

## An isothermal flow calorimeter for high-temperature basic solutions

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### Abstract

An isothermal flow calorimeter suitable for measuring heats of reaction in basic aqueous solutions is described. The calorimeter was constructed of materials capable of operating to 773 K and 40 MPa. Corrosion resistance was obtained by using nickel tubing in the calorimeter proper. An automatically controlled pulsed heater and a highly stable heat-leak path are used to maintain the reaction zone at a constant temperature. Energy effects from 0.15 to 120 J min<sup>-1</sup> can be measured to an accuracy of  $\pm 0.8\%$  at constant temperature and pressure. The calorimeter was tested by measuring the heats of dilution of aqueous NaOH solutions at 523 K and 5.5 MPa and was found to produce data in good agreement with literature values.

### INTRODUCTION

Isothermal calorimetry is based on measuring the energy required to maintain the reaction zone at a constant temperature during the course of a reaction. This condition is achieved in the calorimeter described here by adjusting the power output of a controlled heater to balance the rate of energy arising from the chemical reaction plus the power removed by a constant heat-leak path. The method is equally applicable to both endothermic and exothermic reactions. No heat capacity measurements are required and no corrections are necessary for the heat exchange between the reaction zone and the surroundings. These two conditions are inherent in the operation of the type of isothermal calorimeter described here as the fluids enter and leave at the same temperature and the temperature difference between the reaction zone and the surroundings is the same in both the electrical calibration and experimental runs.

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An isothermal titration calorimeter [1], an isothermal microcalorimeter [2], an isothermal, high-pressure flow calorimeter [3], an isothermal, elevated temperature, high pressure flow calorimeter [4], an isothermal flow calorimeter designed for high-temperature, high-pressure operation [5], and an isothermal flow calorimeter for high-temperature acidic aqueous solutions [6] have been described. In addition, the application of isothermal calorimetry to the measurements of heats of reaction [7], equilibrium constants for metal–ligand interaction and proton ionization [7–9], heats of mixing [10,11], and vapor–liquid equilibrium data [12] has been reported.

This paper describes a calorimeter suitable for use with high-temperature aqueous solutions containing inorganic bases, salts or weak acids. The calorimeter is based on using a controlled heat-leak path between the reaction zone and the surrounding container. This calorimeter retains all of the desirable operating characteristics and advantages of previous isothermal flow calorimeters [3–6] while offering the additional advantages of operation at temperatures up to 673 K and solution pH values from 5 to 14. Energy effects can be measured at any temperature–pressure combination in the ranges 373–673 K and 0.1–25.5 MPa, respectively. The data can be collected and displayed in digital form by a Macintosh Plus computer and/or obtained as a strip chart recording.

This instrument was developed to extend the pH range of the existing isothermal flow calorimeter for high-temperature aqueous solutions [6]. A versatile instrument was desired that could be used to measure energies arising from a wide variety of reactions under a wide range of conditions. Many current problems in science involve reactions at high temperatures and pressures including the chemistry in high-temperature ocean vents, corrosion problems in geothermal applications, high-temperature boilers and heat exchangers, and supercritical extraction involving hydrocarbons, alcohols, CO<sub>2</sub>, etc. All tubing used in the calorimeter was made of nickel to enable the instrument to work under the extreme corrosive conditions that arise at high temperatures while using aqueous solutions of inorganic bases. The calorimeter does, however, exhibit severe corrosion in the presence of either chloride solutions or strong acidic solutions.

The calorimeter has been tested by both electrical and heat of dilution (1.8445 m NaOH(aq) + H<sub>2</sub>O at 523 K and 5.5 MPa) calibrations. The data obtained were of approximately the same precision and accuracy ( $\pm 0.8\%$ ) as those obtained from earlier isothermal flow calorimeters.

