INSTANTANEOUS HEAT EFFECT ESTIMATED WITH MICROCOMPUTER-AIDED HEAT EXCHANGE CALORIMETRY INVOLVING ANALOG COMPUTATION *

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ABSTRACT

Microcomputer-aided heat exchange calorimetry involving an analog technique is developed to estimate sensitively instantaneous heat effects or rate of heat evolution, as well as total heat, on line and real time. Heat evolved in one of two vessels placed differentially in a water bath is exchanged freely with the ambient water and the thermal phenomena are expressed by a simple differential equation. First, total heat is estimated from the temperature observed via each thermistor installed in the vessels. Then the values of total heat corresponding to several successive points were fed into a microcomputer and used to calculate a point of instantaneous heat effect by numerical differentiation. The instantaneous heat effect thus obtained was far better than that obtained by solely analog or numerical differentiation.

INTRODUCTION

Total heat is usually measured in titration calorimetry and thermometric or enthalpimetric titration of adiabatic methods. Accurate knowledge of instantaneous heat effects may sometimes be indispensable for following the process of a chemical reaction. However, most conventional calorimeters may 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 calorimetric 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. Unfortunately, the observed temperature does not directly supply instantaneous heat effects nor rate of heat evolution nor total heat. However, heat exchange calorimetry

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* Partly presented at 8th ICTA (1985) held at Bratislava [3].

has several advantages in 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 require any proficiency for operations.

In the previous report [2], an electrical voltage corresponding to the observed temperature was fed into a microcomputer and the desired instantaneous heat effect was obtained by mere numerical calculation. Then double differentiations were needed to obtain an instantaneous heat effect through the process of the calculation. On the other hand, the analog computation technique may be applicable to an 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, which may usually be included in an experimentally produced signal as the indispensable result. On the contrary, however, the analog computation is capable of giving satisfactorily reproducible and accurate values of integrated instantaneous heat effect, as shown in the previous report [1].

In the present report, an analytical method of the thermal data was developed by taking advantage of both analog computation and numerical calculation. The analog computation technique was preferred to obtain total heat from the observed temperature, and then the total heat was fed into a microcomputer followed by the numerical differentiation to estimate the desired instantaneous heat effect.

THEORETICAL

The total heat Q may be obtained from the observed temperature θ according to eqn. (1) [1], where α is a constant relating to the efficiency of heat transfer, β a constant relating to the delay of the measuring system including response of the sensor, and W effective heat capacity. For simplicity, a negligibly small or no volume increment and no change in the effective heat capacity in the sample vessel are considered. As θ involves the delay in response of temperature, strictly speaking the actual temperature T in vessels should be distinguished from θ.

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

$$d\theta/dt = \beta(T - \theta) \tag{2}$$

$$q/W = dT/dt + \alpha T \tag{3}$$

The relation between T and θ was found to be expressed by eqn. (2) [1]. The instantaneous heat effect q can be obtained by differentiating Q with time t, since Q is defined as an integral of q with t. From eqns. (1) and (2), eqn. (3)

which implies the physical meanings of q is easily derived. Therefore, q can be obtained via Q from the measured θ.

EXPERIMENTAL SECTION

Apparatus

The main construction and the configuration of sample and reference vessels fixed in the thermostatted water bath were almost the same as in the previous report [2]. Thermal phenomena occurring in the sample vessel were detected against those in the reference vessel via a thermistor used as a sensor, and the response was fed to a Wheatstone bridge and a pre-amplifier, of which E_i is the output; E_i was proportional to θ as long as θ remained small, thus $E_i = k_1\theta$.

Procedure

The observed signals of thermal phenomena were treated on line in dual steps. As a first step, E_0 corresponding to Q was derived from the analog computation circuit shown in Fig. 1. Subsequently, in a second step, the output voltage of the analog circuit E_0 was fed into a microcomputer as pairs of Q vs. t, and the desired q was calculated numerically.

Analog computation

According to eqn. (1), Q was obtained from θ by the analog computation circuit shown in Fig. 1 [1]. The relation of voltages between input E_i and output E_0 was expressed by eqn. (4). On comparing eqn. (4) with eqn. (1),

$$E_0 = -\frac{R_f}{R_i}\left[R_iC_i\frac{dE_i}{dt} + \left(1 + \frac{R_iC_i}{R_fC_f}\right)E_i + \frac{1}{R_fC_f}\int E_i\, dt \right] \tag{4}$$

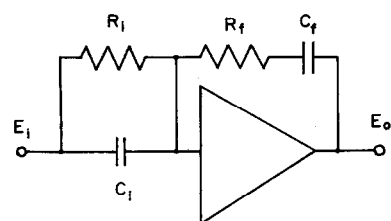it is obvious that the expression $E_0 = -(k_2/W)Q$ is valid, provided that

Fig. 1. Analog computation circuit.

the time constants $R_i C_i$ and $R_f C_f$ are equal to the reciprocals of β and α, respectively. Actually, R_i and R_f were composed of variable resistors, and appropriate values of the time constants could be determined beforehand in electrical heating by adjusting the resistors so as to yield linear trails of an E_0 vs. t curve, of which the details of the treatment have been reported [1].

