STATES
MENT OF
IERCE
CATION

NBS TECHNICAL NOTE 396

U. S.
TMENT
OF
MERCE
ational
Bureau
ndards

Data Analysis for Isoperibol Laser Calorimetry

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

- **Physics and Chemistry**

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $9.50; foreign, $11.75*.

- **Mathematical Sciences**

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $5.00; foreign, $6.25*.

- **Engineering and Instrumentation**

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, $5.00; foreign, $6.25*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—*for engineers, chemists, physicists, research managers, product-development managers, and company executives.* Annual subscription: Domestic, $3.00; foreign, $4.00*.

* Difference in price is due to extra cost of foreign mailing.

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitive data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

Federal Information Processing Standards Publications. This series is the official publication within the Federal Government for information on standards adopted and promulgated under the Public Law 89–306, and Bureau of the Budget Circular A–86 entitled, Standardization of Data Elements and Codes in Data Systems.

CLEARINGHOUSE

The Clearinghouse for Federal Scientific and Technical Information, operated by NBS, supplies unclassified information related to Government-generated science and technology in defense, space, atomic energy, and other national programs. For further information on Clearinghouse services, write:

Clearinghouse
U.S. Department of Commerce
Springfield, Virginia 22151

Order NBS publications from: Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

UNITED STATES DEPARTMENT OF COMMERCE
Maurice H. Stans, Secretary
NATIONAL BUREAU OF STANDARDS ● Lewis M. Branscomb, Director

NBS TECHNICAL NOTE 396

ISSUED FEBRUARY 1971

Nat. Bur. Stand. (U.S.), Tech. Note 396, 34 pages (Feb. 1971)
CODEN: NBTNA

Data Analysis for Isoperibol Laser Calorimetry

E. D. West

Quantum Electronics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

This work was partly supported by the Night Vision Laboratory, U.S. Army Electronics Command, monitored by S. E. Smathers, and by the Advanced Research Project Agency of the Department of Defense, monitored by Lt. Col. John M. MacCallum under ARPA Order No. 891.

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
(Order by SD Catalog No. C13.46:396), Price 40 cents.

Data Analysis for Isoperibol Laser Calorimetry

E. D. West

Isoperibol calorimeters (those operating in a constant-temperature environment) are used to measure the power and energy in laser beams relative to electrical standards. The derivation of the basic formula is reviewed. Two methods are presented for analyzing the data taken at equal time intervals: (1) An approximate manual method with criteria for avoiding significant errors of approximation and (2) A least squares method for use with automatic digital computers.

Key Words: Calorimetry; laser; laser calorimetry; laser energy; laser power.

Laser calorimetry affords a method of comparing the power and energy in laser beams directly to electrical power and energy. Laser calorimetry thus provides an accurate and convenient means of calibrating devices for laser power and energy measurements in terms of the absolute joule or watt. The electrical standards required -- standard resistors and standard cells -- are far more accurate than is now required for laser power and energy measurement; they are easy to use and available in most laboratories or obtainable at reasonable cost.

Calorimeters used at the National Bureau of Standards for these measurements[1,2] operate in a constant-temperature environment and are termed isoperibol calorimeters. The simplified theory of operation of these calorimeters is given in various books.[3,4,5,6] The same measurement method can be derived from a slightly less simplistic model[7] and more rigorously from detailed considerations of the heat flow problem in the calorimeter and its relationship to the first law of thermodynamics.[8] The detailed theory shows that the natural response of the calorimeter to a sudden energy input is an infinite series of exponential terms decaying with time. This theory shows how heat exchange due to these higher order terms is taken into account by proper attention to calorimeter design and operation.

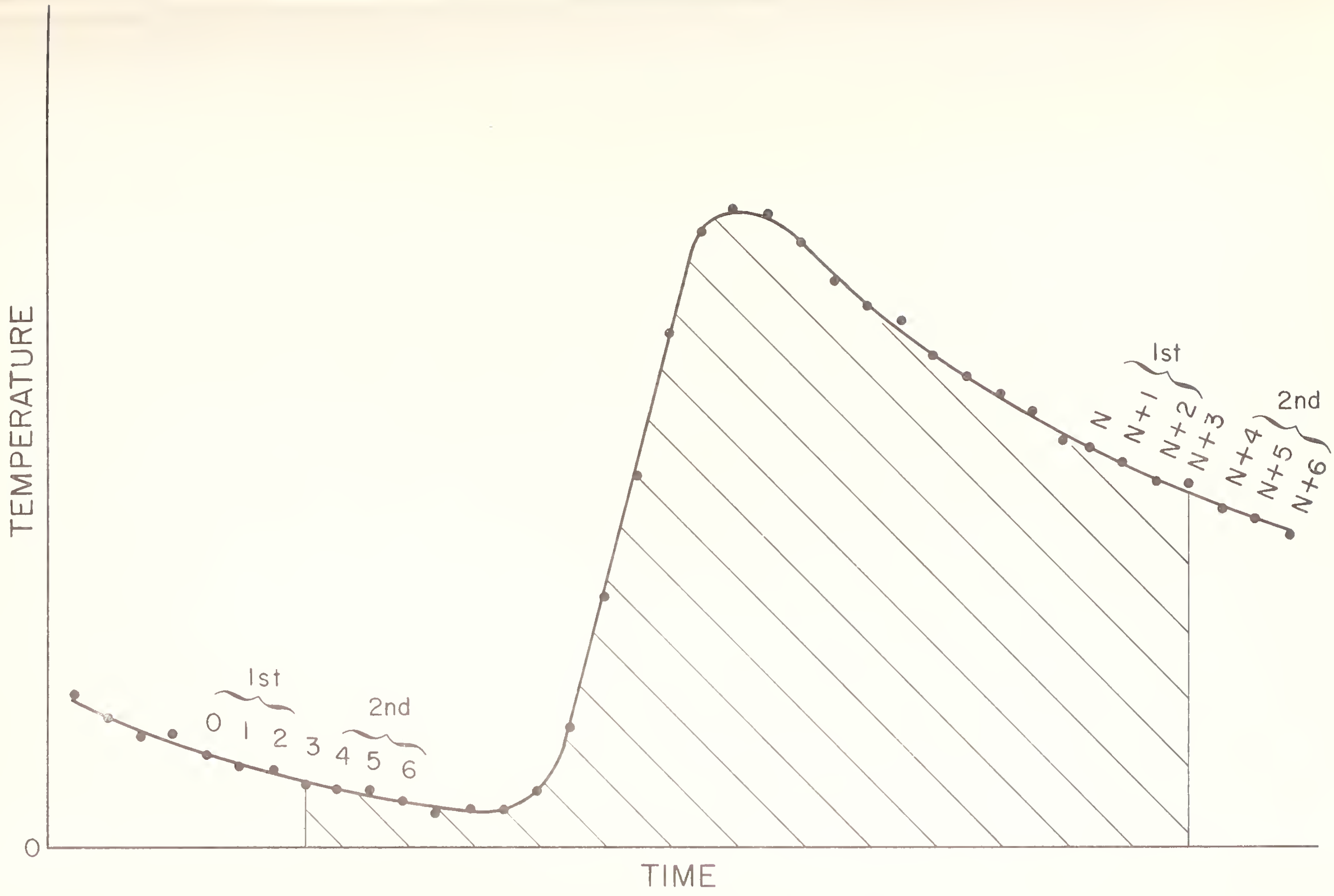
A temperature-time curve for an isoperibol calorimeter is shown in Fig. 1. This curve is typical for calorimeters operating at a temperature above the average temperature of the surroundings. In the first part of the experiment, the temperature is decreasing as a single exponential function of time. Then an electrical or laser input raises the temperature. Some time after this input the temperature again decreases as a single exponential function of time. Although this curve is certainly the usual one for laser calorimetry, the data analysis in this Note applies equally well to any method of operating the calorimeter -- including processes which absorb heat.