## APPARATUS

The calorimeter is very similar to the isothermal high-temperature flow calorimeter described by us [6] and only a brief description will be given of those components that have not been changed extensively. The main changes are in the use of nickel tubing to resist corrosion by basic solutions, the

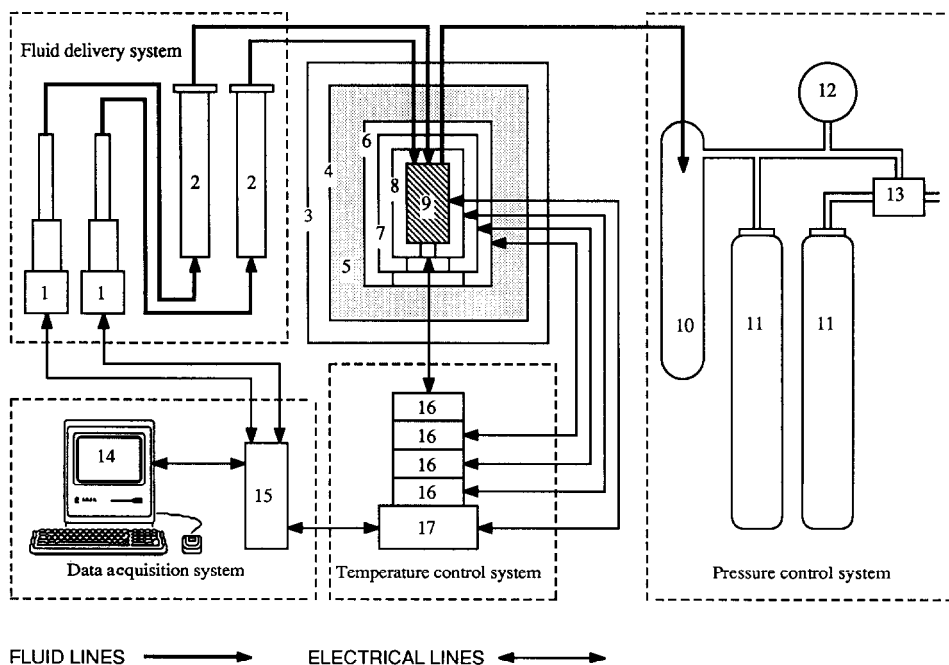


Fig. 1. A schematic diagram of the main components of the calorimeter: 1, pump; 2, pusher; 3, outer can; 4, insulating container; 5, insulation; 6, outer shield; 7, inner shield; 8, reaction vessel; 9, isothermal cylinder; 10, waste solution container; 11, nitrogen tank; 12, pressure gauge; 13, back-pressure regulator; 14, Macintosh Plus computer; 15, computer interface; 16, Tronac PTC-41 temperature controller; 17, Hart Scientific 3704 isothermal control unit.

addition of the pre-heating and heat-exchanging areas to reduce the time required to achieve thermal equilibration, and the use of high-pressure pushers and shrinkable Teflon bags in the fluid delivery system to eliminate solution contamination by corrosion of the pump barrels.

The main components of the calorimeter are the reaction vessel, the isothermal cylinder, the thermal shields and insulating container, the fluid delivery system containing the high-pressure pumps and pushers, the pressure control system which contains a waste solution container, a pressure gauge, a back-pressure regulator and two nitrogen tanks, the temperature control system which contains four Tronac PTC-41 temperature controllers and a Hart Scientific 3704 isothermal control unit, the data acquisition system which contains a Macintosh Plus computer, and an interface between the isothermal control unit and the computer. The Macintosh Plus computer also controls the operation of the pumps. A schematic diagram showing the main components of the calorimeter is given in Fig. 1. The reaction vessel and its contents are shown in Fig. 2.

