

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).

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The Analysis of a Temperature-Controlled Scanning Calorimeter

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► 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

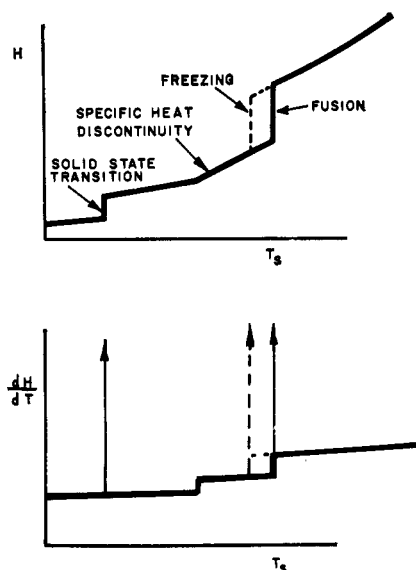


Figure 1. Enthalpy and specific heat functions

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

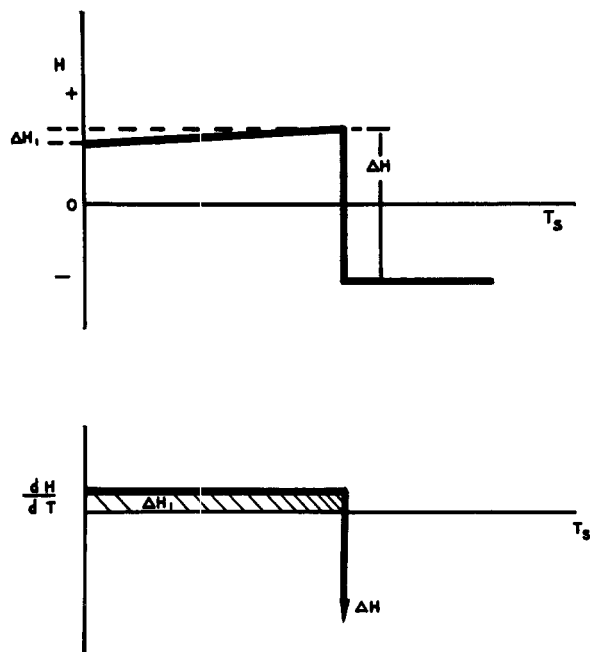


Figure 2. Combustion analysis

isothermal and adiabatic calorimetry is illustrated. Since equivalent thermal circuit parameters will be extensively employed hereafter, a brief discussion of the circuit elements is in order. In the equivalent circuit, voltage represents temperature, and current represents heat flow rate. There are only two passive circuit elements, thermal resistance and thermal capacitance. The four elements and their dimensions are shown in Table I.

In an electrical circuit a voltage source, by definition, has a resistance of zero, while a current source has an infinite resistance. The thermal analog of a current source is a device generating heat at a rate independent of its own temperature, such as a heating element with a constant electrical power input. The thermal analog of a voltage source is difficult to realize; it is a temperature source, capable of delivering or absorbing heat at any rate without any change in its temperature. Any thermal system may be represented by a suitable combination of these ideal elements. For example, a real temperature-controlled surface may be represented by a temperature source in series with a thermal resistance. The values of these two circuit parameters may be determined by temperature and heat flow measurements under two different thermal loading conditions. The thermal capacity of the system, together with the resistances in the circuit, determines its dynamic behavior.

In Figure 3a, a sample is shown totally enclosed by a sample holder, to which it is coupled by the resistance R_0 . The sample holder is supported inside an enclosure which is at the ambient tem-

perature T_A , and is coupled to it via R_T . The equivalent thermal circuit of the sample holder is shown in Figure 3b. C_0 represents the total thermal capacity of the sample holder, and the sample itself is represented by a two-terminal pair.

Coupled to the sample holder, but not shown in the figure, are a source of heat and a temperature-measuring device. In principle, either adiabatic or isothermal calorimetry may be accomplished with this system, by suitable manipulation of these two elements. For adiabatic operation, the sample holder is driven by the circuit of Figure 3c, which is a heat flow source shunted by a thermal voltmeter. For isothermal operation a temperature source in series with a thermal ammeter is utilized, as shown in Figure 3d.

It will be realized at once that in

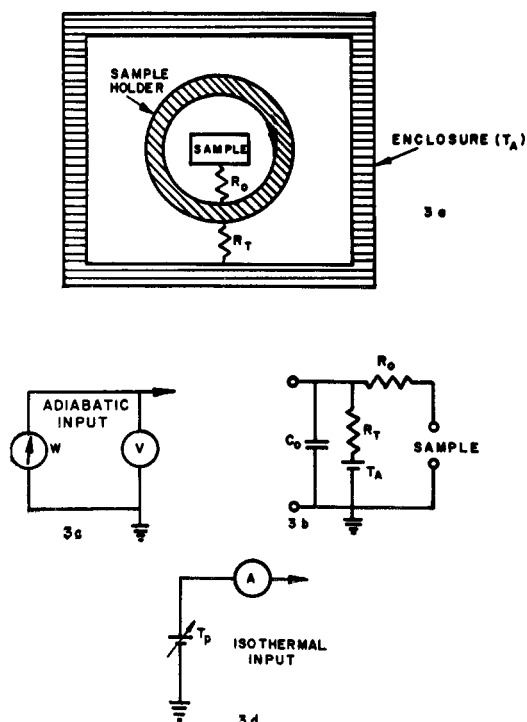


Figure 3. Isothermal and adiabatic calorimetry

Table I. Equivalent Thermal Circuit Elements

Electrical	Thermal	Dimension
Voltage	Temperature	$^{\circ}\text{C.}$
Current	Heat flow rate	cal. sec.^{-1}
Resistance	Resistance	$^{\circ}\text{C. sec. cal.}^{-1}$
Capacity	Capacity	$\text{cal. } ^{\circ}\text{C.}^{-1}$

either of these systems the heat flow through R_0 to the sample is indistinguishable from the heat flow through R_T to the enclosure. The obvious solution in the case of isothermal calorimetry is differential operation, in which two sample holders are supplied from the same temperature source. Such a system is shown in Figure 4. The heat flow rate into an empty reference holder

