A FLOW MICROCALORIMETER FOR MEASURING THE HEATS OF MIXING OF BINARY LIQUIDS BY A CONTINUOUS PROCESS

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In order to measure heats of mixing or heats of dilution for many solutions by a continuous process accurately, a twin conduction type flow microcalorimeter has been constructed, improving the design of the same type of calorimeter reported previously. The thermal stability of the heat sink was enhanced by enlarged contact area of the main heat sink block with a thermostated water bath. Mixing efficiency of the mixing cell and the stability of the base line were improved by the use of a new mixing cell having a long mixing zone and symmetrically arranged sample and reference cells. Waiting time for establishment of thermal steady state was also reduced by sandwiching each of the cell by a pair of wide thermopiles plates and a pair of sub-blocks. Heats of dilution of aqueous urea solutions were measured by a continuous process, and results obtained well agreed with accepted values by Gucker *et al.* The accuracy and thermal resolution in this calorimeter were estimated to be less than 0.05% and 3 $\mu J \cdot s^{-1}$.

Keywords: binary liquids, flow microcalorimeter, heat of mixing

Introduction

Since a flow microcalorimeter for measuring the heats of mixing or dilution of solutions was developed by Stoesser and Gill [1], improved apparatus based on the same principle have been reported by many investigators [2–5]. Especially, twin conduction type flow calorimeter, originally developed by Monk and Wadsö [2], has often been used [6–8]. In our previous study [9], two types of flow calorimeters were constructed and compared. It was shown conclusively that the conduction type unit was better than the isoperibol type because of its higher precision, shorter measurement time and easier procedure of the measurement.

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However, some problems were also found in certain types of conduction flow calorimeters. For a long series of measurement carried out continuously, the temperature of the cell changes appreciably by the heats generated in the cell, because the heat sink block of most apparatus is thermally insulated from the outer thermostat by an air gap. Also mixing efficiency of the cell is often insufficient for measurement on viscous or dense fluids. Therefore, to obtain precise data using such a calorimeter, the operator must take a long interval between the measurement points so as to restore the temperature of the heat sink to that of the thermostat, and forgo measurements on viscous or dense solution. These restrictions offset the advantages of the flow method to a considerable extent.

In order to expand the applicability of the calorimeters of this type by removing these deficiencies, a twin conduction type flow microcalorimeter having a thermally stable heat sink and a mixing cell with high mixing efficiency was constructed.

Features required of a calorimeter and their realization

To determine the excess heat capacity of a binary mixture of organic liquids to an inaccuracy of less than 1% from temperature dependence of the excess enthalpy, the imprecision of the calorimeter has to be less than 0.1% for a measurement spanning a temperature interval of 10 K, as described in the previous paper [10]. For such precision, the temperature of the sample must be constant within 0.01 K even when large excess enthalpies are observed. In addition, for a continuous series of a number of measurements, especially for determination of a small heat, the baseline of the electrical output of the calorimeter must be stable near 0 V regardless of magnitude of the observed heat and length of the determination time.

A flow twin conduction type calorimetric unit was designed and constructed so as to satisfy these requirements. Schematic diagram of the calorimetric unit is shown in Fig. 1. The heat generated in the mixing cell is conducted first to a pair of sub-blocks through a pair of thermopile plates (thermomodules), then to the main block, and finally to the thermostated water bath. The following two points in the construction are the improvement over our previous design [9];

(i) to reduce the time required for attainment of thermal steady state during mixing of liquids, a pair of large-area thermomodules are used for each cell,

(ii) to enhance the thermal leak efficiency of the heat sink, all area of the upper end of the rectangular main heat sink block is firmly attached to the top plate of the thermostated outer vessel in accordance with the following estimation.