A reaction is initiated by starting the pumps thus expelling the reactants at a constant rate from the pushers through the nickel equilibration coil on the isothermal cylinder. A controlled heat-leak path removes energy from

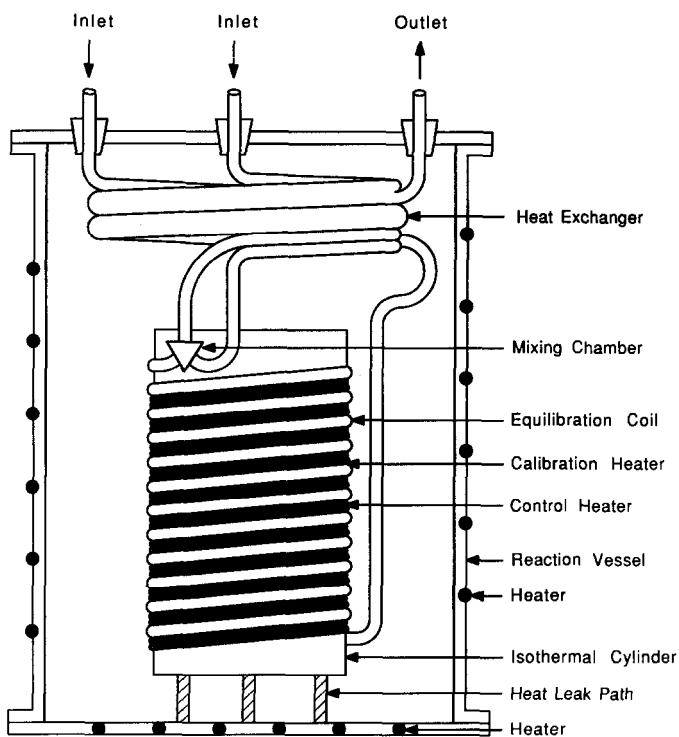


Fig. 2. Reaction vessel and contents.

the isothermal cylinder at a constant rate and discharges it to the reaction vessel bottom. The reaction vessel bottom is temperature-controlled to  $\pm 0.0005$  K and serves as a constant temperature heat-sink. A controlled heater compensates for the energy liberated or absorbed by the reaction and maintains the isothermal cylinder at a constant temperature. The differences in the rates of energy supplied by the heater before, during, and after the reaction are a direct measure of the energy of the reaction. The frequency of electrical pulses ( $0-10^5$  s $^{-1}$ ) supplied to the heater is measured, displayed in digital form, and recorded on a Macintosh Plus computer. Energy effects due to the heat of reaction can be measured in the range  $0.15-120$  J min $^{-1}$  with an error of less than 0.8%. Two high-pressure pumps coupled with a back-pressure regulator allow the calorimeter to be run at any pressure from 0.1 to 25.5 MPa. The flow rates of the two feed streams are controlled by the Macintosh Plus computer and any flow ratio can be introduced into the equilibration coil.

#### *Reaction vessel and shields*

The nickel reaction vessel (9.5 cm ID, 12.7 cm high) contains the isothermal cylinder and equilibration coil (Fig. 2). The nickel cylinder is 4.4 cm

OD, 8.2 cm high, with a wall thickness of 0.238 cm at the top and 0.476 cm at the bottom. The bottom of the cylinder is closed and is 0.635 cm thick. Three 0.635 cm OD nickel bolts connect the bottom of the cylinder to the bottom of the reaction vessel. The distance between the bottom of the cylinder and that of the reaction vessel is 1.27 cm. The cylinder has three adjacent spiral grooves machined into its side, each having 15 turns. The grooves accommodate the equilibration coil tubing and clad wires used for the calibration heater and the control heater. The equilibration coil is constructed of approximately 2 m of 0.159 cm OD, 0.265 mm wall thickness, nickel tubing (Superior Tube Co., Norristown, PA). All flow tubing used in the calorimeter is made of nickel and the total length is about 20 m. Three thermistors (Thermometrics, Inc., Edison, NJ) with resistances of 0.5, 1, and 1.5 M $\Omega$ , respectively, at 125°C are attached with high-temperature cement in the holes drilled in the bottom of the isothermal cylinder. The thermistors are used to monitor and control continuously the cylinder at a constant temperature. Three thermistors are used to cover the entire range of operating temperatures. A chromel–alumel type-K thermocouple and a 100  $\Omega$  (at 0°C) platinum resistance thermometer (PRT) (Omega Engineering, Inc., Stamford, CT) are also attached into holes drilled in the bottom of the isothermal cylinder and they are used to measure the absolute temperature of the cylinder. The thermocouple and PRT have been calibrated from 25 to 300°C on the Hart Scientific (Pleasant Grove, UT) 1006 digital thermometer which is traceable to IPTS-68. The absolute temperature can be measured to an accuracy of  $\pm 0.2$  K with the thermocouple and  $\pm 0.1$  K with the PRT.

