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An Isochronal Differential Microcalorimeter*

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ABSTRACT

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MAS

An isochronal differential-type microcalorimeter has been designed and constructed. As a result of its simple design it is very easy to handle the samples and assemble the calorimeter. Important to the operation of the calorimeter is a program, also working on the differential principle, that provides linear temperature rise of the samples.

This calorimeter is used to measure very small energy releases such as those found in precipitation, stored energy, etc. It is demonstrated that the calorimeter is easily capable of measuring 0.005 cal with a probable error of the order of 1% to 2%.

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INTRODUCTION

In order to measure the small energy released in processes such as stored energy release and precipitation, a microcalorimeter of the differential type is required. In recent years some isothermal microcalorimeters have been constructed using differential techniques. The Borelius¹ type calorimeter of Gordon² is capable of detecting 3×10^{-3} cal/hr. Calorimeters constructed by Orr, et. al.³ and Attree, et. al.⁴ have sensitivities near that of Gordon. It is interesting to note that the development of the breaker-type DC amplifier has been a boon to microcalorimeters of both isothermal and isochronal type.

The microcalorimeter described here is different from those above in that the temperature is a linear function of time rather than constant. Another feature of this calorimeter is the sensitive temperature controller that is used to keep the temperature difference between the calorimeter and its surroundings equal to zero. The fact that only one differential thermocouple is used to measure energy release makes for considerable ease in assembly.

DESCRIPTION OF THE CALORIMETER

The main parts of the calorimeter are a copper block which serves as a heat reservoir, an evacuated Pyrex tube which contains the copper block, and an oil bath surrounding the Pyrex tube. The copper block, which has a mass of about 200 grams and to which the samples are fastened, is shown in Fig. 1a. This block is a cylinder of 1.5 inches long and 1.0 inches in diameter.

Two holes in the block receive the samples. (We have been using iron cylinders 0.2 cm in diameter, 2.0 cm long and mass of about 0.75 grams. For

demonstration purposes we place a small amount of a low melting point metal on one, hereafter known as the sample. The other cylinder is referred to as the dummy.) The sample and dummy are connected by an iron wire (0.013 in diameter) which rests on the thin bridge that separates the two holes. A small, thin strip of copper (0.040 in thick, ~ 200 mg) is secured to the block by screws and holds the iron support-wire in place. It is important that this copper strip be of very small mass so that any variation of the thermal contact with the block will not appreciably affect the heating of the samples. Energy for heating the copper block is supplied by storage batteries. The heating coil is insulated from the block by a fiberglass sleeve and consists of 14 ohms of 0.008 in constantan wire. The block temperature is monitored by a copper-constantan thermocouple that is cemented to the block with Sauereisen cement. A constantan wire is spot welded to each iron sample and, with the iron support wire, forms a differential thermocouple. All thermocouples are made from 0.003 in wire to reduce heat losses.

The copper block rests on a mica pedestal at the bottom of a Pyrex tube of 35 cm length and 3.5 cm diameter and is held away from the walls of the tube by two insulating rings. Heater leads and thermocouple wires are brought out of the tube via feed-through insulators placed in the cap of the tube (see Fig. 1b). The pyrex tube is evacuated to a pressure of 10^{-4} mm Hg or less. This vacuum eliminates convection currents within the tube and insures that the thermal conductivity of the residual gas is at least two orders of magnitude less than the conductivity of the support wire.

Surrounding the Pyrex tube is a dewar filled with Dow Corning XF-10184 silicone heat transfer fluid. This fluid is liquid from below room temperature to its rated flash point of 370°C . The oil is heated by two

500 watt A.C. heaters and is stirred with a motor driven propeller. A copper-constantan thermocouple is placed in the oil bath and, with the thermocouple in the copper block, forms a differential thermocouple that provides the signal for the bath temperature controller. The thermocouple in the bath is attached to a piece of copper (not to be confused with the copper block in the Pyrex tube) which acts as a thermal stabilizer so that small thermal gradients in the oil will not cause the controller to be constantly turning on or off. This is particularly important for the lower temperatures where the viscosity of the oil prevents its mixing as rapidly as at the higher temperatures. The total thermal capacity of the system is about 1200 calories.

An important part of the equipment associated with the calorimeter is the temperature controller. This controls the power to the knife blade heaters in the oil bath. One of the knife blade heaters is powered by a variable transformer and is the largest source of heat. The second heater is powered from a voltage supply that is modulated by a mercury wetted relay and is used to keep the temperature difference between the copper block and the oil bath equal to zero. Consequently, since there is no heat flow between the copper block and the oil bath, all of the power put into the heater of the copper block goes into raising the temperature of the block. This temperature rise will be linear since the power input is constant. The difference of the voltages of the thermocouples in the bath and the copper block is fed into a Brown Electronic amplifier that has been modified by the Brookhaven Instrumentation Division. This difference signal is amplified and used to control the mercury wetted relay (Clare HG-1002). In this way the temperature difference between the bath and the copper block is held to $\pm 0.05^{\circ}\text{C}$ and a temperature rise constant to ± 0.03 . See Fig. 2 for a circuit diagram of the controller.

