論 文

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A New Method for the Precise Thermometry Using Thermistor Bridges

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A new method is proposed for a highly precise thermometry which is used in the reaction calorimetry. The adoption of the thermistor bridge with a constant voltage supply and the improvement of the method for the conversion of unbalanced voltage of bridge into temperature make it possible to determine the temperature with the precision of $2\sim5\times10^{-4}$ K.

1. Introduction

The resistance R_t of a thermistor depends on the absolute temperature T non-linearly, and is approximately represented by the following equation,[1]

$$R_t = A\exp\left(\frac{B}{T+C}\right) \tag{1}$$

where A, B, and C are constant over a limited temperature range.

The thermistor thermometry utilizing the large negative temperature coefficient of resistance is widely adopted for the precise measurement of small temperature change, such as the reaction calorimetry.[2),3)]

In order to use thermistor as a temperature sensor in the reaction calorimetry, two methods have been used. In the first method, the resistance of thermistor is directly measured by means of the Wheatstone bridge, and the temperature is calculated by Eq. (1).[4] In the second method, the unbalanced voltage of the bridge circuit is measured.[5]

The modern calorimetry has become to adopt automated data acquisition system. The first method needs complicated and expensive measuring apparatus.[6] Today, the reliable constant voltage IC and microprocessor system are available at a reasonable price, so it is preferable to measure the unbalanced voltage. When a constant voltage is applied between A and C, as shown in Fig. 1, the unbalanced voltage E appears between B and D. It is represented by the following equation,

$$E = \frac{R_1R_t - R_2R_3}{(R_1+R_3)(R_2+R_t)}V \tag{2}$$

Equations (1) and (2) show that E has a non-linear dependance on T. Many methods have been proposed to convert the unbalanced voltage into temperature. They are the use of complicated equation directly solved from Eq. (2),[7] the representation of T by the power series of E,[8] and the design of modified bridge circuits which give linear relationships between T and E approximately.[5),9)]

Recent advances of computer have made it possible to convert the unbalanced voltage into temperature easily. When computers are available it is favorable that the circuit is as simple as possible and that the data are stored in a microprocessor system, since conversion of E into temperature is carried out easily by the microprocessor or the high speed host computer.

When a temperature precision of 1 mK is required, the relative error in T has to be of the order of 10^{-6}. So R_t and the parameters in Eqs. (1) and (2) must be determined with a precision of 10^{-6}. This kind of highly precise measurement is very difficult, and sometimes a relatively large round off errors are included in the data processing.

This paper reports a new method for the conversions of unbalanced voltage into temperature and its satisfactory results.

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2. Theoretical

Equation (2) is rewritten as follows,

$$E = \frac{rF-1}{(1+r)(1+F)}V \qquad (3)$$

where $r=R_1/R_3$ and $F=R_t/R_2$. Equation (3) is reformulated into the following equation,

$$F=\frac{1}{r}\frac{1+\frac{1+r}{V}E}{1-\frac{1+r}{Vr}E} \qquad (4)$$

It is noteworthy that F is determined by the measured values, r, V, and E.

Substitution of $R_t=R_2F$ into Eq. (1) gives

$$T=B/\ln(R_2F/A)-C \qquad (5)$$

The value of C is usually 20～40 K, and the first term in the right hand side of Eq. (5) is about 300 K. In order to obtain the precision of temperature within 10^{-3} K, the value of B must be determined with a precision of 10^{-6}. Such a high precision is difficult to obtain. So, instead of Eq. (1), the following expression is adopted.

$$R_t = (R_2/r)\exp\{B(\frac{1}{T+C}-\frac{1}{T_0+C})\} \qquad (6)$$

where T_0 is a temperature at $E=0$. When $T=T_0$, $R_t=R_2/r$. Rewriting Eq. (6) using $R_t=R_2F$, one obtains

$$rF = \exp\{\frac{-B(T-T_0)}{(T_0+C)[(T_0+C)+(T-T_0)]}\} \qquad (7)$$

Equation (7) yields

$$T-T_0=-\frac{(T_0+C)^2}{B}\frac{\ln rF}{1+\frac{\ln rF}{(\frac{B}{T_0+C})}} \qquad (8)$$

In the solution calorimetry $T-T_0$ is generally less than 3 K, and it is not difficult to obtain T_0 with a precision of 10^{-3} K. Since B is several thousands of Kelvin, the determination of B to the order of 10^{-1} K is sufficient for the required precision.

