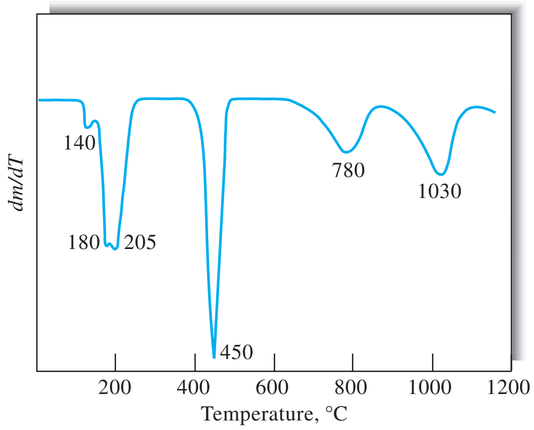
Figure 31-6a illustrates an application of TGA to the quantitative analysis of a mixture of calcium, strontium, and barium ions. The three are first precipitated as the monohydrated oxalates. The mass in the temperature range between 320°C and 400°C is that of the three anhydrous compounds, CaC_2O_4, SrC_2O_4, and BaC_2O_4, and the mass between about 580°C and 620°C corresponds to the three carbonates. The mass change in the next two steps results from the loss of carbon dioxide, as first CaO and then SrO are formed. Sufficient data are available in the thermogram to calculate the mass of each of the three elements present in the sample.

Figure 31-6b is the derivative of the thermogram shown in (a). The derivative curve can sometimes reveal information that is not detectable in the ordinary thermogram. For example, the three peaks at 140°C, 180°C, and 205°C suggest that the three hydrates lose moisture at different temperatures. However, all appear to lose carbon monoxide simultaneously and thus yield a single sharp peak at 450°C.

Because TGA can provide quantitative information, determination of moisture levels is another important application. Levels of 0.5% and sometimes less can be determined.



(a) Thermogram



(b) Differential thermogram

FIGURE 31-6 Decomposition of $CaC_2O_4 \cdot H_2O$, $SrC_2O_4 \cdot H_2O$, and $BaC_2O_4 \cdot H_2O$. (From L. Erdey, G. Liptay, G. Svehla, and F. Paulike, *Talanta*, **1962**, *9*, 489, **DOI**: 10.1016/0039-9140(62)80117-9. With permission.)

31B DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis (DTA) is a technique in which the difference in temperature between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. Usually, the temperature program consists of heating the sample and reference material in such a way that the temperature of the sample T_s increases linearly with time. The difference in temperature ΔT between the sample temperature and the reference temperature $T_r (\Delta T = T_s - T_r)$ is then monitored and plotted against sample temperature to give a differential thermogram such as that shown in Figure 31-7. (The significance of the various parts of this curve is given in Section 31B-2.)

31B-1 Instrumentation

Figure 31-8 is a schematic of the furnace compartment of a differential thermal analyzer. A few milligrams of the sample (S) and an inert reference substance (R) are contained in small aluminum dishes located above sample and reference thermocouples in an electrically heated furnace. The reference material is an inert substance such as alumina, silicon carbide, or glass beads.

The digitized output voltage E_s from the sample thermocouple is the input to a computer. The computer controls the current input to the furnace in such a way that the sample temperature increases linearly and at a predetermined rate. The sample thermocouple signal is also converted to temperature T_s, which is used as the x-axis of the differential thermogram. The output across the sample and reference thermocouples ΔE is amplified and converted to a temperature difference ΔT, which serves as the y-axis of the thermogram.

Generally, the sample and reference chamber in DTA are designed to permit the circulation of an inert gas, such as nitrogen, or a reactive gas, such as oxygen or air. Some systems also have the capability of operating at high and low pressures.

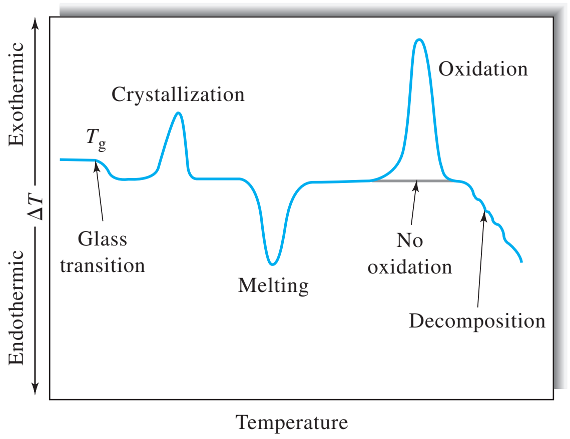


FIGURE 31-7 Differential thermogram showing types of changes encountered with polymeric materials. (From R. M. Schulken Jr., R. E. Roy Jr., and R. H. Cox, *J. Polymer Sci., Part C*, **1964**, *6*, 17, **DOI:** 10.1002/polc.5070060104. Reprinted by permission of John Wiley & Sons, Inc.)

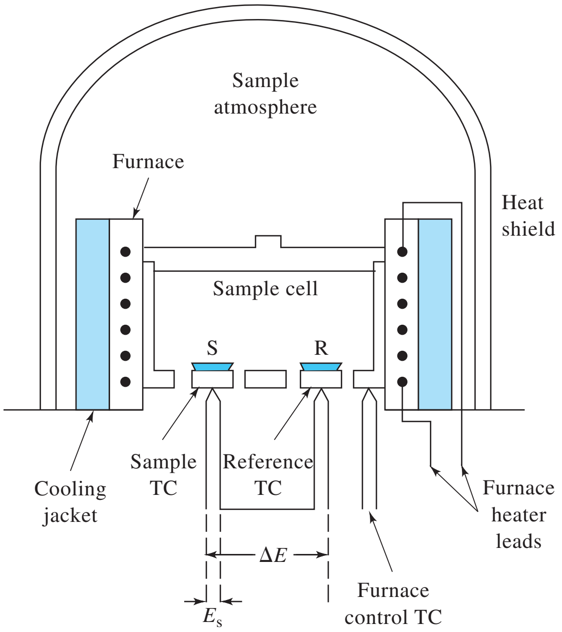


FIGURE 31-8 Schematic diagram of a typical instrument for DTA. TC = thermocouple.