The calibration and control heaters each consist of approximately 1.8 m of Omegaclad wire No. 304-K-MO-040 (0.106 cm OD) (Omega Engineering, Inc., Stamford, CT) having a resistance of approximately 90  $\Omega$  (at 25°C), coiled in the spiral grooves cut in the side of the isothermal cylinder. A heater consisting of 0.5 m of Omegaclad wire No. 304-K-MO-062 (0.159 cm OD) having a resistance of approximately 11  $\Omega$ , is coiled in a spiral groove cut in the bottom plate of the reaction vessel. Three thermistors (one 2 M $\Omega$  at 25°C and two 1 M $\Omega$  at 125°C) are attached in the bottom of the reaction vessel. The heater and the appropriate thermistor, depending on the temperature range to be investigated, are connected to a Tronac (Orem, UT) PTC-41 temperature controller. The temperature of the reaction vessel bottom is controlled to  $\pm 0.0005$  K (as indicated by a thermistor attached to the reaction vessel bottom). The controlled temperature difference between the bottom of the isothermal cylinder and the bottom of the reaction vessel serves as the driving force for the controlled heat-leak path along the three nickel bolts connecting the bottoms of the cylinder and the reaction vessel. The size, number, and length of the bolts were designed to give a heat-leak rate of approximately 1 J s<sup>-1</sup> with a temperature difference of 1 K between the bottoms of these components.

After entering the reaction vessel and before entering the equilibration

coil, the reactants are equilibrated with the products from the coil in a counter-current heat exchanger. This exchanger consists of 0.3 m lengths of the inlet and exit tubing which are wrapped together with silver wires, so that the two inlet streams run counter-current to the exit stream. The two tubes containing the reactants are brought together in a triangular shaped mixing chamber as shown in Fig. 2. The two inlet tubes and the exit tube from the mixing chamber are welded into the nickel mixing chamber. Three thermistors (0.5, 1 and 1.5 M $\Omega$  at 125°C) are attached on the outside surface of the reaction vessel. A 1.2 m length of Omegaclad wire No. 304-K-MO-062 having a resistance of approximately 27  $\Omega$  is coiled into the grooves cut on