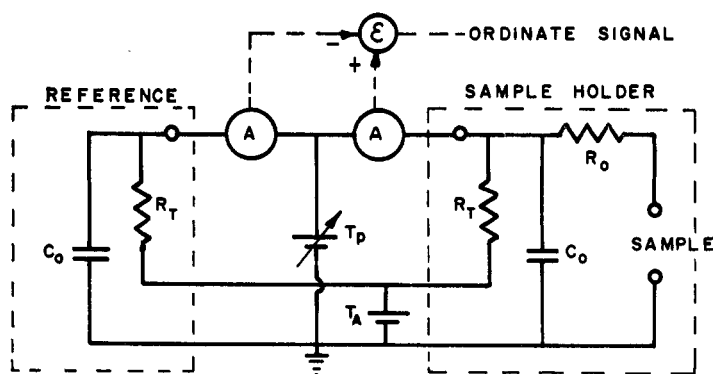


Figure 4. Differential isothermal calorimetry

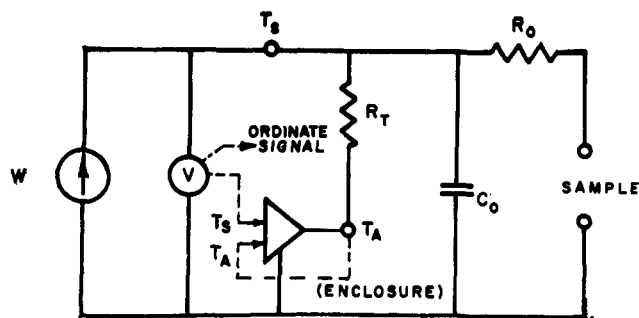


Figure 5. Adiabatic calorimetry

is subtracted continuously from the heat flow rate into the sample holder. The background heat flow rate, through R_T , is determined only by T_P and T_A , which are identical for the sample and reference holders; thus the differential heat flow rate is equal to the heat flow rate into the sample. An additional feature of this system is its ability to perform true differential calorimetry, in which a reference material with known thermal behavior is compared with the sample.

In adiabatic calorimetry, the background cannot be cancelled by differential operation, since the sample and reference temperatures would be neither equal nor reproducible. This is an inevitable consequence of using an extensive parameter as the independent variable. The only alternative is complete elimination of the background; this may be accomplished by making R_T as large as possible, and by making the ambient temperature equal to the sample holder temperature throughout the analysis. Figure 5 illustrates the principle.

Adiabatic calorimetry, accomplished in this manner, is unsatisfactory for routine analytical work. Even without ambient temperature control, it would be a time consuming instrumental technique, because the large thermal resistance necessary for reduction of the background signal contributes to a large thermal time constant. With ambient temperature control, the situation is aggravated, owing to the larger physical dimensions of the enclosure. In practice, multiple enclosures are used, since it is not possible to program the temperature of a single enclosure at a useful speed without generating intolerable gradients within it. It is absolutely essential to maintain uniformity of temperature in the area immediately surrounding the sample holder.

An additional limitation of the controlled-ambient calorimeter is its inability to remove heat from the sample. This capability is essential for the examination of reversible phenomena, and for the control and observation of exothermic processes. The adiabatic calorimeter cannot be programmed downward in temperature, nor can it

measure the energy released in an exothermic reaction. In such a case, the energy release must be inferred from the temperature rise and the thermal capacity of the sample holder.

Differential isothermal calorimetry is not subject to either of these limitations. In the first place, as will be shown, the system is inherently fast. Secondly, it is capable of removing heat from the sample, since there is always a flow of heat through R_T to the environment. In an exothermic reaction, the energy released by the sample contributes to this flow of heat, and less heat is drawn from T_P , the temperature source. In this case, the differential heat flow and the ordinate signal are negative, as required.

Scanning Calorimetry: State of the Art. Adiabatic calorimeters have reached a high degree of perfection, within the basic limitations discussed earlier. Representative designs are described in papers by Dauphinee, MacDonald, and Preston-Thomas (2), and by Westrum, Hatcher, and Osborne (8).

The first nonadiabatic scanning calorimeter was developed by Sykes (6); in this instrument, the enclosure temperature was programmed linearly, while the sample was made to follow the same program by varying the electrical power input to a heating element integral with the sample holder. This electrical power input was measured and recorded.

Differential nonadiabatic calorimetry was performed by Eyraud (3). In his apparatus, the sample and reference materials were made electrically conductive by thorough mixing with powdered graphite, after which a measured quantity of heat could be generated in either material by the passage of electricity through it.

