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FOR
GENERAL RESEARCH
APRIL 16, 1951 TO JULY 30, 1951
(SUPPORTING RESEARCH VOLUME)

Date: September 30, 1951

Approved By:

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SUMMARY

This volume presents the quarterly results of that portion of the research and development endeavor which was directed toward establishing new techniques or instruments and toward improving present methods for determining accurately and safely levels of radioactivity encountered in the course of other phases of work.

No appreciable difference has been found between beta rays and photon-induced secondary electrons by differential counting using a Nuclear Measurements Corporation PC 2 counter with either pure methane or a 90 per cent argon 10 per cent methane mixture as the counter gas. Because of differences in specific activity, particle energy, solid content or backing material, individual samples submitted for routine counting have been found which had counting voltage plateaus which differed from the voltage plateau normally established by counting a RaD E F equilibrium standard (p. 7).

An investigation was initiated to study methods of preparing thin, plastic films for use as absorbers in the study of low energy alpha and beta particles. Films one inch in diameter and having weights in the order of 25 micrograms per square centimeter have been made by placing a drop of an ethylene dichloride solution of Formvar E on the surface of cold water, allowing the solvent to evaporate and then removing the film by raising a wire ring under it (p. 8).

Experimental equipment has been designed for continuous monitoring of emanation contaminated air by observing the scintillations of a phosphor as the contaminated air is drawn past the phosphor. A second method being considered involves adsorption of the emanation on dust particles, filtering out the dust, and then using a scintillation counter to detect the presence of alpha activity on the filter paper (p. 9).

Design has been essentially completed for a parallel plate ionization chamber having plates 4 25 inches in diameter which can be used for evaluating alpha standards (p. 10).

The modern theory of noise has been investigated with the goal of developing methods for treating data which involve noise effects, evaluating methods of noise reduction, and accurate noise level evaluation. With this theory of noise, an equation was developed which expresses the response of a calorimeter to internal and external thermal noises as a function of the damping constant of the calorimeter and the area under the autocorrelation curve of the noise to which the calorimeter is subjected. It appears that the factors which determine the lower limit of detectability of our calorimeters are gross changes in the environment and stirring noise (p. 25).

The noise level of the instrument pier in Room 112^{Mount Laboratory} was investigated and found to be sufficiently low to justify mounting a Coblentz moving magnet galvanometer on it. Studies with a seismic detector on a two micron quartz-fiber suspension indicate that a suspension of this delicacy would be too sensitive in the presence of the existing pier noise (p. 11).

It has been shown that under certain conditions the solution of second order differential equations with given boundary conditions represents very closely the experimental cooling curves of calorimeters loaded with additional heat capacity. These theoretical considerations give added confidence to heat capacities measured by determining the area under a cooling curve. They also make possible calculation of certain properties of a calorimeter from the constants of the materials and the physical dimensions before it is constructed. A method for measuring the heat conductivities of poor thermal conductors has been suggested (p. 42).

Problem Title **Problems in Beta Counting**
Report By **M L Curtis**
Work Done By **M L Curtis**

INTRODUCTION

Two general problems in beta counting in a Nuclear Measurements Corporation PC-2 counter were considered this quarter

- 1 The problem of distinguishing betas from secondary electrons due to photons
- 2 The problem of adapting one procedure to a wide variety of samples

DETAILED REPORT

It has been suggested that one method of distinguishing beta particles from secondary electrons was to count the samples in question in both P 10 gas (90 per cent argon, 10 per cent methane) and methane. The methane is theoretically less efficient for counting gamma or X-rays than argon.

It was necessary to use a one half mil center wire when the counter gas was methane, since the voltage required with methane with the usual one mil center wire was too high to be practical. The alpha plus beta voltage plateaus obtained were surprisingly long and flat compared to those obtained with P 10 gas, but no appreciable difference in the beta count with the two gases was found on the samples tested. Other samples will be tried and helium isobutane will also be tried as the counter gas. It should be less efficient for gammas than methane.

The samples submitted for routine counting at Mound vary greatly in specific activity, energy, solid content, and backing material. Many samples are unknown mixtures of several materials. There is evidence that some of these factors affect the voltage plateau on the Nuclear Measurements Corporation PC-2 counters, so that the plateau changes with the sample. This is a serious matter, since in routine counting, the voltage plateau must be checked with a standard (usually a RaD E F equilibrium standard) and all samples counted at the same voltage. If the voltage plateau changes with the sample, the difficulty is obvious. Of 24 samples selected at random, 9 gave voltage plateaus which differed from those obtained with the standard. The answer at present seems to be to check the plateau with the sample to be counted if the results are in question. Meanwhile, a research group is working to improve the plateau characteristics of the circuits.

Problem Title **Very Thin Plastic Film Absorbers**

Report By **J S Stanton**

Work Done By **J S Stanton**

INTRODUCTION

The research counting group needs a series of absorbers for the continuation of its studies of low-energy alpha and beta particles. The thinnest absorbers presently used are made from electroscope foil but at best are too thick for low energy particles. Very thin films of plastic materials can be made but only in a relatively small size. The problem is to make the films as thin as possible for the area required.

DETAILED REPORT

The minimum weight of the foil absorbers presently used is of the order of 150 micrograms per square centimeter so the plastic film absorbers should range from this weight to the lowest possible value. Formvar E dissolved in ethylene dichloride was chosen as the plastic material for its toughness and strength.

The films are formed by placing a drop of solution on the surface of cold tap water, where it immediately spreads out and the solvent evaporates.¹ A water temperature of 10 to 15°C is required to retard evaporation and give thinner, more uniform films.

The films are picked up from below by means of a wire loop two and one half inches in diameter. The wire loop is secured to the barrel of an inexpensive microscope modified so that the loop can be raised and lowered and rotated in both vertical and horizontal planes. The films are gradually raised from the surface by combining a tilting movement with the upward movement of the loop. After drying the film is transferred to a previously weighed aluminum ring for weighing on a microbalance.

The limiting factor in the weight or thinness of the film is the surface and interfacial forces between the film and the water and many attempts have been made to reduce these forces. The first method was the addition of a wetting agent to the water. Santomerse Joy and Triton NE were tried and resulted in some improvement with perhaps the latter being the best. The thinnest films made so far by this method have weighed approximately 75 micrograms per square centimeter. Films having weights in the range of 25 micrograms per square centimeter have been made but at diameters of one inch. For diameters greater than this the interfacial forces are greater than the tensile strength of the film.

The surface tension of water is a linear function of temperature and as a next approach the water was heated by small immersion heaters after the film was formed. However, at a temperature of 30 to 35°C the film began to noticeably lose its strength. The 20° increase in temperature gave insufficient decrease in surface tension to be of value.

The method now being tried consists of applying a thin film of low-viscosity spindle oil between the plastic film and the water to reduce the effects of interfacial forces. Difficulty is being experienced in getting the oil to penetrate under the film; it tends to work out and over.

REFERENCE

- 1 Fry, L. M. and Overman, R. T., "The Preparation of Very Thin Plastic Films," Clinton National Laboratory, U.S. Atomic Energy Commission, AECD-1800.

Problem Title **The Development of a Method for the Continuous Monitoring of Emanation Contaminated Air**

Report By **W L Hood**

Work Done By **T L Zinn**

INTRODUCTION

The presence of emanation contaminated air in the exhaust systems or the working areas of laboratories requires continuous monitoring to insure that the contamination level remains within the accepted health tolerance limits. The monitoring problem is complicated by the fact that the monitor does not immediately respond to changes in contamination level since some time must elapse before equilibrium is reached among the various decay products whose presence is detected by the monitor. In order for the monitoring system to respond quickly to changes in contamination level the air must be sampled at frequent intervals. On the other hand if the monitor is to be reliable it must respond to the average contamination level over a sufficiently long time interval to minimize statistical fluctuations in counting rate. These two conflicting requirements can be met by a system which makes use of overlapping sampling time intervals.

DETAILED REPORT

The problem of continuously monitoring air for emanation contamination is being approached in two ways.

1 The use of an alpha scintillation counter and rate meter with the output of the rate meter applied to a mechanical integrator which provides overlapping sampling time intervals. This mechanical integrator is described in MLM 561¹. The scintillation counter employs a zinc sulfide coated sphere. Contaminated air is passed continuously over the surface of the sphere. Lightscintillations produced by alpha particles which reach the phosphor-coated surface from the space near the sphere are detected by a type 5819 photomultiplier tube whose photo-cathode is optically coupled to the sphere.

2 The use of an alpha scintillation counter to count the alpha activity deposited on filter paper. The count is then transferred to a mechanical integrator of the type described in 1 above.

To insure maximum collection of emanation the air to be filtered will be mixed with dust of controlled particle size and concentration. It is hoped that the emanation will be absorbed by the dust particles which can then be concentrated on the filter paper and counted by an alpha scintillation counter.

Experimental equipment of the above types has been designed. When completed, it will be tested to determine whether either of these monitoring methods is satisfactory. The better method will then probably be incorporated in the design of an instrument for monitoring emanation levels.

REFERENCE

- 1 Rogers A J Rpt Gen Res MLM 561 p 32 May 21 1951.

Problem Title **A Large Area Parallel-Plate Ionization Chamber for the Evaluation of Alpha Standards**

Report By **E V Zaucha**

Work Done By **E V Zaucha**

INTRODUCTION

The development of a large area gas flow parallel plate ionization chamber was undertaken to provide a suitable means for evaluating alpha standards. This ionization chamber will be capable of pulse height analysis and the counting of samples with mountings up to four inches in diameter.

DETAILED REPORT

The ionization chamber will have circular parallel-plate electrodes 4.25 inches in diameter spaced 1.25 inches apart. The chamber will be gas tight so that it may be operated at small positive or negative pressures. The counting gas may be argon or nitrogen.

The resolving time of the chamber has been calculated to be approximately 5 microseconds. This should make it possible to utilize a pulse amplifier pass band lying above the audio spectrum, resulting in an ionization chamber having low microphonic response.

The lower electrode is retractable by means of a rack and pinion into a slide assembly so that samples may be admitted to the chamber for counting.

The design of the ionization chamber is essentially complete.

Problem Title **Determination of the Operating Characteristics of the 6BN6 Gated Beam Tube**
Report By **W L Hood**
Work Done By **J A Williamson and W L Hood**

INTRODUCTION

There is an urgent need in high resolution pulse counting circuits for devices that will perform the functions of pulse limiter pulse shaper multivibrator and coincidence or anticoincidence gates with a high degree of stability and without adverse effect on the frequency response and resolving time of the associated circuits. The type 6BN6 gated beam tube has design characteristics which should make it suitable for many of these applications. Its operating characteristics under pulsed operation are therefore being investigated.