The calculation of T by Eq. (1) needs determination of three parameters, A, B, and C. However, when Eq. (8) is employed, only two parameters, B and C, are required to be determined. In other words, Eq. (8) is more advantageous than Eq. (1) for the precise determination of T.

3. Experimental

The thermistor used in the thermistor bridge shown in Fig. 1 was supplied by Victory Engineering Corp., and had a nominal resistance of 10 kΩ at 25°C. R_1, R_2 and R_3 were precise metal film resistors with temperature coefficients of less than 5 ppm, and had nominal resistances of 1, 3 and 30 kΩ, respectively. The resistor circuit kept in a glass tube filled with insulation oil was placed in a thermostated water bath. A constant voltage supplied from a stabilized d.c. power source was applied to the thermistor bridge, and the unbalanced voltage was measured by a digital voltmeter. The BCD coded output was fed into a microprocessor system, and the data were printed out. For the calibration of temperature a Hewlett-Packard quartz thermometer 2804A was used. Its resolution was of 0.0001 K. The thermistor and the quartz thermometer were set in a water bath. The unbalanced voltage E and the temperature T were measured in the range of 22～26°C at intervals of about 0.5°C. Measurement was repeated five times at every temperature. T_0 is evaluated by the interporation of T vs E plot independently observed at near $E=0$.

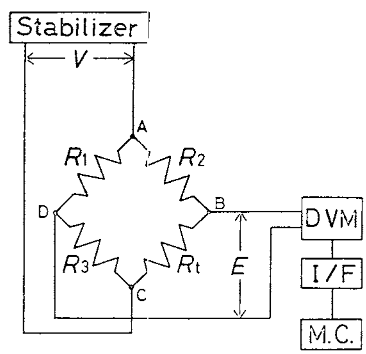

Fig. 1 Thermistor bridge and data sampling system

4. Results and discussion

The measurement of E against T was repeated three times. The results are given in Fig. 2. The resistance R_t of thermistor was calculated by the relation $R_t=R_2F$ and Eq. (4). Instrumental parameters, R_2, r, and V were determined by the measurements of electric potential at each point in the bridge circuit. They are given in Table 1.

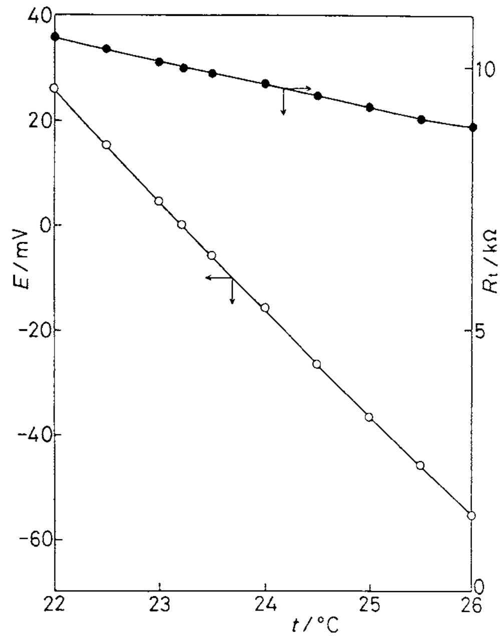

Fig. 2 The unbalanced voltage of thermistor bridge and the resistance of thermistor in the range of 22 ~ 26°C

Table 1 Values of instrumental and thermistor parameters

Instrumental parameters		
T_0 = 296.3634 K		
R_2 = 30.036 kΩ		
r = 2.9941		
V = 2.5170 V		
Thermistor parameters		
	for Eq. (1)	for Eq. (9)
B/K	4696.2	3872.8
C/K	30.025	
$S(E)$*/mV	5.15×10^{-3}	1.17×10^{-2}
$S(T)$**/K	2.55×10^{-4}	5.85×10^{-4}

* defined by Eq. (10)
** defined by Eq. (11)

In order to determine the thermistor parameters, B and C, least squares fitting was made for Eq. (7). The left hand side of Eq. (7) was calculated by Eq. (4). The results are also given in Table 1.