The energy release is determined by measuring the temperature difference between the sample and the dummy with an iron-constantan differential thermocouple. The iron support wire for the sample and dummy forms the common leg of this thermocouple and 0.003 inch constantan wires spot welded to each of the samples (or dummies) form the other two legs. A Keithley model 150AR microvoltmeter amplifies the signal of this thermocouple and its output is placed on one point of a multipoint recorder. An additional thermocouple in the bath measures the oil temperature which is recorded by a second point of the multipoint recorder.

ANALYSIS OF DATA

Consider first the case of the heating of the samples via the iron support wires. Let T be the temperature of the reservoir, T_1 the temperature of one sample, and T_2 the temperature of the other sample. Then the heat conducted to the samples from the reservoir is

$$\frac{dq_1}{dt} = \frac{K_1 S_1}{\ell_1} (T - T_1) \quad (1)$$

where t is the time, q is the heat transferred, K is the thermal conductivity of the support wire, S is the cross section of the wire, and ℓ is the length of the wire. The subscripts, 1, refer to the sample and subscripts, 2, refer to the dummy. The heat required to raise the temperature of the sample is

$$\frac{dq_1}{dt} = m_1 c_1 \frac{dT_1}{dt} \quad (2)$$

where m is the mass of the sample and c is its specific heat. Eliminating $\frac{dq}{dt}$ from equs. (1) and (2) we have

$$\frac{dT_1}{dt} = \frac{K_1 S_1}{m_1 c_1 \ell_1} (T - T_1) \quad (3)$$

Now we define $\frac{dT}{dt} \equiv R_o$. Inserting this into equ. (3) we get

$$\frac{d(T - T_1)}{dt} = R_o - \frac{K_1 S_1}{m_1 c_1 \ell_1} (T - T_1) \quad (4a)$$

$$\text{or} \quad \frac{d(\Delta T)_1}{dt} = R_o - \frac{K_1 S_1}{m_1 c_1 \ell_1} (\Delta T)_1 \quad (4b)$$

The solution to equ. (4b) is

$$(\Delta T)_1 = \frac{m_1 c_1 \ell_1}{K_1 S_1} R_o \left\{ 1 - \exp \left(- \frac{K_1 S_1}{m_1 c_1 \ell_1} t \right) \right\} \quad (5)$$

$(\Delta T)_1$ is the temperature difference between one sample and the copper block. The differential thermocouple, however, measures the temperature difference between the two samples (or dummies). Hence,

$$(\Delta T)_{12} = (\Delta T)_1 - (\Delta T)_2 = \left\{ \left(\frac{m c \ell}{K S} \right)_1 - \left(\frac{m c \ell}{K S} \right)_2 \right\} R_o$$

$$- \left\{ \left(\frac{m c \ell}{K S} \right)_1 \exp \left[- \left(\frac{K S}{m c \ell} \right)_1 t \right] - \left(\frac{m c \ell}{K S} \right)_2 \exp \left[- \left(\frac{K S}{m c \ell} \right)_2 t \right] \right\} R_o$$

(6)

One trace of the recorder is a plot of $(\Delta T)_{12}$ vs. t . If R_0 is constant and if $\left(\frac{mcl}{KS}\right)_1 = \left(\frac{mcl}{KS}\right)_2$ then this plot is a straight line of zero slope. If R_0 is constant but $\left(\frac{mcl}{KS}\right)_1 \neq \left(\frac{mcl}{KS}\right)_2$ then the plot starts out with an exponential rise and eventually levels off to a constant $(\Delta T)_{12}$ determined by the magnitude of $\left(\frac{mcl}{KS}\right)_1 - \left(\frac{mcl}{KS}\right)_2$. Since the value of R_0 is usually a slowly varying function of time, the plot of $(\Delta T)_{12}$ vs. t has a non-zero slope after the exponential term has decayed. For instance, if $R_0 = R(1-rt)$ then

$$(\Delta T) = \left(\frac{mcl}{KS}\right)_1 R + \left(\frac{mcl}{KS}\right)_1 \left\{ \left(\frac{mcl}{KS}\right)_1 - t \right\} rR + R \left(\frac{mcl}{KS}\right)_1 \exp \left[- \left(\frac{KS}{mcl}\right)_1 t \right] \quad (7)$$

In this case, after the exponential term has decayed, the plot of $(\Delta T)_{12}$ vs. t has a slope dependent on r . This non-zero slope can be seen in the $(\Delta T)_{12}$ trace in Fig. 3.