Both of these instruments were limited

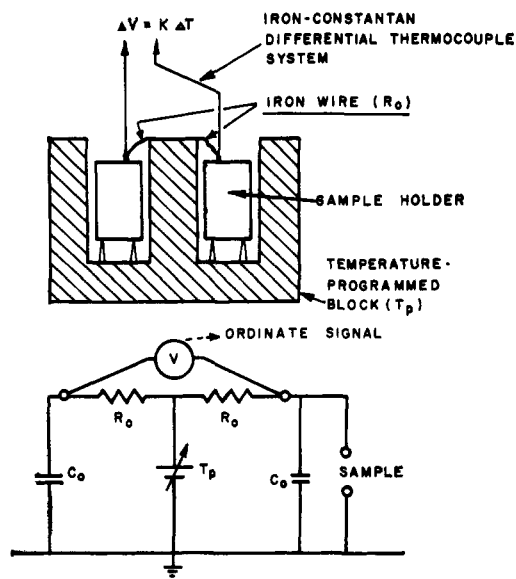


Figure 6. Differential calorimeter

to the analysis of endothermic reactions, since the sample and ambient temperatures were nominally equal at all times. However, in Eyraud's technique, the reference side could be heated during a sample exotherm, for approximate measurement of the energy release.

Most routine scanning calorimetry is performed by a class of instruments in which the flow of heat to the sample is not measured directly, as it is in isothermal or adiabatic calorimetry. In these instruments, the sample holder is coupled to a source of heat through a thermal resistance. The temperature differential appearing across this resistance is measured and recorded, and from this data the heat flow rate may be calculated. Alternatively, the temperature differential may be held at a fixed value, by suitably controlling the source of heat; this creates a constant flow of heat into or out of the sample.

These instruments depend upon the constancy of the coupling resistance for calorimetric accuracy. Such factors as radiative and convective heat transfer, and variations of sample holder geometry from one analysis to the next, must be recognized and dealt with.

A well-designed differential calorimeter based on this principle is described by Arndt and Fujita (1). Figure 6 shows the essential details of this instrument, and its equivalent thermal circuit. Of special interest are the precautions taken to ensure a constant and reproducible source resistance, including the evacuation of the sample holder area to eliminate convection coupling and reduce conduction coupling from the sample holder to the source.

An instrument in which the temperature differential across the source resistance is held at a fixed value is described by Smith (4). This technique is known as heat-leak calorimetry.

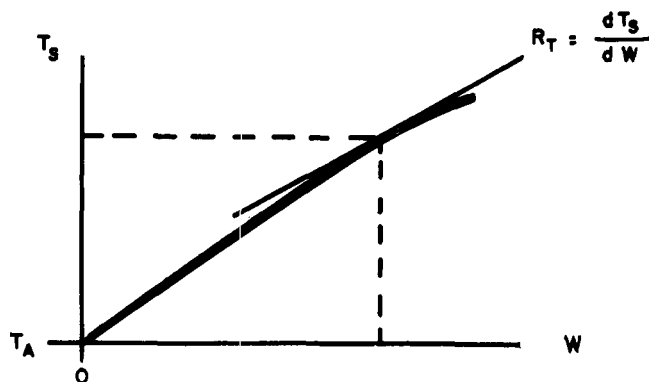


Figure 7. Temperature-heat flow function

A third technique, known as differential thermal analysis (DTA), is equivalent to the differential calorimeter referred to above, except in the control of the source resistance. In all of the many variations of this technique, the temperature measurement is made, not on the sample holder, but in the interior of the sample. Since the thermal resistance of the sample contributes to the total resistance across which temperature measurements are made, the ordinate calibration is sensitive to such factors as the resistivity and the geometry of the sample. The technique is so convenient, however, that it has taken the place of adiabatic calorimetry for many routine determinations. A wealth of literature is devoted to the problem of obtaining accurate calorimetric data with this technique (5, 7).

EQUIVALENT CIRCUIT OF A TEMPERATURE-CONTROLLED SAMPLE HOLDER

We have seen that scanning calorimetry should be improved by the use of a true temperature source, rather than a heat flow source. We now investigate the use of proportional temperature control to approach the performance of a true isothermal calorimeter.

Consider a sample holder with a heat flow source closely coupled to it. T_s , the temperature of the sample holder, is determined by the heat flow rate, W , and the thermal resistance between the sample holder and the environment,

which is at a temperature T_A . The relationship between W and T_s is non-linear, as illustrated in Figure 7, because in any real geometry there will be heat transfer by radiation and convection, as well as by conduction.

R_T is defined as the small-signal thermal resistance between the sample holder and the environment. W is the abscissa and T_s the ordinate in Figure 7, since the heat flow rate is the independent variable.

To determine the response of the sample holder temperature to an incremental heat flow rate, such as a sample exotherm, we may construct the equivalent circuit of Figure 8, in which ΔW_s is the sample signal. If ΔW_s were a step-function, for example, the response would be:

$$\Delta T_s(t) = \Delta W_s R_T [1 - e^{-\frac{t}{R_T C_0}}] \quad (1)$$

This is, of course, the characteristic response of a linear system with a simple low-pass filter. For a time-variable signal, the integral of ΔT_s is just the integral of ΔW_s multiplied by a calibration factor R_T . If the sample holder temperature were increasing or decreasing with time, the response $\Delta T_s(t)$ would appear superimposed on the zero-signal temperature function.

This system will therefore serve as a scanning calorimeter, but its performance is obviously unsatisfactory, since the calibration factor is a function of T_s .

