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HEAT EXCHANGE CALORIMETRY FOR SMALLER SIZE SAMPLES

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ABSTRACT

The heat exchange calorimetry, hitherto developed for ordinary size samples, was modified for diminishing the sample size to one tenth or less of that commonly used in previous reports. Improvements were made with respect to the vessels for sample and reference, the stirrer of the sample solution, the thermistor and the calibration heater. The value of α, a constant relating to the heat transfer and critically affecting the sensitivity to smaller heat effects, was given an appropriately small value. The improved version of the calorimeter employed a sample vessel of a capacity of 6 cm^3 and was suited to accomodate about 3 cm^3 of a solution. The calorimeter proved to give sufficiently precise results when total heats ranging from 0.05 to 0.4 J were evolved.

INTRODUCTION

In the application of calorimetry to chemical problems, an accurate and precise method is often required for estimating small heat effects which correspond to smaller size samples. Then a sufficiently sensitive and reliable means of measuring the small heat effect is necessary for the estimation. Since the heat exchange calorimetry originally proposed by the present authors (ref.1) provides a simple technique which is easy to operate and gives sufficiently precise results, an attempt has been made to modify the calorimetry so as to be adapted to small heat effects.

So far in the heat exchange calorimetry, samples of an ordinary size have been supposed. Thus, for example, the minimum heat to be determined with a tolerable error is approximately around 1 J evolved in 50 s, or a rate of around 0.02 J/s continuing for 50 s. In this paper, how to diminish the sample size is discussed together with the related problems. The primary object is to reduce the minimal amount of heat necessary for the measurement down to one tenth to twentieth of that required in the previous method.

First, an as small effective heat capacity as possible of the calorimeter vessel (or sample vessel) is needed to obtain reliable response in the measuring system. This might be possible by employing a smaller size vessel. Second, the temperature of the liq-

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uid inside the sample vessel should be kept uniform. Adequate and thorough mixing of the liquid without disturbing the smooth surface of the liquid is necessary. Third, contribution of the thermistor and the electrical heater for calibration to the effective heat capacity should remain as small as possible. Fourth, area of the effective heat exchange surface estimated for a unit volume of liquid is relatively larger for smaller vessels than for larger vessels. Consequently heat is exchanged more rapidly and a less elevation of the temperature results. These imply a larger value of the constant α appearing in the equation below. It is therefore necessary to decrease the value of α so as not to introduce lowered sensitivity of response.

These requirements could be met successfully in the modified calorimeter as described below. The discussions are made using electrical heat evolution for the sake of simplicity and the titrimetric procedure which involves increase in the solution volume is not considered in this paper.

THEORETICAL

When heat is evolved at a rate q in the sample vessel, the temperature change with time, dT/dt, is expressed by the following equation:

$$dT/dt = q/W - \alpha T \qquad (1)$$

where W is the effective heat capacity and α is a constant relating to the efficiency of the heat transfer and T is the difference of temperatures in the sample vessel and the ambience. The corresponding difference of temperature θ actually observed with the thermistors may probably not be equal to T on account of the delay of response, and the rate of change with time obeys eq.(2). From eqs.(1) and (2), the following relation is derived as a function of θ.

The q integrated through a period of time, as appearing on the left side of eq.(3), gives a total heat, Q, evolved during the period, and this quantity can be calculated from the continuously observed value of θ according to the same equation. The calculation could be performed by use of the analog computation circuit in Fig.

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

$$(1/W)\int q\,dt = \frac{1}{\beta}\frac{d\theta}{dt} + (1 + \frac{\alpha}{\beta})\theta + \alpha\int \theta\,dt \qquad (3)$$

$$E_o = - \frac{R_f}{R_i} [R_i C_i \frac{dE_i}{dt} + (1 + \frac{R_i C_i}{R_f C_f}) E_i + \frac{1}{R_f C_f} \int E_i dt] \tag{4}$$

1 which involves an operational amplifier, where the output voltage E_o is related to the input voltage E_i by the eq.(4). From the similarity of eqs.(3) and (4), the followings are concluded.

If the time constants $R_f C_f$ and $R_i C_i$ are so adjusted as to be reciprocally equal to α and β , respectively, and the voltage as θ is applied to the input of the circuit, then Q, the heat integrated up to any time t, could be obtained as an output voltage of the circuit.

Details of the circuit including functions and adjustment of variable parts are described in the previous paper (ref.1).

MODIFICATIONS

Some parts of the calorimeter assembly were modified so as to enable precise estimation of small heat effects. Glass bottles with a capacity of 6 cm^3 were used as sample and reference vessels. The outer surface of the bottom was covered with a thin board of polystyrene foam in order to minimize irregular exchange of heat through the bottom. A small thermistor (2.5 kΩ at 25°C) and an electric calibration heater of a minimal dimension (prepared of a 1/16W 100 Ω resistor) were accomodated in each vessel. Stirring the solution in each vessel was achieved without disturbing the smooth surface of the solution by using a tiny Teflon stirrer rod (8 × 1.5 mmØ) which was magnetically driven by a motor placed outside in the water bath.

The constant α plays an important role and a small value of α is preferable to attain a high precision when a smaller sample is involved. It is readily understood that α is directly proportional to the heat exchange area and reciprocally proportional to the volume of the liquid in the vessel. But these quantities are rather difficult to control. The only possible way is to change the thermal conductivity of wall of the vessels so that heat is transferred less readily. Thus, strips of a polyvinyl tape were applied on the outside walls of the vessels to produce a smaller value of α. The observed α 0.0436 s^{-1} before the application of tape was reduced to 0.0220 s^{-1} by applying the tape and the observed θ's could be magnified accordingly.

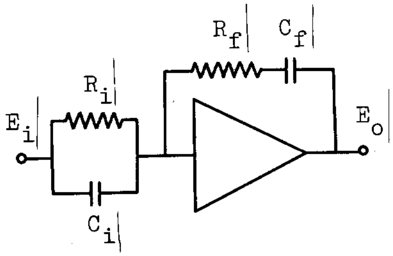

Fig. 1. Analog computation circuit

EXPERIMENTAL AND RESULTS

In this paper heat was evolved electrically with the heater for the sake of convenience. The observed temperature difference θ between the sample and reference vessels appearing at the output of the Wheatstone bridge was fed to the input of the operational amplifier circuit, to obtain the total or integral heat Q.

The rate of evolution of heat or the instantaneous heat, q, might be obtained by a similar analog computation technique, but considerations on this line are omitted in this paper because the electrical noises inherent to the simple circuit **has** to be removed by some other measures. A solution of the problem will be presented in a later paper.

Twenty runs of experiment were carried out with a varied current and time for evolving various small amounts of heat. Thus, the total heat amounted to 0.05 to 0.4 J. The output V of the computation circuit, in terms of volts, at the completion of the heat evolution could be expressed by the following equation:

$$V = 3.071 \times 10^{-3} + 3.754 \times Q \qquad (5)$$

The mean square error was 0.013, showing very good linear relationship. The small first term on the right hand side of the equation confirms that the line substantially passes the origin. In other words, the small total heats could be obtained with sufficiently high precision by using the present modified method.

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