The heat conduction area, S, was calculated to be 22 cm^2, for the condition of the maximum rate of heat generation, $W = 0.1$ J·s^{-1}, the maximum temperature increase allowed in the cell, $\Delta T = 0.01$ K, and the thermal length from the cell to

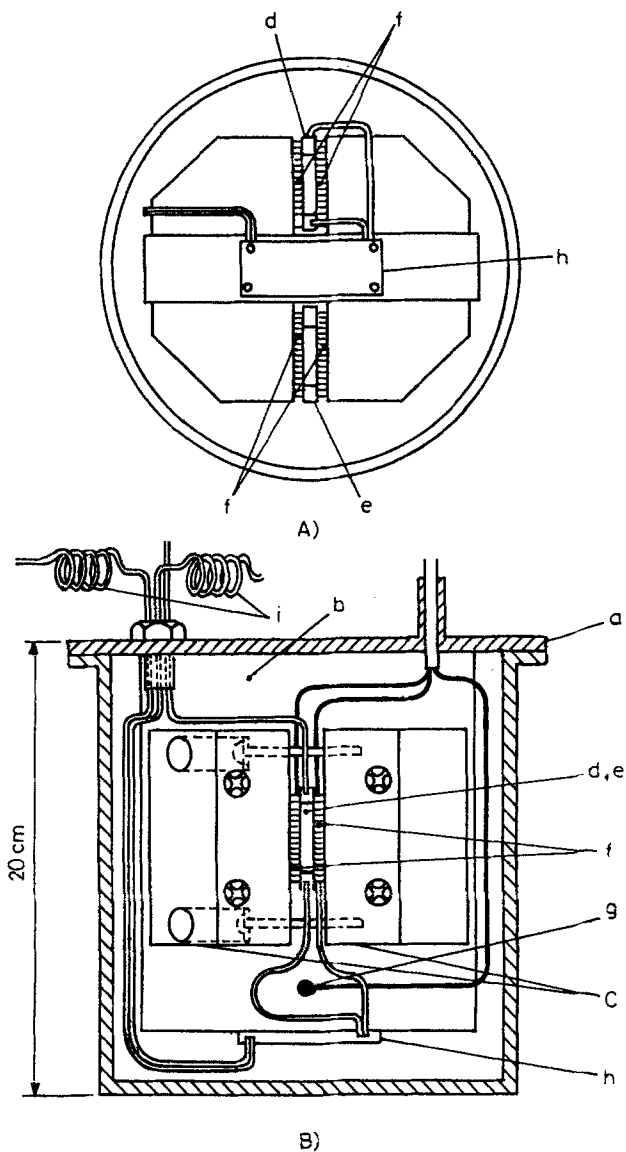**Fig. 1** Schematic diagram of the calorimetric unit. (A), bottom view; (B), side view; a, waterproof vessel; b, main heat sink block (copper); c, sub-block (copper); d, mixing cell; e, reference cell; f, thermomodule (CP1.4–127–10L, Melcor); g, silicon temperature sensor (KTY-10A, Siemens); h and i, heat exchanger (h: with heat sink, i: with water bath)

thermostated water, $L = 9$ cm, using the equation of thermal conduction in a steady state;

$$W = kS\Delta T/L \qquad\qquad (1)$$

where k is the thermal conductivity of copper. In the present apparatus, contact area of the rectangular main block with the lid of the waterproof vessel containing the calorimetric unit was taken as 90 cm^2, to account for the larger thermal resistance in the sub-block and thermopile plate than in the main block. The total mass of the heat sink block is 26 kg.

A pair of thermomodules contacting with both sides of the mixing cell were further sandwiched in a pair of sub-blocks. Two such assemblies for the sample and reference were mounted symmetrically on the both sides of the main block in the opposite directions. The masses of the two sets of the cell and sub-block were balanced within 3%. To equalize the temperature of the flowing liquids to that of the heat sink before mixing, two serially connected heat exchangers were placed in and outside the thermostated vessel. The outer (primary) exchanger was made of coiled 25 cm long stainless-steel tube and inner (secondary) one of the same material was soldered to a copper frame and mounted on the lower end of the main heat sink block. A silicon temperature sensor was attached to the main block near the secondary heat exchanger for the measurement of the temperature of the calorimeter. These details of the design were intended for better stabilization of the baseline of the differential output of thermomodules, both in the flow-stop and liquid-flowing states.