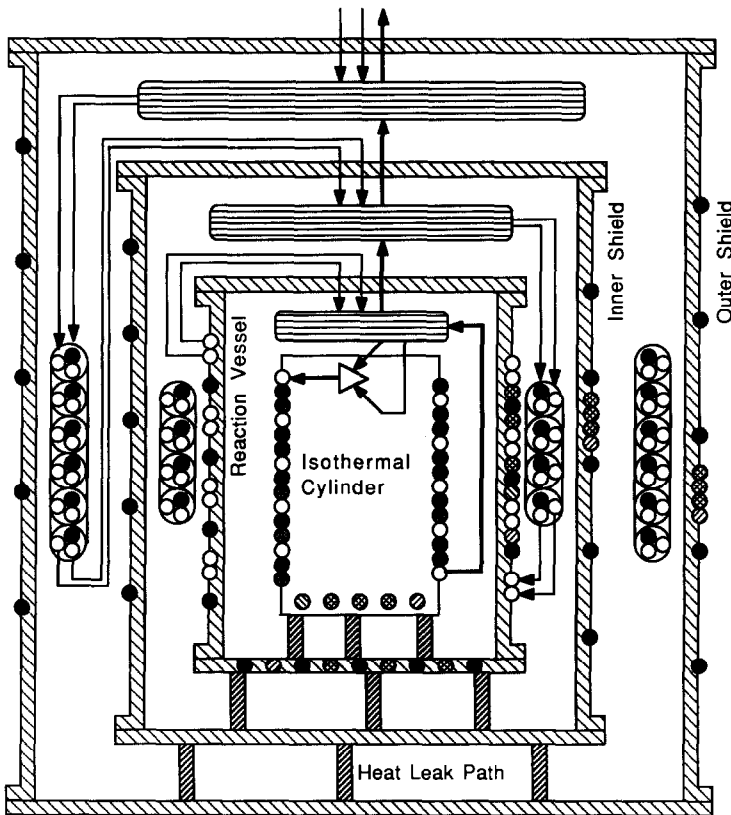


Fig. 3. A schematic diagram of the reaction vessel and thermal shields showing configuration of flow lines, heaters and temperature sensors.

the outside surface of the reaction vessel. The heater and appropriate thermistor are connected to a Tronac PTC-41 temperature controller and the temperature is controlled to  $\pm 0.001$  K. The side of the reaction vessel is controlled at the same temperature as the isothermal cylinder. The bottom of the reaction vessel is controlled at approximately 1 K below the cylinder temperature.

The thermal shields consist of two nickel cans surrounding the reaction vessel as is shown in Fig. 3. The inner shield has a 1.8 m length of Omegaclad wire No. 304-K-MO-062, having a resistance of approximately  $39 \Omega$ , and three thermistors (one  $2 \text{ M}\Omega$  at  $25^\circ\text{C}$ , one  $1 \text{ M}\Omega$  at  $125^\circ\text{C}$  and one  $1.5 \text{ M}\Omega$  at  $125^\circ\text{C}$ ) coiled into the grooves on its outside surface. The heater and thermistor are connected to a Tronac PTC-41 temperature controller and the temperature is controlled to  $\pm 0.005$  K. The outer shield has a 5.5 m length of Omegaclad wire No. 304-K-MO-125 (0.318 cm OD), having a resistance of approximately  $23 \Omega$ , and three thermistors (one  $2 \text{ M}\Omega$  at  $25^\circ\text{C}$ , one  $1 \text{ M}\Omega$  at  $125^\circ\text{C}$  and one  $1.5 \text{ M}\Omega$  at  $125^\circ\text{C}$ ) attached to its outside surface. The heater and thermistor are connected to a Tronac PTC-41 temperature controller and the temperature is controlled to  $\pm 0.01$  K. A thermal path is provided from the reaction vessel through the shields to the insulation through three 0.635 cm OD nickel bolts connecting the reaction vessel to the inner shield and the inner shield to the outer shield. The bolt circles are rotated at  $60^\circ$  between the two shields.

Chromel–alumel thermocouples are attached with high-temperature cement to the reaction vessel bottom and the outside surfaces of the reaction vessel and the thermal shields. A  $100 \Omega$  PRT is also attached to the outside surface of the reaction vessel. The PRT and thermocouples are used to monitor the temperatures of these various surfaces and to aid in setting their temperatures. All internal wiring in the calorimeter is 30 gauge, stranded, nickel-plated copper wire with glass wrap insulation. The upper operating temperature with this wire is approximately 773 K.

### *Fluid delivery*

A schematic diagram of the fluid delivery system is shown in Fig. 1. Two Isco (Lincoln, NE) LC-5000 syringe pumps and two high-pressure pushers are used for the delivery of fluids to the calorimeter. Each pump has a capacity of 500 ml with a flow rate from 0.1 to  $400 \text{ ml h}^{-1}$ . Solutions under study are contained in the Teflon bags inside the pushers (Fig. 4). Pressure to transfer solutions to the calorimeter is transmitted by water from the pumps to the pushers. The pushers are made of stainless steel (7.8 cm OD, 5.2 cm ID, and 109.5 cm high) with openings on the top cap and at the bottom. Each pusher has an adaptor machined from solid Teflon and attached to the top cap which supports a shrinkable Teflon bag (4.0 cm OD and 98.0 cm high). The Teflon bag is heat-shrunk on to the adaptor. The