DETAILED REPORT

The 6BN6 has the following operating characteristics under pulsed operation:

- 1 Pulse limiting characteristics are excellent for positive pulses injected at either the limiter or quadrature grid with pulse limiting occurring at the plate. Minimum pulse amplitude for limiting is 1.5 volts peak at the limiter grid and 4 volts peak at the quadrature grid.
- 2 The 6BN6 may be used for coincidence or anticoincidence counting or pulse height selection by the use of fixed bleeder bias at the cathode and/or grids to provide gating selection or rejection of input pulses.
- 3 The pulse limiting or pulse selection sensitivity of the 6BN6 may be held to close limits by the use of transformer coupling at the pulse input grid. The use of resistance capacitance grid coupling causes the sensitivity to vary with signal level.
- 4 The 6BN6 may be operated as a triggered pulse generator (one shot multivibrator) by capacitive coupling the quadrature grid to the unbypassed accelerator and biasing the grids to prevent oscillation.
- 5 The high frequency characteristics of the 6BN6 are limited in broad band amplifier application because of the low grid plate transconductance of the tube.

Problem Title - A Study of Instrument Pier Noise

Report By - T J Beasley

Work Done By - J R Parks and T. J Beasley

INTRODUCTION

Part of the calorimetry research program has been directed toward the improvement of calorimeter sensitivity. This work has resulted in equipment capable of measuring progressively smaller units of power output. As one would expect, increases in sensitivity have been accompanied by greater manifestations of troublesome second-order effects. In particular, it has been necessary to study the problem of minimizing the effects of the random thermal, electrical, and mechanical disturbances acting upon every calorimetric system. These disturbances are hereinafter referred to as "noise" because of their statistical character.

It has become apparent that further significant attenuation of noise effects resulting from bath-temperature fluctuations, instrument-pier tremors, etc., will require the use of the mathematical tools of modern noise theory.

A recent report by J. R. Parks¹ describes experimental work undertaken to determine the suitability of the instrument pier in Room 112 of the Research Building for use as a platform for a Coblentz moving-magnet galvanometer. The analysis is important because of the extreme sensitivity of a Coblentz galvanometer as compared to the "high sensitivity" galvanometers now used in our Laboratory, i.e., 0.008 microvolt per millimeter at 1 meter for the Coblentz galvanometer and 0.5 microvolt per millimeter at 1 meter for the latter.

The seismic detector was fitted with a 5-micron quartz fiber in order to simulate the Coblentz galvanometer. Experiments with the seismic detector on the pier in Room 112 indicated that the pier is a suitable platform for a Coblentz galvanometer.

Inasmuch as Mound Laboratory was equipped to make 2-micron quartz-fiber suspensions, we were afforded the opportunity of having a Coblentz galvanometer modified by substituting such a suspension and thus increasing its sensitivity. Before recommending this modification, however, it was important to know the pier noise response of a 2-micron quartz-fiber mirror suspension. To this end, the seismic detector was equipped with a 2-micron quartz-fiber suspension for further experiments on the pier.

The 2-micron quartz-fiber suspension was observed to be quite responsive to the low-power noise levels of the pier. This fact indicated qualitatively that the pier probably would not be satisfactory as a platform for a galvanometer with a 2-micron quartz-fiber suspension. Nevertheless, there remained the possibility that the pier noise could be sufficiently isolated from the seismic detector by utilizing an anti-vibration mount of suitable design. "Suitable design" of an anti-vibration mount calls for an analytic knowledge of the noise characteristics.

A decision was made to undertake an analytic investigation of pier noise not only on the basis of the immediate problem but also because such an investigation promised to provide experience and insight which would be useful when the temperature fluctuations of a calorimeter bath are studied.

In addition, the future use of this method at Mound Laboratory could lead to equipment economies. When new sensitive-instrument installations are contemplated it will be possible to assess quantitatively the need for anti-vibration mounts or suspensions, and if such mounts are required, optimum types can be chosen. The ability to determine in advance the optimum suspension parameters involves an aspect of the over-all theory known as filter theory. In this regard it is appropriate to remark that the language of noise theory stems from the terminology of electronics. With this history in mind, the connotations of the term "filter" become evident, and an anti-vibration mount or suspension may be called a mechanical filter.

By direct experimentation, a "stationary time series" was obtained. From this series alone, an "autocorrelation function" was derived and plotted. Considerable information became available at this point, although more work remains to be done in the future. The next step will be to develop a Fourier-integral expression for the autocorrelation function. Finally, the inverse Fourier integral will be derived. This is the "power-density spectrum" of the noise.

In the detailed report, definitions are given for "stationary time series", "autocorrelation function", and "power-density spectrum". For a thorough mathematical development of these entities the reader is referred to the bibliography and, especially, to a report by J. R. Parks entitled "Thermal Noise and Calorimetry."²

DETAILED REPORT

Stationary Time Series

The most direct and useful experimental measure of a noise process is that which correlates the amplitude of the fluctuating parameter with time. Such a record taken over a finite period of time, is a time series by definition. Assuming that the governing statistical processes are invariant with time, the recorded time series represents an arbitrary segment of an infinite time series. Theory shows that appropriate mathematical operations on an infinite statistical time series will generate the autocorrelation function and the power-density spectrum of the noise as well as the governing probability-distribution functions.³ The results of these operations are unchanged by the selection of the time origin, hence the expression "stationary time series".

Experimentally determined finite segments of infinite stationary time series retain, to a close approximation, the "stationary" property of the infinite time series and carry the same information. Such finite segments are also called stationary time series.

Consider the graphical representation of a (finite) stationary time series. It is a continuum of finite length requiring an infinite series of numbers for its complete description. On the other hand a periodic sampling of the continuum will yield a finite series of numbers. By choosing a sample of appropriate size one can arrive at representations for the autocorrelation function and power density spectrum which are accurate to the desired degree.

Experimental Arrangement

In order to sample the fluctuations of the mirror of the seismic detector special motion-picture and timing equipment was used. Referring to Figure 1 the motion-picture camera was placed to pick up the mirror image of the millimeter scale. Timing

equipment energized the camera and lighting equipment for approximately five minutes out of each hour during a period from 5 00 p m March 15 till 12 05 a m March 16. Throughout each active five-minute run, the timing equipment also caused the flash lamp to be activated, synchronized with the camera shutter at one-second intervals. Thus each five-minute run resulted in a sequence of approximately 300 frames on the film.

Visual examination of the eight sequences of frames on the developed film showed that the "quietest" period sampled was from 10 00 p.m. to 10 05 p.m. This series was chosen for detailed analysis.

Each of the 312 frames in the selected film strip was projected in magnified form on the ground-glass screen of a library microfilm reader. The distances from the right-hand edges of the projected images to an arbitrarily chosen index mark of the photographed millimeter scale were measured by superimposing a scale on the ground-glass screen. This method of measurement resulted in units such that 4.76 units equal 1 millimeter on the photographed millimeter scale. The resulting stationary time series appears enumeratively in Table I and graphically in Figure 2-B

Autocorrelation Function

In any noise process there is some measure of coupling between the values of the fluctuating parameter. This coupling or correlation exists only between values separated by less than a characteristic finite interval of time. The nature of the correlation and the measure of its extension in time (known as the "relaxation time" "memory" etc) vary from process to process. These properties define the time correlation of a process with itself or its "autocorrelation function". The values of two points on a "noise" curve are coupled if the value of one point determines the value of the other with non-zero probability.

If $f(t)$ represents a stationary time series of infinite extension then the autocorrelation function $R(\tau)$ is defined by

$$R(\tau) = \lim_{T \rightarrow \infty} \left[\frac{1}{2T} \int_{-T}^T f(t) f(t + \tau) dt \right] \quad (1)$$

where τ a time shift of $f(t)$.

The autocorrelation functions of some processes decay from a maximum at $\tau = 0$ according to some exponential law. In order to retain the useful concept of a "relaxation time" for such processes this time is taken to represent the value of τ such that $(R(0) - R(\tau))$ is some arbitrary fraction of the difference between $R(0)$ and $R(\infty)$.

Consider the graphical representations of $f(t)$, $f(t + \tau)$ and $R(\tau)$. It is seen that $f(t)$ and $f(t + \tau)$ are identical except for a relative displacement of magnitude τ along the time axis. To obtain the value of $R(\tau)$ at any point τ_1 superimpose on $f(t)$ the graph of $f(t + \tau_1)$ and form the products $f(t) f(t + \tau_1)$ for all t . The average of these products as $t \rightarrow \infty$ is then $R(\tau_1)$.

Many of the properties common to the $R(t)$ of any $f(t)$ can be heuristically deduced. Some of these properties are stated without proof:

$$1. R(0) = \bar{y}^2$$

where $y = f(t)$

$$2. R(\tau) \text{ is an even function of } \tau \text{ Symbolically } R(\tau) = R(-\tau)$$

$$3. R(\tau) \leq R(0).$$

4. $R(\tau)$ has (approximately) a constant or zero value for all $\tau >$ some finite value τ_n accordingly as $\bar{y}$ is a constant or zero, except that

(a) $\tau_n = 0$ if $f(t)$ represents a "white noise"

(b) τ_n is undefined if $f(t)$ has a periodic or quasi-periodic component

With regard to Statement 4 (a) white noise cannot exist physically, although its postulation is useful in some special applications which do not enter into this discussion; e.g., in the statistical analysis of Brownian motion. On the other hand, Statement 4 (b) is of direct concern for the seismic detector noise has a quasi periodic component which corresponds to the natural frequency of the suspension.

As mentioned previously the stationary time series available to us through experiment is of necessity in the form of a finite series of N numbers $Y_1, Y_2, Y_3, \dots, Y_N \dots Y_N \approx f(t)$, where $N = 312$

Since $R(\tau)$ is an even valued function Equation 1 can be expressed thus:

$$R(\tau) = \lim_{T \rightarrow \infty} \left[\frac{1}{T} \int_0^T f(t) f(t + \tau) dt \right] \quad (2)$$

Converting to a form suitable to arithmetic solution we have:

$$R(\tau) = \frac{1}{N} \sum_{n=1}^N \frac{\tau}{\Delta t} Y_n Y_{\left[n + \frac{\tau}{\Delta t}\right]}$$

Where τ is restricted to integral multiples of Δt and Δt is the sampling interval.

Let $m = N \frac{\tau}{\Delta t}$ the number of products formed for a specific value of τ and a sample of N numbers

then:

$$R(\tau) \approx \frac{1}{m} \sum_{n=1}^m Y_n Y\left[n + \frac{\tau}{\Delta t}\right] \quad (4)$$

As stated previously, the sampling interval, Δt , utilized in the experiment with the seismic detector was 1 second, therefore our computations yielded values for $R(\tau)$ at the points $\tau_0, \tau_1, \tau_2, \tau_3, \dots$ (where the subscripts represents seconds).

The $R(\tau)$ values calculated are shown graphically in Figure 2 A

It is reasonable to assume that the stationary time series, $f(t)$, represents the sum of three independent processes.

Thus:

$$f(t) = f_B(t) + f_M(t) + f_P(t) \quad (5)$$

Where,

$f_B(t)$ - the noise contribution resulting from Brownian motion of the air in contact with the mirror of the seismic detector,

$f_M(t)$ - the noise contribution resulting from instrument-pier tremors; and

$f_P(t)$ - the noise contribution resulting from the natural periodic response of the suspension of the seismic detector

It can be shown that:

$$R(\tau) = R_B(\tau) + R_M(\tau) + R_P(\tau) \quad (6)$$

This relationship exists as a result of the mutual independence of $f_B(t)$, $f_M(t)$, and $f_P(t)$.

It can also be shown that $R_P(\tau)$ is a quasi-sinusoid which does not "blur" significantly in the interval from $\tau = 0$ to $\tau =$ a moderate magnitude.