31B-2 General Principles

Figure 31-7 is an idealized differential thermogram obtained by heating a polymer over a sufficient temperature range to cause its ultimate decomposition. The initial decrease in ΔT is due to the glass transition, a phenomenon observed in the initial segments of many differential thermograms of polymers. The glass transition temperature T_g is the characteristic temperature at which glassy amorphous polymers become flexible or rubber-like because of the onset of the concerted motion of large segments of the polymer molecules. When heated to the glass transition temperature T_g, the polymer changes from a glass to a rubber. Such a transition involves no absorption or evolution of heat so that no change in enthalpy results—that is, $\Delta H = 0$. The heat capacity of the rubber is, however, different from that of the glass, which results in the lowering of the baseline, as shown in the figure. No peak appears during this transition, however, because of the zero enthalpy change.

Two maxima and a minimum are observed in the thermogram in Figure 31-7. The two maxima are the result of exothermic processes in which heat is evolved from the sample, thus causing its temperature to rise. The minimum labeled "melting" is the result of an endothermic process in which heat is absorbed by the analyte. When heated to a characteristic temperature,

Tutorial: Learn more about **differential thermal analysis** at www.tinyurl.com/skoogpia7 many amorphous polymers begin to crystallize as microcrystals, giving off heat in the process. Crystal formation is responsible for the first exothermic peak shown in Figure 31-7.

The second peak in the figure is endothermic and involves melting of the microcrystals formed in the initial exothermic process. The third peak is exothermic and is encountered only if the heating is performed in the presence of air or oxygen. This peak is the result of the exothermic oxidation of the polymer. The final negative change in ΔT results from the endothermic decomposition of the polymer to produce a variety of products.

As suggested in Figure 31-7, DTA peaks result from both physical changes and chemical reactions induced by temperature changes in the sample. Physical processes that are endothermic include fusion, vaporization, sublimation, absorption, and desorption. Adsorption and crystallization are generally exothermic. Chemical reactions may also be exothermic or endothermic. Endothermic reactions include dehydration, reduction in a gaseous atmosphere, and decomposition. Exothermic reactions include oxidation in air or oxygen, polymerization, and catalytic reactions.

31B-3 Applications

In general, DTA is considered a qualitative technique. Although able to measure the temperatures at which various changes occur, DTA is unable to measure the energy associated with each event.

DTA is a widely used tool for studying and characterizing polymers. Figure 31-7 illustrates the types of physical and chemical changes in polymeric materials that can be studied by differential thermal methods. Note that thermal transitions for a polymer often take place over an extended temperature range because even a pure polymer is a mixture of homologs and not a single chemical species.

DTA is also widely used in the ceramics and metals industry. The technique is capable of studying high-temperature processes (up to 2400°C for some units) and relatively large sample sizes (hundreds of milligrams). For such materials, DTA is used to study decomposition temperatures, phase transitions, melting and crystallization points, and thermal stability.

An important use of DTA is for the generation of phase diagrams and the study of phase transitions. An example is shown in Figure 31-9, which is a differential thermogram of sulfur, in which the peak at 113°C corresponds to the solid-phase change from the rhombic to the monoclinic form. The peak at 124°C corresponds to the melting point of the element. Liquid sulfur is known to exist in at least three forms, and the peak at 179°C apparently involves these transitions, whereas the peak at 446°C corresponds to the boiling point of sulfur.

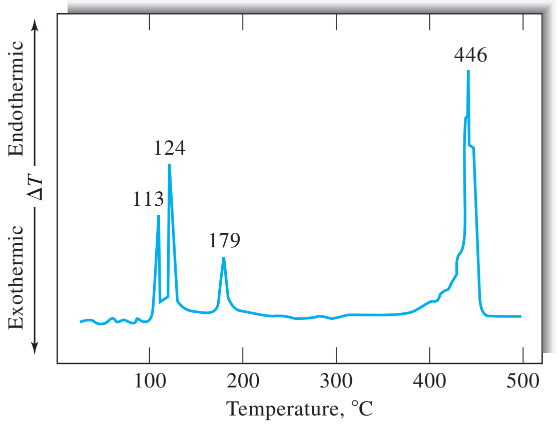


FIGURE 31-9 Differential thermogram for sulfur. (Reprinted with permission from J. Chiu, *Anal. Chem.*, **1963**, *35*, 933, **DOI:** 10.1021/ac60200a052. Copyright 1963 American Chemical Society.)

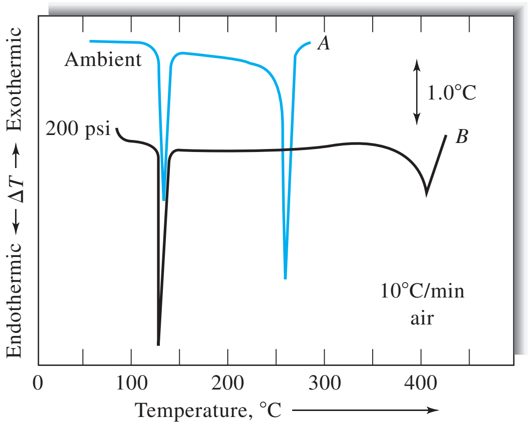


FIGURE 31-10 Differential thermogram for benzoic acid. Curve *A* taken at atmospheric pressure. Curve *B* taken at a pressure of 13.79 bar (200 lbs/in.^{2}). (From P. Levy, G. Nieuweboer, and L. C. Semanski, *Thermochim. Acta*, **1970**, *1*, 429, **DOI:** 10.1016/0040-6031(70)85013-4. With permission.)