Consider now, the case of energy being supplied to, or taken from, one of the samples and not the other. The measured energy release or absorption will show up as a difference in the energy absorbed from the reservoir. Using equ. (1) we write the energy of the reaction as the energy transferred to the sample on a run when the reaction takes place, subscript A, minus the energy transferred when there is no reaction, subscript B.

$$q = \left(\frac{KS}{\ell}\right)_1 \int_A (T - T_1) dt - \left(\frac{KS}{\ell}\right)_1 \int_B (T - T_1) dt \quad (8)$$

Now substitute for T in each term on the right side of equ. (8) according to

$$(\Delta T)_2 = T - T_2 \quad (9)$$

Then

$$q = \left(\frac{KS}{\ell} \right) \int_1^A [(\Delta T)_2 + T_2 - T_1] dt - \left(\frac{KS}{\ell} \right) \int_1^B [(\Delta T)_2 + T_2 - T_1] dt \quad (10)$$

Since the integration over $(\Delta T)_2$ is the same for both A and B we have the energy of the reaction proportional to the Difference in the areas under the $(\Delta T)_{12}$ vs. t curves of runs A and B.

RESULTS

Figure 3 is the recorder trace of $(\Delta T)_{12}$ vs. t for a 1.20 mg piece of Rose's metal as a sample. The area of this peak is 0.36 in.² and represents an energy of 0.0099 cal. On this trace one inch on the time scale is 10 min. and one inch on the $(\Delta T)_{12}$ scale is 0.052°C. The accuracy of the measurement can be increased by changing the temperature scale and time scale. Referring to equ. (10), we see that the sensitivity can also be increased by changing the value of the proportionality constant, $\frac{KS}{\ell}$. Figure 4a is a replica of a trace of $(\Delta T)_{12}$ vs. t for 1.55 mg Rose's metal where one inch on the time scale was 5 min., one inch on the $(\Delta T)_{12}$ scale was 0.017°C, and the value of $\frac{KS}{\ell}$ was decreased to approximately 1/2 its value for Figure 3. The area under the peak in Figure 4a was 4.50 inch² and corresponds to an energy of 0.0128 cal. Figure 4b is a replica of a trace for 1.00 mg of tin using the same conditions as in Figure 3b. Since the temperature controller keeps the bath temperature to within $\pm 0.05^\circ\text{C}$ of the copper reservoir temperature, we then know the reservoir temperature.

Actually the results demonstrated here for tin and Rose's metal are only used to determine the proportionality factor $\frac{KS}{\ell}$. In practice it is difficult

to determine the length ℓ so that the results are best found by calibrating the constant with a reaction of known energy (e.g., heat of fusion of a metal). The accuracy of a measurement then depends on the accuracy of the area measurement and the value of the heat of fusion of the metal used for calibration. Both of these are known within an error of about 1%; the resulting error for a determination in the calorimeter is, therefore, about 2%. Using a heating rate of $1^{\circ}\text{C}/\text{min}$, data (not shown) was obtained with this accuracy for energy releases of 0.005 cal. The accuracy will vary since the time required to complete a given reaction depends on the heating rate of the calorimeter.

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FIGURE CAPTIONS

- Fig. 1a Cross section of copper heat reservoir showing placement of samples and thermocouples. Electric insulation for the copper-constantan thermocouple is provided by Sauereisen cement. Drawing not to scale.
- Fig. 1b Pyrex tube showing location of reservoir and thermocouple connections. The reservoir sits on a mica pedestal.
- Fig. 2 Circuit diagram of bath-temperature controller showing modification of Brown amplifier.
- Fig. 3 Recorder trace of $(\Delta T)_{12}$ vs. t for 1.20 mg Rose's metal. One major division on the ordinate is $0.75 \mu v$. One major division on the time scale is 10 min. Area is 0.36 in.^2 .
- Fig. 4a Replica of recorder trace for 1.55 mg Rose's metal. The base line has been subtracted from the value for $(\Delta T)_{12}$. The area was 4.50 in.^2 , corresponding to 0.0128 cal.
- Fig. 4b Replica of a recorder trace for 1.00 mg of tin. The base line has been subtracted from the value for $(\Delta T)_{12}$. The area was 4.71 in.^2 , corresponding to 0.0140 cal.

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FIGURE 1

MODIFICATION OF BROWN AMPLIFIER

FIGURE 2

FIGURE 3

FIGURE 4

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