Specifically:

$$R_P(\tau) \approx K \cos \left\{ \frac{2\pi\tau}{T_P} \right\} \quad (7)$$

where:

τ is not large

$K =$ a constant

$T_P =$ the period of $f_P(t)$

The considerations leading to the development of Equation 7 are admittedly quite vague because the terms "quasi-sinusoid", "blur", "moderate magnitude", and "large" are

not defined. For clarification the reader is referred to the literature.⁴ For our purposes the reasonable assumption is made that the quasi sinusoid of $R_p(\tau)$ is not blurred significantly for several cycles beyond the value τ_n of the relaxation time of $R_B(\tau) + R_M(\tau)$. It should be remembered that $R_B(\tau) + R_M(\tau) \approx 0$ or a constant when $\tau \leq \tau_n$.

By studying the graph of $R(\tau)$ in a region where it is a quasi sinusoid, we can adjust the position of the τ axis so that $Y_n \approx 0$ and also approximately determine the values of K and T_p of Equation 7. (Note: In all of the following discussion the values of $R(\tau)$ and its member functions are measured from the τ axis corresponding to $\bar{Y}_n \approx 0$.)

Subtracting $R_p(\tau)$ from $R(\tau)$ the graph of $R_B(\tau) + R_M(\tau)$ can be obtained.

The problem of analyzing the graph of $R_B(\tau) + R_M(\tau)$ into separate functions is somewhat more involved. By recourse to statistical mechanics, however, it is possible to calculate the value of $R_B(0)$.

Thus

$$R_B(0) = A^2 \frac{kT}{\gamma} \quad (8)$$

Where,

$$A = \frac{U}{\text{radian}} \quad 8044 \text{ } \mu$$

$$A^2 = 6.4712 \times 10^7$$

$$U = 4.76 \text{ millimeter} \quad \text{the units of } R(\tau) \text{ and member functions } 1 \text{ millimeter on the scale } \frac{1}{1690} \text{ radians displacement of mirror (geometry of experiment)}$$

$$k = \text{Boltzmann's constant} = 1.3805 \times 10^{-16} \text{ erg/mol } ^\circ\text{K}$$

$$T = \text{absolute temperature} = 298^\circ\text{K}$$

$$\gamma = \text{the torsion constant of the suspension} = 7.05 \times 10^{-8} \text{ erg/radian}^2$$

whence:

$$R_B(0) = 0.378 U^2$$

The relaxation time of the autocorrelation function of the response of a physical system to Brownian motion of a gas is known to be about 0.01 seconds. Combining this information with our knowledge of the value of $R_B(0)$ it is seen that the contribution of $R_B(\tau)$ to $R_B(\tau) + R_M(\tau)$ is quite small. Considering the orders of magnitude involved, $R_M(\tau)$ can be very closely represented by subtracting $R_B(0)$ from $R_B(0) + R_M(0)$ and leaving the rest of the points on $R_B(\tau) + R_M(\tau)$ unaltered.

In other words set

$$R_B(\tau) = 0$$

except at the origin where

$$R_B(0) = 0.378 U^2$$

Because of the ratio of the relaxation time of $R_B(\tau)$ with respect to the experimental sampling interval, it is not possible to obtain a curve for $R_B(\tau)$. Comparing the values of $\sqrt{R_B(0)}$ and $\sqrt{R_M(0)}$, it is found that the power contribution of Brownian motion to the noise is only one fifteenth of that resulting from pier tremors

Power Density Spectrum

Suppose that it is desired to reduce the noise which the pier transmits to an instrument. It is obvious that some sort of suspension or mount could be used; however, frequency bands carrying most of the noise power should be known in order to design the filter (suspension). To obtain this information, use is made of the "power density spectrum". The power density spectrum, $G(f)$, of a noise process, $f(t)$, is a representation of power as a function of frequency. When $f(t)$ is a statistical process, the determination of $G(f)$ of $f(t)$ is quite laborious if one proceeds to a solution directly from some representation of $f(t)$. In most cases it is much more expedient to generate the power density spectrum, $G(f)$, in terms of the autocorrelation function, $R(\tau)$, of $f(t)$. This is possible as a result of the fact that $G(f)$ is a Fourier transform of $R(\tau)$. The usefulness of autocorrelation function theory is enhanced as a result of this last consideration.

Thus:

$$G(f) = 4 \int_0^{\infty} R(\tau) \cos(2\pi f \tau) d\tau \quad (10)$$

In addition:

$$R(\tau) = \int_0^{\infty} G(f) \cos(2\pi f \tau) df \quad (11)$$

Since $R_M(\tau)$ represents most of the noise picked up by the mirror of the seismic detector, let us consider the power density spectrum, $G_M(f)$, of $f_M(t)$.

From Equation 10:

$$G_M(f) = 4 \int_0^{\infty} R_M(\tau) \cos(2\pi f \tau) d\tau \quad (12)$$

To determine the Fourier integral expression from the graph of $R_M(\tau)$ several techniques are available including a number of iterative numerical processes.

SUMMARY

The noise level of the pier in Room 112 of the Research Building is low enough to justify mounting a Coblentz moving-magnet galvanometer on it. If the suspension of a Coblentz galvanometer were modified by substituting a 2-micron quartz fiber, the increased sensitivity might be obscured by pier noise.

The above conclusions were obtained by considering the root-mean-square values of the angular displacements of the mirror of the seismic detector.

Thermodynamic theory of the Brownian motion of a gas led to the estimation of the power contribution from this source of noise. It was found that pier noise contributes about 15 times as much power to the mirror as does the Brownian motion of the surrounding air.

It will be observed that the foregoing results are obtainable without the utilization of autocorrelation theory. There are, however, numerous instances in calorimetric practice where a knowledge of noise level is not enough. In such cases the fundamental problem is that of noise reduction, noise level measurement merely representing a first step. Thus we are led to utilize autocorrelation functions and power density spectra.

Determination of the autocorrelation function of the pier noise by desk calculating machine methods proved to be prohibitively time consuming. These methods were abandoned in favor of I.B.M. electronic calculating machine methods before the autocorrelation curve of the function was completely determined.

Many innovations in technique were developed during the course of this experiment and some have been used in subsequent work on other problems. These innovations will appear in future reports. Further work on the pier noise problem has been postponed because of more pressing noise problems which relate to other aspects of calorimetry.

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TABLE I

STATIONARY TIME SERIES

TENS/DIGITS	0	1	2	3	4	5	6	7	8	9
0	25	23	24	23	22	21	21	22	22	
1	23	24	24	23	22	22	22	21	21	21
2	22	25	29	32	32	29	27	22	20	21
3	23	25	28	28	26	26	26	26	24	22
4	23	26	27	29	27	25	24	21	21	20
5	19	19	22	24	22	27	28	26	25	23
6	22	23	25	25	27	27	27	25	24	22
7	21	21	22	23	25	26	26	25	24	23
8	24	25	25	26	24	24	22	22	21	21
9	22	23	25	26	26	26	26	26	26	25
10	25	24	25	24	23	23	22	21	21	21
11	22	23	22	21	20	19	18	19	21	23
12	25	25	25	26	25	24	22	22	23	24
13	24	25	24	24	26	26	25	24	24	25
14	27	28	28	28	27	27	27	27	27	27
15	27	27	27	27	27	27	29	30	31	32
16	34	36	37	38	36	32	29	26	24	22
17	22	25	27	28	26	24	22	22	23	25
18	26	27	27	26	25	25	26	26	27	26
19	25	24	23	24	25	27	28	29	29	29
20	29	29	29	29	28	28	29	30	32	34
21	32	30	29	29	30	30	31	33	36	39
22	40	36	29	26	26	27	27	28	30	32
23	32	32	29	27	27	29	32	35	35	33
24	32	32	34	36	37	35	33	30	28	28
25	29	30	31	31	31	29	28	28	29	31
26	31	31	32	35	32	32	32	35	36	32
27	38	33	34	30	26	24	25	27	30	34
28	40	42	40	35	32	34	35	35	35	35
29	35	35	33	34	38	37	36	36	34	30
30	25	21	19	19	20	21	21	21	22	23
31	25	26	25							

TABLE OF VALUES FOR $Y_n = f(t)$ IN UNITS U 4.76 MILLIMETERS. $n = 1, 2, 3, \dots, N$ where $N = 312$

EXPERIMENTAL LAY-OUT

22

F18.2

UNCLASSIFIED

FIGURE 2

MLM-603

AUTOCORRELATION FUNCTION.

PIER NOISE SAMPLE.

UNCLASSIFIED

Problem Title - **Thermal Noise and Calorimetry**

Report By **J. R. Parks**

Work Done By - **J. R. Parks**

INTRODUCTION

Thermometry is a very important factor in calorimetry. The precision limit to which the temperature can be measured determines the precision limit of usefulness of the calorimeter, and the precision limit of measurement of temperature is the blurring motion of the thermometric element. It is this background, upon which precise measurement may be attempted, that decreases and probably destroys the precision.

Thermometers vary in form and construction but the more important variants are their sensitivity and their decay constant. The latter factors determine how much and to what degree thermometers respond to temperature changes in their environment. The sensitivity is a magnification factor that expands the responses of thermometers so that they can be read to as many significant figures as desired.

It might be thought that within the possibilities of good construction, the sensitivity of a thermometric element may be made as great as desired in order to obtain an ever increasing number of significant figures in the temperature measurement. These additional significant figures may be looked upon as additional information, concerning a temperature measurement, gained by merely increasing the sensitivity of the thermometer.

This is a worthy idea; however, in any given calorimetric experiment as the sensitivity of the temperature detector is increased, the significance of the figures desired begin to be blurred by thermal disturbances in both the thermometer and its environment. In this case any further increase of sensitivity gives no additional information since the extraneous disturbances are proportionately magnified. Those thermal disturbances are referred to as noise inasmuch as they tend to limit the ability to gain information.

The problem of the limits of precision of the calorimeters and calorimetric techniques at Mound Laboratory are important since the problem of measuring about 0.03 calorie per hour of power output by a power source to one per cent precision is necessary for the standardization of other instruments.

The first part of the detailed report will deal with the concept of noise in an effort to make clear the physics and mathematics used in the study of noise. The latter part contains the development of an equation that expresses the response of a calorimeter to internal and external thermal noise as a function of the damping constant of the calorimeter and the area under the autocorrelation curve of the noise to which the calorimeter is subjected. This equation is helpful in understanding the instabilities experimenters find in their calorimeters.

DETAILED REPORT

Research was begun to determine the sources of the thermal noise in a calorimeter, thereby making it possible to reduce it to a minimum. It would be surprising indeed if the

thermal noise in calorimeter experiments could be reduced to the irreducible level. However, for any given experimental arrangement there should be a minimum, dependent on the apparatus, which may be sufficiently low to make it possible to obtain the information desired.

The ideas discussed here have a general aspect. The seismic detector was constructed to study the mechanical noise level of the pier in Room 112 of the Research Building. It was shown that the pier, during the quietest period of the night, has a mechanical noise level that is 15 times that of the irreducible thermodynamic level.