1. THE WORKING EQUATION

The first law of thermodynamics states that the work W done on a calorimeter by a laser beam or in an electrical calibration is given by the increase in the energy ΔU stored in the calorimeter minus the heat Q transferred from the constant-temperature surroundings:

$$W = \Delta U - Q. \tag{1}$$

The experimental problem is to determine the heat exchange and the stored energy. Of course, it must be shown that one is applying the



Plot of time-temperature data for an imaginary experiment with an isoperibol calorimeter. The data points are separated by equal time intervals of z seconds and scatter about the smooth curve because of imperfections in the observing system.

first law properly for each calorimeter. For example, tests must be made to show that various combinations of ΔU and Q give the same value for the work W and that $\Delta U = Q$ during rating periods ($W = 0$ during rating periods; that is, there is no electrical heating or laser input.) Such tests are made to demonstrate the adequacy of a particular design and are essential to the estimation of the accuracy of a particular calorimeter. Discussions of design and testing calorimeters are scattered through the literature, but some of these have been collected.[9-11] Restrictions which the theory imposes on the experimental measurements are derived from the detailed consideration of the heat flow problems.[8] This paper will not treat the problems of design and testing, but will instead be concerned with the analysis of data from proven isoperibol calorimeters.

To use Eq. (1) for measurement, the quantities ΔU and Q must be determinable in terms of observed quantities. In the linear theory of isoperibol calorimeters,[8] the change in internal energy of the calorimeter is shown to be proportional to the change in temperature

$$\Delta U = C(T - T_I), \tag{2}$$

where $T - T_I$ represents the change in the observed temperature. (T_I may be looked on as a reference temperature at which U has the value of U_I.) The constant of proportionality C will be different for each particular calorimeter. This constant is a sum of heat capacities weighted according to the temperature gradient in the calorimeter.[8] The procedure described below takes this weighting into account.

The determination of the heat transferred from the environment is such a complicated problem that the development given here is more illustrative than rigorous. We begin with the observation that sometime after an electrical or laser input to the calorimeter, the observed temperature T changes according to the relation

$$dT/dt = -\epsilon(T - T_\infty) \tag{3}$$

where T_∞ is the observed temperature for which $dT/dt = 0$ and ϵ is termed the cooling constant. Equation (3) is a representation of Newton's law of cooling. Multiplication by the constant C gives the relation

$$C\, dT/dt = -(C\epsilon)(T - T_\infty). \tag{4}$$

It is apparent from Eq. (2) that the left-hand side of Eq. (4) is the rate of change of the internal energy. Since the electrical or laser work term must be zero when Eq. (3) holds, the right-hand side of Eq. (4) must represent heat transfer as required by Eq. (1). For a calorimeter behaving as in Fig. 1, the internal energy is decreasing and heat is flowing from the calorimeter because $T > T_\infty$. The constant $C\epsilon$ has the dimensions of a heat transfer coefficient and is frequently so called; in this instance, T is merely an observed temperature and not the temperature of the calorimeter surface from which heat is lost. When the existence of a temperature gradient in the calorimeter is acknowledged, $C\epsilon$ loses this physical meaning. It has been shown[8] that ϵ is the smallest eigenvalue in the heat flow problem.

When Eq. (3) holds, the calorimeter is said to be in a rating period. Another criterion for the rating period is obtained by integration of Eq. (3) between limits and placing it in the exponential form

$$T - T_\infty = (T_I - T_\infty)\, e^{-\epsilon(t - t_I)} \tag{5}$$

where the constant of integration is obtained from knowledge of the temperature T_I at the time t_I. Eq. (5) is reached in practical calorimeters because the other eigenvalues are appreciably greater than ϵ and the corresponding exponentials usually become negligible in a reasonable time. The heat exchange due to these higher order terms can be accounted for if the calorimeter is properly calibrated electrically and care is taken that temperature observations extend from an initial rating period, in which Eq. (3) [or (5)] holds through the "main" period, in which the laser or electrical energy is added, into a final rating period in which Eq. (3) [or (5) with new integration constants T_F and t_F] again holds. If the data are analyzed by methods outlined below, the measurement does not require that dT/dt is small. These methods therefore speed up the measurement by eliminating the "infinite" time required for T to equal T_∞ in Eq. (5). A principal source of systematic error is that the heat transfer due to the higher order terms depends on the location of the source. Since the laser energy obviously cannot be absorbed exactly where the electrical energy is generated, the calorimeter must be designed so that the two sources appear to be equivalent as far as accounting for the heat transfer by the use of the observed temperature. This problem is discussed in reference 8. With these restrictions the small heat transfer q due to the transients is shown to be proportional to the electrical work on the calorimeter heater or to the electromagnetic work of the laser beam.

$$q = kW. \tag{6}$$

The balance of the heat exchange, and probably the greater part of it, is obtained by integrating the right-hand side of Eq. (4). The quantity Q in Eq. (1) is then the sum

$$Q = - C\epsilon \int (T - T_\infty)\, dt + kW. \tag{7}$$

The heat quantity Q is usually negative in laser work because T is usually greater than T_∞; that is, the calorimeter is usually heated above its equilibrium temperature. Substituting from Eqs. (2) and (7) into Eq. (1) and rearranging, we obtain the working equation for isoperibol calorimetry

$$W = \frac{C}{1 - k} [T_F - T_I + \epsilon \int_{t_I}^{t_F} (T - T_\infty)\, dt], \tag{8}$$

where T_I and T_F are the observed temperatures at times t_I and t_F respectively. The quantity in brackets in Eq. (8) is usually called the corrected temperature rise. It is a constant when Eq. (3) holds, as is apparent from integrating Eq. (3) to obtain

$$T'_F - T_F = \epsilon \int_{t_F}^{t'_F} (T_F - T_\infty) dt,$$

which shows that the decrease in T_F is just equal to the increase in the integral term. One must be on guard at this point that the data really fit Eq. (3), that is, that deviations from the smooth curve are really random. To check on this point, the computer program described below prints out the deviations, which can be examined to see if the positive and negative deviations are grouped or in patterns. The calculations can also be done manually, but manual calculations require considerable time.