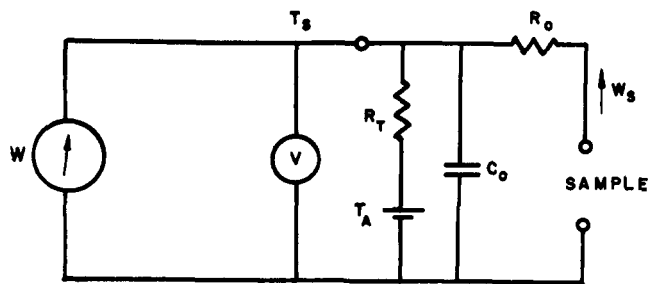


Figure 8. Equivalent thermal circuit

and because all signals are modified by a filtering time constant $R_T C_0$. However, the system can measure exothermic reactions, and can scan in both directions, since there is a steady flow of heat to the environment.

To improve the performance, T_s may be measured and compared with a desired temperature T_P . The difference between these two temperatures may be amplified and used to control the input heat flow rate W . A block diagram of this system is shown in Figure 9. The amplifier has a transfer function K , with dimensions $\text{cal. sec.}^{-1} \text{ } ^\circ\text{C.}^{-1}$. It will be realized that in a practical embodiment of this system, T_s is not directly compared with a temperature T_P . In fact, a transducer such as a platinum resistance thermometer generates an electrical signal related to T_s , and this signal is compared with one produced by a potentiometer or some other convenient device. In the block diagram, the transducer transfer function is included in K , the amplifier transfer function.

As the amplifier gain is increased from zero, three important changes take place in the system. First, the temperature response to the sample signal approaches zero; the steady-state response is given by:

$$\frac{dT_s}{dW_s} = \frac{R_T}{1 + K R_T} \quad (2)$$

Second, the heat flow W compensates accurately for W_s , the sample heat flow rate. This steady-state relationship is given by:

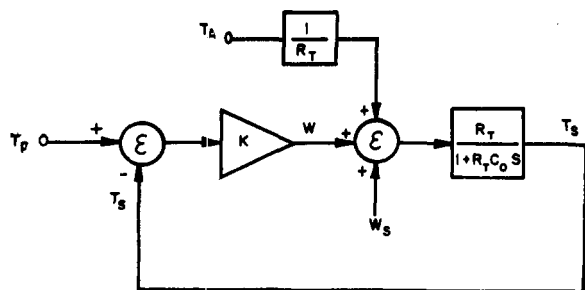


Figure 9. Temperature control system

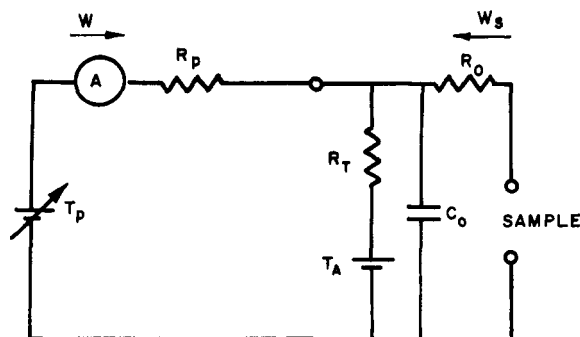


Figure 10. Equivalent thermal circuit

$$\frac{dW}{dW_s} = -\frac{KR_T}{1 + KR_T} \quad (3)$$

Finally, the speed of response is improved. The system time constant is:

$$\tau_1 = \frac{R_T C_0}{1 + KR_T} \quad (4)$$

Equation 2 demonstrates that the source resistance of the sample holder is very much smaller than the original value R_T . In fact, the source resistance is exactly R_T in parallel with a smaller resistance R_P equal to K^{-1} , which approaches zero as the amplifier gain is increased. Since the difference between T_S and T_P also approaches zero, the sample holder behavior approaches that of a temperature source T_P , and T_P may be used as the abscissa in the read-out presentation.

Equation 3 shows that nearly all of the sample heat flow rate is supplied by the amplifier. We may therefore measure and record W as a function of time, which corresponds to putting a thermal ammeter in series with R_P . The equivalent circuit of the whole system is shown in Figure 10.

One advantage of the smaller source resistance is immediately apparent. When a signal W_s is applied, the heat flow divides between R_P and R_T . If K^{-1} were equal to $R_T/100$, for example, then 99% of W_s would flow through R_P and the measuring system, and 1% would flow through R_T . At some higher temperature, R_T might be only one half of its original value, and the division would then be 98% and 2%. Thus we observe that a variation in R_T which would have caused a 50% change in calibration in the previous system causes a 1% change in this system.

The smaller system time constant allows rapid programming, and reduces the filtering of signal information. Thus, in every respect, a temperature-controlled calorimeter is realizable. It

remains only to cancel the component of W due to losses through R_T , and this is readily accomplished by using two identical sample holders, operating at the same temperature, and measuring the difference between the two total heat flow rates.

The preceding discussion has been confined to the case where an arbitrarily specified signal is applied, and has enabled us to derive equivalent circuit parameters. This treatment is useful in the case where sample phenomena are initiated and completed at a fixed temperature. Now we examine the general case, where reactions are produced by scanning the sample temperature through a range where there are characteristic transitions. Since the calorimeter measures heat flow rate, the input signal under scanning conditions should be given by the specific heat function and the scanning speed:

$$W = \frac{dH}{dT} \cdot \frac{dT}{dt} \quad (5)$$

One might expect the ordinate presentation to be an exact duplicate of the specific heat function, modified only by instrumental filtering. In fact, this is precluded by the thermal resistivity of the sample, and by the resistance at the interface between the sample and the instrument, which together modify the analysis of all sample phenomena, especially the sharp transitions.