The DTA method also provides a simple and accurate way of determining the melting, boiling, and decomposition points of organic compounds. Generally, the data are more consistent and reproducible than results obtained with a hot stage or a capillary tube. Figure 31-10 shows thermograms for benzoic acid at atmospheric pressure (*A*) and at 13.79 bar (*B*). The lower temperature peak corresponds to the melting point and the second peak to the boiling point of the acid.

31C DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) is the most often used thermal analysis method, primarily because of its speed, simplicity, and availability. In DSC a sample and a reference are placed in holders in the instrument. Heaters either ramp the temperature at a specified rate (e.g., 5°C/min) or hold the DSC at a given temperature. The instrument measures the difference in the heat flow between the sample and the reference. The basic difference

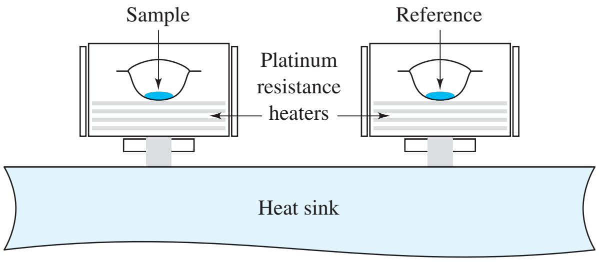


FIGURE 31-11 Power-compensated DSC sample and reference holders and heaters. A temperature program is generated by the computer system. Platinum resistance thermometers, in contact with the sample and reference holders, sense any difference between the programmed temperature and the temperatures of the sample and reference. The error signal is used to adjust the power applied to the sample and the power applied to the reference platinum resistance heaters. The DSC output signal is the difference in the power required between the sample and the reference so that both equal the programmed temperature.

between DSC and DTA is that DSC is a calorimetric method in which differences in *energy* are measured. In contrast, in DTA, differences in temperature are recorded. The temperature programs for the two methods are similar. DSC is considered to be a quantitative technique in contrast to DTA.

31C-1 Instrumentation

There are three different types of DSC instruments: *power-compensated DSC*, *heat-flux DSC*, and *modulated DSC*. Each produces a plot of power or heat flow versus temperature, called a *thermogram*.[3]

Power-Compensated DSC Instruments

In power-compensated DSC, the temperatures of the sample and reference are kept equal to each other while both temperatures are increased or decreased linearly. The power needed to maintain the sample temperature equal to the reference temperature is measured.

A diagram of a power-compensated DSC sample holder and heating unit is shown in Figure 31-11. Two independent heating units are employed. These heating units are quite small, allowing for rapid rates of heating, cooling, and equilibration. The heating units are embedded in a large temperature-controlled heat sink. The sample and reference holders have platinum resistance thermometers to continuously monitor the temperature of the materials. Both sample and reference are maintained at the programmed temperature by applying power to the sample and reference heaters. The instrument records the power difference needed to maintain the sample and reference at the same temperature as a function of the programmed temperature.

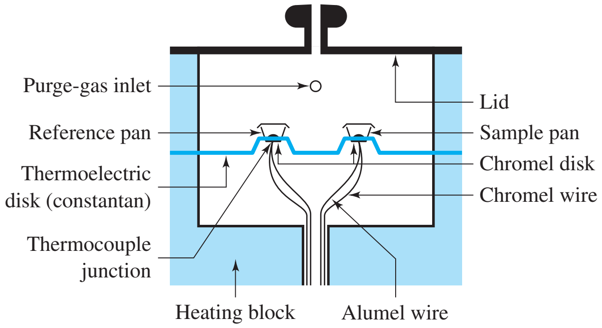


FIGURE 31-12 Heat-flux DSC. (Courtesy of TA Instruments, New Castle, DE.)

Power-compensated DSC has lower sensitivity than heat-flux DSC, but its response time is more rapid. This makes power-compensated DSC well suited for kinetics studies in which fast equilibrations to new temperature settings are needed. Power-compensated DSC is also capable of higher resolution than heat-flux DSC.

Heat-Flux DSC Instruments

In heat-flux DSC, the difference in heat flow into the sample and reference is measured while the sample temperature is changed at a constant rate. Both sample and reference are heated by a single heating unit. Heat flows into both the sample and reference material via an electrically heated constantan thermoelectric disk, as shown in Figure 31-12. Small aluminum sample and reference pans sit on raised platforms on the constantan disk.[4] Heat is transferred through the disks and up into the material via the two pans. The differential heat flow to the sample and reference is monitored by Chromel-constantan area thermocouples formed by the junction between the constantan platform and Chromel disks attached to the underside of the platforms. The differential heat flow into the two pans is directly proportional to the difference in the outputs of the two thermocouple junctions. The sample temperature is estimated by the Chromel-alumel junction under the sample disk.

In heat-flux DSC, we can write the total heat flow dH/dt as

$$\frac{dH}{dt} = C_p\frac{dT}{dt} + f(T,t) \tag{31-1}$$

where H is the enthalpy in J mol^{-1}, C_p is the specific heat capacity (heat capacity per mole) in J K^{-1} mol^{-1}, and $f(T, t)$ is the kinetic response of the sample in J mol^{-1}. We can thus see that the total heat flow is the sum of two terms, one related to the heat capacity, and one related to the kinetic response. A typical DSC thermogram is shown in Figure 31-13. We can see in the plot several processes that occur as the temperature is changed. An increase

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[3] For a discussion of DSC instruments and designs, see P. Gabbott in *Principles and Applications of Thermal Analysis*, P. Gabbott, ed., Oxford, UK: Wiley-Blackwell, 2008, Chap. 1.