Temperature is not observed directly, but is calculated from some other observed quantity. The temperature is frequently a linear function of an observed quantity x, such as a thermopile voltage. In such a case, that is, when

$$T = a + bx, \tag{9}$$

it is not necessary to convert to temperature. This linear relationship is frequently an adequate representation of the temperature and is used in our work to relate the temperature to the output of a difference thermocouple or thermopile when the temperature difference is small. Substitution for T from Eq. (9) into Eq. (8) will show that the quantity a cancels and the quantity b can be factored and placed outside the bracket. Putting $\frac{bC}{1-k} = E$, which is customarily called the energy equivalent of the calorimeter, the working form of Eq. (6) becomes

$$W = E\left[x_F - x_I + \epsilon \int_{t_I}^{t_F} (x - x_\infty)\, dt\right]. \tag{10}$$

The quantities x, x_F, x_I, t, t_F, t_I, may be observed directly; the quantities ϵ and x_∞ are calculated from observations of x and t during rating periods using Eq. (5). Although x_∞ may be observed directly, it is commonly not done.

Equation (10) is identical to Eq. (8) so that x is merely a new temperature scale with a different zero and a different sized degree. The quantity E in Eq. (8) or (10) is to be determined from a known work quantity, an electrical calibration, for example. It may accordingly be regarded as the calibration factor. Note that it is not a sum of the heat capacities of the "parts" of the calorimeter.[7, 8]

The quantities E, x_∞, and ϵ are constants which are properties of the calorimetric system. It is prudent to maintain control charts on each of these quantities. The calibration factor E should remain constant within the required accuracy, although a predictable drift with time is almost equally useful. The quantity x_∞ is affected somewhat by changes in the room because the calorimeter exchanges some heat with the room through the opening for the laser beam. This quantity might therefore be expected to show small variations with time, perhaps related to room temperature. The cooling constant ϵ is markedly affected by the gas pressure in the calorimeter and affords an operating check on the vacuum system if the calorimeter is evacuated. The calibration factor E should not be appreciably affected if x_∞ and ϵ are different for different experiments, but it is incumbent on the user to show that this is true.

The direct computation of Eq. (10) can be carried out with a manually-operated desk calculator. Historically, much attention was given to simplifying the problem of evaluating the integral, but, when readings of x or T are spaced equally in time, the direct manual computation may be less time-consuming than establishing the validity of a shortcut method. The straightforward calculation may avoid some of the pitfalls of the shortcut methods. Actual data lack the smoothness of the analytical equations and various schemes are employed to reduce the effects on the calculated quantity W of the "noise" or "scatter" in the observations. The computation outlined in the next section uses averaging of a number of points to smooth the data. If the temperature-time data are recorded on a chart, the smoothing and the integration can be done graphically. Data analysis by the method of least squares with a digital computer provides the best smoothing and the most information about the experiment. The least squares procedure used at NBS is discussed in later sections of this Note.

The question of whether to use a manual or an automatic digital method should be resolved, as usual, on the basis of how much work is to be done and what accuracy is required. The extra work of programming the computer can be offset by its greater speed and accuracy, if enough work is to be done. The computer should probably be used for the most accuracy work, in order to obtain a more thorough analysis of the results, even though the difference in computed values may be slight.

2. DIRECT MANUAL EVALUATION OF THE TEMPERATURE-TIME DATA

The method of data analysis presented in this section is suggested for use when automatic digital computers are not available and when the user does not wish to develop his own methods. The basis of the method can be readily understood from a simple illustration of how the constants required in Eq. (8) or (10) are extracted from discrete and noisy temperature observations spaced equally in time.

Temperature-time data plotted in Fig. 1 indicate the typical course of an experiment with an isoperibol calorimeter. The smooth curve is sketched to emphasize that the individual data points do not slavishly follow the theoretical single exponential. Points to be used in our illustration are given numbers from 0 to N + 6. Ordinarily, seven points in each rating period will be too few, but they are sufficient to illustrate the method. From these points we must obtain T_F, T_I, ϵ and T_∞ for Eq. (8) and the integral from t_F to t_I.

Equation (3) is the basic equation for determining the four constants. The derivative dT/dt can be approximated by $\Delta T/\Delta t$ using any pair of points in a rating period, but a derivative based on adjacent points will likely be a poor approximation because of the scatter in the data. Spacing the points farther apart will reduce the effects of scatter but may get into the problem of how well the slope of a chord approximates the derivative of an exponential curve. This problem will be considered at the end of this section.

To apply Eq. (3) to the data in Fig. 1, the slope of the chord is taken as an approximation to the derivative at the time corresponding to the midpoint of the. chord. The following approximation to Eq. (3) is obtained from the points, spaced at equal time intervals z, and numbered 0 to 4 and point 2, which is midway between

$$\frac{T_4 - T_0}{4\,z} = -\,\epsilon\,(T_2 - T_\infty)\,. \tag{11}$$

The time interval is just four times the fixed interval z between observations. From the first seven points, two more equations can be written:

$$\frac{T_5 - T_1}{4z} = -\,\epsilon\,(T_3 - T_\infty)$$

$$\frac{T_6 - T_2}{4z} = -\,\epsilon\,(T_4 - T_\infty).$$

The average of these equations is

$$\frac{1}{4z}\left(\frac{T_4 + T_5 + T_6}{3} - \frac{T_0 + T_1 + T_2}{3}\right) = -\,\epsilon\,\frac{T_2 + T_3 + T_4}{3} + \epsilon\,T_\infty. \tag{12}$$

If the initial rating period is divided into a first section preceding the midpoint and a second section following the midpoint (see Fig. 1), the preceding equation represents the average temperature of the first section minus the average temperature of the second section divided by the time interval and equal to the cooling constant ϵ times the average temperature of the interval less the quantity ϵT_∞.

Seven points are usually not enough to get the noise out of the data. We therefore need to generalize Eq. (12) to deal with a larger number of points. The number of points is not arbitrary but is restricted by Eq. (11) which requires that there be an observed temperature (e.g., T_2) midway between two observed temperatures (e.g., T_4 and T_0). This method of computation works if we take 2K equal intervals in each rating period where K is an odd integer. Then the more general form of Eq. (12) for the initial rating period can be written

$$\frac{\sum_{i=K+1}^{2K} T_i - \sum_{i=0}^{K-1} T_i}{(K+1)\, z} = -\epsilon \sum_{i=\frac{1}{2}(K+1)}^{\frac{1}{2}(3K-1)} T_i + \epsilon K T_\infty . \tag{14}$$

For the final rating period starting at point number N and extending for 2K time intervals, as in Fig. 1, the corresponding equation can be written

$$\frac{\sum_{i=N+K+1}^{N+2K} T_i - \sum_{i=N}^{N+K-1} T_i}{(K+1)\, z} = -\epsilon \sum_{i=N+\frac{1}{2}(K+1)}^{N+\frac{1}{2}(3K-1)} T_i + \epsilon K T_\infty . \tag{15}$$

