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HEAT EXCHANGE CALORIMETRY FOR ESTIMATING HEATS OF SOLUTION

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ABSTRACT

A simplified calorimeter has been developed for estimating heats of solution by means of heat exchange calorimetry which was originally proposed by the authors. An analog operational technique is preferred for analyses of thermal phenomena observed in the sample vessel. Two recommended chemical systems are utilized to test the validity of the proposed methodology and instrumentation, the correct performance of the constructed assembly, and to evaluate the device in terms of accuracy and precision. The heat of reaction of solid THAM (tris(hydroxymethyl)aminomethane) with 0.100 M HCl as an exothermic reaction, and the heat of solution of potassium chloride crystals in water as an endothermic reaction were estimated in this paper. Both of the estimated results agreed satisfactorily with literature values to prove the suitability of the proposed calorimetry.

INTRODUCTION

Theoretical and fundamental considerations of the heat exchange calorimetry, originally proposed by the authors, were previously reported [1]. The heat evolved in a sample vessel, which resulted from endothermic or exothermic chemical reactions, or from an electrical heating, was allowed to exchange freely with an ambient medium around the vessel. Thus, the Newtonian cooling equation could be exactly applied to express the change of temperature in the vessel, and the temperature observed was related to the rate of heat evolution by means of differential equations. The temperature as a function of time was followed by the on-line and real time analog treatment with an appropriate operational amplifier circuit. The total heat evolved could be obtained by integration of the instantaneous heat effect with time. Fortunately, the technique greatly shortened the waiting time before the measuring system reached thermal equilibrium, and needed neither expensive equipment, nor skilled operators.

In this paper, a simplified technique to estimate heats of solution directly was established by applying the essential concept of heat exchange calorimetry. For certification of the validity of the proposed calorimetry, including

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the performance of the calorimeter assembly constructed in this study, and for evaluation of the accuracy and reproducibility of the heat of solution estimated in an aqueous solution, two calorimetric processes were executed as test runs [2]: one is the reaction of THAM (tris(hydroxymethyl)aminomethane) with 0.100 M hydrochloric acid, which was recommended as the standard exothermic reaction; and the other, the solution of solid potassium chloride in water for an endothermic reaction.

THEORETICAL CONSIDERATIONS

Two vessels having the same geometry and heat capacity or thermal effects should be used as sample and reference vessels in the differential configuration. When heat is evolved in a vessel, the temperature in the vessel must be uniform with instantaneous mixing. As far as a small amount of solid samples is concerned, the increment in volume owing to sample additions may be negligibly small. The temperature change with time obeys the following equation [1]

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{q}{W} - \alpha T \tag{1}$$

where q is heat evolving rate, W effective heat capacity, and α a constant concerning heat transfer with which heat evolved in a vessel is exchanged freely with a large amount of the ambient water.

In a practical measuring system, however, the temperature observed via thermistor as a sensor, θ, may include the delay of response which is expressed as the following equation [1]

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \beta(T - \theta) \tag{2}$$

where β is a constant concerning the delay of response.

Therefore, T is derived from θ by eqn. (2), and then, total heat Q is obtained from integrating q with time. Provided that q/W in eqn. (1) is a constant, the differential equation can be solved mathematically. However, it is seldom the case in general chemical reactions. In this paper, an analog computation technique, instead of numerical calculations, was preferred to realize the analytical processing of thermal phenomena.

INSTRUMENTATION

Equations (1) and (2) can be rewritten as eqns. (3) and (4), respectively.

$$\frac{q}{W} = \frac{\mathrm{d}T}{\mathrm{d}t} + \alpha T \tag{3}$$

$$T = \frac{1}{\beta} \cdot \frac{\mathrm{d}\theta}{\mathrm{d}t} + \theta \tag{4}$$

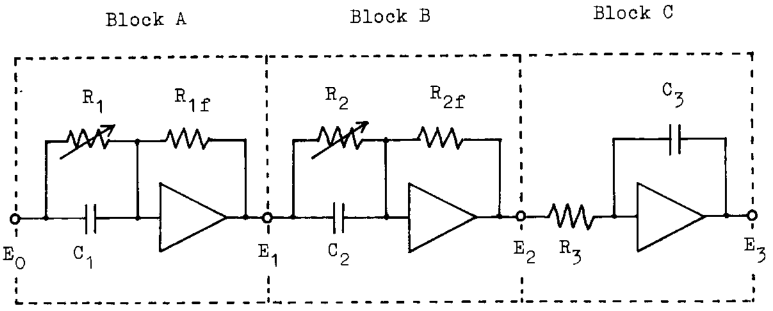

Fig. 1. Analog computation circuit.