In a practical instrument, the sample cannot be allowed to come in direct contact with the temperature-controlled surface discussed above; the surface would become contaminated. Therefore, the sample is generally sealed into a metal container, which is then placed on the sample holder. This procedure also facilitates the handling and weighing of small samples. However, the thermal resistance which appears at the plane of contact, which has been designated R_0 , contributes to the source resistance of the instrument. R_0 is generally

much larger than R_P in a real instrument, and in the following discussion R_P will be neglected. R_0 is somewhat under the control of the analyst, since it is possible to reduce it by ensuring good thermal contact between the sample container and the sample holder, or to increase it by allowing foreign matter to intrude.

Provided that the sample is totally enclosed by the sample holder, as shown in Figure 3a, neither R_0 nor the resistance of the sample has any effect upon the calorimetric accuracy of an instrument. However, a given quantity of heat can be delivered to a sample in a shorter time, and therefore in a smaller temperature interval, if the thermal resistances in the circuit are small.

We shall now investigate the influence of R_0 and the sample resistance on the resolution of a sharp transition. It can be shown that the dynamic temperature gradients within the sample due to its distributed thermal capacity are orders of magnitude smaller than the gradients created by the flow of heat during such a transition. However, it is possible for R_0 and the total thermal capacity of the sample to constitute a low-pass thermal filter which does modify the flow of heat. It will be assumed in the following analysis that the sample is so small that this effect can be neglected. Filtering effects will be considered separately, in connection with the signal-to-noise ratio of the instrument.

Analysis of a Sharp Transition. It will be assumed that the calorimeter may be represented by an isothermal platform, connected through a resistance R_0 and a thermal ammeter to a temperature source T_P , as shown in Figure 11. The sample rests on the platform in a layer of uniform thickness, which is such that end effects may be neglected. A fusion will be described, although the analysis is applicable to any sharp endothermic transition. The following parameters will be used:

\dot{T}_P Scanning speed ° C. sec.⁻¹
 T_0 Platform ° C.
 temperature

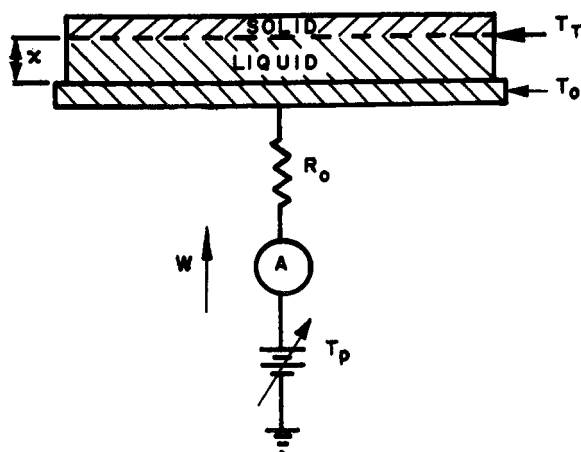


Figure 11. Sample geometry

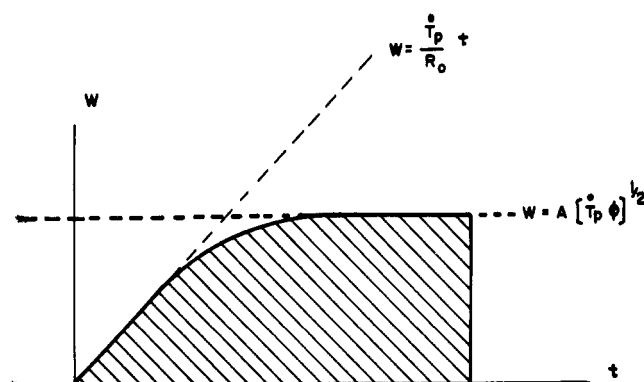


Figure 12. Fusion analysis

T_T	Transition temperature	$^{\circ}\text{C.}$
A	Platform area	cm.^2
ΔH	Transition energy	cal.
r	Sample resistivity	$^{\circ}\text{C. cm. sec. cal.}^{-1}$
η	Specific transition energy	cal. g.^{-1}
ρ	Sample density	g. cm.^{-3}

The transition begins when T_P equals T_T . At this time, a solid-liquid interface appears at the lower surface of the sample, in contact with the platform. As T_P increases, this interface moves up through the sample. Between the platform and the interface, in the liquid portion of the sample, there is a temperature gradient. Above the interface the sample temperature is T_T .

The heat flow rate is determined by the rate at which the sample melts, which is proportional to the interface velocity. Denoting the thickness of the liquid layer by x , the heat flow rate is given by:

$$W = A\rho\eta \frac{dx}{dt} \quad (6)$$

The thermal resistance of this layer is equal to rx/A , and the temperature differential is $(T_0 - T_T)$. Therefore:

$$\frac{A(T_0 - T_T)}{rx} = A\rho\eta \frac{dx}{dt} \quad (7)$$

Similarly, considering the resistance R_0 we have:

$$\frac{T_P - T_0}{R_0} = A\rho\eta \frac{dx}{dt} \quad (8)$$

From these two equations, T_0 may be eliminated:

$$AR_0\rho\eta \frac{dx}{dt} + r\rho\eta x \frac{dx}{dt} = T_P - T_T \quad (9)$$

This differential equation describes the motion of the solid-liquid interface as a function of T_P . We are interested here in the case where T_P increases linearly with time:

$$T_P = T_T + \dot{T}_P t \quad (10)$$

Substituting this expression for T_P , and integrating once, we have an equation in x and t :

$$\frac{r\rho\eta}{2} x^2 + AR_0\rho\eta x = \frac{\dot{T}_P}{2} t^2 \quad (11)$$

Solving for x :

$$x = \left[\frac{A^2 R_0^2}{r^2} + \frac{\dot{T}_P t^2}{r\rho\eta} - \frac{AR_0}{r} \right]^{1/2} \quad (12)$$

