

EVALUATION OF HEAT EXCHANGE CALORIMETRY OF THE BATCH TYPE BY ESTIMATING KNOWN HEATS OF SOLUTION

SHUKO FUJIEDA

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

(Received 29 June 1987)

ABSTRACT

In the method of heat exchange calorimetry developed by the author, step-wise instantaneous thermal phenomena were estimated sensitively. The batch technique heat exchange calorimeter, which was preferred to titrimetry because of easy handling and simplified procedure, was tested by estimating known heats of solution. To investigate an exothermic reaction, tris(hydroxymethyl)aminomethane was added to aqueous 0.1000 M hydrochloric acid, heat of solution being estimated as $89.38 \pm 0.44 \text{ J g}^{-1}$ at $25.0 \pm 0.1^\circ \text{C}$. The heat of solution of crystalline potassium chloride in water was estimated as $17.58 \pm 0.08 \text{ J mol}^{-1}$ in an example of an endothermic reaction at the same temperature. Validity of the proposed method of calorimetry was evaluated from the accuracy of estimated heats of solution.

INTRODUCTION

In the method of heat exchange calorimetry originated by Nakanishi and Fujieda [1], good response and reproducibility were obtained for such sudden thermal phenomena as step-wise heat effects [2]. The measuring system was simply constructed using readily available equipment. Ease of handling of a whole system without loss of precision and accuracy may be required for analytical applications; therefore, in estimating heats of solution of solid substances, a batch technique may be preferred to titrimetry. The change in heat capacity due to increase in volume in the sample vessel may be small, even on addition of a solid sample. Moreover, no titrant system is required to be in thermal equilibrium, and the electric circuits for data processing are also simplified as mentioned below. As a result, the time necessary for the whole calorimeter system to attain thermal equilibrium may be reduced.

Prior to applications of the proposed method of batch calorimetry to unknown materials, precision and accuracy had to be tested using standard chemical reactions, to certify the reliability of the calorimeter. Montgomery

et al. [3] reviewed the background to this problem and proposed separate experiments for endothermic and exothermic reaction systems.

In the present paper, a heat exchange calorimeter of the batch type was constructed involving an analog computation circuit in which only one operational amplifier was used. Total heat evolved was estimated in order to evaluate the validity of the method of calorimetry and the accuracy. As recommended by Montgomery et al. [3], the heat of reaction of solid tris(hydroxymethyl)aminomethane (THAM) with 0.100 M aqueous hydrochloric acid was measured to investigate an exothermic reaction, and the heat of solution of crystalline potassium chloride in water to investigate an endothermic reaction. The observed heats were compared with those in the literature.

INSTRUMENTATION

Sample and reference vessels are fixed in the thermostatted water bath, where heat evolved or absorbed in the sample vessel is exchanged freely with the ambient water. In mathematical expressions, endothermic phenomena may be included in exothermic expressions as usual. Any information in a sample vessel is expressed compared with that in a reference vessel. Temperature T in the sample vessel and time t are related as follows

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

where q , W and α are heat evolving rate, effective heat capacity, and a constant concerning heat exchange efficiency, respectively. Usually the letter C is used for heat capacity, but to avoid confusion W is preferred to C in this paper. It is assumed that in the calorimeter heat evolved spreads uniformly and instantly throughout the vessel, and that the temperature remains uniform in the water bath. Strictly speaking, the temperature signal θ , observed via a thermistor used as the temperature sensor, is distinguished from T . The value of θ should include a delay in the response of the measuring system. The relation between T and θ is expressed by

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

where β is a constant concerning delay of response. From eqns. (1) and (2)

$$\frac{Q}{W} = \frac{1}{W} \int q dt = \frac{1}{\beta} \frac{d\theta}{dt} + \left(1 + \frac{\alpha}{\beta}\right) \theta + \alpha \int \theta dt \quad (3)$$

Total heat Q , therefore, may be obtained from the observed signal θ by computing the right hand side of eqn. (3).

A simple analog computation circuit in which only one operational amplifier is utilized may be used to estimate Q from θ , provided that only the total heat is needed. Resistor R_1 and capacitor C_1 connected in parallel,

and resistor R_2 and capacitor C_2 in series are attached to the inverting input terminal and feedback circuit of the operational amplifier, respectively. Fundamental knowledge of the analog circuit gives eqn. (4) below. The constants, α and β depend upon the construction of calorimeter used. In addition, α is affected by the sample volume in the vessels, the effective heat exchange area and the materials of the vessels. When the time constants R_1C_1 and R_2C_2 in the operational amplifier circuit are adjusted [1] to be equal to $1/\beta$ and $1/\alpha$, respectively, of the working calorimeter, the value of Q/W expressed by eqn. (3) may be observed as output voltage of the analog circuit according to eqn. (4)

$$E_0 = -\frac{R_2}{R_1} \left[R_1C_1 \frac{dE_i}{dt} + \left(1 + \frac{R_1C_1}{R_2C_2} \right) E_i + \frac{1}{R_2C_2} \int E_i dt \right] \quad (4)$$

because E_i and E_0 are directly proportional to θ and Q/W , respectively.

EXPERIMENTAL

Reagents

Sample crystals of THAM, which were commercially available from Sigma Chemical Co. as a primary standard reagent, were used without further purification, the nominal purity being about 99.9%. Drying was performed according to the literature [4]. The crystalline potassium chloride used was guaranteed grade reagent available from Wako Junyaku Co. and dried for 3 h at 110°C before use. Aqueous hydrochloric acid of the required concentration was prepared by diluting more concentrated stock solution, and standardized to 0.1000 M by titration against weighed amounts of sodium carbonate. Deionized water was distilled just before use.

Calorimeter assembly

Two glass bottles of about 100 cm³ served as sample and reference vessels. Apparatus and parameters such as the thermistor, the heater element, the sample inlet and the geometry of the vessels, the arrangement of the two vessels, in the water bath, the motor driven agitator, the heater, and the cooler were essentially the same as those used in ref. 2. The heat exchange effect of the vessels was balanced by covering the bottom of each vessel with an insulator of styrene foam as previously reported [5]. A resistor (100 Ω , 1/8 W) coated with epoxy resin to protect it from water and chemicals was used as an electrical heating element for the heat calibration. A selected pair of thermistors (NLSB type, Shibaura Electronic Co.) was used in the vessels as the temperature sensors. The B constant of the thermistors was about

3500 K. Resistances of the thermistors in the sample and reference vessels were 2.570 k Ω and 2.454 k Ω , respectively, at 25°C. The water bath was constructed from 8-mm thick acryl boards, and contained about 27 dm³ of water. Six faces including a lid were covered with 25-mm thick styrene foam insulator. Stirrer bars placed in each vessel for mixing were remotely controlled from outside the water bath by magnets and synchronous motors.

Analog computation circuit

The thermistors used for the sample and reference vessels were constituted in a Wheatstone bridge. The unbalanced voltage, which was within $\pm 300 \mu\text{V}$, was amplified to ca. $\pm 2 \text{ V}$ by the preamplifier (PM-16A, Toa Electric Co.), and fed into the analog computation circuit as an E_i on line. The operational amplifier used was type LF356 (National Semiconductors Co.). In the circuit, large capacitance was preferred in order to provide the required time constant, so polycarbonate film capacitors were used. The output voltage of the operational amplifier circuit was monitored by a $Y-t$ recorder. For the calorimeter assembly, the reciprocals of the two time constants (R_1C_1 for the input circuit and R_2C_2 for the feedback circuit) were $0.52 \pm 0.05 \text{ s}$ and $(8.5 \pm 0.1) \times 10^{-3} \text{ s}$, respectively, in a typical run. Details of the optimum adjustment of time constants to α and β of the working calorimeter were almost the same as those reported in ref. 2.

Procedure

Sample and reference vessels contained 60 cm³; 0.1000 M hydrochloric acid for the THAM experiment, and water for potassium chloride. After a period of about 30 or 40 min, thermal equilibrium was attained in the water bath. This was almost the same time as the warming-up period for the Wheatstone bridge and preamplifier. The two time constants for the analog circuit were adjusted to the constants of the working calorimeter (in the order of α and β) by using electrical heating generated at a constant rate. The calorimeter should be maintained in the optimum heat range; in the present report, therefore, the sample was added little by little to the sample vessel, so that instantaneous heat effects did not exceed the mixing limit in the sample vessel. Irregular heat conduction to the thermistors would give large errors in the estimated values. For the sake of simplified handling, the solid sample was directly introduced into the sample vessel via the sample inlet, from outside of the covered water bath, without removing the cover. Before and after the sample addition, electrical heating was carried out, and Joule heats were estimated in the usual manner from trails recorded on a strip chart. Samples were weighed with an electric balance (Electrobalance, Cahn).

RESULTS AND DISCUSSION

If q/W in eqn. (1) is a constant, this equation may be solved mathematically. In a general chemical reaction, however, q/W should not be constant. One of the advantages of the analog computation technique is the capability of treating differential equations, such as eqns. (1) and (2), without any restrictions. An analog computation circuit composed of three operational amplifiers has been reported for the estimation of heats of solution [2]. In the present report, however, the use of a single operational amplifier was preferred, because of such advantages as simplification of the hardware, ease of handling for an unskilled operator, simple off-set adjustment, and the small drift in final output voltage, provided that direct determination of total heat, rather than the instantaneous caloric effect, is needed. The handling procedure of the calorimeter was also simplified. Therefore, as mentioned above, the solid sample was introduced directly into the sample vessel from outside of the water bath without taking off the cover. Even when the difference in temperature between the sample crystals and the liquid in the vessel is about $\pm 10^\circ\text{C}$, the total heat estimated was considered not to be affected. Moreover, thermal insulation of the water bath was improved so that stable output of the analog circuit including the differential circuit may be maintained during the measuring period. The temperature drift in the water bath was within $\pm 0.2^\circ\text{C}$ during a series of measurements, even if no temperature control system was introduced. It was not used (for simplicity) during runs. In the differential circuit of an operational amplifier, some resistance is generally introduced in series with the capacitor to remove or minimize noisy signals. In the present paper, however, no resistance was introduced. The final output voltage of the analog circuit recorded on the strip chart of a $Y-t$ recorder was measured to test the repeatability and precision of the proposed calorimeter, for which reproducible electrical heating was preferred. In the heat range 1–15 J, error expressed by the ratio of heat released to output voltage of the analog computation circuit, which was shown as a trace on the analog recorder, was 0.49% (standard deviation), obtained from twenty runs. Before and after each addition of a solid sample, electrical heating was applied to estimate output voltage per joule in the adjusted time constants, since the effective heat capacity in the sample vessel may have changed.

Montgomery et al. [3] after detailed discussions recommended the use of THAM and potassium chloride as test substances for determining the energy equivalent. The heat of reaction of THAM with 0.100 mol dm^{-3} aqueous hydrochloric acid was $245.54 \pm 0.04\text{ J g}^{-1}$ at a concentration of $0.0500\text{ mol dm}^{-3}$ at 298.15 K . This value was obtained as the weighted mean of the chronological plot. In their results, another value of 245.76 J g^{-1} was also reported, and discussed concerning the difference between the two values. Corresponding values found in other papers are $7107.0 \pm 0.9\text{ cal mol}^{-1}$ [4],

$29.744 \pm 0.003 \text{ kJ mol}^{-1}$ [6], and $7114 \pm 4 \text{ cal mol}^{-1}$ [7]. However, in the present report, the higher value reported by Montgomery et al. was used. The aim of the present report was to test the accuracy of the batch heat exchange calorimeter. Every batch of heat smaller than several joules should be treated for the optimum conditions of each run. In a series of measurements, therefore, specimens of crystalline THAM less than 20 mg were added twenty times to aqueous hydrochloric acid to obtain respective total heats, which were summed to estimate the heat of reaction. To match seriously the recommended value, a small excess of the sample was introduced, and the corresponding heat effect at the indicated sample weight was calculated between the last two values. The mean of two series of runs was $89.38 \pm 0.44 \text{ J g}^{-1}$, which was 0.08% larger than the value recommended by Montgomery et al. [3].

To test the accuracy of the calorimeter in an endothermic system, heats of solution of crystalline potassium chloride in water were measured. It was pointed out that the observed heat of solution may depend on the drying method employed for the potassium chloride crystals used as the specimen. In the present report, the drying method for the sample crystals was not as severe as that reviewed in the literature [3]. Crystalline potassium chloride was dried for 3 h at 110°C . The measuring procedure was almost the same as those of the THAM experiment. The heat of solution of potassium chloride in water was estimated as $17.58 \pm 0.08 \text{ J mol}^{-1}$ for two series of runs, which was within $\pm 0.47\%$ of the corresponding value ($17.4992 \pm 0.0059 \text{ kJ mol}^{-1}$) reported [3] as the enthalpy of solution calculated for 1 mol of potassium chloride not heated above 600 K in 1110 moles of water (molality of $\text{KCl} = 0.0500 \text{ mol kg}^{-1}$).

In the estimation of heats of solution of THAM, only two series of results were obtained, but each heat of solution of twenty samples was observed in each series, and expressed as the summation of them. The situation was the same for estimating the heats of solution of potassium chloride in water. Therefore, accuracy and validity of the proposed calorimetry may be confirmed from the estimated heats, as correct results would not be obtained from erroneous measurements.

REFERENCES

- 1 M. Nakanishi and S. Fujieda, *Anal. Chem.*, 44 (1972) 574.
- 2 S. Fujieda and M. Nakanishi, *Thermochim. Acta*, 111 (1987) 167.
- 3 R.L. Montgomery, R.A. Melaugh, C.C. Lau, G.H. Meier, H.H. Chan and F.D.R. Rossini, *J. Chem. Thermodyn.*, 9 (1977) 915.
- 4 S.R. Gunn, *J. Phys. Chem.*, 69 (1965) 2902; E.W. Wilson, Jr. and D.F. Smith, *Anal. Chem.*, 41 (1969) 1903.
- 5 M. Nakanishi and S. Fujieda, *Thermochim. Acta*, 43 (1981) 189.
- 6 J.O. Hill, G. Ojelund and I. Wadsö, *J. Chem. Thermodyn.*, 1 (1969) 111.
- 7 D.J. Eatough, J.J. Christensen and R.M. Izatt, *J. Chem. Thermodyn.*, 7 (1975) 417.