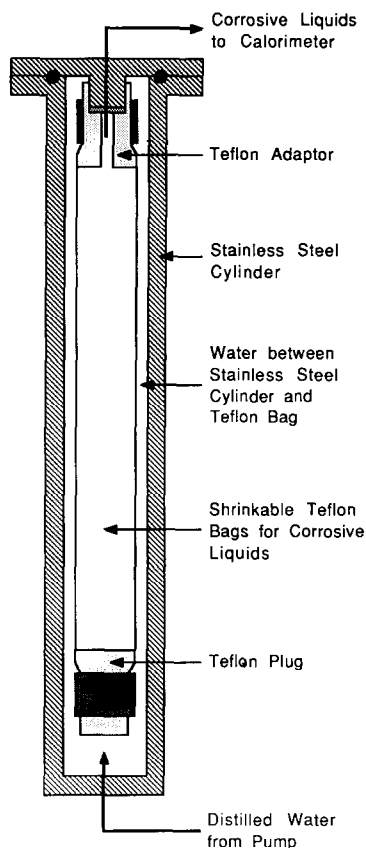


Fig. 4. A schematic diagram of the pusher.

lower end of each Teflon bag is heat-shrunk around a plug machined from solid Teflon. The pushers are similar to that described by Busey et al. [13].

The pressure in the system is controlled by a back-pressure regulator (Grove Valve and Regulator Co., Oakland, CA, model S-91XW, Teflon diaphragm). Pressure is monitored with a 0–21 MPa Heise (Newton, CT) gauge. The control gas to the back-pressure regulator is supplied by a compressed nitrogen gas cylinder. The available pressure in the gas cylinder limits the pressures attainable by this arrangement to less than 14 MPa. Pressure fluctuations are less than  $\pm 0.5\%$  of the system pressure as indicated by repeated observations of the Heise gauge. The two inlet streams are thermally equilibrated to the temperature of the isothermal cylinder by passing through (1) a 1.2 m long counter-current heat exchanger between the tops of the outer and inner shields, (2) a 2.4 m long  $51 \Omega$  pre-heater between the sides of the outer and inner shields, (3) a 0.8 m long counter-current heat exchanger between the tops of the inner shield and the reaction vessel, (4) a 0.6 m long  $13 \Omega$  pre-heater between the sides of the inner shield and the reaction vessel, (5) 1.2 m of tubing attached to the outside surface of the



reaction vessel, and (6) a 0.3 m long counter-current heat exchanger contained in the reaction vessel. In the entire flow circuit the fluids come in contact with only Teflon bags, nickel tubing and Monel fittings. The flow circuit inside the calorimeter consists of only nickel tubing and the nickel mixing chamber. Thus, the fluid only contacts nickel metal when at a temperature above ambient.

### *Insulating container*

The insulating container consists of a 38 cm OD stainless-steel can containing an 8 cm layer of Fiberfax S-Durablanket fiberglass insulation (Carborundum, Resistant Materials Co., Chicago, IL). This container is surrounded by a 46 cm OD aluminum cylinder which provides a 4 cm air-gap between it and the insulating container and has a small fan at its base to circulate air through the air gap.

### *Isothermal control unit*

The isothermal cylinder and attached equilibration coil are held at a constant temperature (as indicated by a thermistor sensor attached to the cylinder) by maintaining a constant temperature difference across the heat-leak path while varying the energy input to the isothermal cylinder with the control heater. The control circuit is very similar to those described previously [1-6] and is available either as a Tronac 550 isothermal control unit or as a Hart Scientific 3704 iso-therm isothermal control unit. The present unit uses a Hart Scientific 3704 iso-therm unit. The frequency of pulses supplied to the heater ( $0-10^5 \text{ s}^{-1}$ ) is recorded and displayed on a Macintosh Plus computer.