Equations (14) and (15) are solved simultaneously to obtain the following formula for calculating the cooling constant ϵ

$$\epsilon = \frac{1}{(K+1)\,z} \; \frac{\displaystyle\sum_{i=N+K+1}^{N+2K} T_i - \sum_{i=N}^{N+K-1} T_i - \sum_{i=K+1}^{2K} T_i + \sum_{i=0}^{K-1} T_i}{\displaystyle\sum_{i=\frac{1}{2}(K+1)}^{\frac{1}{2}(3K-1)} T_i - \sum_{i=N+\frac{1}{2}(K+1)}^{N+\frac{1}{2}(3K-1)} T_i} \qquad (16)$$

This value of the cooling constant is inserted in Eq. (14) or (15), which is then solved for T_∞, giving two of the quantities required by Eq. (8). The scheme of computation indicated in Fig. 1 requires the temperature T_1 and T_F at the midpoints of the rating periods and integration between those points. We use the average temperatures obtained by dividing the sums from the right hand side of Eqs. (14) and (15) by K, the number of temperatures in the sums

$$T_I = \frac{1}{K} \sum_{i=\frac{1}{2}(K+1)}^{\frac{1}{2}(3K-1)} T_i$$

$$T_F = \frac{1}{K} \sum_{i=N+\frac{1}{2}(K+1)}^{N+\frac{1}{2}(3K-1)} T_i . \qquad (17)$$

The integration required in Eqs. (8) and (10) is carried out between the midpoints of the rating periods; that is, the time $t_I = t_K$ and $t_F = t_{N+K}$ are limits on the integration in Eqs. (8) and (10). The integration is performed by the trapezoidal rule, which approximates the curve between adjacent points by a straight line. By this rule, the integral I is equal to the product of the length of the time interval z and the sum of one-half the first and last temperatures plus all the temperatures in between:

$$I = z\left(\tfrac{1}{2}\, T_K + \sum_{i=K+1}^{N+K-1} T_i + \tfrac{1}{2}\, T_{N+K}\right).$$

The analytical formula of Eq. (8) or (10) can now be represented in terms of the temperature observations

$$W = E\left[\frac{1}{K}\left(\sum_{i=N+\frac{1}{2}(K+1)}^{N+\frac{1}{2}(3K-1)} T_i - \sum_{i+\frac{1}{2}(K+1)}^{\frac{1}{2}(3K-1)} T_i\right) + \epsilon I - \epsilon\, N z\, T_\infty\right]. \tag{18}$$

There is a problem, as mentioned earlier, of possible errors from taking the time interval z too long or from taking the rating periods too long. The problem arises because the theoretical exponential curve has been approximated by a straight line to obtain the derivatives in Eqs. (14) and (15) and the average temperatures T_F and T_I in Eqs. (17) and (18). Neglecting the scatter in the data, we will consider just the error in these approximations.

The temperature in the initial rating period is given by Eq. (5). To remove any reference to a particular rating period or part of a rating period, we write the equation in the form

$$T - T_\infty = Ae^{-\epsilon t}, \tag{19}$$

where A is the value of $T - T_\infty$ at the time chosen for $t = 0$. A shift of the time scale (from initial to final rating period, for example) will merely require a change in the value of A and will not affect our argument on the relative magnitude of the errors. We first consider the error in the derivative in Eq. (11). For chosen value of K an approximate value of the derivative is computed by the left-hand side of Eq. (11).

$$\left.\frac{dT}{dt}\right)_{app} = \frac{T_{K+1} - T_0}{(K+1)\,z}$$

Substitution into this equation from Eq. (19) gives

$$\left.\frac{dT}{dt}\right)_{app} \quad \frac{A\,(e^{-\epsilon(K+1)\,z} - 1)}{(K+1)\,z}. \tag{20}$$

From Eq. (19) the actual derivative at the midpoint of this interval is

$$\frac{dT}{dt} = -\,A\epsilon e^{-\frac{1}{2}\epsilon(K+1)\,z}. \tag{21}$$

To evaluate the error, we expand the exponentials in a series and subtract Eq. (20) from Eq. (21) obtaining

$$\text{Error} = \epsilon A\left(\frac{\epsilon^2(K+1)^2\,z^2}{24} - \frac{\epsilon^3(K+1)^3\,z^3}{48} + \ldots\right).$$

Dividing by Eq. (21), we obtain the fractional error

$$\text{Fractional Error} = \frac{\frac{1}{24}\,\epsilon^2(K+1)^2\,z^2 - \frac{1}{48}\,\epsilon^3(K+1)^3\,z^3 + \ldots}{e^{-\epsilon(K+1)\,z/2}}.$$

Evidently the fractional error increases as larger values are chosen for K and z. Proper choice of K and z may make the error as small as required. As an example of a practical case, for K = 9, z = 5 sec., and the calorimeter cooling constant = .002 sec^{-1}, the fractional error in the derivative is only .0004, which is acceptable for most work.

The error in the derivatives causes an error in Eq. (16).

Usually the derivative in the initial rating period is small, so that the fractional error in the cooling constant is about the same as the fractional error in the derivative. The corresponding error in Eq. (18) can be calculated when the integral I and the temperature T_∞ are known.

The average temperatures also appear in Eq. (18) and these also have small errors introduced by the method of computation. In Eq. (17) we average K successive points. The temperature of the n^{th} point T_n is obtained according to Eq. (19):

$$T_n = T_\infty + A\, e^{-\epsilon n z} .$$

Numbering these points from 0 to K-1 and writing the exponential in series form we obtain the average temperature T_{av} in the following form

$$T_{av} = \frac{1}{K} \sum_{n=0}^{K-1} T_n = T_\infty + \frac{A}{K} \sum_{n=0}^{K-1} \left[1 - n\epsilon z + \frac{(n\epsilon z)^2}{2} - \ldots \right]. \tag{22}$$

The temperature T at the midpoint, when $t = \frac{1}{2} z(K-1)$, is also obtained from Eq. (19)

$$T = T_\infty + A\left[1 - \frac{(K-1)\,\epsilon z}{2} + \frac{(K-1)^2\, \epsilon^2\, z^2}{8} - \ldots \right]. \tag{23}$$

From Eqs. (22) and (23) we find the error

$$T - T_{av} = A\left[\frac{(K-1)^2\, \epsilon^2\, z^2}{8} - \frac{1}{2} \sum_{n=0}^{K-1} n^2\, \epsilon^2\, z^2 + \ldots \right]$$

or, after simplifying and using $\sum_{n=0}^{r} n^2 = r(r+1)\,(2r+1)/6$,

$$T - T_{av} = A \epsilon^2 z^2 \left[(K-1)^2/8 - (K-1)\,(2K-1)/12 + \ldots\right].$$