The ideas and concepts concerning noise have been clarified in the last 50 years by the development of the theory of the correlation function. The ideas behind the correlation function began with the studies of Brownian motion by Einstein, Smoluchowski, and Langevin and are now being expanded by Wiener, Shannon, and Chandrasekar into a general theory of noise. In between these two groups of scholars has been a host of other contributors.

The autocorrelation function of any function of time is defined by Equation 1.

$$R(\tau) = \lim_{t \rightarrow \infty} \left[\frac{1}{2t} \int_{-t}^t f(t) f(t + \tau) dt \right] \quad (1)$$

It is a relatively simple problem to calculate the autocorrelation function of a bounded function that has a countable number of finite discontinuities. Most of the functions encountered in physics are bounded and continuous. Let us assume that the function, $f(t)$, is a voltage varying as a cosine function of time across a resistance of 1 ohm as given in Equation 2.

$$f(t) = V(t) = e_0 \cos (\omega t + \alpha) \quad (2)$$

Where e_0 = maximum amplitude in volts

ω = angular velocity in radians seconds⁻¹

t = time in seconds

α = phase angle in radians

The application of Equation 1 gives the autocorrelation function as

$$R(\tau) = \frac{e_0^2}{2} \cos \omega \tau \quad (3)$$

Here we see that, since the power dissipated in the 1-ohm resistance is the voltage squared, the autocorrelation function given in Equation 3 is the mean power of $V(t)$ multiplied by the periodic factor of $V(t)$ with the phase deleted. It can be shown that, if the function, $f(t)$, is a sum of sinusoids with various phases, the autocorrelation function will

be the sum of one half the maximum amplitude of each component of the $f(t)$ squared, multiplied by the cosine of the angular velocity times the corresponding periodic factor with the phase angles deleted.

$$R(\tau) = \sum_{i=0}^n \frac{e_i^2}{2} \cos(\omega_i \tau) \quad (4)$$

In general, the functions dealt with in physics are response functions of physical systems, hence, the autocorrelation function is the mean power of the response of the system. In this case, from the Wiener-Kintchine Theorem, the energy density spectrum can be obtained as a Fourier transform of the autocorrelation function as shown in Equation 5

$$E(f) = 2 \int_{-\infty}^{\infty} R(\tau) \cos(2\pi f \tau) d\tau \quad (5)$$

where $E(f)$ = the energy density spectrum function in ergs cycle⁻¹

f = frequency in cycles seconds⁻¹

Hence if the autocorrelation function of a response is known then the energy density as a function of the frequency, f , can be obtained. This is a highly important idea

Usually the practice, when setting up an experiment, is to isolate the system from those disturbing forces that are obvious and as many as possible of those that are not so obvious. The good experimenter either intelligently isolates his experiment or accounts for the disturbing forces. However there can be disturbances that are beyond the ken of the experimenter, and it is here that the techniques of the autocorrelation function can be a great aid. If the autocorrelation function is known then the energy density function can be found from which it may be determined what frequency ranges contain energy from undesirable sources. This knowledge aids in the design and construction of suitable mechanical, electrical, and thermal filtering systems.

The functions of time discussed so far are expressible in the usual fashion. However, as far as the application of the autocorrelation function is concerned, the function can be any continuous or discontinuous time series. An example of a continuous time series is a continuous record of the temperature variations of a bath drawn by the usual type of recording equipment. Figure 1 gives an example of the continuous time series which can not be given the usual type of functional expression. It is a record of the thermal noise of a calorimeter bath. This record was made with a resistance bridge type thermometer. The output of the thermometer is put into a Leeds and Northrup direct current microvolt amplifier and then fed to the strip chart recorder.

An example of the discontinuous time series is given in a paper by T. J. Beasley¹ where the time series is composed of photographs of an illuminated scale taken through the vibrating mirror of the seismic detector. The photographs were taken at 1 second intervals over a period of 5 minutes. The motion of the mirror was caused by the mechanical noise of the pier.

Both of these time series illustrate a type of function that has the property that a precise knowledge of the function in the past does not predicate a knowledge of it in the future. This property is characteristic of functions representing responses of physical systems to noise.

For the purposes of calculation Equation 1 can be written as

$$R(\tau) = \frac{1}{N} \sum_{n=0}^{n=N-\tau/\Delta t} f(n\Delta t) f(n\Delta t + \tau) \quad (6)$$

$$\text{where } \Delta t = \frac{t_1 - t_2}{N}$$

where $t_1 - t_2$ = total time interval in seconds selected for the determination of $R(\tau)$ from $f(t)$

N = total number of equal intervals of time, Δt , into which the time interval $t_1 - t_2$ is divided

τ = integral number of subintervals, Δt in seconds.

There are restrictions on Δt and τ in order that Equation 6 gives the autocorrelation function with reasonable accuracy. The subinterval, Δt , should be chosen so small that $f(t)$ does not change significantly in that interval, and the time range, τ , of the autocorrelation function should not exceed $\frac{1}{5}(t_1 - t_2)$, since for larger values of τ the amount of data for calculating $R(\tau)$ is reduced by more than 20 per cent. The time intervals, Δt , may be taken as the unit of τ . Continuous time series, after the selection of the time intervals, $t_1 - t_2$, and Δt are reduced to a discontinuous time series by reading $f(n\Delta t)$ from the strip chart so that Equation 6 may be applied by the method developed by T. J. Beasley.¹

A calorimeter or a thermometer responds to its internal temperature changes as well as to external temperature changes. Since the calorimeters and thermometers to be discussed here are of the twin bridge type, their internal temperatures will be a few degrees higher than the ambient temperature because of the heat introduced by the bridge current. The differential equation that is satisfied by the heat flow in a calorimeter with a resistance bridge thermometer is given by Equation 7

$$C \frac{du}{dt} + Ku = K \left[U_0(t) + \frac{q(t)}{K} \right] \quad (7)$$

Where C = lumped thermal capacity of the calorimeter in calories degree⁻¹

u = temperature of the calorimeter in degrees centigrade

K = lumped thermal conductivity of the gradient medium that semi isolates the calorimeter in calories degree⁻¹ seconds⁻¹

$U_0(t)$ = temperature of the environment in degrees centigrade

$q(t)$ = power introduced into the calorimeter by the bridge current in calories second⁻¹.

A schematic representation of a calorimeter or a thermometer is shown in Figure 2. The calorimeter is region R_1 separated from its environment, region R_2 , by a thermally conducting membrane, M , the conductivity of which is K . From the macroscopic point of view if $q(t)$ is a constant, Equation 7 reduces to

$$u = U_0(t) + \frac{q(t)}{K} \quad (8)$$

This equation means that after long enough time $\frac{du}{dt} \rightarrow 0$, and the maximum temperature of the calorimeter is given by Equation 8 where the temperature rise of the calorimeter above the temperature of the environment is the term $\frac{q(t)}{K}$.

However, after macroscopic equilibrium has been reached, there are microscopic variations of temperature in the various parts of regions R_1 and R_2 that cause microscopic variations of the temperature of the calorimeter. These microscopic changes in temperature in R_1 , the internal region of the calorimeter, and in R_2 , the region external to the calorimeter, are random and hence may be thought of as thermal noise to which the calorimeter is subjected. The physics of this situation may be described by considering a small region of R_1 . If a spontaneous temperature change occurs in this small region, the rest of the region R_1 will respond by an amount dependent on the thermal capacity of the region R_1 and the amount by which the region R_2 is affected by the conductivity K_1 of the separating membrane M . Now consider a spontaneous temperature fluctuation in a small region of R_2 , again the R_1 will be affected by an amount dependent on the thermal capacity, C , of R_1 and the thermal conductivity, K , of the membrane M . Since the response of the calorimeter is a solution of a linear differential equation, then we may consider that the response of the calorimeter as a whole to the spontaneous temperature changes in R_1 and R_2 is a solution of the differential equation expressing the exchange of power between R_1 and R_2 through the membrane, M . This equation is Equation 9.

$$C \frac{du}{dt} + Ku = K U(t) \quad (9)$$

Where $U(t)$ = the continuous stationary time series of temperature variation in regions R_1 and R_2 (thermal noise) in degrees when there is a constant input of power into region R_1 of $q(t)$ calories second⁻¹

This equation holds for the case in which the power input, $q(t)$ is zero, so that we have from Equation 7 the following equation

$$C \frac{du}{dt} + Ku = K U_0(t) \quad (10)$$

In this equation, $U_0(t)$ is the continuous stationary time series of temperature variation of the environment, R_2 , and the internal region, R_1 , since $q(t)$ is assumed to be zero.

Just as in the case of mechanical noise studied by means of the seismic detector, thermal noise is composed of two parts. One part is the thermodynamic noise and the other

part is that introduced by the experimental equipment. When heat is introduced into the calorimeter the variations in the power caused by changes in the external battery circuit are noise introduced by the experimental facilities. The thermodynamic noise is a function of temperature and is such that the higher the temperature the higher the thermodynamic noise level.

In the following discussion Equation 9 will be taken as fundamental since Equation 10 is a special case. The function, $U(t)$, will be considered to contain all the noise components due to the experimental equipment as well as those due to thermodynamic causes. Furthermore the calorimeter and bath must be in equilibrium for a time that is very long compared to the time constant and therefore may be considered an infinite time.

Equation 9 has the form of the equation proposed by Langevin in his study of Brownian motion. In Equation 9 the thermal capacity is analogous to the mass of the colloidal particle in Brownian motion, and the thermal conductivity is analogous to the coefficient of viscous friction between the environment and the particle, and the temperature is analogous to the velocity of the particle. The function, $U(t)$, is analogous to $f(t)$ in the Brownian motion case in that it represents random spontaneous fluctuations of temperature to which the calorimeter has a response. Therefore Equation 9 can be discussed in the manner of Brownian motion, provided we define $U(t)$.