Finally, W is calculated from Equations 6 and 12:

$$W = \frac{\dot{T}_P t}{R_0} \left[1 + \frac{\dot{T}_P r t^2}{A^2 R_0^2 \rho\eta} \right]^{1/2} \quad (13)$$

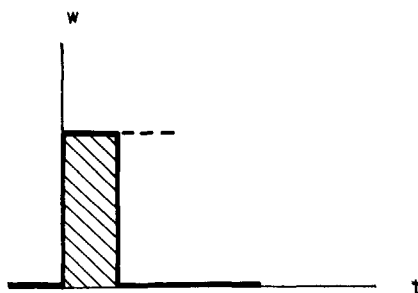


Figure 13. Sample-limited analysis

This expression for W is valid while there exists an interface at which heat is being absorbed by the solid-liquid transition. When the interface arrives at the upper surface of the sample, the transition is complete, and W becomes zero. Thus the transition is measured and recorded as a peak, with a shape as shown in Figure 12. The area of the peak, of course, is equal to ΔH .

To determine the peak width Δt , the sample thickness $\Delta H/A\rho\eta$ may be substituted for x in Equation 11, which yields:

$$\Delta t = \left[\frac{\Delta H}{\dot{T}_P} \left(2R_0 + \frac{r\Delta H}{A^2 \rho\eta} \right) \right]^{1/2} \quad (14)$$

Inspection of Equation 13 reveals that the signal waveform is determined by two asymptotes, and by the magnitude of ΔH . For small values of t , the denominator of the expression is unity, and W is given by:

$$W = \frac{\dot{T}_P}{R_0} t \quad (15)$$

This equation defines an asymptote passing through the origin. The flow of heat is governed only by the scanning speed and the source resistance. If the sample is sufficiently thin, or if R_0 is very large, the transition will be completed without any appreciable departure from this asymptote. Since the thermal resistance of the sample has no effect upon the analysis, this asymptote represents instrument-limited performance.

For large values of t , W is given by:

$$W = A \left[\frac{\dot{T}_P \rho\eta}{r} \right]^{1/2} \quad (16)$$

This equation defines a horizontal asymptote, and represents a situation where R_0 is negligible compared with the thermal resistance of the sample. This asymptote represents sample-limited performance. From Equation 12 it may be shown that the interface velocity approaches a limiting value:

$$\left. \frac{dx}{dt} \right|_{t \rightarrow \infty} = \left[\frac{\dot{T}_P}{r\rho\eta} \right]^{1/2} \quad (17)$$

In this very interesting case we see that the thickness of the liquid layer,

and the temperature differential across it, are each increasing linearly with time; the heat flow rate is therefore constant. Equation 12 shows also that when R_0 equals zero the interface velocity assumes its limiting value immediately; in this case, the initial asymptote is vertical, and the peak is rectangular, as shown in Figure 13. The peak width is given by:

$$\Delta t = \frac{\Delta H}{W} = \frac{\Delta H}{A} \left[\frac{r}{\dot{T}_P \rho\eta} \right]^{1/2} \quad (18)$$

Every transition begins under instrument-limited conditions and, if sufficient energy is involved, will eventually become sample-limited. Some numerical values may be used to illustrate the above analysis. Consider the fusion of 1 mg. of ice at a scanning speed of $5^{\circ}\text{C. minute}^{-1}$ on a sample holder with an area of 0.45 sq. cm. (the sample-holder area of the Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1). In this case ΔH is 0.08 cal., and the parameter $\rho\eta/r$, to which we will assign the symbol ϕ , is $0.1 \text{ cal.}^2 \text{ } ^{\circ}\text{C.}^{-1} \text{ cm.}^{-4} \text{ sec.}^{-1}$. The sample-limited value of W , from Equation 16, is $0.041 \text{ cal. sec.}^{-1}$. If there were no source resistance at all, the energy would be delivered to the sample in 1.95 seconds, and the transition would be completed in a temperature interval of 0.16°C.

An average value of R_0 for this instrument might be $200^{\circ}\text{C. sec. cal.}^{-1}$. In this case, Δt , from Equation 14, is 19.8 seconds, the temperature interval is 1.65°C. , and the maximum rate of heat transfer, from Equation 13, is $0.008 \text{ cal. sec.}^{-1}$. The two analyses are illustrated in Figure 14.

A Figure of Merit for Scanning Calorimeters. A measure of the performance of a calorimeter with a sharp transition is the ratio of the temperature interval ΔT to the peak height W_P . Ideally, this ratio should approach zero.

From Equations 13 and 14, W_P may be expressed as a function of Δt . Substituting $\Delta T/\dot{T}_P$ for Δt , the following relationship between W_P and ΔT is derived:

$$\frac{\Delta T}{W_P} = R_0 + \frac{\Delta H}{A^2 \phi} \quad (19)$$

It is remarkable that this expression does not include the scanning speed \dot{T}_P . The temperature and heat flow rate coordinates of every point on the signal waveform are proportional to $(\dot{T}_P)^{1/2}$, and therefore the shape of the peak is independent of scanning speed.