[4] Constantan is an alloy of 60% copper and 40% nickel. Chromel is a trademark for a series of alloys containing chromium, nickel, and at times, iron. Alumel is an alloy of nickel with 2% aluminum, 2% manganese, and 1% silicon.

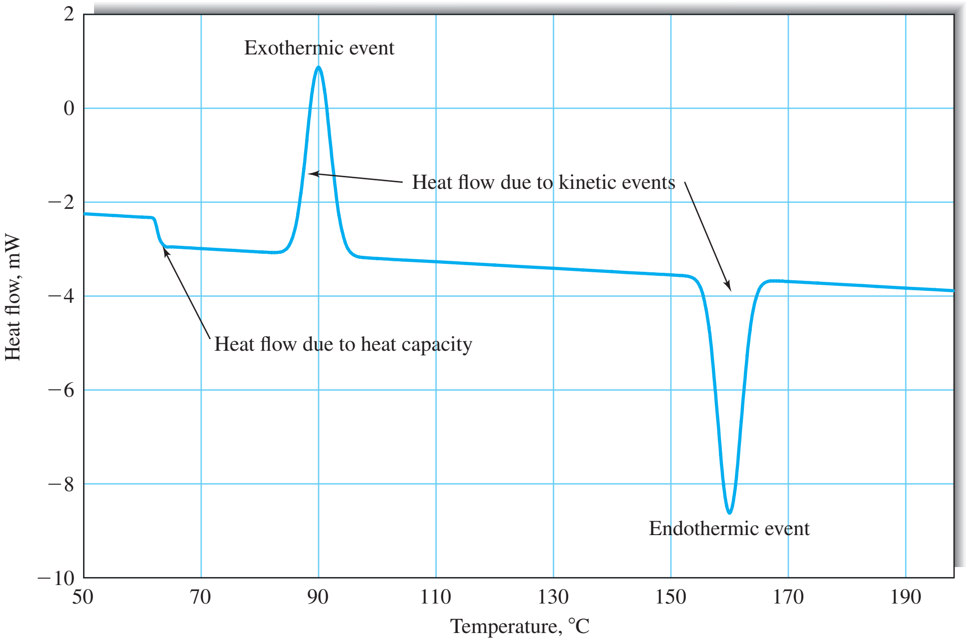

FIGURE 31-13 Typical DSC scan for a polymeric material. Note the step transition at about 63°C. There is an exothermic event at approximately 90°C and an endothermic event at 160°C. Note that the thermogram represents the sum of the heat flow due to heat capacity and kinetic processes. (Courtesy of TA Instruments, New Castle, DE.)

in heat flow signifies an exothermic process, and a decrease indicates an endothermic process.

Modulated DSC Instruments

Modulated DSC (MDSC) uses the same heating and cell arrangement as the heat-flux DSC method. In MDSC, a sinusoidal function is superimposed on the overall temperature program to produce a micro heating and cooling cycle as the overall temperature is steadily increased or decreased. Using Fourier transform methods, the overall signal is mathematically deconvoluted into two parts, a reversing heat flow signal and a nonreversing heat flow signal. The reversing heat flow signal is associated with the heat capacity component of the thermogram, and the nonreversing heat flow is related to kinetic processes. Usually, step transitions, such as the glass transition, appear only in the reversing heat flow signal, and exothermic or endothermic events may appear in either or in both signals.

A plot showing the decomposition of the total heat flow signal into reversing and nonreversing components is shown in Figure 31-14. Note that the transition near 60°C appears in the reversing heat flow component associated with the heat capacity part of the total heat flow. The endothermic process near 250°C also appears in the reversing component, and the exothermic event near 150°C appears in the nonreversing component.

A different type of modulated DSC was introduced by Rösgen and coworkers, termed *pressure-modulated DSC*.[5] In this experiment, a sawtooth pressure ramp or another pressure format is superimposed on a standard DSC temperature scan. Pressure modulation permits the simultaneous, synchronous determination of heat capacity and expansibility.

DSC Accessories

Autosamplers are available for most, modern DSC instruments. Many also permit a photocalorimetry attachment, which allows calorimetric measurements to be made while irradiating a light-sensitive sample with UV-visible radiation. Pressurized cell accessories allow the cell pressure to be controlled and manipulated. In addition, refrigerated cooling systems are available to extend the low-temperature range.

The DSC Experiment

A typical DSC experiment begins by weighing an empty sample pan. The pans are most often made of aluminum, although gold, platinum, graphite, stainless steel, and glass ampoules can be used. Hermetic pans are often used. A small portion of the sample is then transferred to the pan so as to provide a uniform layer at the bottom of the pan. The pan is hermetically sealed and then weighed again. When the sample and reference pans are in position, the purge gas is applied. Some DSC units have autosamplers that allow multiple sample pans placed in a holder to be run sequentially. Helium or nitrogen is the usual purge gas, although occasionally air or oxygen is employed to study oxidation processes. The purge gas helps to rid the sample of moisture and oxygen and aids in transferring heat to the sample pan.

Modern DSC instruments are computer controlled so that the experiment is performed automatically after the user enters

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[5] J. Rösgen and H. J. Hinz, *Anal. Chem.*, **2006**, *78*, 991, **DOI**: 10.1021/ac0516436; K. Boehm, J. Rösgen, and H. J. Hinz, *Anal. Chem.*, **2006**, *78*, 984, **DOI**: 10.1021/ac0509760.