Eq. (18) requires the temperature difference $T_F - T_I$. The error in this difference is obtained from the preceding equation:

$$\text{Fractional Error} = \frac{(A_F - A_I)\,\epsilon^2 z^2 \left[(K-1)^2/8 - (K-1)\,(2K-1)/12 + \ldots\right]}{(A_F - A_I)\, e^{-\frac{1}{2}\epsilon z(K-1)}}.$$

For a practical case in which $K = 9$, $z = 5$ sec, and $\epsilon = .002\ \text{sec}^{-1}$, the fractional error is about 3×10^{-4}. The preceding discussion indicates that there is a compromise between taking a large number of points to avoid systematic errors in the computation. That the manual method can be quite adequate is shown by comparison with results of the least squares method described in the next section. For a calorimeter used at the National Bureau of Standards having a cooling constant of $.0024\ \text{sec}^{-1}$ and with $K = 9$, $z = 2$ sec, the manual method gives 4287 for the bracket in Eq. (18), compared to 4285 for the least squares method. Using twice as many points to obtain the average temperatures T_F and T_I, the manual method gives 4288. The precision of the calorimeter is a few tenths of a percent, so these results would probably be acceptable. The main disadvantage of the manual method, aside from the time involved in the computation, is that one must be continually on guard against these systematic errors. For similar repetitive measurements the systematic errors need be examined only once and the manual method should prove quite satisfactory.

3. DERIVATION OF THE LEAST SQUARES SOLUTIONS.

General discussions of the method of least squares for the treatment of experimental data can be found in many books on experimental physics or statistics. Natrella[12] deals carefully with the problem and gives many worked examples to illustrate the applications. This treatment is recommended reading for those who would develop their own methods of data analysis. Young[13] gives a readable introduction for those who would like a better understanding of the power and elegance of the method and the basis of the development which follows.

For isoperibol calorimetry, the relationships required by the least squares data analysis are derived from Eq. (5). Using subscripts I and F to designate temperatures and time in the initial or "fore" rating period and the final or "after" rating period, we have the two equations

$$
\begin{aligned}
T - T_\infty &= (T_I - T_\infty)\, e^{-\epsilon(t - t_I)} && \text{Initial} \\
T - T_\infty &= (T_F - T_\infty)\, e^{-\epsilon(t - t_F)} && \text{Final}
\end{aligned}
\qquad (24)
$$

These equations contain the quantities T_I, T_F, T_∞, and ϵ which are required in the calculation of Eq. (10). These are the quantities for which we want to make the best possible evaluation from the data available.

The actual data points will not lie exactly on the smooth curves of Eq. (24), so we define residuals $\underline{r}$ for each observation as the difference between the observed temperature at the time of the observation and the corresponding value calculated from Eqs. (24). In order to simplify the work, the substitutions $A = T_\infty - T_I$ and $B = T_\infty - T_F$ are made to give the following expressions for the residuals -- r_i for the i^{th} point in the fore period and r_j for the j^{th} point in the after period.

$$r_i = T_i - T_\infty + A\, e^{-\epsilon(t_i - t_I)} \qquad \text{Initial} \tag{25a}$$

$$r_j = T_j - T_\infty + B\, e^{-\epsilon(t_j - t_F)} \qquad \text{Final} \tag{25b}$$

Note that the difference $T_F - T_I$ required by Eq. (8) is equal to the difference A-B. The least squares calculation is set up to minimize the sum S of the squares of the residuals. If there are $\underline{\ell}$ time intervals in the initial rating period and $\underline{m}$ time intervals in the final rating period,

$$S = \sum_{i=0}^{\ell} r_i^2 + \sum_{j=0}^{m} r_j^2 . \tag{26}$$

Although the A and B contain T_∞, which is also to be determined from the data, it can be shown that substitution of these parameters does not alter the values obtained for T_I, T_F, ϵ, and T_∞ by the method of least squares. Ordinarily one should plan the experiment so that ℓ and m are approximately equal, say within a factor of two of one another. If ℓ is very different from m, the estimates of T_∞ and ϵ will depend primarily on the larger set of data, as is apparent from Eq. (13). In most of the work in this laboratory, the uncertainties in the temperature (in microvolts) and time (in seconds) are the same for both periods, so that we usually take $\ell = m$. However, the development which follows will allow for $\ell \neq m$, to allow for flexibility. (The computer program in the next section requires that both ℓ and m be even numbers.)

For the sum S to be a minimum the partial derivatives of S with respect to the four constants -- A, B, T_∞, and ϵ -- shall be zero. Substituting from (25) into (26), taking the derivatives and putting $Z_i = t_i - t_I$ and $Z_j = t_j - t_F$ we obtain the equations

$$\frac{\partial S}{\partial A} = 2 \sum_{i=0}^{\ell} e^{-\epsilon Z_i} (T_i - T_\infty + A e^{-\epsilon Z_i}) \tag{27a}$$

$$\frac{\partial S}{\partial B} = 2 \sum_{j=0}^{m} e^{-\epsilon Z_j} (T_j - T_\infty + B e^{-\epsilon Z_j}) \tag{27b}$$

$$\frac{\partial S}{\partial T_\infty} = -2 \left[\sum_{i=0}^{\ell} (T_i - T_\infty + A e^{-\epsilon Z_i}) + \sum_{j=0}^{m} (T_j - T_\infty + B e^{-\epsilon Z_j}) \right] \tag{27c}$$

$$\frac{\partial S}{\partial \epsilon} = -2 \left[\sum_{i=0}^{\ell} A Z_i e^{-\epsilon Z_i} (T_i - T_\infty + A e^{-\epsilon Z_i}) + \sum_{j=0}^{m} B Z_j e^{-\epsilon Z_j} (T_j - T_\infty + B e^{-\epsilon Z_j}) \right] \tag{27d}$$

The least squares problem is now reduced to finding values of A, B, T_∞, and ϵ which make all four partial derivatives simultaneously equal to zero. This task is complicated by the appearance of ϵ in the argument of an exponential, but the solution can be found by successive approximations. We will now develop the equations needed for this procedure. To reduce the number of symbols which must be written in the subsequent development, we define the following symbols in terms of the observed quantities.

$$s_1 = \sum_{0}^{\ell} e^{-\epsilon Z_i} \qquad s_2 = \sum_{0}^{m} e^{-\epsilon Z_j}$$

$$s_3 = \sum_{0}^{\ell} T_i e^{-\epsilon Z_i} \qquad s_4 = \sum_{0}^{m} T_j e^{-\epsilon Z_j}$$

$$s_5 = \sum_{0}^{\ell} (e^{-\epsilon Z_i})^2 \qquad s_6 = \sum_{0}^{m} (e^{-\epsilon Z_j})^2$$

$$s_7 = \sum_0^{\ell} T_i \qquad s_8 = \sum_0^{m} T_j$$

$$s_9 = \sum_0^{\ell} T_i\, Z_i\, e^{-\epsilon Z_i} \qquad s_{10} = \sum_0^{m} T_j\, Z_j\, e^{-\epsilon Z_j}$$

$$s_{11} = \sum_0^{\ell} Z_i\, e^{-\epsilon Z_i} \qquad s_{12} = \sum_0^{m} Z_j\, e^{-\epsilon Z_j}$$

$$s_{13} = \sum_0^{\ell} Z_i\, (e^{-\epsilon Z_i})^2 \qquad s_{14} = \sum_0^{m} Z_j\, (e^{-\epsilon Z_j})^2$$