Numerical calculation

The E_0 value was acquired via an AD converter (ADC80AG-12, Burr Brown) linked to an 8-bit microcomputer. The sampling was usually made every 1 or 2 s during the steady progress of the thermal phenomena, but more frequent samplings were required particularly when q suddenly changed. To meet the situation, the sampling was conducted every 0.5 s. Several later readings were stored for the calculations, which included the linear least-squares fitting of the baseline prior to the region of heat evolution. If necessary, the following acquired E_0 should be corrected on-line for the extended baseline. On each sampling of E_0, the least-squares fitting was followed using several successive readings of E_0, the best fit was used to obtain the best value of q which was assigned to the middle of the several points. The starting or terminating point of a heat evolution could be taken as a point where a sudden change in q occurred, that is, the calculated error, as mentioned below, exceeded a preset threshold value. The point was estimated as an intersection of two lines obtained with a least-squares approximation of acquired successive readings. The program was written for the most part in BASIC, but partly in the assembly language of Zilog Z-80 to accept the signal pulse from the converter and to carry out the lengthy calculations. Traces of E_i and E_0 vs. t curves, the calculation processes of the least-squares 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 recorded.

RESULTS AND DISCUSSION

For the accurate determination of q, the method of treatment of such a sudden change in q as the beginning or end of heat evolution was significant. Heat evolution in a step function was preferred to test whether the proposed calorimetry could follow the quick change in thermal phenomena. In this report, the heat effect was supplied electrically, instead of chemical phenomena, 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 unknown in the data analyses.

Reproducibility of ten E_0 values estimated by the analog circuit shown in Fig. 1 was within the range better than 0.6% relative standard deviation (r.s.d.) for about 4–24 J of total heat analyzed conventionally on the E_0 vs. t curves.

Every time a pair of t and E_0 values was fed into the microcomputer on-line, q was calculated by using the latest 7 pairs. Since q was treated as a constant in this report, the linear relation was selected for convenience, and calculated with least-squares approximation. The square of the difference between the calculated value and the observed value was summed for the 7 pairs to estimate the error. When at least one datum 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 time delay.

Typical outputs in the cases of single and triple heat evolutions are shown in Figs. 2 and 3, respectively; A is the trail of the output voltage E_0 of the
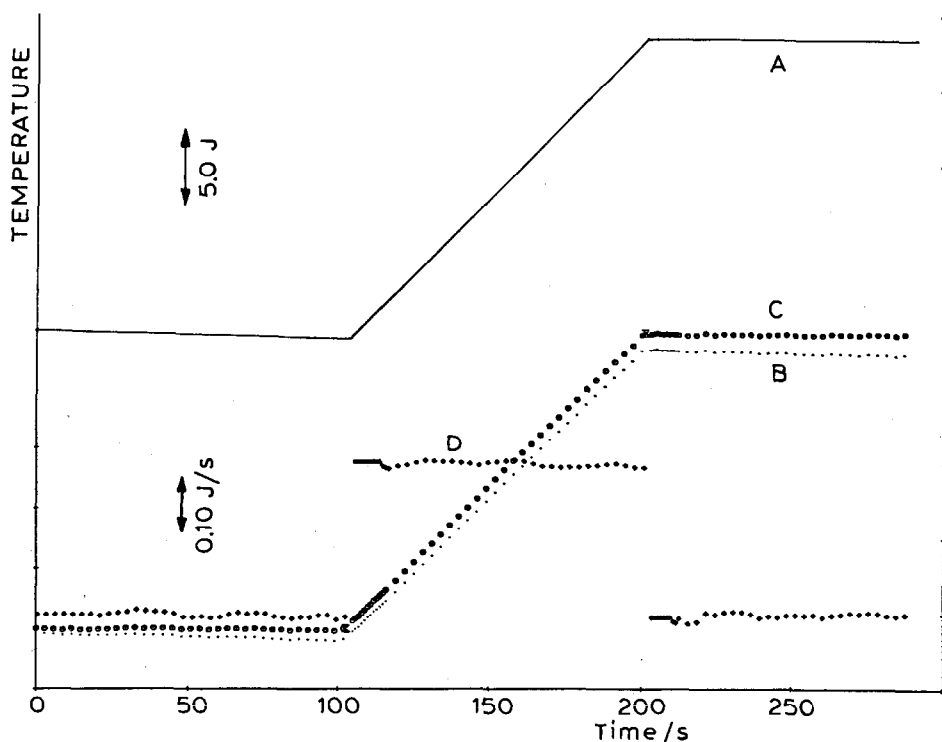