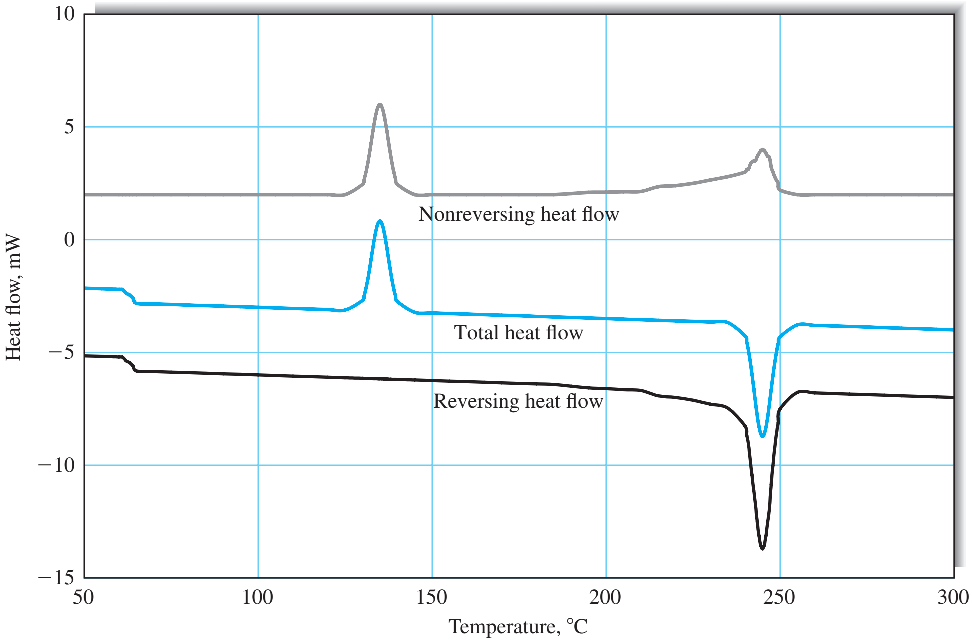

FIGURE 31-14 Deconvoluted thermogram from an MDSC apparatus showing nonreversing and reversing heat flow components. (Courtesy of TA Instruments, New Castle, DE.)

parameters such as the temperature program and various calibration parameters.

DSC Calibration

The DSC system is usually calibrated in several ways. Baseline calibration is performed with no pans in place. The calibration measures the baseline slope and offset over the temperature range of interest. The computer system controlling the DSC stores these values and subtracts baseline slope and offset from subsequent sample runs to minimize their effects.

After baseline calibration is performed, heat flow calibration is done by melting a known quantity of a material with a well-known heat of fusion. Indium is the most often used standard. Indium is placed in the sample pan and scanned against an empty reference pan. The area of the melting peak is related to the known enthalpy of fusion by a calibration factor known as the *cell constant*. This procedure also calibrates the temperature axis from the known melting temperature of indium. Temperature calibration should also be performed over a wider temperature range, by measuring the melting points of several well-known standards.

For heat capacity determinations with normal DSC and MDSC systems, heat capacity calibration is performed by scanning a heat capacity standard, such as sapphire. This calibrates the system for C_p values and is used in separating the heat capacity component from the total heat flow.

DSC Data Analysis

With modern DSC instruments, software is available to aid the user in determining melting points, glass transition temperatures, and heat capacity values. The temperatures of step transitions and kinetic events are usually determined as onset temperatures. The onset temperature is defined as the temperature at which a line tangent to the baseline intersects another line tangent to the slope of the transition, as illustrated in Figure 31-15. In some cases temperatures of transitions, such as the glass transition, are taken as the midpoint of the transition rather than the onset.

The step in a transition, such as the glass transition, is related to the change in heat capacity as the material goes through the transition from one state to another. The change in heat capacity is usually determined as the difference between the heat capacity at the onset and at the end of the transition. The enthalpy of melting or crystallization is determined by finding the area of the representative endotherm or exotherm through integration.

31C-2 Applications

DSC finds many applications in characterizing materials. Quantitative applications include the determination of heats of fusion and the extent of crystallization for crystalline materials. Glass transition temperatures and melting points are useful for qualitative classification of materials, although thermal methods cannot be used alone for identification. Melting points are also very useful in establishing the purity of various preparations. Hence, thermal methods are often used in quality control applications.

Glass Transition Temperatures

Determination of the glass transition temperature T_g is one of the most important applications of DSC. The physical properties of a polymer undergo dramatic changes at T_g, where the material goes from a glassy to a rubbery state. At the glass transition, the polymer undergoes changes in volume and expansion, heat flow, and heat capacity. The change in heat capacity is readily measured by DSC.

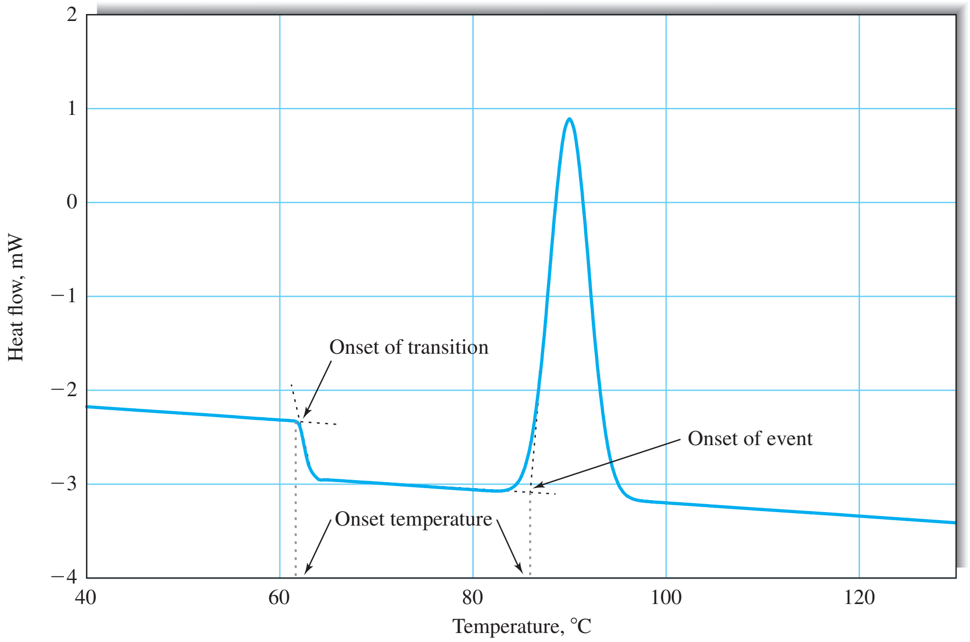

FIGURE 31-15 Determination of onset temperatures for a transition and an exothermic event (crystallization).