Setting Eqs. (27) equal to zero, which is the condition for a minimum value of S, substituting the above definitions, and rearranging, we obtain the following four equations:

$$A = \frac{s_1\, T_\infty - s_3}{s_5} \tag{28a}$$

$$B = \frac{s_2\, T_\infty - s_4}{s_6} \tag{28b}$$

$$T_\infty = \frac{s_7 + s_8 - s_1\, s_3/s_5 - s_2\, s_4/s_6}{\ell + m + 2 - s_1^2/s_5 - s_2^2/s_6} \tag{28c}$$

$$A\, s_9 - A\, T_\infty\, s_{11} + A^2\, s_{13} + B\, s_{10} - B\, T_\infty\, s_{12} + B^2\, s_{14} = 0 \tag{28d}$$

These equations can be solved for A, B, T_∞, and ϵ. The procedure used is to make a first estimate of ϵ by the method outlined in the preceding section and to use this value to estimate T_∞ in Eq. (28c). Both quantities are then used in Eqs. (28a) and (28b) to estimate A and B. Newton's method (discussed in books on calculus) is then used to estimate a new value for ϵ from Eq. (28d), based on the values just obtained for T_∞, A and B. If we call the left-hand side of Eq. (28d) $F(\epsilon)$, an $(i+1)^{th}$ estimate of ϵ is obtained from the relationship

$$\epsilon_{i+1} = \epsilon_i + \frac{\epsilon_i - \epsilon_{i-1}}{F_i - F_{i-1}} F_i,$$

where the derivative is approximated by $\Delta\epsilon/\Delta F$. The value of ϵ_0 is arbitrarily taken to be 1.001 ϵ_1 and is used to calculate F_0. After the new value of ϵ is obtained, new values of T_∞, A and B are estimated and the procedure is repeated until successive estimates of ϵ differ by a negligible amount.

4. THE COMPUTER PROGRAM

The computer program which carries out the isoperibol calculation is written in a version of BASIC language for use on a time-sharing, remote access computer. This version of BASIC does not require the use of LET in a replacement statement (e.g., line 145). The lines and their functions are as follows:

```
80 DATA 2,1,40,40,15
90 READ Z,N2,L,M,N5
```

The data supplied in 80 and identified with variables in 90 are: Z = constant length of time interval (normally seconds, but may be arbitrary if constant); N2 = the number of successive blocks of data to be used from the after period to give N2 separate solutions; L = number of equal time intervals in the fore period; M = number of time intervals in the after period; N5 = the number of points beyond the maximum temperature where the final rating period is to be started. The number N2 will ordinarily be one. Putting N2 = 2 will cause the problem to be done twice and will require new values of L, M, and N5, which will be read in line 715. This procedure checks whether different combinations of ΔU and Q give the same answer.

```
100 OPEN /C/,INPUT
```

Instructs the computer to open the data file /C/ in which the temperature data have been stored. The data must be in the order in which they were taken. The temperature may be in any scale or on an arbitrary X scale (See Eq. (9)). The last entry in the data file is a fake 100, 000 used for identification. For this program, the data must be taken at equal time intervals and no temperature observation may be omitted from the file /C/.

```
110 DIM T(200),I(200),S(14)
```

A dimension statement reserving storage for 200 temperatures, 200 integrals, and 14 summations.

```
120 FOR I=0 TO 200
130 INPUT FILE T
140 IF T=100000 THEN 170
145 N1=I
150 T(I)=T
160 NEXT I
```

Reads the data into storage and assigns each temperature a subscript. Line 140 ends the read-in when it sees the false 100, 000. Line 145 counts the number of data points and line 175 prints the total.

```
170 I(0)=0
175 PRINT"TOTAL POINTS = "N1 + 1
180 FOR I=1 TO N1
190 I(I)=I(I-1)+Z*T(I-1)/2+Z*T(I)/2
200 NEXT I
```

Sets the integral to zero and computes by the trapezoidal approximation and stores the integral from the first point to each point used in the calculation.

```
210 T9=T(0)
220 FOR I=L TO N1
230 IF T(I)<T9 THEN 250
240 T9=T(I)
245 N9=I
250 NEXT I
252 PRINT "MAX TEMP IS T ("N9")"
253 PRINT
254 PRINT"TIME  CORR RISE  COOLG CONST  CONV TEMP  INIT T   FINAL T"
255 N=N9+N5
```

Selects the maximum temperature by a series of comparisons, assigns it the number N9, and prints it out. In 255 the point N, which is the beginning of the final rating period, is taken N5 points beyond the maximum. This number will depend on the particular calorimeter. If point N consistently shows a large deviation from the smooth curve (deviations are calculated beginning with Line 660) the after period should be started farther beyond the maximum. The maximum temperature is stored in 240 and printed out in 252.

```
256 T1=0
257 T2=0
258 T3=0
259 T4=0
260 FOR I=0 TO (L/2-1)
262 T1=T1+4*[T(L-I)-T(I)]/(L↑2+2*L)/Z
```

```
264 NEXT I
266 FOR I=0 TO L
268 T2=T2+T(I)/(L+1)
270 NEXT I
272 FOR I=0 TO (M/2-1)
274 T3=T3+4*[T(N+M-I)-T(N+I)]/(M↑2+2*M)/Z
276 NEXT I
278 FOR I=0 TO M
280 T4=T4+T(N+I)/(M+1)
282 NEXT I
300 E(1)=(T1-T3)/(T4-T2)
```

Following the procedure very similar to that outlined in Section 2, these lines make a first estimate of ϵ from the data, using Eq. (3). The average derivative is T1 in the initial rating period and T3 in the final rating period. The average temperature is T2 in the initial rating period and T4 in the final rating period.

```
310 E(0)=1.001*E(1)
```

Computes a fake cooling constant for later use in Newton's method of approximation.

```
315 N4=0
```

Sets the index N4 to zero. N4 counts the number of complete least squares solutions using different blocks of data.

```
320 FOR I=0 TO 9
```

Starts the successive approximations and limits the number of passes to ten. The computation for I = 0 is not based on the data, but it provides values for the next approximation.

```
330 FOR J=1 TO 14
340 S(J)=0
350 NEXT J
```

Sets all sums to zero. The subscripts correspond to those in Eqs. (28).

```
360 FOR J=0 TO L
370 X=EXP(-Z*E(I)*J)
380 S(1)=S(1)+X
390 S(3)=S(3)+T(J)*X
400 S(5)=S(5)+X↑2
410 S(7)=S(7)+T(J)
420 S(9)=S(9)+Z*J*T(J)*X
430 S(11)=S(11)+Z*J*X
440 S(13)=S(13)+Z*J*X↑2
442 NEXT J
```