Fig. 2. Temperature variations shown as outputs of the analog computation circuit and the microcomputer and estimated instantaneous heat effect. The scales indicated between two arrows near A and D corresponded to the total heat and the instantaneous heat effect, respectively.
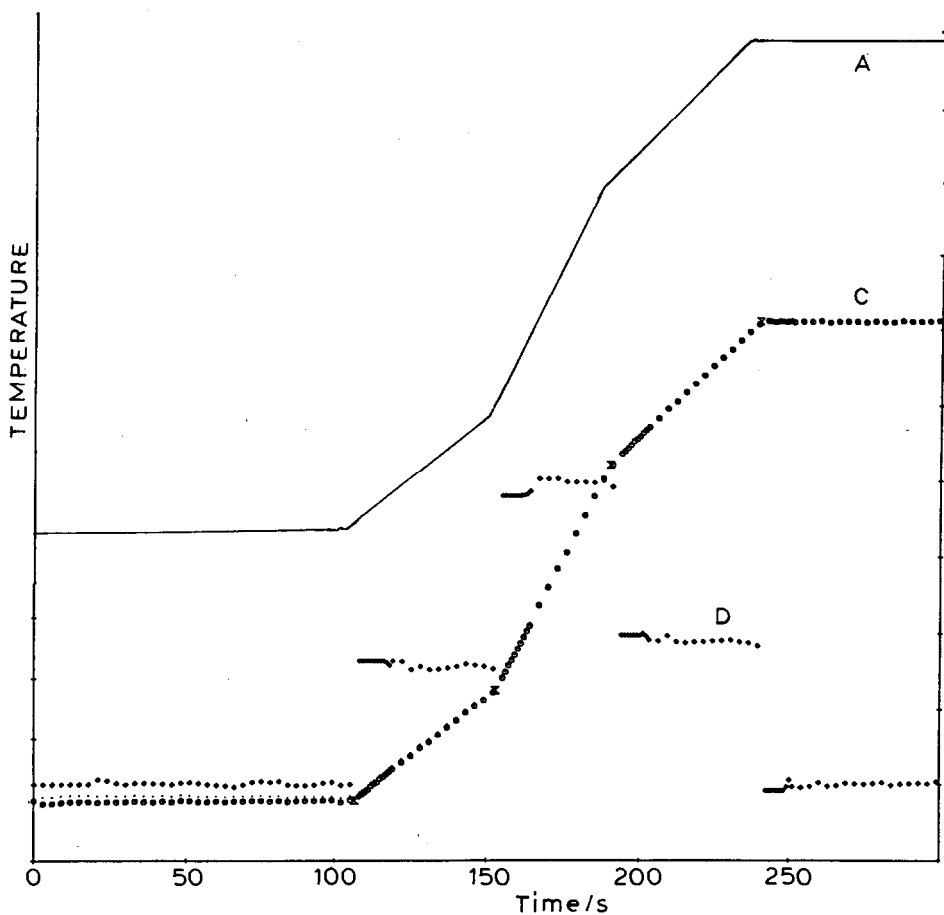
Fig. 3. Continuous heat evolutions in different q values at the same situation as in Fig. 2.

operational amplifier circuit shown in Fig. 1; B, C, and D are outputs from the microcomputer drawn by an XY-plotter. The value of B corresponds to the E_0 fed into the microcomputer, to which the baseline was corrected to give data C; D is the instantaneous heat effect estimated with the proposed method.

From 16 runs executed in the range from 0.1 to 0.3 J s^{-1}, the q values were estimated with error better than 1.1% r.s.d.

Heat released in the sample vessel, which was placed in a thermostatted water bath, should be exchanged freely with the ambient water in heat exchange calorimetry. Consequently, the calorimetric measurement will be carried out at a more constant temperature than in the case of adiabatic measurement, provided that the ambient water is controlled in a narrow range of temperature. In addition, elimination of analog differentiation allowed the expansion of the range of temperature control. In this report, the temperature of the water bath was kept within the range ± 5–6×10^{-4} °C.

The use of the analog operation combined with the numerical calculation proved to afford satisfactory results in the estimation of instantaneous calorimetric effects that were not expected with the analog or numerical operation alone.

ACKNOWLEDGMENT

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