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# SOME IMPROVEMENTS IN THE HEAT EXCHANGE CALORIMETER FOR ESTIMATION OF SMALL HEAT EFFECTS

SHUKO FUJIEDA

*Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112 (Japan)*

JUNKO KAWAHITO

*The Doctoral Research Course in Human Culture, Ochanomizu University, Bunkyo-ku, Tokyo 112 (Japan)*

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## ABSTRACT

In heat exchange calorimetry, sample and reference vessels are fixed in a temperature-controlled water-bath. Heat evolved in the sample vessel is exchanged freely with ambient water. Therefore, the measuring temperature can be easily selected by changing the temperature of the bath water. In the estimation of small heat effects, the measurement of temperature via a thermistor used as a sensor must be accurate and precise. Some improvements in the water-bath of the heat exchange calorimeter are reported.

To find the influence of close agreement between $B$ constants on the thermal fluctuation range of the bath water, a pair of thermistors with $B$ constants of 3396 and 3342 K, used in the sample and reference vessels respectively, were compared with thermistors with $B$ values of 3404.09 and 3404.07 K, respectively.

A hand-made heater block was introduced into the temperature control system of the water-bath, and was found to shorten the delay time of heat evolution. The heat evolution from an area instead of a point source was effective in mixing the water throughout the water-bath. To demonstrate the proposed improvements, the total heat effects by electric heating were compared in the range 0.5–0.05 J. On the whole, reasonable repeatability and simple handling of the vessels were obtained.

## INTRODUCTION

In heat exchange calorimetry [1], sample and reference vessels are fixed differentially in a temperature-controlled water-bath. Heat evolved in the sample vessel as a result of chemical reactions or electrical heating is exchanged efficiently with the ambient water. The thermal behavior is expressed by a simple differential equation which obeys the Newtonian cooling law. A thermistor as a temperature sensor is installed in each vessel and forms part of a Wheatstone bridge. The temperature observed in the

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sample vessel $\theta$, as opposed to that in the reference vessel, is converted to an electric signal $E_0$. The $\theta$ may include a delay in response, which is related to the real temperature by a simple differential equation. The heating rate $q$ and the total heat effect $Q$ are estimated from $E_0$ followed by analogue, digital, and hybrid computations. In calorimetry, therefore, the measuring temperature is selected easily by changing the temperature of the bath water.

The accuracy and precision of the observed values are highly dependent upon the thermal fluctuation and temperature drift of the bath water. For estimation of a small heat effect, in particular, observed values of good quality are indispensable, even if any data processing is applied. For this reason, a temperature control system for a precision water-bath by the modified PID (proportional, integral, and differential) method has been proposed earlier [2]. Optronic heating system without immersion of a heater element in the sample or reference solution has also been reported for measurements of joule heat in calorimetry of a smaller heat effect which was prevented from thermal leakage via heater wires [3].

In this paper, the facilities needed in the water-bath for accurate observation of $\theta$ were improved. A pair of thermistors in each vessel was changed to a new product with better resistance vs. temperature characteristic. A hand-made heater block was used to diminish delay time of heat evolution in temperature control of the bath water. At the same time, an area rather than a point heat source was preferred. To demonstrate the extent of improvement, joule heats from 0.5–0.05 J were observed.

## EXPERIMENTAL

### *Apparatus*

The fundamental concept and essential parts of the assembled heat exchange calorimeter were almost the same as reported earlier [4].

A plastic box of 27 cm × 47 cm × 28 cm, which was used as the bath, was covered with Styrofoam insulator boards of 3 cm thickness and was filled with 28 $dm^3$ of water. The temperature of the bath water was automatically controlled by modified PID programs [2] executed on an 8-bit microcomputer (M5, SORD Co, Tokyo, operated with Z-80, Zilog). The fluctuation range was within about $\pm 2$ per 10000 K. Cooling water, which was kept a little below the set temperature with an electronic cooler (CTE-220 and CTR-220, Komatsu Electronics, Tokyo), was circulated by using a glass spiral tubing, shown as C in Fig. 1A. The difference between the set temperature and the observed temperature of bath water was controlled by a heater (placed at H in Fig. 1A). The electric power to the heater was adjusted by control signals from the microcomputer. A commercially available heater (500 W at 100 V a.c., Hakko Denki Seisakusho, Tokyo) was

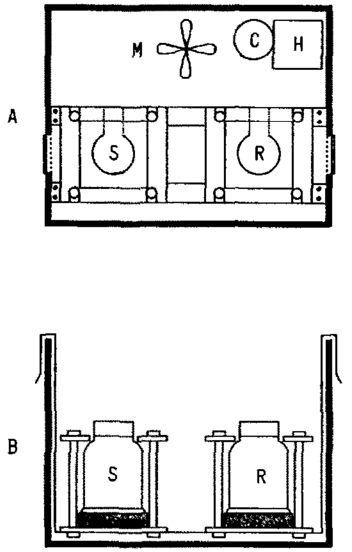

Fig. 1. Water-bath of heat exchange calorimeter. S, Sample; R, reference. A, Top view; B, side view.

compared with the hand-made heater shown in Fig. 2A, which was made from about 260 cm of nichrome wire wound onto plastic sticks of 5 cm side and coated with epoxy resin. The resistance of the heater element was 20.20 Ω. A maximum of about 27 V d.c. was applied across the heater and the maximum current was about 1.4 A.