The computations for obtaining Q/W from θ were realized by means of the following operational amplifier circuits which can be composed of 3 unit blocks illustrated in Fig. 1:

Block A: computation of T from θ after eqn. (4);
Block B: computation of q/W via T after eqn. (3);
Block C: computation of Q/W by integrating q/W with time.

The relation of voltage between the input E_0 and the output E_1 in Block A is expressed as eqn. (5).

$$E_1 = -\frac{R_{1f}}{R_1}\left(R_1C_1\frac{\mathrm{d}E_0}{\mathrm{d}t} + E_0\right) \tag{5}$$

Equation (5) corresponds to eqn. (4), when $E_0 = k_0\theta$ and the time constant R_1C_1 is adjusted to be equal to the reciprocal of β or $1/\beta$ [1], where k_0 is the conversion coefficient. From eqns. (4) and (5), the following relation is obtained.

$$E_1 = k_1T \tag{6}$$

where $k_1 = -(R_{1f}/R_1)k_0$.

The circuit in Block B has the same configuration as that in Block A where the input–output relation is given by the following expression.

$$E_2 = -\frac{R_{2f}}{R_2}\left(R_2C_2\frac{\mathrm{d}E_1}{\mathrm{d}t} + E_1\right) \tag{7}$$

When the time constant R_2C_2 is adjusted to be equal to $1/\alpha$ [1] and $k_2 = -(R_{2f}/R_2)\ k_1/\alpha$, eqn. (8) is obtained

$$E_2 = k_2\left(\frac{q}{W}\right) \tag{8}$$

from which the voltage E_2 proportional to q is derived.

The integration circuit or Block C gives E_3 proportional to Q at the output terminal.

$$E_3 = -\frac{1}{R_3C_3}\int E_2\mathrm{d}t = \frac{k_3}{W}\int q\mathrm{d}t = k_3\frac{Q}{W} \tag{9}$$

where $k_3 = -k_2/R_3C_3$.

The corresponding values of θ, T, q/W, and Q/W at any time are obtained at the outputs E_0, E_1, E_2, and E_3, respectively, in the analog computation circuits.

EXPERIMENTAL

Reagent

Sample crystals of THAM (tris(hydroxymethyl)aminomethane) available as a primary standard material from Sigma Chemical Co., of which the written purity was ca. 99.9%, were used without further purification after being dried for 2 h at 100–103°C [3] before use. All of the other reagents used in the report was guaranteed grade. Potassium chloride crystals were dried at a sufficiently high temperature. Deionized water was distilled before use.

Apparatus

Each of two cylindrical glass vessels installed a glass thermistor as a sensor, a heater element for calibration of heat effect, and a glass sample inlet for throwing down solid samples from the outside of a covered water bath. The resistance of thermistors placed in the sample and the reference vessels was ca. 38 kΩ at 298.15 K, their B constants being 3557 and 3537 K, respectively. Two thermistors were so adjusted as to be equal in the relation between the resistance and temperature to order of 1 Ω at 298.15 K by applying resistors in parallel or series connections. A 100 Ω resistor of 1/8 W coated with epoxy resin was used as a heater element, of which lead wires being immersed in the liquid were prolonged so that heat evolved from the heater element may be released into the liquid without any loss. The content of vessels was ca. 80 cm^3, and in a typical run, 40 cm^3 of sample volume were utilized. The smaller the dead space in the vessels, the better. The Teflon coated iron bar in each vessel was controlled by synchronous motors (8 W, 300 rpm, Japan Servo Motor Co.) placed at the outside of the water bath. The water bath made of acryl resin boards was covered with styrol foam boards as a thermal insulator, and contained about 42 l of water which was agitated vigorously by three motor-driven stirrers. To keep the temperature of the water within a range less than ± 0.001 K, PI-controlled heating was made on circulating water colder than the temperature to be kept constant. Thermistors placed in sample and reference vessels were incorporated in a Wheatstone bridge followed by a preamplifier and the output voltage was applied to the analog operational amplifier circuit shown in Fig. 1 as E_0 of the input voltage. Most parts of the electric circuit including operational amplifiers (LF356, NS), except the operation board, were placed in a water bath to keep the thermal circumstance constant. The accurate values of a constant direct current (0–85 mA) applied to the heater circuit, which was supplied from a booster circuit, were directly measured by digital voltmeters.