The mixing cell is shown in some details in Fig. 2. To ensure complete homogeneous mixing, longer than 1 m of length may be required in the flow path made of 1,0 mm inside diameter stainless-steel tube [10]. Two calorimetric liquids meet at a T-piece placed at the centre of the cell, and mix homogeneously while flowing through a 105 cm long coiled mixing tube. In order to improve the mixing efficiency, turbulence is created in the mixing cell by flattening the tube at several points along the mixing zone. The reference cell is same in construction as the mixing cell, but sample liquid does not flow in it. A 100Ω of manganin wire heater for electrical calibration was wound round the mixing tube. To avoid large temperature distribution over the cell, the mixing tube assembly was fitted in a copper frame plate with epoxy resin containing copper powder. The mass of the cell was 82 g, which is 40% larger than our previous design. But it is sufficiently small compared with heat sink.

The vessel housing the calorimetric unit was immersed in a water bath, maintained within ±0.0003 K of an intended temperature by means of a constant cooling and heater control using a cooling pump (CH-150BP2, Taitec, Japan) and a precision temperature controller (PTC-40, Tronac, USA). The two liquids for mixing were pumped in the calorimeter through teflon tubing by a pair of peris-
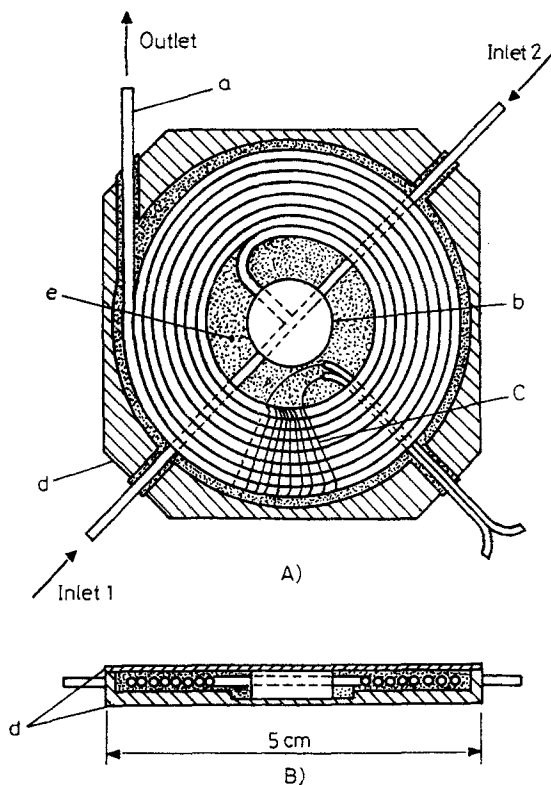
Fig. 2 A perspective (*A*) and a cross section (*B*) of the mixing cell. *a*, mixing zone made of stainless-steel tube with several frictions (1.0 mm in i.d. and 105 cm long); *b*, stainless-steel T-piece; *c*, manganin wire heater (100Ω); *d*, copper frame; *e*, epoxy resin containing copper powder

taltic pumps (SJ-1211H, Atto, Japan) equipped with an elastic tube (PharMed tube, Norton, USA).

The circuit for electrical calibration consists of a D.C. stabilized power supply (PW18-IT, Kenwood, Japan), attenuator, 100Ω standard resistor and digital multimeter (Fluke 87, USA). The current supplied to the calibration heater was calculated from the voltage drop across the standard resistor. The differential outputs of the thermomodules and the bridge of the silicon sensor were amplified by a low noise low drift D.C.-amplifier (AM-1001B, Ohkura, Japan). The output was digitized and monitored using a multimeter (VOAC7511, Iwatsu, Japan) and a recorder (U-125, Shimadzu, Japan), respectively.

Results and discussion

The apparatus was examined about a some performance considered to be important for the flow calorimetry. In the flow method, heats of mixing are calculated from the displacement ΔV of the output voltage, relative to the base line, measured during continuous mixing of two sample liquids flowing at a constant rate. The approach of ΔV from 0 to the saturated value ΔV_{sat} is expected to follow a relaxation equation;