These lines compute the summations for the value of E(I). These summations are based on the data in the initial rating period.

```
444 FOR J=0 TO M
446 X=EXP[-Z*E(I)*J]
448 S(2)=S(2)+X
450 S(4)=S(4)+T(N+J)*X
455 S(6)=S(6)+X↑2
460 S(8)=S(8)+T(N+J)
470 S(10)=S(10)+Z*J*T(N+J)*X
474 S(12)=S(12)+Z*J*X
476 S(14)=S(14)+Z*J*X↑2
480 NEXT J
```

These lines compute the corresponding summations from the data in the final rating period.

```
490 T8=S(7)+S(8)-S(3)*S(1)/S(5)-S(4)*S(2)/S(6)
495 T7=L+M+2-S(1)↑2/S(5)-S(2)↑2/S(6)
500 T8=T8/T7
```

The value of T_∞ is computed according to Eq. (28c).

```
510 A=[T8*S(1)-S(3)]/S(5)
520 B=[T8*S(2)-S(4)]/S(6)
```

The values of A and B are computed according to Eqs. (28a) and (28b).

```
530 F(I)=A*S(9)+B*S(10)-A*T8*S(11)-B*T8*S(12)+A↑2*S(13)+B↑2*S(14)
```

This line computes the value of the left-hand side of Eq. (28d), which we seek to make zero. The quantity F is given a subscript because two successive approximations are used in Line 580.

```
550 IF I<1 THEN 590
560 IF F(I)=F(I-1) THEN 800
570 IF I=9 THEN 592
580 E(I+1)=E(I)-[E(I-1)-E(I)]*F(I)/[F(I-1)-F(I)]
582 IF ABS[E(I+1)-E(I)]<1E-7 THEN 740
590 NEXT I
592 PRINT "RAN TEN TIMES"
```

These lines compute the next approximation to the cooling constant E(I + 1). Line 550 avoids the computation for I = 0 because it cannot be computed until two successive values of E and F are available. Line 560 prevents the possibility of division by zero in 580. Line 570 stops the number of approximations at nine, but completes the calculation using E(9). Line 580 computes the next approximation E(I + 1) by Newton's method, using the chord $\Delta E/\Delta F$ to approximate the derivative. Line 582 terminates the approximations provided that 3 successive values differ by less than 10^{-7}. This criterion may have to be altered to suit a particular calorimeter or time scale. It is selected for a typical cooling constant of .002 $\sec^{-1}$; it would probably not be suitable for very much smaller cooling constants. Line 592 provides printout to indicate a possible fault.

```
605 T5=A-B+E(I)*[I(N)-T8*Z*N]
610 PRINT Z*N;T5;1E-6*INT(1E6*E(I));1E-3*INT(1E3*T8);T8-A;T8-B
```

Line 605 calculates the corrected temperature rise, which is the quantity in brackets in Eq. (8).

```
664 U=0
668 FOR J=0 TO L
670 C=T8-A*EXP[-E(I)*Z*J]
674 U=U+[C-T(J)]↑2
678 PRINT T(J);C;1E-4*INT((T(J)-C)*1E4)
680 NEXT J
684 FOR J=N TO N+M
686 Z1=Z*(J-N)
688 C=T8-B*EXP[-E(I)*Z1]
690 U=U+[C-T(J)]↑2
694 PRINT T(J);C;1E-4*INT((T(J)-C)*1E4)
696 NEXT J
698 PRINT "RESIDUAL STD DEV= "SQR(U/(L+M-2))
```

These lines compute the smooth exponential curves for the initial and final rating periods and the deviations of the experimental points from these curves. The number of points L + M + 2 is decreased by four in 698 because four constants have been determined from the data.

```
700 IF N4=N2-1 THEN 730
710 N4=N4+1
715 READ L,M,N5
720 GO TO 320
730 STOP
```

Line 700 determines whether another calculation has been asked for. If so, line 710 increases the index N4 and line 715 reads the parameters which determine the data to be used in the next computation.

```
740 IF ABS[E(I)-E(I-1)]<1E-7 THEN 605
750 GO TO 590
```

These lines complete the criterion for terminating the successive approximations.

```
800 PRINT "F(I)=F(I-1)";"F(I)= "F(I)
810 GO TO 605
```

Line 800 serves as an alert to a possible fault.

5. SAMPLE CALCULATIONS WITH THE COMPUTER PROGRAM.

As an illustration of its operation and the interpretation of results, two computations have been made on the data in Table I, which are from a typical experiment with a small calorimeter -- one of a group designated the C-series and having energy equivalents corresponding to 1 or 2 joules per kelvin and cooling constants between .002 and .003 sec^{-1}.

The print-out for the first computation is shown in Table II. This computation took the first 40 points for the initial rating period and 40 points for the final rating period starting 15 points past the maximum temperature. The first two lines of the print-out give information to judge whether the data are sufficient. In this case, the computation used 55 points beyond the maximum, which occurred at the 49^{th} point. There were thus 104 points used, comfortably less than the total of 119 available.

The next line shows the length of time between the initial and final temperatures, the corrected rise, which is the desired quantity in the bracket in Eq. (8), the cooling constant ϵ, the convergence temperature T_∞, and the initial and final temperatures. Note that T_∞ is well below any observed temperature, which is consistent with the decrease in temperature during the initial rating period.

The balance of the print-out consists of a column of the input data, a column of the calculated temperatures for the times corresponding to the input data, and a column of the differences. The differences indicate how well the computation fits the data for the rating periods. It is extremely useful in discovering points which have been entered incorrectly, or an improper fit of the data. The last entry is the standard deviation of the observations from the smooth curves. Points with deviations three or more times this quantity should be checked.

A long run of deviations of the same sign indicates a poor fit of the data. An example is given in Table III, which shows the deviations for the same set of data, but with the final rating period starting only one point past the maximum. Note the long series of points which lie above the smooth curves and followed by the long series of points which lie below the smooth curves. The standard deviation also indicates a poor fit, but it is a less sensitive indicator.

Table I

Data for an Experiment with an Isoperibol Calorimeter.