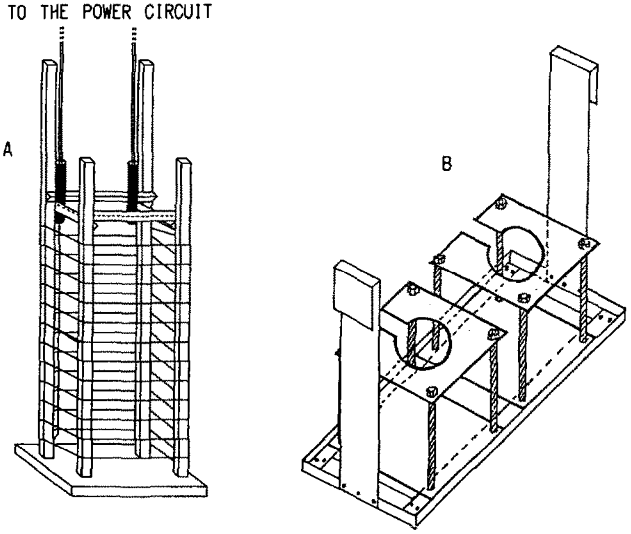

Fig. 2. Hand-made improvements for water-bath of heat exchange calorimeter. A, Heater block; B, frame for fixing the vessel and the magnetic stirrer.

A thermistor was installed in each glass vessel (the vessels were of volume 100 $cm^3$). A pair of thermistors sealed in each glass tubing (of diameter 1.2 mm) (NBS, Shibaura Denshi, Tokyo) were compared with a pair of Teflon-coated thermistors (NBS, Shibaura Denshi, Tokyo) which had $B$ constants (defined as $R = A \exp(B/T)$) in good agreement with each other. Two thermistors in the sample and reference vessels comprised two arms of a Wheatstone bridge, the resistance being twice as large to prevent self-heating. The unbalanced voltage $E_1$, which is directly proportional to $\theta$, was adjusted by a preamplifier (PM-17A, Toa Dempa, Tokyo), and $Q$ was then calculated by the analogue computation circuit, the output voltage of which was recorded on a $y$–$t$ recorder (R-02, Rika Denki, Tokyo).

Mixing in each vessel was carried out by rotation of an iron bar placed in the vessel and controlled by a magnetic stirrer of submarine type, as shown by the shaded area in Fig. 1B, in which all of facilities are not drawn. The vessel and the stirrer were fixed with an aluminum frame, as shown in Fig. 2B, and placed inside the water-bath, as shown in Fig. 1A and 1B. The geometry of the bath, including a motor-driven stirrer, M, as shown in Fig. 1A, was selected for effective mixing.

### *Procedure*

Sample and reference vessels containing 50.0 g of water were set in the frame shown in Fig. 2B and fixed in the water-bath. The temperature control system of the water-bath was activated. When thermal equilibrium was attained (after about 40 min), time constants of the analogue computation circuit were adjusted to those of the calorimeter by variable resistors in the circuit. Joule heat was measured in almost the same manner as reported earlier [4]. In this study, however, a smaller heat effect was estimated by diminishing the voltage applied to the heater element in the sample vessel, instead of shortening the working time by taking the measurement error into consideration.

## RESULTS AND DISCUSSION

Fluctuations in signals obtained from the calorimeter may contain signals caused by small temperature changes in the water-bath, as well as electric noise. Noise reduction techniques, such as an electric noise filter, which are commonly used in signal processing, may remove fluctuations in signals by electric treatment, but, simultaneously, the true values to be observed may also be altered.

The observation of temperature signals which include very few thermal fluctuations should be indispensable for the estimation of smaller heat effects, because the selective elimination of noise signals from observed signals may be impossible. In this study, the following points were examined for improvement.

(1) Selection of thermistor pair: Matching of the $B$ constant is required for a pair of thermistors. The degree of match may depend on the minimum temperature difference of the bath water and the minimum heat effect to be measured. The thermal characteristics of a specific thermistor pair can be adjusted commonly as a combination of several resistors [5]. However, it is tedious to select resistors for the adjustment, and the working temperature is limited to within a narrow range. Fortunately, a matched thermistor pair may be easily available. A pair of thermistors sealed in glass tubing, $Th_{1S}$ and $Th_{1R}$, which had been used in sample and reference vessels, respectively, was compared with a pair of thermistors coated with Teflon, $Th_{2S}$ and $Th_{2R}$. Precise $B$ constants and specifications of resistance, $R$, vs. temperature, $T$, were necessary for two pairs of thermistors. Therefore, the required data were simply observed, instead of using the values stated by the manufacturer. The pair of thermistors were placed inside a double jacket composed of two beakers and magnetic stirrers. The temperature was changed stepwise, for both cooling and heating, and controlled at the outer beaker. A commercially available standard thermometer was used for the temperature observation.

The plots of $\ln R$ vs. $T^{-1}$ for all four thermistors, $Th_{1S}$, $Th_{1R}$, $Th_{2S}$ and $Th_{2R}$, were linear in the range from 10 to 40 °C. The $B$ constant was obtained as the slope of the line calculated by the least-squares method, as was the relation between $R$ and $T$. For $Th_{1S}$ and $Th_{1R}$, $\ln R = 3396T^{-1} - 10.49$ and $\ln R = 3342T^{-1} - 10.35$, and $R$ values were calculated as 2.460 and 2.361 kΩ at 25.0 °C, respectively. For $Th_{2S}$ and $Th_{2R}$, $\ln R = 3404.09T^{-1} - 9.706$ and $\ln R = 3404.07T^{-1} - 9.709$, and $R$ values were 5.5382 and 5.5202 kΩ at 25.0 °C, respectively. $Th_{2S}$ and $Th_{2R}$ were a well-matched pair with respect to the $B$ constant.

The relative temperature difference between sample and reference vessels, which may depend upon the degree of match in thermal characteristics of a pair of thermistors and may cause drift of the base-line on the thermogram, was taken into consideration for a slight change in temperature of the bath water (from 25.0 to 24.9 °C). The temperature difference to be caused in vessels was calculated to be 0.004 K for the $Th_1$ pair and 0.0001 K for the $Th_2$ pair, because the $R$ values of $Th_{1S}$, $Th_{1R}$, $Th_{2S}$ and $Th_{2R}$ at 24.9 °C were 2.4692, 2.3700, 5.5595 and 5.5414 kΩ, respectively, from the estimated expressions. The temperature difference corresponded approximately to a heat effect of 0.8 and 0.02 J, respectively, in the calorimeter, and an unbalanced voltage in the Wheatstone bridge of 38.3 and 1.4 $\mu$V, respectively.

The results obtained were affected by the number of figures in numerical calculations. When the temperature of the bath water was changed by a larger amount (from 25.0 to 24.3 °C), unbalanced voltages were observed via the preamplifier and $y$–$t$ recorder in the calorimeter. Experimental results supported the calculations.

The temperature range of the bath water required for estimation of a heat effect of $\pm 0.1$ J within an error of 1% might be $(1–2) \times 10^{-4}$ K for the $Th_1$ pair and $5 \times 10^{-3}$ K for the $Th_2$ pair. The temperature control system constructed using the $Th_1$ pair [2] may be expected to perform much better than the system with the $Th_2$ pair.

(2) Heater element for water-bath control: Heat evolution from a commercially available heater element, in which nichrome wire was covered with asbestos and a metal case, delayed the signal from the microcomputer to the heater circuit. However, the hand-made heater element shown in Fig. 2A gave direct heating and served as an area heat source. After addition of a small amount of cold water, the response time of the recovery curve was improved by 1.6-fold.

(3) Mixing in vessels: In the theoretical treatment of heat exchange calorimetry, heat evolved in the vessels should be mixed instantaneously; thus, efficient agitation is indispensable. The remote-type magnetic stirrer [4] was changed to a submarine-type stirrer, and tightly fixed in the frame as shown in Figs. 1 and 2B. Handling of the vessels was also improved. The rotation of the iron bar coated with resin was markedly stabilized by shortening the distance between the vessel and the permanent magnet. As a result, the thermal insulation of bottom part of the water-bath was also improved. Heat evolved from submarine-type magnetic stirrers to the bath water served as part of the heater element.

After improvements in factors (1)–(3), joule heats were measured with $Th_1$ and $Th_2$ pairs in the heat range 0.5–0.1 J (0.57–0.086 J) and at 0.05 J (0.054–0.046 J). Standard deviations of the total heat effect, for five to seven runs, recorded on a strip-chart recorder were found to be 0.62 and 1.1% for $Th_1$, and 0.30 and 0.61% for $Th_2$, respectively. Introduction of the thermistor pair $Th_2$, an area heat source, and a submarine-type magnetic stirrer significantly improved the performance of the heat exchange calorimeter.

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