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An isothermal flow calorimeter for use with corrosive solutions from 50 to 125°C

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Abstract

An isothermal flow calorimeter suitable for measuring heats of mixing of two fluid streams which may or may not contain reactive solutes is described. The calorimeter proper was constructed of a platinum–10% rhodium alloy (tubing) and platinum–10% iridium alloy (mixing chamber) in order to obtain corrosion resistance to both strong acids and strong bases. Endothermic and exothermic processes can be studied from 323 to 398 K and from 0.1 to 20 MPa with the calorimeter. Energy effects from 0.0025 to 0.50 J sec^{-1} are measured at a constant temperature and pressure through the use of an automatically controlled pulsed heater and a constant cooling Peltier device. The calorimeter was tested (pressures given in parentheses) by measuring the heat of mixing of ethanol and water at 348.15 K (1.52 MPa) and the heat of dilution of aqueous sodium chloride at 323.15 (0.34 MPa), 348.15 (0.34 MPa), 372.85 (6.6 MPa) and 398.15 K (1.03 MPa), and was found to produce data in good agreement with literature values.

Keywords: Alloy; Binary system; Corrosion; Flow calorimeter; Heat of mixing; Isothermal

1. 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

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output of a controlled heater to balance the rate of energy arising from the chemical reaction plus the power removed by a constant Peltier cooler. The method is applicable to either endothermic or 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 conditions exist in the operation of the 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.

An isothermal, high-pressure flow calorimeter [1], an isothermal flow calorimeter with a modified insert [2], and an isothermal flow calorimeter for high-temperature basic solutions [3] have been described. The present paper describes a calorimeter suitable for use with corrosive aqueous solutions, strong acids or strong bases, inorganic salts, and organic compounds at moderate temperatures. The calorimeter retains the desirable operating characteristics and advantages of previous isothermal flow calorimeters [1-3] while offering the additional advantages of corrosion-resistant platinum alloy tubing and mixing chamber, operation at temperatures from 323 to 398 K, and operation at pressures to 20 MPa.

The calorimeter has been tested (pressures given in parentheses) by measuring the heats of mixing of ethanol and water at 348.15 K (1.52 MPa) and of aqueous sodium chloride in water at 323.15 (0.34 MPa), 348.15 (0.34 MPa), 372.85 (6.6 MPa) and 398.15 K (1.03 MPa). The results obtained were in good agreement with literature data.

2. Apparatus

The calorimeter insert is a modification of that used in the isothermal, high-pressure flow calorimeter described by Ott et al. [2]. The main changes are in the use of platinum-10% rhodium alloy tubing to resist corrosion, the use of control and calibration heaters which extend the length of the equilibration coil, the use of a triangular platinum-10% iridium mixing chamber instead of annular mixing, and the addition of high pressure pushers and shrinkable Teflon bags in the solution delivery system to eliminate solution contamination by corrosion of the pump barrels.

The equilibration coil (referred to in Ott et al. [2] as a mixing tube) is not vacuum silver-brazed to the copper cylinder. Instead, the equilibration coil, and calibration and control heaters are wound tightly in machined grooves around the cylinder. Small screws secure the equilibration coil at both ends of the cylinder. This allows for easy assembly and replacement if a plug or hole should occur in the equilibration coil. The equilibration coil can be replaced without replacing the machined cylinder.

The calibration heater in the present calorimeter is located in such a way that it lies parallel to the mixing coil along the entire length of the isothermal cylinder. Therefore, the calibration heater and the mixing coil are affected in the same manner by the heat leaks which results from hot or cold spots along the surface of