Equation 19 indicates also whether a transition will be sample-limited. For small ΔH values, the ratio is equal to R_0 , and the transitions will be instrument-limited. As ΔH increases, the thermal resistance of the sample begins to limit the heat flow rate. It is readily shown that $\Delta H/A^2 \phi$ is in reality the total

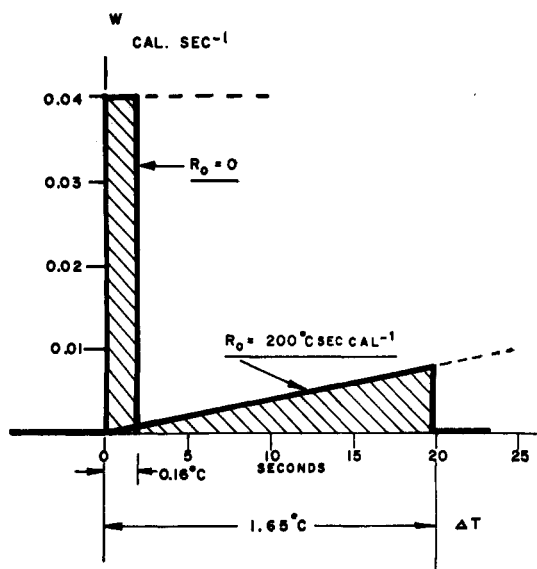


Figure 14. Fusion of ice

thermal resistance of the sample. It is concluded that for good resolution the second term in Equation 19 should be small with respect to the first term. If this condition is satisfied, $\Delta T/W_P$ is also independent of sample size.

For a given value of R_0 , ΔT may be reduced to any desired value, by reducing the scanning speed sufficiently. It will be observed that the analyst pays a high price in analysis time for better temperature resolution; to improve ΔT by a factor of 2, for example, costs a factor of 4 in Δt . As ΔT is reduced, W_P is reduced proportionately, and the peak will eventually disappear in the instrumental noise level. We may combine the $\Delta T/W_P$ ratio and the noise level W_N to form a figure of merit M :

$$M = \frac{W_P}{W_N \Delta T} \quad (20)$$

This figure of merit is significant and useful, for it represents the signal-to-noise ratio per unit temperature resolution, and may be conveniently evaluated from recorded data. It is invariant with respect to sample size and scanning speed. Finally, it may be used to measure and optimize the thermal coupling between the sample and the instrument. If a sample were uniformly distributed on the sample holder, and if there were no air gaps at the interface, the source resistance would approach R_P , the effective output resistance of the temperature control system. In fact, samples are frequently distributed nonuniformly, and air gaps do exist. The smallest conveniently realizable source resistance of the DSC-1 is approximately $200^\circ \text{C. sec. cal.}^{-1}$. The instrumental noise level is less than $4 \times 10^{-3} \text{ cal. sec.}^{-1}$. Combining these two numbers, we have:

$$M = \frac{1}{R_0 W_N} = 125^\circ \text{C.}^{-1}$$

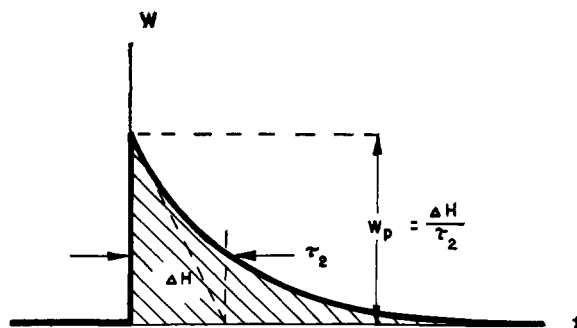


Figure 15. Bandwidth-limited analysis

$$\frac{\Delta T}{W_P} = \frac{\tau_2^2 \dot{T}_P}{\Delta H} \quad (21)$$

Figure 16 shows the variation of $\Delta T/W_P$ with respect to τ_2 . Clearly, the figure of merit is optimized when the temperature resolution is determined primarily by R_0 .

When large sample quantities are involved, the bandwidth of the instrument may be limited by R_0 and C_s , the lumped thermal capacity of the sample and its container. In addition, since the total thermal resistance of the sample will be large in this case, sharp transitions will be somewhat sample-limited, and the temperature resolution will be poor. An analytical solution is available only if the gradients in the sample are assumed to be negligible, in which case the $\Delta T/W_P$ ratio is given approximately by:

$$\frac{\Delta T}{W_P} = \frac{R_0^2 C_s^2 \dot{T}_P}{\Delta H} \quad (22)$$

Application of Figure of Merit to Other Techniques. It is interesting to consider the evaluation of non-quantitative techniques such as DTA with the aid of the figure of merit defined above. The heat flow rate during a sharp transition is determined by the same instrumental and sample parameters as in scanning calorimetry, but the ordinate signal is the temperature differential across R_0 :

$$T_Y = R_0 W \quad (23)$$

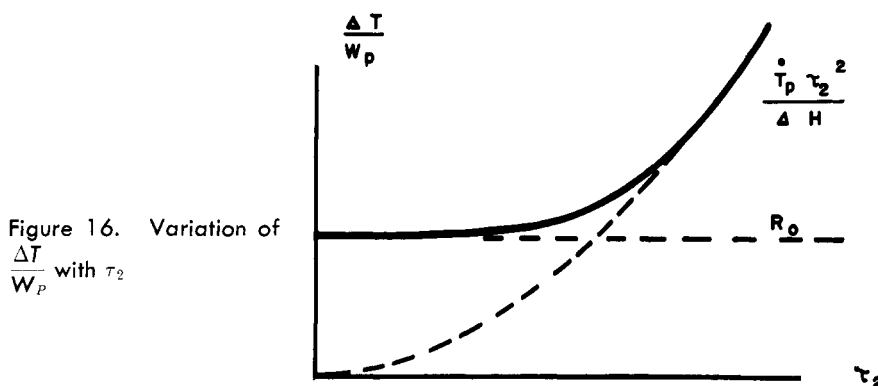


Figure 16. Variation of $\frac{\Delta T}{W_P}$ with τ_2

The noise level will be defined as T_N . The figure of merit can therefore be expressed as follows:

$$M' = \frac{T_Y}{T_N \Delta T} \quad (24)$$

M' is invariant with respect to scanning speed, for the reasons already outlined. It is also invariant with respect to ΔH , since this type of instrument always has a large source resistance.