$$\Delta V / \Delta V_{sat} = 1 - \exp(-t / \tau) \tag{2}$$

where τ is a time constant. The time t is measured from the beginning of the mixing or heating (for the electric calibration). As seen in Fig. 3, the present apparatus well conforms to Eq. (2). By a least-squares method applied to the plots in Fig. 3, τ was estimated to be 85 s. For ΔV to exceed 99.98% of ΔV_{sat}, t must be longer than 8.5τ. The waiting time for establishment of the steady state was determined to be 12 min, which is approximately equal to a half the value of the previous apparatus.
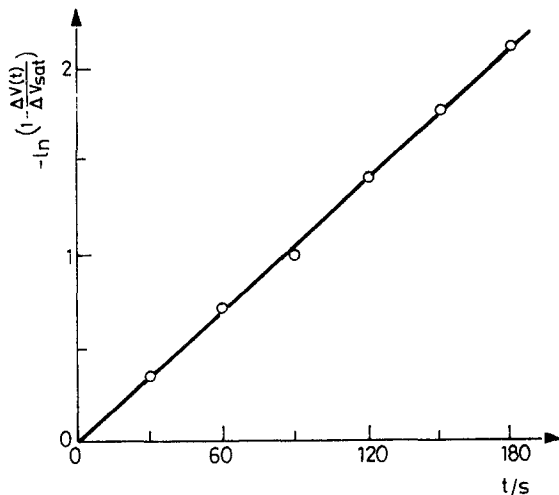

Fig. 3 Plots of $-\ln[1 -\Delta L(t)/\Delta V_{sat}]$ against time t for a constant electrical heating of $0.1\ Js^{-1}$, compared with Eq. (2)

Ideally, ΔV(V) at a steady state should be proportional to the observed heat of mixing $W(J \cdot s^{-1})$ as follows:

$$\Delta V = \varepsilon W \tag{3}$$

where ε is a calibration constant. It depends slightly on materials and different flow rates. The value of ε was determined as $0.147\ VJ^{-1}s$ from electrical calibra-

tion experiment by pumping water into the mixing cell at a constant flow rate of $1 \times 10^{-2} cm^3 s^{-1}$. Figure 4 shows the deviation of ΔV from Eq. (3) against the electrical heating power. As shown in this figure, deviation from linearity of the output was within 0.02% for a large observed heat. Taking into account the accuracy of the digital voltmeter and standard resistor, accuracy was believed to be better than 0.05%. For measurement of the smaller heat, deviation was somewhat larger, affected by noise and drift of the base line.
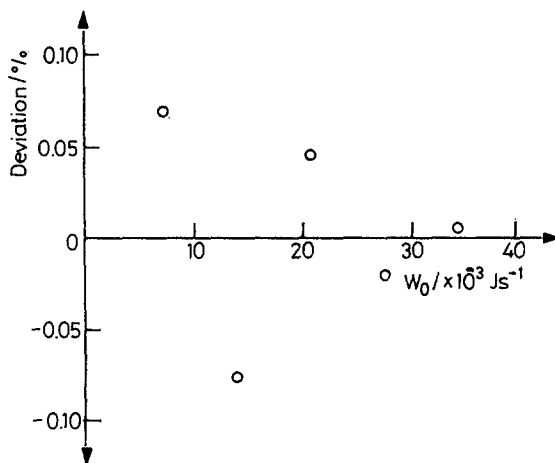

Fig. 4 Deviation plot of the output voltage ΔV from the linear relation of Eq. (3) in the text against the electrical heating power W_O

The absolute value of the base line was $0.2 \mu V$ when the flow was stopped and $0.5 \mu V$ when water was flowing at a rate of $1.0 \times 10^{-2} cm^3 s^{-1}$. Fluctuation of the base line caused solely by the flow of liquid was $0.4 \mu V$ in the peak to peak value. For the case of the large and unstable flow base line, correction for this effect is very important and might be complicated. But the baseline fluctuation met in this study was not inordinately large compared with the $0.15 \mu V$ noise and drift of the D.C.-amplifier. Thermal resolution was estimated to be $3 \mu J \cdot s^{-1}$ from these values. Such precision will be adequate for determination of excess molar enthalpy up to $0.02 J \cdot mol^{-1}$.

