510. *Improvements in Temperature Measurement for a Recently Described Heat-of-mixing Calorimeter*

By E. A. FAULKNER, M. L. McGLASHAN, and D. STUBLEY

The resistance thermometry of Larkin and McGlashan's heat-of-mixing calorimeter has been improved by operating the bridge with low frequency A.C. instead of with D.C. In particular fluctuations due to thermal e.m.f.'s have been eliminated, the power dissipated in the resistance thermometer has been substantially reduced, and the output voltage has been amplified sufficiently to operate an ordinary pen recorder.

IMPROVEMENTS have been made to the resistance thermometry of Larkin and McGlashan's heat-of-mixing calorimeter[1] with the following results. (1) D.C. potential fluctuations due to thermal e.m.f.'s have now been eliminated. (2) The power dissipated by the resistance thermometer (thermistors) in the Wheatstone bridge has been reduced by about a factor of ten. (3) The output voltage has been amplified sufficiently to operate an ordinary 10 mv pen recorder, thereby eliminating the need for point-by-point plotting of galvanometer–time readings.

These improvements have been effected by operating the thermistor bridge with about 15 cycles/sec. A.C. instead of with D.C. At this low frequency the bridge is still effectively

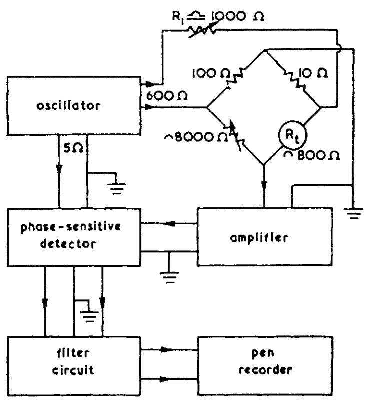

FIGURE 1. Block diagram of measuring circuit

a resistance bridge and no modifications are necessary, although it is better to connect the thermistors in series than in parallel to increase the output voltage from the bridge. After amplification the bridge output is rectified in a phase-sensitive detector. The use of such an element rather than a simple rectifier is essential if the required linearity is to be obtained, and has the additional advantage of improving the signal–noise ratio of the system by reducing the bandwidth.

A general-purpose phase detector of the required linearity and zero stability (zero drift less than $\pm 0{\cdot}025\%$ full scale deflexion per hour) has recently been developed[2] and we have used the commercial version of this instrument.

The circuit diagram is shown in Figure 1. The A.C. generator is an Advance Electronics Ltd., type J1 oscillator; this instrument has two outputs: one of impedance 600 Ω with both ends floating which is used to energise the bridge, the other of impedance 5 Ω with one side earthed, which supplies the reference signal for the phase-sensitive detector.

[1] J. A. Larkin and M. L. McGlashan, *J.*, 1961, 3425.
[2] E. A. Faulkner and R. H. O. Stannett, *Electronic Engineering*, 1964, **36**, 159.

The bridge output is fed *via* a Brookdeal type LA635 low-noise amplifier to a Brookdeal type PD629 phase-sensitive detector, the D.C. signal from which is applied to a Honeywell 10 mv recorder (type 153 X 17). A filtering circuit (Figure 2) is interposed between the phase-sensitive detector and the recorder to eliminate unwanted A.C. components and to increase the time constant of the detection system.

The input impedance of the amplifier is about 0·5 MΩ which is much larger than the thermistor resistance. Provided that the resistor in series with the thermistors has a high enough value (*e.g.*, ten times the thermistor resistance) and that the resistors in the

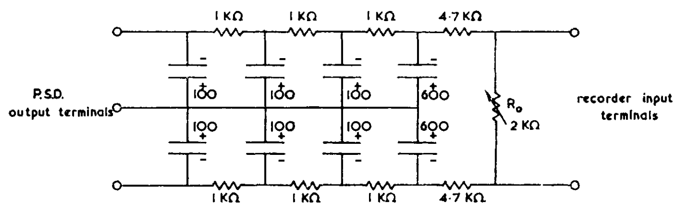

FIGURE 2. Circuit diagram of filter (capacitances in μF)

other arms have a low enough value, the voltage output of the bridge for a given temperature change is proportional to the product of the thermistor resistance R_t and the current flowing i_t. The power dissipated in the thermistors is $R_t i_t^2$ and therefore, by increase of R_t and decrease of i_t, the power can be reduced whilst keeping the output signal constant.

Most D.C. amplifiers have a much lower input impedance than the present A.C. amplifier and the input impedance of the mirror galvanometer used previously was 33 Ω. The value of R_t is limited when using such amplifiers or galvanometers of low impedance; the fact that R_t can be increased is one of the main advantages to be gained by using an A.C. system in preference to a D.C. system.

In recent work with the previous D.C. set-up considerable difficulty has been experienced in obtaining a stable galvanometer–time baseline; it is thought that thermal e.m.f.'s in the bridge circuit were the primary cause of the instability. By converting the bridge from D.C. to A.C. the effects of these thermal e.m.f.'s have now been eliminated.

EXPERIMENTAL

In the present case $R_t \simeq 800$ Ω obtained by wiring two Stantel M52 thermistors in series. The two fixed arms of the bridge are wire-wound standard resistors of 100 and 10 Ω. The fourth arm of the bridge is a six-decade resistance box with a value of $\simeq 8000$ Ω actually in the circuit.