## PROCEDURE

All the controllers are adjusted so the calorimeter is operating at the desired temperature. The isothermal cylinder and reaction vessel wall are set at the same temperature. The reaction vessel bottom is set at a temperature approximately 1 K lower than the isothermal cylinder temperature. The inner shield is set at a temperature approximately 3 K lower than the reaction vessel bottom temperature. The outer shield is set at a temperature approximately 6 K lower than the inner shield temperature. A temperature gradient is thus provided for the heat generated in the equilibration coil to be transferred to the surrounding cans and room by conduction. The reaction vessel wall temperature is finely adjusted by monitoring the heat pulse rate with no fluid and with one stream of fluid flowing through the coil. When the heat pulse rate is the same for the two conditions, the

temperature of the fluid is the same as the temperature of the isothermal cylinder.

The pumps are charged with distilled water which is pumped into the pushers to expel the reactants into the calorimeter. A run consists, first, of running one pump at the total flow chosen for the reaction to determine a baseline heater pulse rate. Then, both pumps are run at their respective flow rates and the reaction steady-state heater pulse rate is determined, followed by the other pump being run at the total flow rate and the baseline heater pulse rate being determined again. The calorimeter can be calibrated chemically by carrying out a standard reaction or electrically by adding a known amount of heat via a calibration heater. For most runs only electrical calibrations are made. The chemical calibration is done periodically to confirm the electrical calibration.

## PERFORMANCE

Chemical calibrations were made earlier on the low-temperature version of the calorimeter using the systems  $\text{HClO}_4\text{-NaOH}$ ,  $\text{HClO}_4\text{-tris(hydroxymethyl)aminomethane}$ , and  $n\text{-hexane-cyclohexane}$  at 298 K [3] and on the elevated temperature calorimeter using the system  $n\text{-hexane-cyclohexane}$  at 298 K [4] and water-ethanol at 383 [4] and 413 K [5]. These calibrations showed that the calorimeters are capable of producing accurate measurements over a wide range of flow rates and concentrations. To test the performance of the present calorimeter, heats of dilution of 1.8445 M  $\text{NaOH(aq)}$  were determined at 523 K and 5.5 MPa and compared with literature values [14]. A comparison of the heat of dilution values given in Table 1 shows agreement to  $\pm 0.8\%$  or better. No literature values are available for the heat of dilution of  $\text{NaOH(aq)}$  at temperatures above 523 K. The results show that this calorimeter is capable of producing accurate heat data at temperatures up to 523 K.

TABLE 1  
Heats of dilution of 1.8445 m  $\text{NaOH(aq)}$  at 523 K and 5.5 MPa

$m_f$ (mol $\text{kg}^{-1}$ )	$\Delta L_\phi$ (J $\text{mol}^{-1}$ )		$n^b$	$\Delta^c$
	Literature <sup>a</sup>	This study		
1.4752	-2188	-2175 $\pm$ 15	6	+13
1.2293	-3997	-3992 $\pm$ 27	6	+5
0.9219	-6416	-6367 $\pm$ 46	18	+49
0.6146	-9623	-9643 $\pm$ 60	8	-20
0.3688	-13221	-13219 $\pm$ 91	12	+2

<sup>a</sup> Literature values are obtained by interpolation from ref. 14.

<sup>b</sup> Number of duplicate runs.

<sup>c</sup>  $\Delta = \Delta L_\phi(\text{this study}) - \Delta L_\phi(\text{literature})$ .

## DISCUSSION

By combining the principles of isothermal calorimetry with the chemical resistance of nickel metal to basic solutions, a flow calorimeter has been developed that can measure heats of reaction in aqueous solution over a wide range of concentrations, flow rates, temperatures, and pressures. The lack of any dependence on the heat capacity of the solution makes the method particularly applicable to systems which may undergo large heat capacity changes. In addition, no correction is necessary for heat exchange between the calorimeter and its surroundings. The upper temperature limit of the instrument is dependent only on the temperature limits of the materials of construction and is not dependent on the use of a Peltier cooler device.

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