It will be realized that, in the absence of filtering effects, T_Y and ΔT should be identical. T_Y , the temperature differential across R_0 at the conclusion of the transition, is exactly the amount by which the sample temperature lags the program temperature as a result of the transition. Therefore, M' cannot exceed the reciprocal of the temperature noise:

$$M' \leq \frac{1}{T_N} \quad (25)$$

In practice, transitions are always limited by the thermal bandwidth of the system, characterized by the time constant $R_0 C_s$, and ΔT is considerably larger than T_Y . Temperature resolution and sensitivity are incompatible in this type of instrument, since the former requires a small value of R_0 , while the latter requires a large value of R_0 .

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LITERATURE CITED

(1) Arndt, R. A., Fujita, F. E., *Rev. Sci. Inst.* **34**, 868 (1963).

SYMBOLS		
Symbol	Dimensions	Definition
T_s	$^{\circ}\text{C.}$	Sample holder temperature
T_0	$^{\circ}\text{C.}$	Platform temperature
T_T	$^{\circ}\text{C.}$	Transition temperature
T_P	$^{\circ}\text{C.}$	Temperature source
T_A	$^{\circ}\text{C.}$	Ambient temperature
T_P	$^{\circ}\text{C. sec.}^{-1}$	Scanning speed
ΔT	$^{\circ}\text{C.}$	Temperature resolution of sharp transition
ΔH	cal.	Transition energy
ΔH_1	cal.	Energy
W_s	cal. sec. $^{-1}$	Sample heat flow rate
W	cal. sec. $^{-1}$	Measured heat flow rate (ordinate)
W_N	cal. sec. $^{-1}$	Ordinate noise level
W_P	cal. sec. $^{-1}$	Peak value of W
C_0	cal. $^{\circ}\text{C.}^{-1}$	Thermal capacity of sample holder
C_s	cal. $^{\circ}\text{C.}^{-1}$	Thermal capacity of sample and container
R_T	$^{\circ}\text{C. sec. cal.}^{-1}$	Thermal resistance between sample holder and environment
R_P	$^{\circ}\text{C. sec. cal.}^{-1}$	Output resistance of temperature control system
R_0	$^{\circ}\text{C. sec. cal.}^{-1}$	Thermal resistance between sample and sample holder
K	cal. sec. $^{-1} ^{\circ}\text{C.}^{-1}$	Amplifier transfer function
τ_1	sec.	Temperature control system time constant
τ_2	sec.	Ordinate readout time constant
r	$^{\circ}\text{C. cm. sec. cal.}^{-1}$	Sample resistivity
η	cal. g. $^{-1}$	Specific transition energy
ρ	g. cm. $^{-3}$	Sample density
$\phi = \rho\eta/r$	cal. 2 cm. $^{-4} ^{\circ}\text{C.}^{-1} \text{sec.}^{-1}$	Convenient sample parameter
A	cm. 2	Platform area
M	$^{\circ}\text{C.}^{-1}$	Figure of merit
T_Y	$^{\circ}\text{C.}$	DTA ordinate
T_N	$^{\circ}\text{C.}$	DTA ordinate noise level
M'	$^{\circ}\text{C.}^{-1}$	DTA figure of merit

- (2) Dauphinee, T. M., MacDonald, D. K. C., Preston-Thomas, O., *Proc. Roy. Soc.* **221**, 267 (1954).
 (3) Eyraud, C., *Compt. Rend.* **238**, 1511 (1954).
 (4) Smith, C. S., *Trans. A.I.M.E.* **137**, 236 (1940).
 (5) "Differential Thermal Analysis," Smothers, W. J., Chiang, Y., Chemical Publishing Co., New York, 1958.

- (6) Sykes, C., *Proc. Roy. Soc.* **148**, 422 (1935).
 (7) Vold, M. J., *ANAL. CHEM.* **21**, 683 (1949).
 (8) Westrum, E. F., Jr., Hatcher, J. B., Osborne, D. W., *J. Chem. Phys.* **21**, 419 (1953).

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Continuous Quantitative Electrolysis

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► The construction and operation of a continuous electrolytic cell, designed for the quantitative electrolysis of material in a flowing stream, are described. Some applications to analysis are presented: quantitative oxidation of Ce(III), selective prereduction of Fe(III)-(UVI) mixtures, and separation of Cu-Pb-Cd-Zn mixtures. At low concentrations, the selectivity of the cell approaches that of controlled potential devices, but selectivity decreases as the concentration of electroactive material increases.

THIS article presents the design and operation of a simple apparatus that can be used to electrolyze substances quantitatively in a flowing solution, and some applications to analysis and separations. The continuous electrolytic cell is essentially a short column packed with a material that can act as an electrode.

The cell has several advantages when compared to a metal reductor column, which it resembles in many respects. The cell is packed with a conducting material whose potential can be varied.

Only one packing material is necessary for a wide variety of tasks. Since the potential is applied from an external source, it is independent of the supporting electrolyte, and there is a wide choice of supporting electrolytes for use in a particular situation. Contamination of samples by the introduction of metal ions is less than in metal reductor columns. The cell can be used for tasks which cannot be performed by

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