Crystallinity and Crystallization Rate

With crystalline materials, the level of crystallinity is an important factor for determining polymer properties. Degrees of crystallinity can be determined by IR spectroscopy, X-ray diffraction, density measurements, and thermal methods. In most cases DSC is one of the easiest methods for determining levels of crystallinity. The crystallinity level is obtained by measuring the enthalpy of fusion for a sample $(\Delta H_f)_{sample}$ and comparing it to the enthalpy of fusion for the fully crystalline material $(\Delta H_f)_{crystal}$. The fractional crystallinity is then given by

$$\text{Fractional crystallinity} = (\Delta H_f)_{sample}/(\Delta H_f)_{crystal} \qquad (31\text{-}2)$$

Calorimetric methods are also used to study crystallization rates. Crystallization is an exothermic event, as shown in Figure 31-15. The rate of heat release and thus the crystallization kinetics can be followed by DSC.

Reaction Kinetics

Many chemical reactions, such as polymer formation reactions, are exothermic and readily monitored by DSC methods. Here, the determination of the rate of heat release, dH/dt, is used to determine the extent of reaction as a function of time. Polymerization kinetics can be studied in both a temperature scanning and an isothermal mode. With some polymer systems, factors such as monomer volatility and viscosity can affect the measured kinetics.

Protein Stability and Structure

The characterization of proteins is another important application of DSC. Protein unfolding, decompostion, and the binding of ligands and metals are among these characterizations. To facilitate studies on microgram quantities of proteins, microcalorimeters are available commercially.

Tutorial: Learn more about **differential scanning calorimetry** at www.tinyurl.com/skoogpia7

31D MICROTHERMAL ANALYSIS

Microthermal analysis[6] combines thermal analysis with atomic force microscopy. It is actually a family of scanning thermal microscopy techniques in which thermal properties of a surface are measured as a function of temperature and used to produce a thermal image. In microthermal analysis the tip of an atomic force microscope is replaced by a thermally sensitive probe such as a thermistor or thermocouple. The surface temperature can be changed externally or by the probe acting both as a heater and as a temperature-measuring device.

A photomicrograph of a thermal probe is shown in Figure 31-16. The most common type of thermal probe is the resistive probe based on a Wollaston wire. This wire has a thick coating of silver on top of a thin core of platinum or a platinum-rhodium alloy. At the tip of the probe, the silver is etched away to expose the bare wire. Micromachined probes have also been developed. With these probes, almost all of the electrical resistance is located at the tip. As a result, when an electric current is applied, only the tip becomes hot. The electrical resistance of the tip is also a measure of the temperature.

A microthermal analysis apparatus, pictured in Figure 31-17, can be operated in either a constant-temperature mode or a

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[6] For reviews on microthermal analysis and its applications, see H. M. Pollock and A. Hammiche, *J. Phys. D: Appl. Phys.*, **2001**, *34*, R23, **DOI**: 10.1088/0022-3727/34/9/201; C. Q. M. Craig, V. L. Kett, C. S. Andrews, and P. G. Royall, *J. Pharm. Sci.*, **2002**, *91*, 1201, **DOI**: 10.1002/jps.10103.

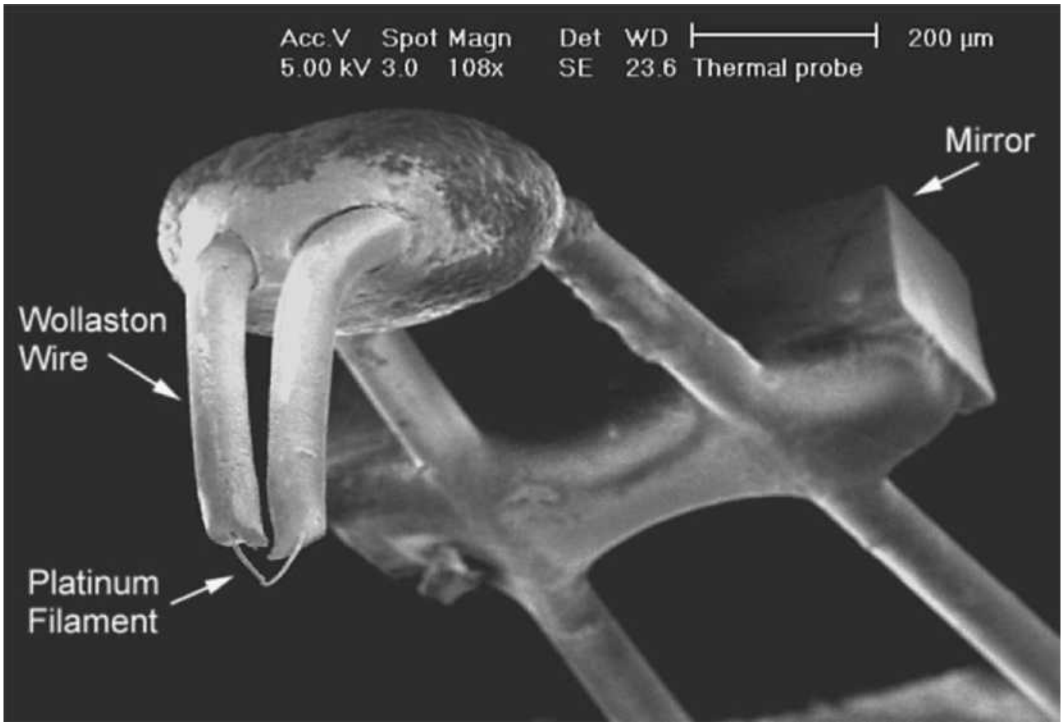

FIGURE 31-16 A microthermal analysis probe. (Reprinted from P. G. Royall, D. Q. M. Craig, and D. B. Grandy, *Thermochim. Acta*, **2001**, *380* (2), 165–173, **DOI**: 10.1016/S0040-6031(01)00667-0, with permission from Elsevier.)