The function, $U(t)$, is considered to have the following properties. The average, $\overline{U(t)}$, is a constant.

$$\overline{U(t)} = \lim_{t \rightarrow \infty} \left[\frac{1}{2t} \int_{-t}^t U(t) dt \right] = a \quad (11)$$

The autocorrelation function of $U(t)$ is given by Equation 12. and is

$$R(\tau) = \lim_{t \rightarrow \infty} \left[\frac{1}{2t} \int_{-t}^t U(t) U(t + \tau) dt \right] \quad (12)$$

The function, $U(t)$, is such that for large τ the autocorrelation function, $R(\tau)$, is very nearly equal to a^2 , or, in the form of an equation, we have Equation 13.

$$R(\tau) \simeq a^2, \text{ for } \tau \rightarrow \infty \quad (13)$$

For small τ the autocorrelation function, $R(\tau)$, is given by Equation 14.

$$R(\tau) \simeq b^2 + a^2, \text{ for } \tau \simeq 0 \quad (14)$$

where b^2 is proportional to the power exchange across the membrane. M , due to the spontaneous fluctuations of the temperature about the mean value a . This function, $R(\tau)$, appears similar to the graph of the autocorrelation function of the thermal noise obtained from the oil and water baths and shown in Figure 3

Before continuing we may define the functions $U(t)$ and $R(\tau)$, by virtue of Equations 11, 13, and 14, as functions with the quantities, a or a^2 , subtracted from them. This means that we will consider that Equations 11, 13, and 14 are as follows.

$$\overline{U(t)} = 0$$

$$R(\tau) = 0, \text{ for } \tau \rightarrow \infty$$

$$R(\tau) = b^2, \text{ for } \tau \simeq 0$$

By applying the methods of Langevin, Wiener and MacDonald to Equation 9 a value of the autocorrelation function, $\rho(\tau)$, of the calorimeter temperature response can be found in terms of the autocorrelation function, $R(\tau)$, of the environment temperature fluctuations, $U(t)$, and is given in Equation 15

$$\rho(\tau) = \frac{\beta}{2} e^{-\beta|\tau|} \int_{-\infty}^{\infty} R(\nu) d\nu \quad (15)$$

Where $\beta = \frac{K}{C}$ and is the damping constant of the calorimeter in inverse seconds, and $\rho(\tau)$ is the autocorrelation function of the calorimeter response in degrees squared. Equation 15 balances dimensionally, since the integral of $R(\nu)$ is in degrees squared seconds and the damping constant is in inverse seconds. Upon referring to Equation 5 it is seen that the integral in Equation 15 is proportional to the power density of the thermal noise at zero frequency as is shown by Equations 16 and 17

$$E(f) = 2 \int_{-\infty}^{\infty} R(\nu) \cos(2\pi f\nu) d\nu \quad (16)$$

and for $f = 0$, we see that

$$\int_{-\infty}^{\infty} R(\nu) d\nu = \frac{1}{2} E(0) \quad (17)$$

This integral is the area under the autocorrelation curve, $R(\tau)$, as shown in Figure 3. The physics of this problem may be investigated by substituting Equation 17 into Equation 15. Thus we have Equation 18.

$$\rho(\tau) = \frac{\beta}{4} e^{-\beta\tau} E(0) \quad (18)$$

Since $\rho(\tau)$ is the autocorrelation function of the calorimeter response, then

$$\rho(0) = \bar{u}^2 \quad (19)$$

Hence at $\tau = 0$ we have Equation 20

$$\bar{u}^2 = \frac{\beta}{4} E(0) \quad (20)$$

or

$$(\bar{u}^2)^{1/2} = \frac{1}{2} \sqrt{\beta} [E(0)]^{1/2} \quad (21)$$

Since $E(0)$ is the power density at zero frequency then $[E(0)]^{1/2}$ may be considered as a constant temperature deviation being impressed on the calorimeter by the spontaneous temperature fluctuations in the environment caused by the interchange of power across the conducting membrane. The sensitivity of the calorimeter to this constant temperature deviation is $\sqrt{\frac{\beta}{2}}$. Let σ denote the sensitivity of the calorimeter to its environment, then we have Equation 22.

$$\sigma = \sqrt{\frac{\beta}{2}} \quad (22)$$

and since $\beta = \frac{K}{C}$ then

$$\sigma = \frac{1}{2} \sqrt{\frac{K}{C}} \quad (23)$$

This equation is supported by experiment because a calorimeter, when zero power is put into it can be made less sensitive to bath noise by increasing the thermal resistance (reducing K) of its insulation, thus increasing its thermal isolation from the bath, and/or by increasing its thermal capacity, C . These ideas are true when power is not put into the calorimeter

When power is put into the calorimeter, the problem is different since the temperature in region R_1 (returning to Figure 2) is higher than that of the external region, R_2 (the bath), and therefore the thermodynamic noise level is higher within the calorimeter. For the moment let us analyze the sources of noise in experimental equipment. Consider a stirred bath maintained at a constant temperature, U_0 . Suppose that a calorimeter is in the bath and a constant power, q , in calories per second has been put into the calorimeter for a considerable length of time, maintaining it at a constant temperature, u_1 . The temperature of the calorimeter is given by the following equation

$$u_1 = U_0 + \frac{q}{K} \quad (24)$$

It has already been remarked that the noise to which a calorimeter is subject is composed of two parts, the thermodynamic noise, which is a function of temperature, and the noise introduced by the experimental equipment. This latter type, for the purposes of discussion, we shall assume to be caused predominantly by stirring the bath. Intuitively it is suspected that the stirring of the bath has an effect on the calorimeter that can be said to be random but is characteristic of the mode of stirring. The experimentalist attempts to obtain as random stirring as possible with a minimum of power input into the bath by stirring. It is reasonable to expect that the statistical law governing the noise of stirring is different from that governing the thermodynamic noise to such an extent that the two laws have a zero cross-correlation. From Equation 24 it is seen that the temperature, u_1 , of the calorimeter and the bath temperature, U_0 , statistically contain each other, and their combined effect on the calorimeter is given by Equation 7.

This equation should be extended to include the effect of stirring. Suppose that the effect of stirring appears to the calorimeter as a statistical temperature function, $U_2(t)$. The differential equation governing the response of the calorimeter to these various sources of thermal noise is given by Equation 25.

$$C \frac{du}{dt} + Ku = K \left[\left\{ U_0(t) + \frac{q(t)}{K} \right\} + U_2(t) \right] \quad (25)$$

Here, as before, we will consider that the experimental set up has been in equilibrium for a long time and that the constant temperatures have been subtracted from Equation 25 thus leaving the equation referring only to the statistical variations.

The solution to Equation 25 is obtained in the same manner in which the solution of Equation 9 was obtained and is given by Equation 26.

$$\rho(\tau) = \frac{\beta}{2} e^{-\beta|\tau|} \int_{-\infty}^{\infty} R_T(\nu) d\nu \quad (26)$$

Where $R_T(\nu)$ is the autocorrelation function of the function, $U_0(t) + \frac{q(t)}{K} + U_2(t)$.

Since it is assumed that the noise, $U_2(t)$, caused by stirring is not correlated to that caused by temperature, $\{U_0(t) + \frac{q(t)}{K}\}$, then the cross-correlation of these functions is zero; or

$$\lim_{t \rightarrow \infty} \left[\frac{1}{2t} \int_{-t}^t \left\{ U_0(t) + \frac{q(t)}{K} \right\} U_2(t + \nu) d\nu \right] = 0 \quad (27)$$

Then the autocorrelation function, R_T , is given by Equation 28

$$R_T(\nu) = R_1(\nu) + R_2(\nu) \quad (28)$$

where

$$R_1(\nu) = \lim_{t \rightarrow \infty} \left[\frac{1}{2t} \int_{-t}^t u_1(t) u_1(t + \nu) dt \right] \quad (29)$$

The function, $u_1(t)$, is given by Equation 24.

$$R_2(\nu) = \lim_{t \rightarrow \infty} \left[\frac{1}{2t} \int_{-t}^t U_2(t) U_2(t + \nu) dt \right] \quad (30)$$

Equation 26 then becomes Equation 31.

$$\rho(\tau) = \frac{\beta}{2} e^{-\beta|\tau|} \int_{-\infty}^{\infty} R_1(\nu) d\nu + \frac{\beta}{2} e^{-\beta|\tau|} \int_{-\infty}^{\infty} R_2(\nu) d\nu \quad (31)$$

At

$$\tau = 0, \rho(0) = \overline{u^2} \quad (32)$$

Hence the mean square variation of the temperature of a calorimeter with power put into it and with the bath stirred is given by Equation 33.

$$\overline{u^2} = \frac{\beta}{2} \int_{-\infty}^{\infty} R_1(\nu) d\nu + \frac{\beta}{2} \int_{-\infty}^{\infty} R_2(\nu) d\nu \quad (33)$$

This equation is a generalization of Equation 15. In Equation 15 the autocorrelation function, $R(\nu)$, can be considered as containing the functions for the thermodynamic noise and the noise of stirring in the same fashion as in Equation 28. The integral, $\int_{-\infty}^{\infty} R_2(\nu) d\nu$, the area under the autocorrelation curve for noise of stirring, must be found from experiment. This is possible if the integral, $\int_{-\infty}^{\infty} R_1(\nu) d\nu$, is known, since a run with a calorimeter with a known damping constant in which $\overline{u^2}$ is determined leaves the integral, $\int_{-\infty}^{\infty} R_2(\nu) d\nu$ as a single unknown.

The integral, $\int_{-\infty}^{\infty} R_1(\nu) d\nu$, may be evaluated by analogy with the concept of the equal partition of energy in the mechanical case, which states that kT ergs of energy

are possessed by each degree of freedom of a particle of a system in thermodynamic equilibrium, with one-half of it being distributed to the kinetic energy and the other half being assigned to the potential energy. This statement is illustrated by Equation 34.

$$\frac{1}{2} M \bar{V}^2 = \frac{1}{2} kT \quad (34)$$

Where

M = mass of the particle in grams

$\bar{V}^2$ = mean square of the speed of the particle in centimeters second⁻²

k = Boltzmann's constant in ergs degree⁻¹ absolute

T = temperature of the system of which the particle is a part in degrees absolute

The analogy of the calorimeter in equilibrium with its environment to a particle in equilibrium with its environment may be expressed as follows.

$$\text{If } M = \frac{C}{T} \quad (35)$$

$$\text{and } \bar{V}^2 \sim \bar{u}^2 \quad (36)$$

where C = thermal capacity of the calorimeter in calories degree⁻¹

T = temperature of the calorimeter in degrees absolute

and $\bar{u}^2$ = mean square of the deviation of the temperature of the calorimeter from the temperature, T, in degrees²,

then from Equation 34 we have

$$\bar{u}^2 = \frac{kT^2}{C} \quad (37)$$

For dimensional correctness the thermal capacity, C, should be expressed in ergs per degree, in which case Equation 37 becomes Equation 38.

$$\bar{u}^2 = \frac{kT^2}{C \times 4.186} \times 10^7 \quad (38)$$

Equation 38 gives that part of $\bar{u}^2$ in Equation 33 that is caused by thermodynamic noise, so that we may write Equation 39.

$$\frac{\beta}{2} \int_{-\infty}^{\infty} R_1(\nu) d\nu = \frac{kT^2}{C \times 4.186} \times 10^7 \quad (39)$$

From this we evaluate the integral

$$\int_{-\infty}^{\infty} R_1(\nu) d\nu = \frac{2}{\beta} \times \frac{kT^2}{C \times 4.186} \times 10^{-7} \quad (40)$$

therefore we have for Equation 33 the following equation.

$$\bar{u}^2 = \frac{kT^2}{C \times 4.186} \times 10^{-7} + \frac{\beta}{2} \int_{-\infty}^{\infty} R_2(\nu) d\nu \quad (41)$$

Now the absolute temperature, T , of the calorimeter is given by Equation 42 if it has a power input of q calories per second

$$T = u_0 + \frac{q}{K} + 273 \quad (42)$$

If we let T_0 be the absolute temperature of the bath, we may write Equation 41 as follows:

$$\bar{u}^2 = \frac{k(KT_0 + q)^2}{K^2 C \times 4.186} \times 10^{-7} + \frac{\beta}{2} \int_{-\infty}^{\infty} R_2(\nu) d\nu \quad (43)$$

This equation gives the limit of temperature sensitivity of a calorimeter when the noise of stirring the damping constant of the calorimeter, the power input, and the bath temperature are known. If the sensitivity of the temperature detector is such that the response to noise is greater than the step of the temperature measuring device, then nothing is gained by the excess sensitivity

Usually the temperature detecting and measuring devices are of an electrical nature with sensitivities which have units of microvolts per degree. The damping constants of the detecting and measuring circuits are usually considerably greater than that of the calorimeter so that we may write Equation 44 for the response of the temperature measuring instrument.

$$\bar{e}^2 = s^2 \bar{u}^2 \quad (44)$$

where

$\bar{e}^2$ = mean square response of the temperature measuring device in microvolts²
 s = sensitivity of the measuring device in microvolts degree⁻¹.