-Ø263	-Ø263	-Ø264	-Ø265	-Ø265	-Ø266	-Ø267	-Ø267	-Ø268	-Ø268
-Ø269	-Ø270	-Ø270	-Ø271	-Ø271	-Ø272	-Ø273	-Ø273	-Ø274	-Ø275
-Ø275	-Ø276	-Ø276	-Ø277	-Ø277	-Ø278	-Ø278	-Ø279	-Ø280	-Ø280
-Ø281	-Ø281	-Ø282	-Ø282	-Ø283	-Ø283	-Ø284	-Ø284	-Ø285	-Ø286
-Ø286	-Ø220	+Ø486	+1391	+2342	+33Ø4	+3738	+383Ø	+3852	+3852
+3844	+3832	+3817	+38Ø1	+3783	+3764	+3745	+3726	+37Ø7	+3688
+3668	+3649	+363Ø	+3611	+3591	+3572	+3553	+3535	+3516	+3497
+3479	+346Ø	+3442	+3424	+34Ø6	+3387	+3369	+3351	+3334	+3316
+3299	+3281	+3264	+3246	+3229	+3212	+3195	+3178	+3161	+3144
+3127	+3111	+3Ø94	+3Ø78	+3Ø61	+3Ø45	+3Ø28	+3Ø12	+2996	+298Ø
+2964	+2948	+2932	+2917	+29Ø1	+2885	+287Ø	+2854	+2839	+2824
+28Ø9	+2793	+2778	+2763	+2749	+2734	+2719	+27Ø4	+269Ø	+2675
1ØØØØØ									

Table II

Print-out from Data Analysis Program

TOTAL POINTS = 119
MAX TEMP AT PT NO 49

TIME	CORR RISE	COOLG CONST	CONV TEMP	INIT T	FINAL T
128	4285.322	.2374E-02	-397.253	-262.815	3590.653

-263	-262.815	-.185	3591	3590.653	.3465
-263	-263.4521	.4521	3572	3571.757	.2425
-264	-264.086	.086	3553	3552.95	.49E-01
-265	-264.7171	-.283	3535	3534.233	.7664
-265	-265.345	.345	3516	3515.604	.3951
-266	-265.9701	-.3E-01	3497	3497.064	-.0644
-267	-266.5921	-.4079	3479	3478.611	.3881
-267	-267.2113	.2112	3460	3460.247	-.2467
-268	-267.8274	-.1726	3442	3441.968	.314E-01
-268	-268.4407	.4407	3424	3423.777	.223
-269	-269.0511	.51E-01	3406	3405.672	.3283
-270	-269.6585	-.3415	3387	3387.652	-.6522
-270	-270.2631	.263	3369	3369.718	-.718
-271	-270.8648	-.1352	3351	3351.869	-.8688
-271	-271.4636	.4636	3334	3334.104	-.1042
-272	-272.0597	.597E-01	3316	3316.424	-.4238
-273	-272.6529	-.3471	3299	3298.827	.1728
-273	-273.2433	.2433	3281	3281.313	-.3139
-274	-273.8309	-.1691	3264	3263.884	.1164
-275	-274.4157	-.5843	3246	3246.536	-.5359
-275	-274.9978	-.23E-02	3229	3229.27	-.2704
-276	-275.577	-.423	3212	3212.087	-.0867
-276	-276.1535	.1535	3195	3194.984	.156E-01
-277	-276.7274	-.2727	3178	3177.963	.368E-01
-277	-277.2985	.2984	3161	3161.023	-.226E-01
-278	-277.8669	-.1332	3144	3144.162	-.1623
-278	-278.4325	.4325	3127	3127.382	-.3819
-279	-278.9955	-.45E-02	3111	3110.681	.319
-280	-279.5558	-.4442	3094	3094.059	-.592E-01
-280	-280.1136	.1135	3078	3077.516	.4838
-281	-280.6686	-.3314	3061	3061.051	-.516E-01
-281	-281.221	.221	3045	3044.664	.335
-282	-281.7708	-.2292	3028	3028.356	-.356
-282	-282.318	.318	3012	3012.124	-.1243
-283	-282.8626	-.1374	2996	2995.969	.305E-01
-283	-283.4046	.4046	2980	2979.891	.1087
-284	-283.944	-.56E-01	2964	2963.889	.1107
-284	-284.4809	.4809	2948	2947.963	.37E-01
-285	-285.0153	.153E-01	2932	2932.112	-.1123
-286	-285.5471	-.4529	2917	2916.337	.6634
-286	-286.0764	.0764	2901	2900.636	.3643

RESIDUAL STD DEV= .3331032

Table III

Print-out for Rating Period Started Too Soon.

3844	3860.785	-16.7851
3832	3840.762	-8.7619
3817	3820.833	-3.8328
3801	3800.997	.26E-02
3783	3781.255	1.7448
3764	3761.606	2.3942
3745	3742.049	2.9512
3726	3722.583	3.4163
3707	3703.21	3.7899
3688	3683.927	4.0725
3668	3664.735	3.2644
3649	3645.634	3.3662
3630	3626.621	3.3781
3611	3607.699	3.3007
3591	3588.865	2.1343
3572	3570.12	1.8795
3553	3551.463	1.5365
3535	3532.894	2.1058
3516	3514.412	1.5879
3497	3496.017	.9831
3479	3477.708	1.2918
3460	3459.485	.5145
3442	3441.348	.6515
3424	3423.297	.7033
3406	3405.33	.6702
3387	3387.447	-.4473
3369	3369.649	-.6489
3351	3351.934	-.9341
3334	3334.303	-.3026
3316	3316.753	-.754
3299	3299.288	-.2878
3281	3281.903	-.9038
3264	3264.601	-.6014
3246	3247.38	-1.3804
3229	3230.24	-1.2403
3212	3213.18	-1.1808
3195	3196.201	-1.2014
3178	3179.301	-1.3019
3161	3162.481	-1.4818
3144	3145.741	-1.7407
3127	3129.078	-2.0784

RESIDUAL STD DEV= 2.591687

REFERENCES

1. D. A. Jennings, IEEE Transactions on Instr. and Meas. IM 15, 161 (1966).
2. D. A. Jennings, E. D. West, K. M. Evenson, A. L. Rasmussen, and W. R. Simmons, NBS Technical Note 382 (1969).
3. J. Coops, R. S. Jessup, and K. Van Nes in Reference 9.
4. J. M. Sturtevant in Technique of Organic Chemistry, A. Weissberger, ed., Interscience Publishers, Inc., New York (1959).
5. W. P. White, The Modern Calorimeter, Chemical Catalog Co., New York (1928).
6. W. A. Roth and F. Becker, Kalorimetrische Methoden zur Bestimmung Chemischer Reaktionswarmen, F. Vieweg and Son, Braunschweig, Germany (1956).
7. E. D. West and K. L. Churney, J. Appl. Physics 39, 4206 (1968).
8. E. D. West and K. L. Churney, J. Appl. Phys. 41, 2705 (1970.
9. Experimental Thermochemistry, F. D. Rossini, ed., Interscience Publishers, Inc., New York (1956).
10. Experimental Thermochemistry, Vol. II, H. A. Skinner, ed., Interscience Publishers, Inc., New York (1962).
11. Experimental Thermodynamics, Vol. I, J. P. McCullough and D. W. Scott, ed., Plenum Press, New York (1967).
12. M. G. Natrella, Experimental Statistics, Nat'l. Bur. Stds. Handbook 91, U. S. Gov't. Printing Office, Washington, D. C. (1963).
13. H. D. Young, Statistical Treatment of Experimental Data, McGraw-Hill Book Co., New York (1962).

GPO 833-296

U.S. DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20230

OFFICIAL BUSINESS

PENALTY FOR PRIVATE USE, $300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE