Thermochimica Acta, 161 (1990) 147–153
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A HEAT EXCHANGE CALORIMETER FOR SMALLER HEAT EFFECTS INVOLVING AN OPTRONIC HEAT SOURCE

SHUKO FUJIEDA and JUNKO KAWAHITO *

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

(Received 25 September 1989)

ABSTRACT

In a heat exchange calorimeter, the heat evolved in the sample vessel is freely exchanged with the bath water. For measuring the smaller heat effects generated by samples of the size usually involved in chemical experiments, the use of light irradiation, such as a wireless heat source, giving a known heat effect to the calorimeter was examined. A visible light beam was introduced by a bundle of glass fibres and irradiated onto a light-receiving plate fixed horizontally in the sample solution. The total heat irradiated Q_{opt}, ranging from 0.09 J to 1 J or from 1.8 mJ cm^{-3} to 20 mJ cm^{-3}, was obtained from the product of the voltage drop across the lamp E_{lamp}, ranging from 2.37 V to 14.30 V, and the irradiating time t, ranging from 80 s to 120 s. Plots of Q_{opt} versus E_{lamp} were linear. Plots of q_{opt}, calculated from Q_{opt}/t, versus E_{lamp} were also linear: $q_{opt} = 0.683\ E_{lamp} + 0.105$, obtained by the method of least-squares. To test the effect of light irradiation on sample solutions, aqueous $CuSO_4$ solutions were used as a model material, having an absorption maximum at almost the same wavelength as the maximum intensity of the irradiated light. As scattering materials, $CaCO_3$ and activated charcoal were used for white and black suspensions, respectively. The white suspension had no significant effect, in contrast to the $CuSO_4$ solution and the black suspension. In general, heat calibration by light irradiation is recommended. However, in samples which absorb or disperse light, the calibration should be carried out in the same sample solution so that an unknown enthalpy can be estimated in the usual manner in precision calorimetry.

INTRODUCTION

In a heat exchange calorimeter [1], the sample and reference vessels are fixed differentially in a temperature-controlled water bath. The heat released in the vessels is freely exchanged with the ambient water. The thermal behaviour is expressed by a simple differential equation: $dT/dt = q/C - \alpha T$, where T represents the temperature in the sample vessel defined against that

---

* The Doctoral Research Course in Human Culture, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan.

of a reference, q is the rate of heat evolution and t is the time. The efficiency of heat exchange is shown by a constant term α, which is directly proportional to the heat exchange area and inversely proportional to the effective heat capacity C of the vessel contents [2]. The two terms, α and C, control the rate of temperature change in the vessels. The extent of heat exchange also depends on the material of the vessels.

The temperature signal θ observed by thermistors installed in each vessel, may include a delay in the response of the sensing device, and is related to T by the differential equation: $\mathrm{d}\theta/\mathrm{d}t = \beta(T - \theta)$, where β is a constant relaxed to the extent of the delay. Electric signals generated by θ were treated by means of analogue and/or digital computations to estimate q and the total heat Q.

In a previous study [3] estimating comparatively small heat effects in smaller samples, vessels were devised to diminish the heat exchange between the sample solution and the ambient water, so that α becomes small. In the circumstances, the temperature change in the vessels and the electric signals were large, even if the same heat was evolved. Unfortunately, however, it took time to exchange the heat with the ambient water. In measuring a Joule heat, as a result of a small α value, the heat evolved from a heater element immersed in the sample solution may leak out to the outside of the calorimeter system via the lead wires. In the previous study [3], a small 1/16 W resistor coated with epoxy resin was used as the heater element and the lead wires were lengthened and immersed in the sample solution so that the leaking heat was released in the solution. For an accurate treatment of smaller heat effects, any method of heating without direct contact with the solution or without immersion in the solution is required for a Joule heat measurement.

With a chemical reaction in a homogeneous system, the heat may be evolved over the whole area of the vessel, whereas the Joule heat evolved from a heater element is a point source of heat [3]. Therefore, a heat supply throughout the solution in the vessel is also required for the heat calibration.

In the present work with a wireless heat source, light was introduced by a bundle of glass fibres from a light source placed outside the calorimeter, and irradiated onto a small black board fixed in the sample solution. A platinated platinum plate was used as the black board. Joule heat was measured without connecting the sample solution with the outside of the calorimeter via lead wires. Three kinds of model materials were selected as samples to test the specific effect of light irradiation on the Joule heating. For solutions absorbing light, aqueous $CuSO_4$ solutions were used. As materials scattering light, $CaCO_3$ was used for a white solid, and activated charcoal for a black solid. When observing a smaller heat effect, the volume of the solution to be treated in a run should be taken into consideration; therefore, the dimension J cm^{-3} was preferred to J for comparison with other caloric estimations.

EXPERIMENTAL

Reagents

All the reagents used were of guaranteed grade. For preparing the platinated platinum, $H_2PtCl_6 \cdot 6H_2O$ and $Pb(CH_3COO)_2 \cdot 3H_2O$, Wako Chemical Co., Tokyo, were used. Deionized water was boiled before use.

Aqueous solutions of $CuSO_4$ were prepared in the range 1.00×10^{-2} M–4.00×10^{-1} M. Precipitated calcium carbonate, Kanto Chemical Co., Tokyo, was used as a white suspension material, the content being from 0.020 to 0.200 wt.%. The activated charcoal, Takeda Chemical Co., Tokyo, used as the black suspension in the range 0.010 wt%–0.140 wt.%, was treated once by water to lower the activity and to improve the floating property.

Apparatus

The essential parts of the heat exchange calorimeter and the analogue computation circuit were constructed in almost the same manner as reported previously [2]. Vessels installed with the black board and the light-emitting system were incorporated into the heat exchange calorimeter.

The platinated platinum board used as the light-receiving plate was 10 mm^2, because each vessel was a 100 cm^3 glass bottle and the volume of sample and reference solutions was typically 50 cm^3. The electroplating was carried out at a current density of 60 mA cm^{-2} for 5 min in the usual manner. The plate was fixed horizontally 25 mm away from the condensing lens set at one end of the bundle. The size of the light spot was 5 mm in diameter at 10–15 mm below the surface of the solution. The thermistor installed in each vessel was screened from direct heating by scattered light. In the present work, the same plates were installed in each vessel so that sample and reference have an equal heat capacity. Electronic heater elements were also installed in the vessels in order to carry out a calibration run.

Light-emitting system

A commercially available light-source system (HLS 2500, Hoya Co., Tokyo) was used for the light irradiation. A source-power voltage lower than 15 V a.c. was applied to a halogen lamp with a dychroic mirror (JCR 15V 150W, Hoya Co.) and the voltage drop across the lamp, E_{lamp}, during the irradiation was monitored by a digital voltmeter. The light introduced by the bundle of glass fibres was irradiated onto a light-receiving plate fixed in each vessel. The bundle, 2.0 m long and 1.2 mm in diameter, was made from 312 glass fibres 50 μm in diameter. A small lens was set at one end so that the irradiated light could be condensed into a small spot on the plate. To protect the glass fibre from heating, a heat-absorbing filter (HA-50, Hoya Co., Tokyo) was installed between the outlet of the lamp housing and the bundle. The spectroscopic characteristic of the lamp light was specified by a relative maximum intensity at about 740 nm [4]. However, if the spectroscopic characteristics of both the filter and the glass fibres are taken into consideration, the relative maximum intensity of the irradiated light as a whole may be at 650 nm [4].

Procedure

50 g of water or copper sulphate solution were weighed, for good reproducibility, into each vessel and set in the water bath in almost the same manner as reported previously [2]. For experiments involving the suspension material, $CaCO_3$ or activated charcoal was added to water in each vessel. The optically added total heat effect Q_{opt} was recorded on a strip chart recorder as an output of the analogue computation circuit. The absolute value of Q_{opt} was experimentally related to the total heat evolved by the electric heating Q_{el} carried out in the same sample solution. All of the caloric measurements were executed at 25.0 °C in a precisely controlled water bath [5].

RESULTS AND DISCUSSION

When smaller heat effects are treated in solution calorimetry, the problems encountered may differ according to the volume of sample solution in which heat is being evolved. In the present work, the sample size used in common chemical experiments, was selected for the sake of applicability and simplicity of the calorimeter. Estimations of the heat evolved per sample size in J cm^{-3}, as well as the absolute heat in J, are recommended in describing the smaller heat effects in microcalorimetry. A heat effect ranging from 0.09 to 1 J was treated in the present work, which covers an estimated range from 1.8 to 20 mJ cm^{-3}, respectively.

In the present work, visible light was selected as a heat source from those available, even though an infrared light provides a better heat source. Because there was no stabilisation circuit for the power supply of the lamp, during light irradiation, the voltage drop across the lamp, E_{lamp}, was monitored by a digital voltmeter. The fluctuation of E_{lamp} was within ± 0.04 V (a.c.), which was considered acceptable.

A typical chart recorder strip of total heat constantly irradiated, Q_{opt}, is shown in Fig. 1; this is almost the same as that given by electric heating. The beginning and end of the irradiation show no significant delay in the response. In a typical run, for example, a 50.00 g water sample was irradiated by an E_{lamp} of 4.33 V (a.c.) for 100.88 s, corresponding to 0.3072 J

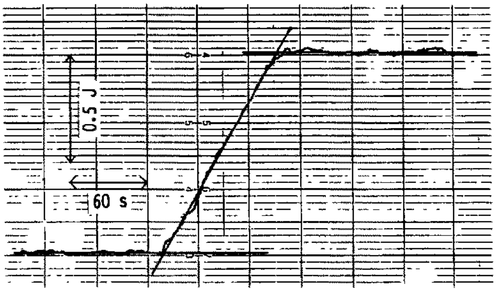

Fig. 1. A typical thermal trace of the total heat evolved by continuously irradiated light in 50 g water.

by electric heating. As the delay time in the irradiation at the beginning and end of a run due to the on-off actions of the lamp was about 0.6 s maximum over the whole measuring system, t was selected to be longer than about 100 s so that the influence of the delay time on t may be neglected. In Fig. 2, E_{lamp}/V (a.c.) was varied as: A, 2.37 ± 0.02; B, 4.33 ± 0.04; C, 5.85 ± 0.04; D, 7.52 ± 0.04; E, 10.01 ± 0.03; and F, 14.30 ± 0.04. At each E_{lamp}, the total irradiated heat effect, Q_{opt}(J), was measured in water several times in the range 1.8–20 mJ cm^{-3} or 0.09–1 J, respectively. Plots of Q_{opt}(J) versus t(s) gave a linear result as shown in Fig. 2. The instantaneous heat effect or the rate of heat evolved, q_{opt}(mJ s^{-1}), calculated from Q_{opt}/t, was 1.10(3.6%), 3.72(0.98%), 4.15(0.72%), 5.21(0.58%), 6.86(0.58%) and 9.92(0.30%) at each E_{lamp}, respectively. The figures in parentheses are the standard deviations of five values at different values of t. Fairly good results were obtained. A plot

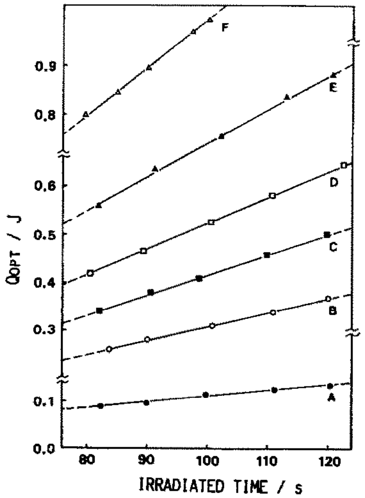

Fig. 2. Linear plots of the total heat irradiated Q_{opt} versus irradiated time t for water at E_{lamp} (a.c.) values: A, 2.37V; B, 4.33V; C, 5.85V; D, 7.52V; E, 10.01V; and F, 14.30V.

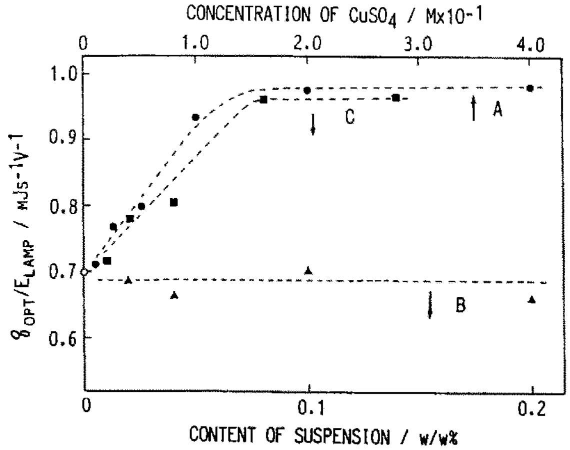

Fig. 3. Plots of q_{opt}/E_{lamp} versus concentrations of: A, $CuSO_4$; B, $CaCO_3$; and C, activated charcoal as light-absorbing substance, white and black suspensions, respectively. The circle on the left axis is the result for water.

of q_{opt} versus E_{lamp} obtained from the results was also linear and was calculated to be $q_{opt}(\text{mJ s}^{-1}) = 0.683E_{lamp} + 0.105$ by the method of least-squares. In practice, Q_{opt} may be estimated from observations of t and E_{lamp} by the expression $Q_{opt}(\text{mJ}) = (0.683\ E_{lamp} + 0.105)t$.