Procedure

In the sample vessel, 40 cm^3 each of 0.1001 M hydrochloric acid and of water were placed for measuring the heat of reaction of solid THAM and for the heat of solution of solid potassium chloride, respectively. The same amount of water was used in the reference vessel. Both vessels were tightened in the holder placed in the water bath. It took almost the same time as necessary for warming up the electronic devices as that for the whole reaction system to be measured to attain thermal equilibrium in the water bath. The operational amplifier used for an integral circuit had to be adjusted so as to keep the offset voltage small enough for the measuring time. Solid samples were introduced into the sample vessel directly from the outside of the covered water bath. For a reasonable measurement, a small aliquot of weighed THAM or potassium chloride should be added little by little to the sample vessel, so that the heat evolving rate might not exceed the mixing ability in the vessel. In a typical run, the application of 10–30 mA of a direct current to the sample vessel was suitable for accurately estimating the heat effect evolved. During the observation of an enthalpogram, E_0 was monitored against time and, in a conventional manner, the corresponding value of total heat Q was estimated as the height of a graphical trail of E_3 vs. t. After every addition of small portions of the solid sample, electrical heating was carried out for calibrating the change in the heat capacity before and after the reaction.

RESULTS AND DISCUSSION

The differential eqn. (1) is solved mathematically as mentioned above, provided that q/W is a constant. Most chemical reactions, however, cannot satisfy this condition. In this report, an analog computation technique was preferred for treating the differential equation without any restrictions. On the other hand, unfortunately, analog differentiation is impractical in heat exchange calorimetry, since with such a noisy output, the high differentiated signals follow small thermal fluctuations in the input signal of the analog circuit, but the integration of the differentiated signal, q, with time resulted in total heat, Q, which was suitable for the present purpose. If thermal phenomena expressed by eqns. (1) and (2) occur strictly in the constructed assembly, the analog circuit shown in Fig. 1, which obeyed two differential equations, should conduct the correct analysis of the experimentally observed thermal phenomena, and the final output of the analog circuit may give the direct reading proportional to Q.

In this technique, it is the most significant point that heat evolved in the vessel should be made uniform instantaneously with the mixing and exchanged freely with the ambient water in the water bath, as previously reported [1]. Experimental fulfillment of the requests depended upon the extent of agitation in both vessels and the water bath. Incomplete mixing around the thermistors will result in deflection from the correct value. In addition, uniformity must be kept in the temperature of the ambient water in the bath, so that phantom thermal phenomena may not be involved.

Since the proposed method was characteristic in its simplified handling, the solid sample was introduced directly via the sample inlet of the vessel from the outside of a water bath, instead of breaking ampoules containing the sample placed in the vessels. The difference in the temperature between sample crystals and the liquid in the sample vessel was, in this case, considered to barely influence the total heat to be estimated. If any, it should have a negative effect.

The accuracy and precision of the proposed calorimetric method for estimating heats of solution in aqueous systems were demonstrated by dissolving solid potassium chloride in water and THAM crystals in 0.100 M hydrochloric acid recommended as standard reactions for endothermic and exothermic reactions, respectively. As for the heat of solution of potassium chloride crystals, the values reported in the literatures varied depending upon the drying method of the sample crystals. Montgomery et al. reported 17.5360 ± 0.0034 kJ mol^{-1} for the case of a sample heated well above 600 K and 17.4992 ± 0.0059 kJ mol^{-1} for an unheated sample [2]. The drying condition of the sample utilized in this report was not so severe as that of Montgomery et al. The estimated value in this report was 17.56 kJ mol^{-1} at 298.15 ± 0.01 K with an uncertainty of less than ±0.4%, which was calculated for 1 mole of potassium chloride in 1110 moles of water (molality of KCl = 0.0500 mol kg^{-1}). The estimated value was 0.1–0.3% larger than the literature values. On the other hand, about 0.2 g of THAM were added in one-tenth portions to 40 cm^3 of 0.1001 M hydrochloric acid over a period of about 10 min. The heats of solution of 0.2075, 0.2017, 0.2011, 0.1999, and 0.1959 g of THAM in 0.1001 M hydrochloric acid solutions, $-\Delta H$, were observed to be 29.66, 29.72, 29.75, 29.76, and 29.71 kJ mol^{-1}, respectively, at 298.15 ± 0.01 K. The mean value of the five runs was 29.72 kJ mol^{-1}, and the uncertainty expressed by the standard deviation was 0.04 kJ mol^{-1}. A few corresponding values found in the literatures were 7107.0 ± 0.9 cal mol^{-1} (29.736 ± 0.004 kJ mol^{-1}) [3], 29.744 ± 0.003 kJ mol^{-1} [4], and 7114 ± 4 cal mol^{-1} (29.76 ± 0.02 kJ mol^{-1}) [5]. The data in parentheses were calculated from the literature values by us so as to be compared easily with that in this report. Montgomery et al. reported $-\Delta H$ to be 245.76 ± 0.06 J g^{-1} (29.771 ± 0.007 kJ mol^{-1}) [2], and from a chronological plot, 245.54 ±

0.04 J g^{-1} (29.745 ± 0.005 kJ mol^{-1}). The estimated heats of solution were 0.08% smaller than the corresponding value recommended by Montgomery et al.

Although, in this report, a simplified apparatus was used for the estimations without any air conditioning, the results obtained were considered to be reasonable.

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