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# HEAT EXCHANGE CALORIMETRY FOR THE ESTIMATION OF INSTANTANEOUS CALORIC EFFECT

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## ABSTRACT

In the heat exchange calorimetry, heat evolved in a vessel placed in a water bath is exchanged freely with the ambient water. The thermal phenomena are expressed by a simple differential equation. An instantaneous caloric effect or rate of heat evolution q, as well as total heat Q, is estimated on line from the temperature $\theta$ observed via each thermistor in sample and reference vessels. After the estimation of Q from $\theta$ by using an analog computation technique, the values of Q corresponding to several successive points were used to calculate a point of q by the on-line numerical differentiation carried out with a microcomputer. The q thus obtained was by far better than that obtained by solely analog or numerical differentiation.

## INTRODUCTION

Accurate knowledge of instantaneous caloric effects may sometimes be indispensable for following the process of a chemical reaction. However, most conventional calorimeters do not respond so quickly as to supply accurate data for the instantaneous effect.

In the heat exchange calorimetry proposed originally by the present authors [1], exchange of heat occurs freely between a sample vessel in which a caloric effect takes place and a large amount of the ambient water. The temperature of the sample vessel as measured against that of the reference vessel is continuously converted into the electrical signal, so that the thermal phenomena may be analyzed on line. Treatments of the observed data will be discussed below, but the heat exchange calorimetry has several advantages that it takes only a short time to attain the thermal equilibrium, that the measuring equipment is assembled from common and simple devices, and that the system does not request any proficiency for operations. Unfortunately, however, the observed temperature $\theta$ does not directly supply q nor Q.

In the previous report [2], an electrical voltage corresponding to $\theta$ was acquired to a microcomputer and the desired q was obtained by mere numerical calculation. Then double differentiations were

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needed to obtain a q through the process of the calculation. On the other hand, the analog computation technique may be applicable to analysis of the same phenomena. But the analog differentiation is not suitable for the present treatment, because the differentiation circuit responds with fidelity even to small fluctuations in the input signal, of which experimentally produced signal cannot get rid.

On the contrary, however, the analog computation is capable of giving satisfactorily reproducible and accurate values of integrated q, as evidenced in [1]. In the present report, an analytical method of the thermal data was developed by taking advantages of both analog computation and numerical calculation. The analog computation technique was preferred to obtain Q from $\theta$ , and then the Q was acquired to a microcomputer followed by the numerical differentiation to estimate desired q.

## THEORETICAL

The Q may be obtained from $\theta$ according to eq.(1) [1], where $\alpha$ is a constant relating to the efficiency of heat transfer, $\beta$ a constant relating to the delay of the measuring system including response of the sensor, and W effective heat capacity. For simplicity, the volume increment in the sample vessel is neglected. As $\theta$ involves the delay in response of temperature, the actual temperature T in vessels should be distinguished from $\theta$ for the sake of strictness. The

$$\frac{Q}{W} = \frac{1}{\beta}\frac{d\theta}{dt} + \left(1 + \frac{\alpha}{\beta}\right)\theta + \alpha\int\theta\,dt \qquad (1)$$

$$d\theta/dt = \beta\,(T - \theta) \qquad (2)$$

$$q/W = dT/dt + \alpha T \qquad (3)$$

relation between T and $\theta$ was found to be expressed by eq.(2) [1]. The q can be obtained by differentiating Q with time, since Q is defined as an integral of q with time. From eqs.(1) and (2), eq.(3) which implies the physical meanings of q is easily derived. Therefore, q can be obtained via Q from the measured $\theta$.

## EXPERIMENTAL

The construction and the configuration of vessels in the water bath were almost the same as the previous report [2]. Thermal phenomena occurring in the sample vessel were estimated with a thermistor, and the response was fed to a Wheatstone bridge and a preamplifier, of which $E_i$ is the output. $E_i$ was proportional to $\theta$ as far as

$\theta$ remained small, thus $E_i = k_1 \cdot \theta$.

According to eq.(1), Q was obtained from $\theta'$ by the analog computation circuit shown in Fig.1 [1]. The relation of voltages between input $E_i$ and output $E_o$ was expressed by eq.(4). On comparing eq.(4)

$$E_o = - \frac{R_f}{R_i} [ \; R_iC_i \frac{dE_i}{dt} + (1 + \frac{R_iC_i}{R_fC_f}) \; E_i + \frac{1}{R_fC_f} \int E_i dt \qquad (4)$$

with eq.(1), it is readily seen that the expression $E_o = -(k_2/W)Q$ is valid, provided that the time constants $R_iC_i$ and $R_fC_f$ are equal to the reciprocals of $\beta$ and $\alpha$, respectively. Actually, $R_i$ and $R_f$ were composed of variable resistors, and appropriate values of the time constants could be determined beforehand in an electrical heating by adjusting the resistors so as to yield linear trails of an $E_o$ vs. t curve, of which details of treatment were already reported [1].

The $E_o$ was acquired via an AD converter (ADC80AG-12) to a microcomputer. The sampling might usually be made every 1 or 2 s during the steady progress of thermal phenomena, but more frequent samplings were required particularly when the q suddenly changed. To meet the situation, the sampling was conducted every 0.5 s, and several latest contiguous readings were stored for the calculation mentioned below. On each sampling of $E_o$, the least square fitting was followed using several successive readings of $E_o$, and the best fit was used to obtain the best value of q which was assigned to the middle of the sevetal points. The starting or terminating point of a thermal phenomenon could be noticed as a point where a sudden change in q occurred. The program was written for the most part in BASIC, but partly in the assembly language to accept the signal pulse from the converter and to carry out the lengthy calculations. Traces of $E_i$ and $E_o$ vs. t curves, the calculation processes of the least square approximation and the error, and estimated results were, when necessary, monitored in real time by peripheral devices, so that the run of the whole system might be grasped.

## RESULTS AND DISCUSSION

For the accurate determination of q, the treating method of such a sudden change in q as start or stop of heat evolution was significant. In this report, the caloric effect was supplied electrically so that the heating may be reproducible and efficient in any conditions. The applied q, therefore, was a constant at an arbitrary value, but the timing of the change in q was considered to be un-

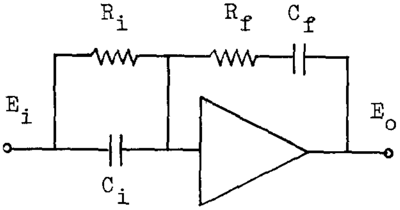

Fig. 1. Analog computation circuit

known in the data analyses.

Reproducibility of $E_o$ estimated by the analog circuit was within the range better than ±0.6 % for about 8 - 24 J of the caloric effect analyzed conventionally on the $E_o$ vs. t curves.

Every time a pair of t and $E_o$ was acquired to the microcomputer on line, q was calculated by using the latest 7 pairs. Since the q was treated as a constant in this report, the linear relation was selected for the convenience, and calculated with least square approximation. The square of the difference between the calculated value and the observed value was summed up for the 7 pairs to estimate the error. Then at least one of data departs from the line, the error became so large as to exceed a predetermined threshold value, so that the sudden change in q could be detected without delay. The data acquisition interval was preferred to be small for accurate detection of changing in q without delay of time.

The 16 runs of q given as constant values in the range from 0.1 to 0.3 J/s were estimated within the range better than ±1.1 % of relative standard deviation, and for 0.02 J/s, q was estimated with about 1.3 % of rsd.

The use of the analog operation combined with the numerical calculation proved to afford satisfactory results in the estimation of instantaneous caloric effect that was hardly expected with the analog or numerical operation alone.

## REFERENCES

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