And it is seen from Equation 44 that the sensitivity of the measuring device should not exceed the following value if the steps of the device are one microvolt

$$s \leq \left(\frac{1}{\bar{u}^2} \right)^{\frac{1}{2}} \quad (45)$$

It may be more practical to state that the sensitivity, s , should not exceed $1/7$ times the value given in Equation 45 since the peak-to-peak value of the variation in temperature, u , is approximately $7(\bar{u}^2)^{\frac{1}{2}}$

From Equation 43 it may be deduced that decreasing the thermal conductivity of the gradient medium which isolates the calorimeter from its environment while keeping the thermal capacity constant, tends to decrease the noise due to stirring but tends at the same time to increase the noise due to power being put into the calorimeter. However increasing the thermal capacity of the calorimeter tends to decrease the noise due to stirring and the power input. Furthermore if the conductivity of the gradient medium and the thermal capacity of the calorimeter are reduced proportionately so that the damping constant, β , remains constant, the sensitivity of the calorimeter to stirring noise remains the same and the sensitivity to power input noise increases

At this point a calculation of the sensitivity to the internal noise of two of the calorimeters was made. The calorimeters chosen for comparison were Numbers 39 and 53. The power input to these calorimeters was considered to be that introduced by the bridge. Only the internal thermal noise was considered since the noise of stirring is unknown

TABLE I

DATA FOR CALCULATING NOISE RESPONSES OF CALORIMETERS 39 AND 53

	NO 39	NO 53
T_0 BATH TEMPERATURE, DEGREES ABSOLUTE	300	300
q POWER INPUT BY BRIDGE, CALORIES SECOND ⁻¹	0.005	0.007
K THERMAL CONDUCTIVITY OF GRADIENT MEDIUM, CALORIES DEGREE ⁻¹ SECOND ⁻¹	0.049	0.0024
C THERMAL CAPACITY OF CALORIMETER, CALORIES DEGREE ⁻¹	21.7	1.1
K BOLTZMANN CONSTANT, ERGS DEGREE ⁻¹	1.38×10^{-16}	

From Equation 43 and without regard to the heat derived from stirring, the following are values of $(\bar{u}^2)^{\frac{1}{2}}$ calculated for the calorimeters.

For calorimeter 39	$(\bar{u}^2)^{\frac{1}{2}} = 1.2 \times 10^{-10}$ degrees
For calorimeter 53	$(\bar{u}^2)^{\frac{1}{2}} = 5 \times 10^{-10}$ degrees

Calorimeter 39 is a macrocalorimeter and Number 53 is one of the sensitive microcalorimeters at Mound Laboratory. Calorimeter 53 is about four times more sensitive to internal thermal noise than Calorimeter 39. By dividing K by C for both calorimeters the damping constants, β , are found to be about the same, 0.0023 inverse seconds and 0.0022 inverse seconds for Calorimeters 39 and 53, respectively with the result that their responses to noise in the bath are about the same. This supports the remarks made in the discussion of Equation 43.

The temperature sensitivities of both calorimeters are around 50,000 microvolts per degree. Even with these high sensitivities, the response to thermal noise is very negligible. Therefore it appears that gross changes in the environment and in stirring noise are the limiting factors of the lower limit of detectability of our calorimeters. Also there is evidence here that the power input of the bridge is not a limiting factor. It has also appeared in the experimental work that the noise in the bath from stirring is the present limiting factor for the macrocalorimeters.

A twin microcalorimeter is now under construction. It is to be made with the highest degree of balance attainable in our Laboratory and is to be submerged in a bath of oil with no stirring. The detecting and measuring device is a Coblentz moving magnet galvanometer mounted on a pier that is singularly free of mechanical noise. The entire calorimeter system and detector will be well protected from the gross changes in temperature of the room. Noise studies with this calorimeter should give positive evidence of the effect of stirring and should point out other less apparent sources of noise.

REFERENCE

- 1 Parks, J. R. and Beasley, T. J. This Report p. 12

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FIGURE 1

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NOISE ANALYSIS CONDITIONS.

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39

FIG. 3

CORRELATION CURVES FOR OIL AND WATER BATHS.

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FIGURE 3

MLM-603

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Problem Title **The Dynamics of Heat Flow in a Steady-State Twin Bridge Calorimeter**

Report By **K C Jordan**

Work Done By **K C Jordan**

INTRODUCTION

In a previous report ¹ an equation was developed which represented the cooling curves of the twin resistance bridge calorimeters of both the macro and micro types. This equation was

$$V = V_m e^{\frac{\alpha R_0 t}{1440 C S}} \quad (1)$$

where

- V bridge potential in microvolts
- V_m bridge potential at t = 0
- α coefficient of resistivity of bridge in ohm ohm⁻¹ degree⁻¹
- R₀ effective bridge resistance in ohms
- t time in seconds
- C effective heat capacity of calorimeter in calories degree⁻¹
- S sensitivity of calorimeter in microvolts hours-millicalorie⁻¹

Equation 1 was derived using the assumptions that the effective heat capacity of the calorimeter could be lumped in a single term C and that the heat conductivity of all parts of the calorimeter which contribute to the effective heat capacity is sufficiently large that the flow of heat through these parts is relatively unimpeded in comparison to the flow of heat across the gradient medium. These assumptions are justified for the calorimeters under discussion because all the calorimeters at this site are essentially composed of good conducting metals and have gradient mediums such as air, vacuum, Santocel or Styrafoam.

In the same report ¹ Equation 1 was shown to represent the experimental cooling curves very closely even when a large additional heat capacity, in the form of a solid brass slug placed in the sample container, was added to the heat capacity C of the calorimeter. However, if the slug within the sample container did not have a large thermal conductivity or if the thermal contact between a slug of large thermal conductivity and the sample container were not excellent, a single lumping of the thermal capacity and thermal conductivity would not be valid in the derivation of the heating and cooling equations of the calorimeters. These are very important cases in calorimetry; the latter case which is simpler is discussed in this report.

A solid cylinder of copper 2.75 inches long and 0.680 inch in diameter was inserted in Calorimeter 51 a standard macrocalorimeter when connected as a twin calorimeter with a single bridge.⁴ The diameter of the copper slug was such that there was an air gap of 0.117 inch between the outer surface of the copper and the inner surface of the heater built into the calorimeter thereby introducing a region of low thermal conductivity between the sample and the thermel of the calorimeter. A 146-ohm heater of fine manganin wire was wound around the copper slug facilitating the introduction of heat either by this heater or by the built-in heater.

The equations of the heating curves when heat is applied through either the heater on the copper slug or the built-in heater were derived using two lumped heat-capacity terms and two heat-conductance terms. The equations of the cooling curves may be obtained by dropping the steady state term from the equations of the heating curves. Both the experimental and theoretical cooling curves were plotted on the same graph (Figure 2).

The times required to come within 0.01 per cent of equilibrium value were calculated from the equations and compared with the equivalent equilibrium times for the experimental curves which were plotted on four place semilog paper for this purpose (Figure 3).

It was shown by using the heating-curve equation derived for heat introduced through the built in heater of the calorimeter that the area under the cooling curve is independent of the thermal conductivity of the air gap between the copper slug and the calorimeter proper. Therefore the accuracy of a specific heat determination is independent of the thermal conductivity of the sample. This has been verified experimentally.³ The difference between the areas under the cooling curves of both the heater wound on the copper slug and the heater built into the calorimeter suggests a method of measuring the heat conductivities of materials, especially those materials with low thermal conductivities and low thermal capacities. The areas under the cooling curves, which resulted from heat introduced through either the built-in heater or the heater wound on the copper slug were calculated from the equations of the curves and compared with the areas under the experimental curves as measured with a planimeter.

DETAILED REPORT

A solid slug of copper was suspended inside the thermel² of Calorimeter 51 and was centrally located in the built in heater by two Lucite spacers 0.01 inch thick. A spiral of No. 38 manganin wire of 156.2 ohms resistance was wound coaxially with the copper slug to serve as a heater. The physical characteristics of the copper slug were as follows:

Length	2.75 inches
Diameter	0.680 inches
Mass	144.7 grams
Specific Heat	0.093 calories gram ⁻¹ degree ⁻¹

The inside diameter of the built in heater was 0.915 inch. Thus the air gap between the copper slug and the built in heater had a thickness of 0.117 inch.

The experimental procedure was as follows. A current was supplied to the built in heater and maintained until the bridge potential reached a steady state condition. The power dissipated in the heater was calculated from I^2R and the joule equivalent to be 8.150×10^5 millicalories hour⁻¹. The current was then removed and the bridge potential in microvolts was read and recorded as a function of time until the bridge potential was again at a steady state. A sensitivity of 0.13162 microvolts per millicalorie per hour was calculated by dividing the total change in bridge potential by the power input. A cooling curve was then plotted (Curve I of Figure 2). The area under this cooling curve was measured with a planimeter.

As the next step in the experiment, current was supplied to the heater wound on the copper slug. After a steady state had been reached, the current was removed and a cooling curve recorded as before. The sensitivity of the calorimeter was calculated as before and found to be 0.1 per cent lower. This can be attributed to either inaccuracies in the heater resistance or to loss of heat around the bridge. For convenience the power introduced into the heater was calculated from the sensitivity determined with the built in heater. This was 6.9617×10^5 millicalories hour⁻¹. This second cooling curve is reproduced as Curve II of Figure 2. Both cooling curves were plotted on five place semilog paper (Curves I and II of Figure 3) to facilitate determination of the times to reach within 0.01 per cent of equilibrium.

Figure 1 shows a very simplified axial section of the calorimeter containing the copper slug to indicate the parameters under discussion in this report. The meaning of the symbols is as follows:

- C_2 in calories-degree⁻¹ is the total effective heat capacity of the calorimeter proper which includes all parts of the thermel and the built in heater
- C_1 in calories degree⁻¹ is the heat capacity of the copper slug
- T_1 is the temperature difference in degrees centigrade between the copper slug and the bath.
- T_2 is the temperature difference in degrees centigrade between the calorimeter proper and the bath.
- K_1 is the total heat conductance of the air gap between the copper slug and the calorimeter in calories second⁻¹-degree⁻¹
- q_1 is the rate of heat transfer in calories second⁻¹ across the air gap between the copper slug and the calorimeter
- K_2 is the total heat conductance in calories second⁻¹-degree⁻¹ of the air gap between the thermel and the jacket of the calorimeter
- q_2 is the rate of heat transfer in calories second⁻¹ across the air gap between the thermel and the jacket.
- Q_1 and Q_2 are the rates of heat input in calories second⁻¹ in the heater wound on the copper slug and in the built in heater respectively

A balance equation of heat flow can now be set up for any time t . Thus for heat being introduced at the copper slug:

$$Q_1 = C_1 \frac{dT_1}{dt} + C_2 \frac{dT_2}{dt} + K_2 T_2 \quad (2)$$

Equation 2 states that given a certain rate of heat input, Q_1 , heat is stored at the rate of $C_1 \frac{dT_1}{dt}$ in the copper slug and at the rate of $C_2 \frac{dT_2}{dt}$ in the calorimeter proper, and that the remaining heat is flowing out of the calorimeter to the bath at the rate of q_2 or $K_2 T_2$ calories per second.