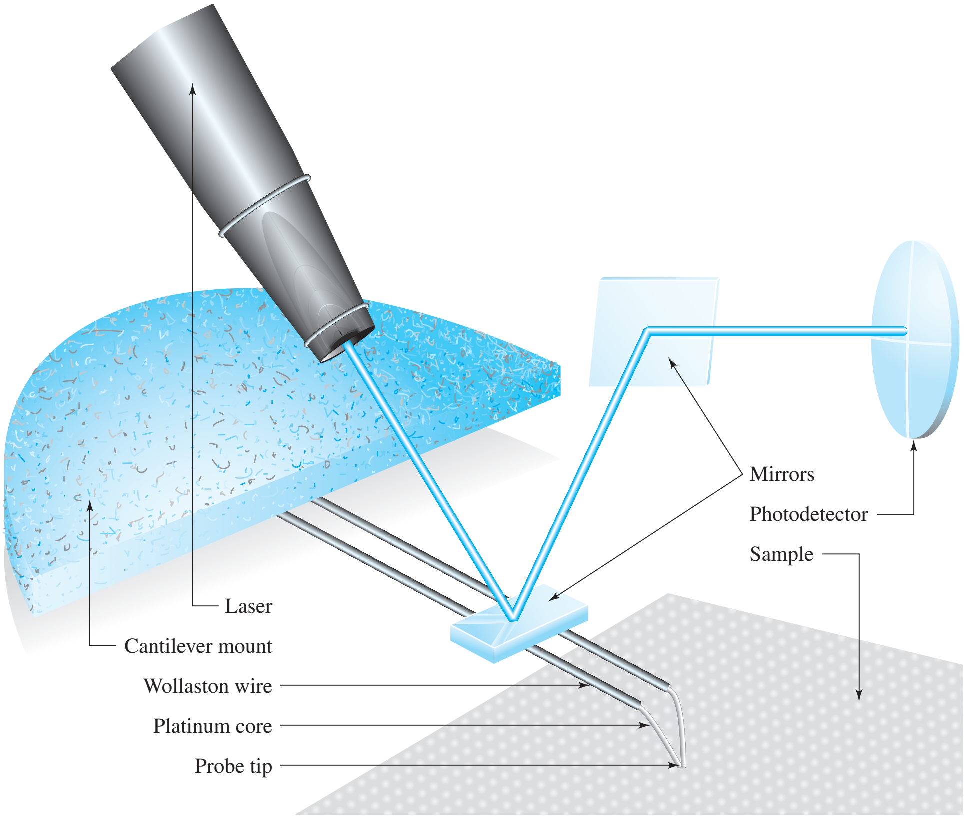

FIGURE 31-17 Microthermal analysis apparatus.

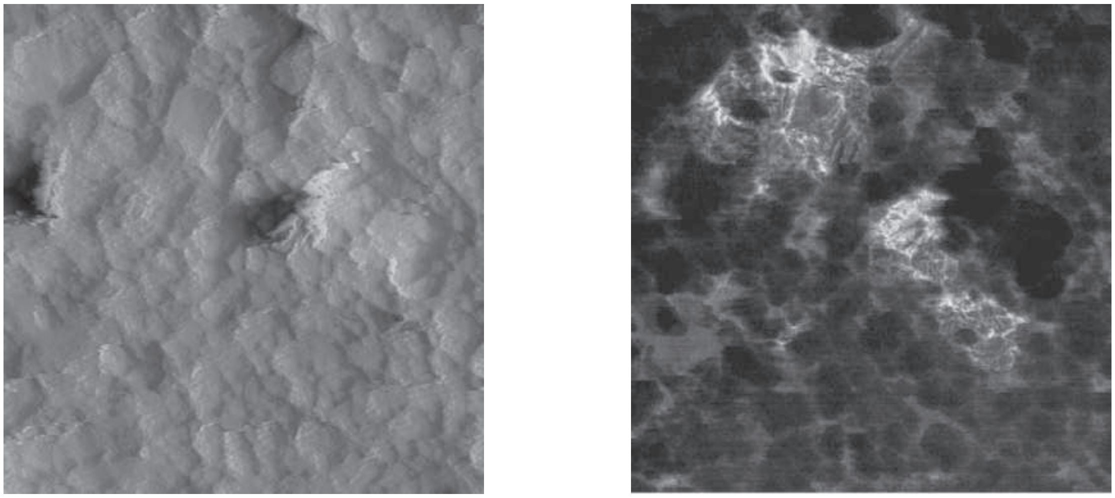
(a) (b)

FIGURE 31-18 Comparison of conventional atomic force microscopy topographic image (a) with thermal image (b) of a paracetamol pharmaceutical tablet. (Reprinted from H. M. Pollock and A. Hammiche, *J. Phys. D: Appl. Phys.*, **2001**, *34*, R23. With permission.)

constant-current mode. The constant-temperature mode is simplest and most often used. In constant-temperature mode, the electrical power needed to keep the probe temperature constant is obtained as the probe is rastered over the sample surface in contact mode (see Section 21G-2). As the probe encounters parts of the surface that differ in thermal properties, varying amounts of heat flow from the probe to the sample. When the probe touches a region of high thermal conductivity, it cools off, and more power is required to keep it at a constant temperature. Conversely, when it touches a region of low thermal conductivity, less power is required. Hence, the thermal conductivity of a sample surface can be imaged. Figure 31-18 compares the thermal image of a pharmaceutical preparation to that of the conventional topographic image. Various modulation techniques are also employed to allow the thermal conductivity at different depths of the sample to be monitored by varying the modulation frequency.