In order to see the precision of the present method the differences between the observed and calculated temperatures are plotted in Fig. 3 (a). Random errors up to $\pm 5 \times 10^{-4}$ K are seen. Some systematic ones depending on each run are also found. These errors are probably caused by the non-uniform temperature distribution in a water bath.

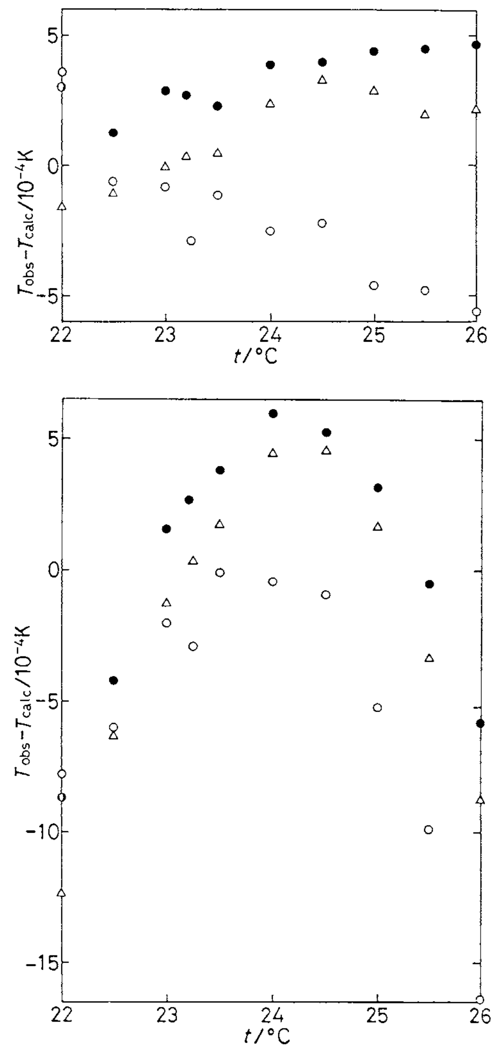

Fig. 3 Temperature dependance of ($T_{obs} - T_{calc}$)
(a) by the employment of Eq. (1)
(b) Eq. (9)
● : 1st run
△ : 2nd run
○ : 3rd run

The temperature dependence of thermistor resistance is usually represented by the equation,

$$R_t = A \exp (B/T) \qquad (9)$$

To evaluate the errors when this conventional expression was employed, the parameter B were determined by the least squares fitting. Result are also given in Table 1. Figure 3 (b) gives the differences between the observed and calculated temperatures. It is clearly seen that large systematic errors up to 10^{-3} K are inevitable when Eq. (9) is employed.

As a method of evaluation, $S(E)$ and $S(T)$, defined by Eqs. (10) and (11), were calculated:

$$S(E) = \frac{1}{n}\sum\left|E_i(\mathrm{obs}) - E_i(\mathrm{calc})\right| \qquad (10)$$

and

$$S(T) = \frac{1}{n}\sum\left|T_i(\mathrm{obs}) - T_i(\mathrm{calc})\right| \qquad (11)$$

where Eqs. (3) and (7) are used to calculate E_i(calc), and Eqs. (4) and (8) are used for T_i(calc).

From these values in Table 1, it is concluded that the present method of calibration of unbalanced voltages of a thermistor bridge circuit has a precision of $2 \sim 5 \times 10^{-4}$ K.

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