The heat stored in the air gaps is very small compared to the heat stored in C_1 and C_2 and is neglected in this treatment. If the heat capacity of the gradient medium between the sample slug of copper and the built-in heater were appreciable, it could be split between C_1 and C_2 , the greater portion being added to C_1 .

The rate of heat flow across the inner air gap is proportional to the temperature difference, the proportionality constant being K_1 . This is given in Equation 3.

$$q_1 = K_1 (T_1 - T_2) \quad (3)$$

Now q_1 must equal the rate of heat storage in C_2 plus q_2 , the rate of heat leaving the calorimeter and going into the bath. This is expressed by Equation 4.

$$q_1 = C_2 \frac{dT_2}{dt} + K_2 T_2 \quad (4)$$

Eliminating q_1 from Equations 3 and 4 gives

$$K_1 (T_1 - T_2) = C_2 \frac{dT_2}{dt} + K_2 T_2 \quad (5)$$

Now, solving Equation 5 for T_1 and differentiating T_1 with respect to time

$$\frac{dT_1}{dt} = \frac{C_2}{K_1} \frac{d^2 T_2}{dt^2} + \left(\frac{K_2}{K_1} + 1 \right) \frac{dT_2}{dt} \quad (6)$$

This value of $\frac{dT_1}{dt}$ can be substituted in Equation 2 to obtain Equation 7, which is in terms of T_2 only:

$$Q_1 = \frac{C_1 C_2}{K_1} \frac{d^2 T_2}{dt^2} + \left(C_1 + C_2 + \frac{C_1 K_2}{K_1} \right) \frac{dT_2}{dt} + K_2 T_2 \quad (7)$$

The temperature difference T_2 of the calorimeter proper above the temperature of the bath is of course proportional to the bridge potential V in microvolts (corrected for zero bridge potential). With a bridge current of 5 milliamperes, Equation 8 correlates T_2 and V :

$$T_2 = \frac{V}{2,500 \alpha R_0} \quad (8)$$

where α and R_0 have the same meaning as in Equation 1. The 99 alloy nickel wire used as bridge wire in Calorimeter 51 has a coefficient of resistivity α of 0.0054 ohms ohm⁻¹ degree⁻¹. The effective resistivity R_0 , of the bridge is 990 ohms determined by a method described earlier.¹ The value of 868 ohms for the effective resistance given in that report is in error. Substituting Equation 8 into Equation 7, and inserting the numerical values of α and R_0 gives Equation 9

$$Q_1 = 7.48 \times 10^{-5} \left[\frac{C_1 C_2}{K_1} \frac{d^2 V}{dt^2} + \left(C_1 + C_2 + \frac{C_1 K_2}{K_1} \right) \frac{dV}{dt} + K_2 V \right] \quad (9)$$

The conductance term K_2 is inversely proportional to the sensitivity of the calorimeter which is expressed in units of microvolts millicalorie⁻¹-hour⁻¹. The experimental sensitivity of Calorimeter 51 was 0.13162 microvolts-millicalorie⁻¹-hour⁻¹. Therefore using the appropriate conversion units

$$K_2 = \frac{1}{1,000 \times 7.48 \times 10^{-5} \times 3,600 \times 0.13162} = 0.028215 \text{ calories second}^{-1} \text{ degree}^{-1}$$

Five places were used here and in subsequent calculations for cross check purposes. If the power in the heater is designated as P_H millicalories hour⁻¹ then

$$Q_1 = \frac{P_H}{3,600 \times 1,000} = 2.7778 \times 10^{-7} P_H \text{ calories second}^{-1}$$

The value of C_1 is the mass of the copper slug times the heat capacity of copper or

$$C_1 = 144.7 \times 0.093 = 13.45 \text{ calories-degree}^{-1}$$

The heat capacity of the calorimeter proper was determined by the experimental methods presented in the previous report¹ to be $C_2 = 9.36 \text{ calories degree}^{-1}$

The method of evaluation of K_1 was similar to that used to determine the sensitivity of a calorimeter described in the previous report.¹ The total conductance K_1 , across the inner air gap will be assumed to be made up of two additive terms, one accounting for the heat transfer by conduction and the other for the heat transfer by radiation. The result is expressed by Equation 10

$$K_1 = \frac{2\pi k_1 L}{\ln \frac{r_2}{r_1}} + 4 T_B^3 \epsilon A \sigma \quad (10)$$

where

k_1 = conductivity of air in calories-second⁻¹-centimeter⁻¹-degree⁻¹.

L = length of copper slug in centimeters

r_2 = radius of inner diameter of the built-in heater

r_1 = radius of outer diameter of the copper slug

T_B = bath temperature in degrees Kelvin

ϵ = net emissivity of the copper surface and factor for the reflectivity of the inside aluminum surface of the built-in heater This is dimensionless

A = area of the copper slug in square centimeters

σ the black body constant in calories-second⁻¹ centimeter⁻² absolute degree⁻⁴

An emissivity of approximately 0.7 was required to make the calculated sensitivities of Calorimeters 51 and 46 equal the measured sensitivities. Since the surfaces and dimensions involved in the evaluation of Equation 10 are similar to those involved in the calculations of the sensitivities of Calorimeters 51 and 46, the use of an emissivity of 0.7 seems justified for the evaluation of K_1 . Thus, from Equation 10,

$$K_1 = 0.0084 + 0.00396 = 0.01236 \text{ calories second}^{-1} \text{ degree}^{-1}.$$

Substituting these values of C_1 , C_2 , Q_1 , T_2 , K_2 , and K_1 in Equation 9 gives Equation 11 as a final result

$$P_H = 2,742,713 \frac{d^2V}{dt^2} + 14408.4 \frac{dV}{dt} + 7.59767 V \quad (11)$$

The general solution of Equation 11 is given by

$$V = 0.131619 P_H + Ae^{0.000594590t} + Be^{0.00466005t} \quad (12)$$

To evaluate the constants A and B of Equation 12 two initial conditions are needed. The first is $V = 0$ at $t = 0$ which reduces Equation 12 to

$$A + B = -0.131619 P_H \quad (13)$$

The second initial condition is $\frac{dV}{dt} = 0$ at $t = 0$. This, in effect, states that at zero time when heat is introduced at the copper slug, no heat reaches the bridge immediately. This second initial condition reduces Equation 12, after differentiating with respect to time to,

$$A = 7.8374 B$$

(14)

The simultaneous solution of Equation 13 and 14 results in

$$B = 0.0192499 P_H$$

and

$$A = -0.150869 P_H$$

The complete solution to the differential equation (Equation 11) is now

$$V = P_H \left[0.131619 \left(0.150869 e^{-0.000594590t} + 0.0191399 e^{0.00466005t} \right) \right] \quad (15)$$

Equation 15 is the heating curve of the bridge potential in microvolts as a function of time in seconds following the addition of P_H millicalories per hour of heat to the heater wound on the copper slug at zero time and henceforth maintained constant. After equilibrium has been reached, if the heat P_H is removed a cooling curve results which is an exact replica of the heating curve. Thus the equation of the cooling curve is given by Equation 16.

$$V = P_H \left(0.150869 e^{-0.000594590t} + 0.0192499 e^{0.00466005t} \right) \quad (16)$$

Several values of bridge potential were calculated using Equation 16 and are shown by Curve II of Figure 2.

The area under the cooling curve, which represents the total amount of heat that is retained by the calorimeter and the copper slug during the heating period is

$$\text{Area} = 0.0150869 P_H \int_0^{\infty} e^{-0.000594590t} dt + 0.0192499 P_H \int_0^{\infty} e^{0.00466005t} dt$$

which upon reduction gives

$$\text{Area} = 249.606 P_H \text{ microvolt seconds}$$

In the corresponding experiment 6.96163×10^5 millicalories per hour were supplied to the heater wound on the copper slug. The calculated area under the cooling curve would then be

$$6.96175 \times 10^5 \times 249.606 = 1.7377 \times 10^8 \text{ microvolt seconds.}$$

The experimental area as measured with a planimeter was 1.7352×10^8 microvolt-seconds. The calculated area thus agrees with the experimental area to within 0.15 per cent. This is one experimental check of the validity of Equation 15.

A second check may be made by investigation of the time to reach a value within 0.01 per cent of equilibrium bridge potential. This time, τ , can be calculated from Equation 15 after dropping the second exponential which is negligible at the time under consideration. The calculation gives $\tau = 262.0$ minutes.

Graph 2 of Figure 3 gave τ an experimental value of 270 minutes which differs from the calculated value by 3.05 per cent.

In the preceding derivations, heat at the rate of Q_1 calories per second was generated in the heater wound on the copper cylinder of heat capacity, C_1 . Now suppose that instead of heat being generated at C_1 heat at the rate of Q_2 calories per second is introduced in the built-in heater which in conjunction with the thermel has a heat capacity of C_2 calories per degree. No other change will be made. The steps in the derivation of the differential equation of heat flow are very similar to the preceding derivations which resulted in Equation 7. The final differential equation for this case is given by Equation 17.

$$\frac{C_1 C_2}{K_1} \frac{d^2 T_2}{dt^2} + \left[C_1 + C_2 + \frac{C_1 K_2}{K_1} \right] \frac{dT_2}{dt} + K_2 T_2 = Q_2 + \frac{C_1}{K_1} \frac{dQ_2}{dt} \quad (17)$$

It is interesting to note that the only difference between Equation 17 and Equation 7 is the term in the derivative of heat flow $\left[\frac{dQ_2}{dt} \right]$ in calories second⁻². In this problem heat at the rate of Q_2 calories per second is supplied at time zero and for any subsequent time, Q_2 is a constant. Since $\frac{dQ_2}{dt} = 0$, then Equation 17 reduces to the same form as Equation 7. The solution of Equation 7 in this case will not, however, be the same as that obtained in the first case. The first initial condition remains the same, that is, the bridge potential is zero at time zero. The second initial condition now is that at zero time the calorimeter proper, of heat capacity C_2 , changes temperature at a rate equal to the adiabatic rate of change of temperature of C_2 when receiving heat at the rate of Q_2 calories per second. This condition is stated in Equation 18 which holds at $t = 0$.

$$\frac{dT_2}{dt} = \frac{Q_2}{C_2} \text{ degrees-second}^{-1} \quad (18)$$

Equation 18 has been shown to be valid by direct experiment. Furthermore, it can be stated that at time zero no heat can escape from C_2 until a temperature difference exists between C_2 and the bath, i.e., between C_2 and C_1 . A temperature difference cannot arise until after heat has been stored in C_2 . Thus, all of the heat will be stored in C_2 at zero time.