Twisted wiring was used wherever possible in the construction of the Wheatstone bridge and the wires were kept as short as possible in order to reduce 50 c./sec. pick-up. The bridge output signal is fed into the amplifier through coaxial cable which is also used in connexions between the amplifier and phase-sensitive detector and between the oscillator reference signal and phase-sensitive detector.

In all respects other than the wiring of the thermistors the details of the construction of the calorimeter and its mode of operation are identical with those described earlier.[1]

The calorimeter is loaded into the thermostat bath and allowed to reach thermal equilibrium over a period of several hours. The electronic instruments, apart from the chart drive, are left on all the time to ensure stability of operation. As a further precaution the oscillator, amplifier, and phase-sensitive detector are run off a constant-voltage transformer (Advance Electronics Ltd., type CV100).

The oscillator output voltage E is adjusted to give a reference signal of suitable amplitude as shown on the " magic eye " incorporated in the phase-sensitive detector (a dark band of about 2 mm. is suggested) and the value of R_1 (see Figure 1) is then set to give the required current through the Wheatstone bridge. In the present experiments $E \simeq 10$ v and $R_1 \simeq 1000$ Ω.

The gain of the amplifier is set to its lowest value and rough balancing of the bridge is achieved by adjusting the value of the resistance box in the variable arm of the bridge until the magic eye in the phase-sensitive detector monitoring the amplifier output shows minimum signal. The amplifier gain is then increased gradually and adjustments are made to the resistance box to keep the signal on the magic eye to a minimum.

At this point the chart drive is switched on and the resistor R_0 (0—2 kΩ wire-wound variable resistor) across the recorder input terminals is adjusted to give a suitable pen response (about 1000 cm. deg.$^{-1}$ in the present experiments).

The gain control in the pen recorder amplifier is set as high as possible to obtain optimum response from the instrument without causing the pen to " hunt."

Finally, it has been found necessary to vary slightly the frequency of the signal from the oscillator to eliminate " beating " between the higher harmonics of the oscillator signal and the 50 c./sec. in the pen-recorder. This phenomenon of " beating " caused a broadening of the pen trace but in no way affected the level of the D.C. signal being recorded. With a little practice it became quite easy to eliminate " beating " and not to confuse it with " hunting " caused by too high a gain in the recorder amplifier.

Once these preliminary adjustments have been made the electronic instruments require no further attention during an experiment. If a series of experiments is being performed at a given temperature the only day-to-day adjustment to be made is the slight adjustment of the variable resistance box in the bridge to set the pen to a suitable point on the chart scale.

RESULTS

A photograph of a typical pen trace obtained in an experiment on the system benzene–carbon tetrachloride is shown in Figure 3. The analysis of such a plot has been fully described in the previous Paper.[1]

It is difficult to assign a definite meaning to the term " signal-to-noise ratio " in considering the relative performances of the present A.C. method and the earlier D.C. method. In one respect the magnitude of the slope of the baseline, due to heating of the calorimeter by the

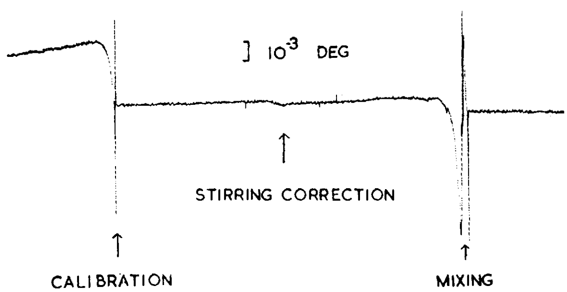

FIGURE 3. A typical recording

thermistor bridge current, can be considered as noise. In this case, the noise developed in the A.C. system has been reduced by a factor of about ten compared with the D.C. system.

The other more usual meaning of the word noise in the present context refers to random fluctuations of the pen trace or galvanometer reading. In the D.C. system the main source of this noise is thought to be thermal e.m.f.'s. These can be reduced considerably, particularly by thermostatting the room where the work is being done and by careful insulation of terminals and junctions. However, in our unthermostatted laboratory the effects of thermal e.m.f.'s varied from day to day and often gave galvanometer deflexions corresponding to temperature changes of as much as $\pm 5 \times 10^{-4}$ deg.

In the A.C. system noise of this type is much lower and it has been found that the noise originates almost entirely within the amplifier rather than in the bridge. Incorporated into the Brookdeal LA635 amplifier is a preamplifier which has very low noise characteristics and if it is desired to operate the system at its limits, then one must switch in the preamplifier circuit.

An experiment was performed in which the A.C. system was run at its maximum sensitivity and the signal–noise ratio observed. The relevant factors are given below together with the corresponding figures for the D.C. system.

	A.C.	D.C.
Power dissipation in thermistors	$4{\cdot}7 \times 10^{-6}$ w	$4{\cdot}0 \times 10^{-5}$ w
Rate of warm-up of calorimeter due to thermistor current	$7{\cdot}6 \times 10^{-6}$ deg./min.	$6{\cdot}5 \times 10^{-5}$ deg./min.
Random fluctuations correspond to	$\pm 1 \times 10^{-5}$ deg.	$\pm 50 \times 10^{-5}$ deg.

M. L. M. and D. S. are grateful for the award of a D.S.I.R. Research Grant.

DEPARTMENTS OF CHEMISTRY AND PHYSICS, THE UNIVERSITY, READING.
[Present address (M. L. M.): DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, EXETER.] [*Received, November 9th*, 1964.]