Solution calorimetry, in contrast to spectroscopy or other methods, presents, in general, no restriction for the sample solution. However, some problems relating to light irradiation were tested in the present work. Aqueous $CuSO_4$ solution, having an absorption maximum at almost the same wavelength as the maximum intensity of the irradiated light, was used as the model material. In six solutions in the concentration range 1.00×10^{-2}–4.00×10^{-1} M, Q_{opt} was observed at a variety of constant E_{lamp} values at several t's. In the range from 0.4 to 1.4 J, or from 8m to 28 mJ cm^{-3}, plots of Q_{opt} versus t fell in a line, almost the same as in Fig. 2. Fluctuation ranges of the observed data were completely within $\pm 0.8\%$ and the repeatability was also good. Plots of q_{opt} versus E_{lamp} fell in a line which passed through the origin. Plots of q_{opt}/E_{lamp} versus concentration of $CuSO_4$ were influenced by the concentration in the range 0–0.20 M, as shown in Fig. 3A. (The dotted lines in Fig. 3 were drawn by hand.)

To test the influence of a solid suspension on the irradiated heat effect, white and black materials were used.

Precipitated calcium carbonate was selected for the white suspension. Four aqueous suspensions from 0.0200 to 0.200 wt.% were used. Suspensions more than 0.1 wt.% were not translucent, so experiments were carried out within the concentration range at which the arrival of irradiated light on the plate is visible to the naked eye. Plots of Q_{opt} versus t were also linear at several values of E_{lamp} measured. Plots of q_{opt} versus E_{lamp} in different suspensions produced lines which almost passed through the origin, and plots of q_{opt}/E_{lamp} versus the amount of suspended $CaCO_3$ (wt.%) gave a horizontal line, as shown in Fig. 3B. In the case of $CaCO_3$, the suspended material had no significant effect on the Joule heat. The thermistor in each vessel was screened from the scattered light. However, if the screen was not installed, scattered light corresponding to heat of about 0.3 J was caught by the thermistor.

Activated charcoal was selected as an example of black material with both absorbing and light scattering properties. Five suspensions in the concentration range 0.0100–0.140 wt.% were used. The plots of Q_{opt} versus t were linear. All plots of q_{opt} versus E_{lamp} were also linear and passed through the origin. Plots of q_{opt}/E_{lamp} versus concentration of suspended activated charcoal are shown in Fig. 3C, where a behaviour similar to that of aqueous $CuSO_4$ solution can be observed.

In measurements of Joule heat in a colourless transparent solution, or water and $CaCO_3$ suspension, Q_{opt} and q_{opt} can be obtained from E_{lamp} and t, within the tested range, 0.09–1 J or 1.8–20 mJ cm^{-3}. The light irradiation method as described here is strongly recommended. The empirical expression written above is generally acceptable. In precision calorimetry, however, heat calibration by known heat effect should be carried out with the same conditions and in the same sample solution in which the unknown enthalpy is to be estimated. The light-receiving efficiency of each plate may also be different. In the presence of materials which absorb and disperse the irradiated light, as shown in Fig. 3, the relation between Q_{opt} and Q_{el} should be determined in estimations of unknown enthalpy.

REFERENCES

1 M. Nakanishi and S. Fujieda, Anal. Chem., 44 (1972) 574.
2 M. Nakanishi and S. Fujieda, Thermochim. Acta, 43 (1981) 189.
3 S. Fujieda and M. Nakanishi, Thermochim. Acta, 88 (1985) 273.
4 K. Kobayashi, S. Niwa and K. Satoh, The Technical Application of Light Fibre, Hoya Information, Hoya Co., Akishima, Tokyo, 1988, p. 2 (in Japanese).
5 S. Fujieda, J. Kawahito and M. Nakanishi, Thermochim. Acta, 157 (1990) 163.