With these initial conditions Equation 17 may be readily solved. The general solution is the same as before and is given again in Equation 19.

$$V = 0.131619 P_H + A e^{-0.000594590t} + B e^{-0.00466005t} \quad (19)$$

The first boundary condition that

$$V = 0 \quad \text{at} \quad t = 0$$

reduces Equation 19 to Equation 20.

$$A + B = 0.131619 P_H \quad (20)$$

The second boundary condition, that at

$$t = 0 \quad \frac{dT_2}{dt} = \frac{Q_2}{C_2}$$

reduces the derivative of Equation 19 to Equation 21.

$$-0.00059459 A - 0.00466005 B = 0.000396756 P_H \quad (21)$$

Solving Equations 20 and 21 simultaneously for A and B results in

$$A = -0.0532777 P_H$$

$$B = -0.0783413 P_H$$

The complete solution of Equation 19 becomes

$$V = P_H \left[0.131619 - 0.053278 e^{-0.000594590t} - 0.0783413 e^{-0.00466005t} \right] \quad (22)$$

As before, the equation of the cooling curve may be taken from Equation 22 and is

$$V = 0.053278 P_H e^{-0.000594590t} + 0.0783413 P_H e^{-0.0046601t} \quad (23)$$

The bridge potential for several values of time, t , were calculated from Equation 23 and are plotted on Curve I of Figure 2. The area under this curve corresponds to $106.42 P_H$ microvolt-seconds.

In the corresponding experiment 8.1503×10^5 millicalories-hour⁻¹ were generated in the built-in heater, so that the calculated area under the cooling curve is $106.42 \times 8.1503 \times 10^5 = 8.6735 \times 10^7$ microvolt-seconds. The area under the experimental cooling curve as measured with a planimeter was 8.75×10^7 microvolt-seconds, a difference of 0.87 per cent.

The time required to obtain a bridge potential within 0.01 per cent of the equilibrium value was calculated to be 232.8 minutes. The experimental time was 238.5 minutes, a difference of 2.40 per cent.

From an analytical point of view, it is quite apparent that the area under the cooling curve, after heat has been applied to the built-in heater and allowed to reach equilibrium, should be independent of the conductance, K_1 , of the air gap between the copper slug and the built-in heater. This can be checked quantitatively by taking the same heat capacity, C_1 , for the copper slug and assuming that the copper is in good metallic contact with the built-in heater. This means that K_1 becomes very large. As $K_1 \rightarrow \infty$, Equation 17 reduces to Equation 24.

$$(C_1 + C_2) \frac{dT_2}{dt} + K_2 T_2 = Q_2 \quad (24)$$

which by substitution can be transformed to

$$\frac{dV}{dt} + \frac{0.028215}{22.81} V = \frac{2.7778 \times 10^{-7} P_H}{22.81 \times 7.48 \times 10^{-5}}$$

The solution of this is given by

$$V = \frac{2.7778 \times 10^{-7} P_H}{0.028215 \times 7.48 \times 10^{-5}} \left[1 - e^{-\frac{0.028215}{22.81} t} \right]$$

The equation of the cooling curve becomes

$$V = 0.131619 P_H e^{-0.001237t} \quad (25)$$

The area under the curve of Equation 25 is

$$A = \frac{2.7778 \times 10^{-7} \times 22.81 P_H}{(0.028215)^2 \times 7.48 \times 10^{-5}} = 106.41 P_H \text{ microvolt-seconds,}$$

which agrees with the value $106.42 P_H$ microvolt-seconds found under the experimental cooling curve of Equation 23. Equation 25 has been plotted as Curve III in Figures 2 and 3.

It can be shown directly from Equation 7 that the area is independent of K_1 . Dividing all terms in Equation 7 by

$$\frac{C_1 C_2}{K_1}$$

gives

$$\frac{d^2 T_2}{dt^2} + \left(\frac{K_1}{C_1} + \frac{K_1}{C_2} + \frac{K_2}{C_2} \right) \frac{dT_2}{dt} + \frac{K_2 K_1}{C_1 C_2} T_2 = \frac{Q_2 K_1}{C_1 C_2} \quad (26)$$

Now let

$$b = \frac{K_1}{C_1} + \frac{K_1}{C_2} + \frac{K_2}{C_2}$$

and

$$c = \frac{K_2 K_1}{C_1 C_2}$$

The general solution of Equation 26 is

$$T_2 = \frac{Q_2}{K_2} + A e^{mt} + B e^{nt} \quad (27)$$

where

$$m = -\frac{b}{2} + \sqrt{\frac{b^2}{4} - c} \quad (28)$$

and

$$n = -\frac{b}{2} - \sqrt{\frac{b^2}{4} - c} \quad (29)$$

The constants A and B can be determined from the initial conditions that (a) at zero time T_2 is zero, and (b) the rate of change of T_2 is equal the adiabatic rate of heating of C_2 . Thus

$$A + B = -\frac{Q_2}{K_2} \quad (30)$$

$$mA + nB = \frac{Q_2}{C_2} \quad (31)$$

Solving Equations 30 and 31 for A and B gives

$$A = -\frac{Q_2 (C_2 n + K_2)}{K_2 C_2 (n - m)} \quad (32)$$

and

$$B = \frac{Q_2 (K_2 + C_2 m)}{K_2 C_2 (n - m)} \quad (33)$$

The area under the cooling curve is then given by Equation 34.

$$\text{Area} = \frac{Q_2(C_2 n + K_2)}{K_2 C_2 (n-m) m} + \frac{Q_2(K_2 + C_2 m)}{K_2 C_2 (n-m) n} \quad (34)$$

Equation 34 reduces to Equation 35 when the values of n and m given in Equations 28 and 29 are substituted into Equation 34.

$$\text{Area} = A_2 = \frac{Q_2(C_2 b - K_2)}{K_2 C_2 c} \quad (35)$$

By substituting the equivalents of b and c in Equation 35, Equation 36 is finally obtained.

$$\text{Area} = A_2 = \frac{Q_2(C_1 + C_2)}{K_2^2} \quad (36)$$

Equation 36 shows that the area is independent of K_1 . This fact is very important in relation to specific heat determinations made with the calorimeter. It was shown experimentally within the limits of measurement (about 0.5 per cent) that the area under the cooling curve was independent of the conductivity of the sample. Equation 36 gives additional verification of the accuracy of specific heat determinations. Previously some consideration was given to using the time to reach equilibrium as a criterion for measuring heat capacities. The amount of labor would be less for measuring an equilibrium time than for measuring an area. The areas under Equation 23 and the cooling curve equation of Equation 25 have already been shown to be equal. The time to reach a value within 0.01 per cent of equilibrium has already been calculated from Equation 23 to be 238.5 minutes. The time to reach a value within 0.01 per cent of equilibrium value is only 124.1 minutes from Equation 25. This difference in time results from a change of K_1 from 0.01236 to a K_1 approaching infinity and means that if the specific heat of the copper slug were calculated by the method of equilibrium times, an error of 250 per cent would be made. However, if Equation 1 represented the cooling curve of the empty calorimeter and also the cooling curve of the calorimeter plus sample, then either the area method or the time-of-equilibrium method would give identical values for the specific heat of the sample. Equation 1 would be valid in both cases so long as the heat capacity of the sample could be lumped to that of the calorimeter in Equation 1. This may be done for most metals in good contact with the calorimeter and for stirred liquid samples.

The difference in areas between the cooling curves (or heating curves), which result from equal quantities of heat supplied first to the built-in heater and then to the heater wound on the copper, will now be shown to be proportional to the conductance term, K_1 , of the air gap between the heaters. If the area difference in microvolt-seconds is divided by the sensitivity of the calorimeter in microvolt-calorie⁻¹-second the resulting calories of heat will represent the amount of additional heat retained in the copper slug by having heat introduced at that point. If this quantity of heat $\frac{A_1 - A_2}{S}$, is divided by the heat capacity of the copper, C_1 , the result is the additional temperature rise of the copper. If Q , the rate of heat generation in either heater, is divided by the additional temperature rise, $\frac{A_1 - A_2}{S C_1}$, the resulting quantity is K_1 , the conductance between heaters. The final result is given by Equation 37.

$$K_1 = \frac{S C_1 Q}{A_1 - A_2} \quad (37)$$

Equation 37 can also be derived from the solutions of Equations 7 and 17. The area, A_2 , in degree-seconds under the curve characterized by Q_2 has already been determined by Equation 36. The area, A_1 , under the curve characterized by Q_1 can be derived in a similar fashion and leads to the value given by Equation 38.

$$\text{Area} = A_1 = \frac{Q_1 (C_2 + C_1 + \frac{K_2}{K_1} C_1)}{K_2^2} \quad (38)$$

After letting $Q_1 = Q_2 = Q$ and subtracting Equation 36 from Equation 38, the difference in area is given by Equation 39.

$$A_1 - A_2 = \frac{Q C_1}{K_1 K_2} \quad (39)$$

or

$$K_1 = \frac{Q C_1}{K_2 (A_1 - A_2)} \quad (37a)$$

Since $K_2 = \frac{1}{S}$ with like units, Equation 37a and Equation 37 are identical.

The preceding discussion suggests a way of measuring the conductivities of various materials, especially poor conductors with low thermal capacities. Since the inverse of K_1 is actually equivalent to a sensitivity as referred to in calorimetry, Equation 37a could well be used for determining optimum gradient material for calorimeters. Since K_1 is actually a composite of the individual conductance terms contributed by conduction, radiation, and convection, the variations of K_1 with heat reflectors and connection baffles could also be studied by the same method.

The correct value of K_1 for the present experiment can now be calculated from the experimental cooling curves, and compared with the value of K_1 as obtained from Equation 10. Thus A_2 was found by a planimeter to equal 1.7352×10^8 microvolt-seconds with a heat input of 6.9616×10^6 millicalories-hour⁻¹. A_1 , when corrected to the same heat input, is equal to 7.474×10^7 microvolt-seconds. Substituting numerical values in Equation 37 ($S = 0.131619$ microvolt-hour-millicallorie⁻¹, $Q = 6.9616 \times 10^{-6}$ millicallorie-hour⁻¹, $C_1 = 13.45$ calories-degree⁻¹, and $A_1 - A_2 = 9.878 \times 10^7$ microvolt-seconds) gives a value for K_1 of 0.01247 calories-second⁻¹-degree⁻¹ which differs from the value of 0.01236 obtained from Equation 10 by only 0.9 per cent.

CONCLUSIONS

This report has shown that under certain conditions the solution of second order differential equations with given boundary conditions represents very closely the experimental cooling curves of calorimeters loaded with additional heat capacity. Also a method

of measuring conductivities of poor thermal conductors has been presented. This report has given added confidence to the method of measuring heat capacities by the area under the cooling curves.

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LEGEND OF FIGURE 1 AND FIGURE 2**CURVE I**

Cooling curve following a steady state with 8.150×10^5 millicalories of heat per hour in the built-in heater. Theoretical points calculated by Equation 23.

CURVE II

Cooling curve following a steady state with 6.9617×10^5 millicalories of heat per hour in the heater wound on the copper slug. Theoretical points calculated by Equation 16.

CURVE III

Theoretical cooling curve following a steady state with 8.150×10^5 millicalories of heat per hour in the built-in heater and with the same mass of copper assumed to be in good thermal contact with the calorimeter. Calculated by Equation 25.

AXIAL SECTION
OF THE
CALORIMETER AND COPPER SLUG.

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