The temperature of the main heat sink was detected by a silicon sensor in a main block with a noise of the bridge output less than 0.18 mK. The temperature of the sink began to increase slowly after calibration heating at a rate of $0.144 J \cdot s^{-1}$ was started, and became constant 40 min later at a value 9.9 mK above the bath temperature. This magnitude of heating corresponds to an excess enthalpy of $2.9 kJ \cdot mol^{-1}$, molar volume of $100 cm^3$ and flow rate of $5 \times 10^{-3} cm^3 s^{-1}$. The temperature of the main heat sink returned to the original value in 40 min when the heating was stopped. The differential output of thermomodules reached

steady state in 12 min from the start of the same heating, and did not drift for 60 min. When the heater was turned off, it returned to the original base line in 12 min. These results show that the output of this calorimeter is not influenced by a considerable variation of thermal state of the heat sink.

In order to check the accuracy of the apparatus, heats of dilution of several aqueous urea solutions were measured by a continuous process. Materials used were Ultra pure urea (Schwarz/Mann., USA) and water purified by deionization and distillation. The base lines were approximated by the time average of the output signals of two blank runs, in which only pure water was flowing, performed at the first and the last stages of the experiments. For each of the dilution steps, the endothermic signal was compensated by electrical heating for calibration. The mass flow rates of solution and solvent were observed with uncertainty less than 0.04% by measuring the mass decrease of the sample liquid and the time pumping it out. No fluctuation of flow rate was found from the recorded output signal. Therefore, the accuracy of the molality after dilution was believed to better than 0.04%.

Heats of dilution per mole of solute thus determined are listed in Table 1, along with the values calculated by an equation reported by Gucker and Pickard [11] in which the average deviation was estimated to be 1.8 J·mol^{-1}. As shown in this Table, the present result agrees well with their values. It confirms the improvement of the heat sink and the cells of present calorimeter. The discrepancy of the result at the low concentration may be caused by the insufficient resolution for the small heat in the present measurement as well as in the measurement reported in the literature.

Table 1 Heats of dilution of water(1) − urea(2) system at 298.15 K against initial and final molality of solutions

$m_{2,i}$[1]	$m_{2,f}$[1]	$W/\text{mJ·s}^{-1}$	$(\Delta H / n^2) / \text{J·mol}^{-1}$	
			exp.	calc.[2]
0.723	0.363	0.395	118.0	118.7
1.584	0.781	1.696	239.4	240.6
2.350	1.149	3.409	330.7	331.6
2.979	1.438	5.095	399.4	399.7
4.080	1.926	8.453	504.5	504.9
4.929	2.264	11.192	583.0	582.9

[1] Units: mol·kg^{-1}

[2] Calculated using Eq. (3) of Gucker and Pickard [11]

The present calorimeter enables a series of accurate measurements to be carried out by a continuous process. However, further investigations will be needed to improve mixing efficiency of the cell for measurements on viscous or dense

solutions. We are also considering automation of this apparatus by developing pair of piston displacement pumps and various interfaces with a computer system.

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Zusammenfassung — Zur genauen Messung von Mischwärmen und Verdünnungswärmen vieler Lösungen in einem kontinuierlichen Vorgang wurde ein Doppelleitungs-Flußmikrokalorimeter entwickelt, wobei die Gestaltung derartiger, bereits beschriebener Kalorimeter verbessert wurde. Die thermische Stabilität der Wärmeableiter wurde durch eine vergrößerte Kontaktfläche zwischen Wärmeableiterblock und thermostatisch geregeltem Wasserbad verbessert. Die Mischwirksamkeit der Mischzellen und die Stabilität der Basislinie wurden durch Anwendung einer neuen Mischzelle verbessert, die über eine lange Mischzone und über symmetrisch angeordnete Proben- und Referenzzellen verfügt. Auch die Wartezeit bis zum Einstellen des thermischen Gleichgewichtszustandes konnte verkürzt werden, indem jede der Zellen durch ein paar breiter Thermosäulenplatten und einem Paar Subblöcke umgeben wurde. Die in einem kontinuierlichen Prozeß gemessene Verdünnungswärme wäßriger Harnstofflösungen stimmte gut mit den akzeptierten Werten von Gucker et.al. überein. Der Fehler und die thermische Auflösung in diesem Kalorimeter wird auf weniger als auf 0,05 % bzw. 3 $J \cdot s^{-1}$ geschätzt.