Although microthermal analysis is a relatively new technique, commercial instruments are available. Applications to pharmaceuticals, polymers, and foods have been reported. The technique also has applications in the ceramics industry and in imaging biomedical samples.

QUESTIONS AND PROBLEMS

*Answers are provided at the end of the book for problems marked with an asterisk.

Problems with this icon are best solved using spreadsheets.

31-1 Describe what quantity is measured and how the measurement is performed for each of the following techniques: (a) TGA, (b) DTA, (c) DSC, and (d) microthermal analysis.

***31-2** A 0.5927-g sample was dissolved, and the Ca^{2+} and Ba^{2+} ions present were precipitated as $BaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot H_2O$. The oxalates were then heated in a thermogravimetric apparatus leaving a residue that weighed 0.5127 g in the range of 320°C–400°C and 0.4362 g in the range of 580°C–620°C. Calculate the percentage Ca and percentage Ba in the sample.

31-3 The following table summarizes some data about three iron(III) chlorides.

Compound	Molecular Mass	Melting Point, °C
$FeCl_3 \cdot 6H_2O$	270	37
$FeCl_3 \cdot \frac{5}{2}H_2O$	207	56
$FeCl_3$	162	306

QUESTIONS AND PROBLEMS (continued)

Sketch the thermogravimetric curve anticipated when a 25.0-mg sample of $FeCl_3 \cdot 6H_2O$ is heated from 0°C to 400°C.

31-4 Why is the low-temperature endotherm for ambient pressure in Figure 31-10 found at the same temperature as that at 13.79 bar, whereas the high-temperature peaks for the two pressures are found at different temperatures?

31-5 It should be possible to at least partially characterize an oil shale sample using techniques discussed in this chapter. Briefly discuss two techniques appropriate to use for this purpose. Sketch typical thermal curves and discuss the information that might be obtained and problems that might be anticipated.

31-6 In thermal analysis methods, why is the thermocouple for measuring sample temperature seldom immersed directly into the sample?

31-7 List the types of physical changes that can yield exothermic and endothermic peaks in DTA and DSC.

31-8 List the types of chemical changes that can yield exothermic and endothermic peaks in DTA and DSC.

31-9 Why are the applications of TGA more limited than those for DSC?

31-10 Why does the glass transition for a polymer yield no exothermic or endothermic peak?

31-11 Describe the difference between power-compensated, heat-flux, and modulated DSC instruments.

Challenge Problem

31-12 In the pharmaceutical industry, close attention must be paid to drug purity, quality, stability, and safety. Pharmaceutical compounds often have several different structural forms with different molecular shapes. These compounds are also susceptible to thermal degradation, to the pickup and retention of water, and to photodecomposition. One of the best methods to characterize pharmaceuticals from raw product to finished product stage is thermal analysis. The following questions deal with applications of thermal analysis methods to pharmaceuticals.

(a) Determining the purity of drugs is one of the most important tests done by the pharmaceutical industry. One such test is based on a determination of the melting point of the drug of interest by DSC and the following relationship from thermodynamics:

$$\frac{d\ln X_1}{dT} = \frac{\Delta H_f}{RT^2}$$

where X_1 is the mole fraction of the drug whose purity is being determined, ΔH_f is the enthalpy of fusion, R is the gas constant, and T is temperature. From this equation, derive the following modified van't Hoff equation:

$$\frac{1}{f} = \frac{\Delta H_f}{R}\frac{(T_0 - T)}{T_0^2}\frac{1}{X_2^0}$$

where f is the fraction of sample melting at temperature T, T_0 is the melting point of the pure drug, and X_2^0 is the mole fraction of the impurity in the original compound.

Hint: Assume the drug is close to pure so that $\ln X_1$ can be approximated by

$$\ln X_1 = \ln(1 - X_2) \approx -X_2$$

As the temperature is increased toward the true melting point T_0, the mole fraction in the liquid state X_2 is constantly reduced according to

$$X_2 = X_2^0(1/f)$$

(b) The fraction f can be found from A/A_T, where A is the area of the melting endotherm up to temperature T and A_T is the total area of the melting endotherm. By dividing the endotherm into partial melting areas, the fraction f can be determined at various temperatures. Rearrange the modified van't Hoff equation to give the melting temperature T as a function of $1/f$. Show that a plot of T versus $1/f$ should be linear with an intercept of T_0 and a slope of $-RT_0X_2/\Delta H_f$. If the heat of fusion is known, X_2 can be determined.

(c) Look up the article by H. Staub and W. Perron, *Anal. Chem.*, **1974**, *46*, 128. Give some of the limitations of the DSC approach to impurity determinations. Describe the "step heating" method used by the authors. How does this differ from normal DSC?

(d) Which type of DSC, power compensated or heat flux, would be most useful in determining purity? Why?

(e) What thermal analysis technique would be suitable for characterizing and quantifying the moisture content in a pharmaceutical sample? Why?

(f) Describe how thermal analysis could be used to determine the degree of hydration of a pharmaceutical compound.

(g) When heated, many pharmaceutical materials show a variety of thermal events, including melting, transitions to glassy states, moisture loss, thermal relaxation, and in some cases, decomposition. How could irreversible kinetic events be distinguished from reversible heat flow events?

(h) Describe how microthermal analysis might be useful in studies of pharmaceutical materials. Consider problems such as polymorphic forms, impurities, and identification of glassy states in your answer.