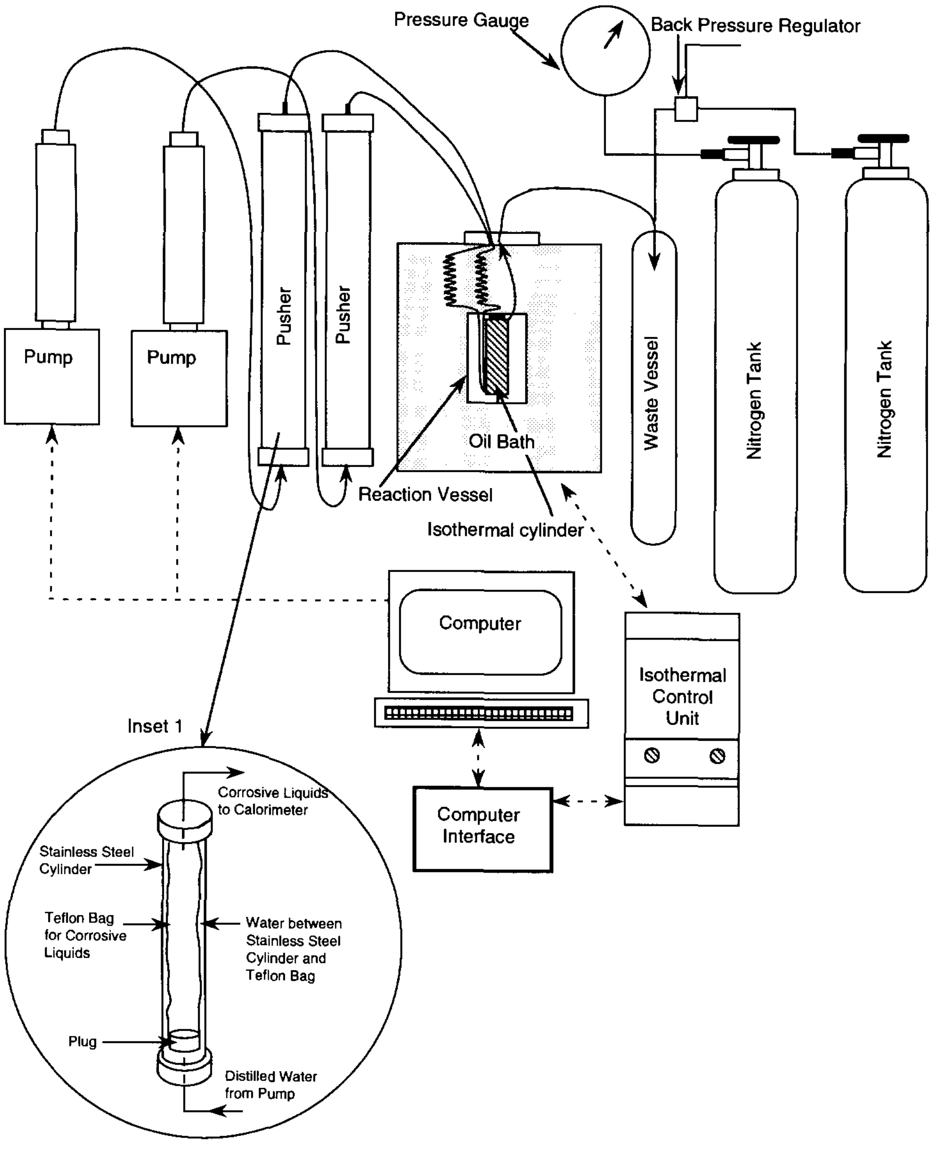

Fig. 1. A schematic diagram of the main components of the calorimeter.

the cylinder. The control heater extending the length of the isothermal cylinder reduces temperature gradients which may occur when the control heater covers only one half of the cylinder as was the case in the calorimeter described by Ott et al. [2].

The earlier annulus design for mixing required fittings made of platinum. To avoid this cost, we used a Y-shaped platinum–10% iridium alloy mixing chamber

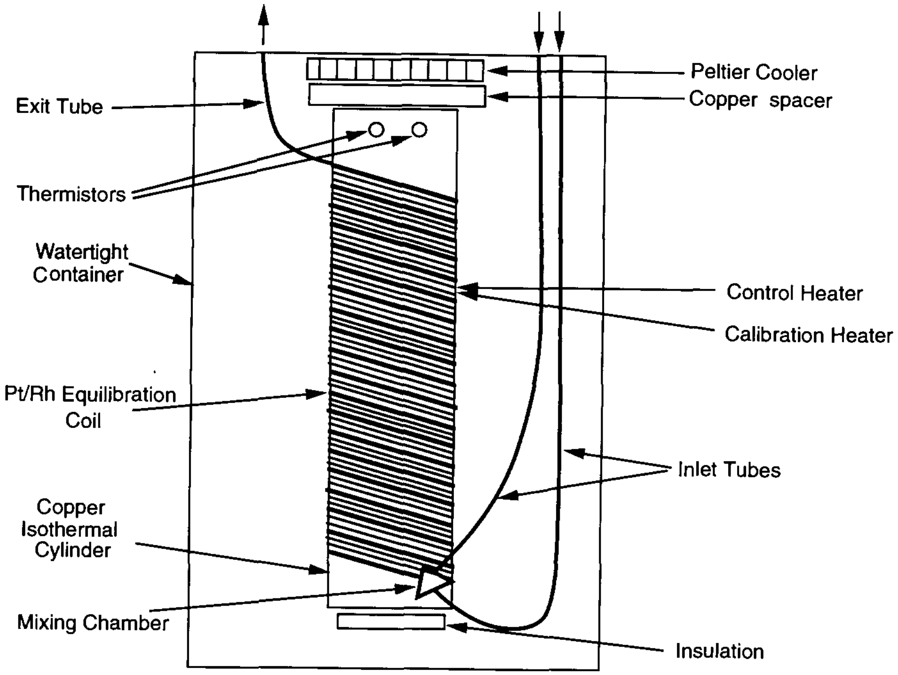

Fig. 2. Reaction vessel and contents.

where the inlet and exit tubing are connected to the mixing chamber by gold brazing. This mixing design has been used successfully in our high temperature calorimeters [3]. The mixing Y is held in good contact with the cylinder using small screws. If a precipitate forms one can access the mixing zone by disconnecting an inlet line.

The main components of the calorimeter (see Fig. 1 for a schematic diagram) are the reaction vessel containing the isothermal cylinder and the mixing and equilibration tubing; the fluid delivery system containing the high pressure pumps and pushers; the pressure control system which contains a waste solution vessel, pressure gauge, back-pressure regulator and two nitrogen tanks; the oil bath; the temperature control system which contains a Tronac 550 isothermal control unit; and the data acquisition component which contains a Macintosh SE computer and an interface between the isothermal control unit and the computer. The Macintosh SE computer also controls the operation of the pumps.

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 platinum–10% rhodium equilibration coil on the isothermal cylinder. A Peltier cooler removes energy from the isothermal cylinder at a constant rate and discharges it to the surrounding oil bath. A control heater compensates for the energy liberated or absorbed by the reaction and the cooling of the Peltier device

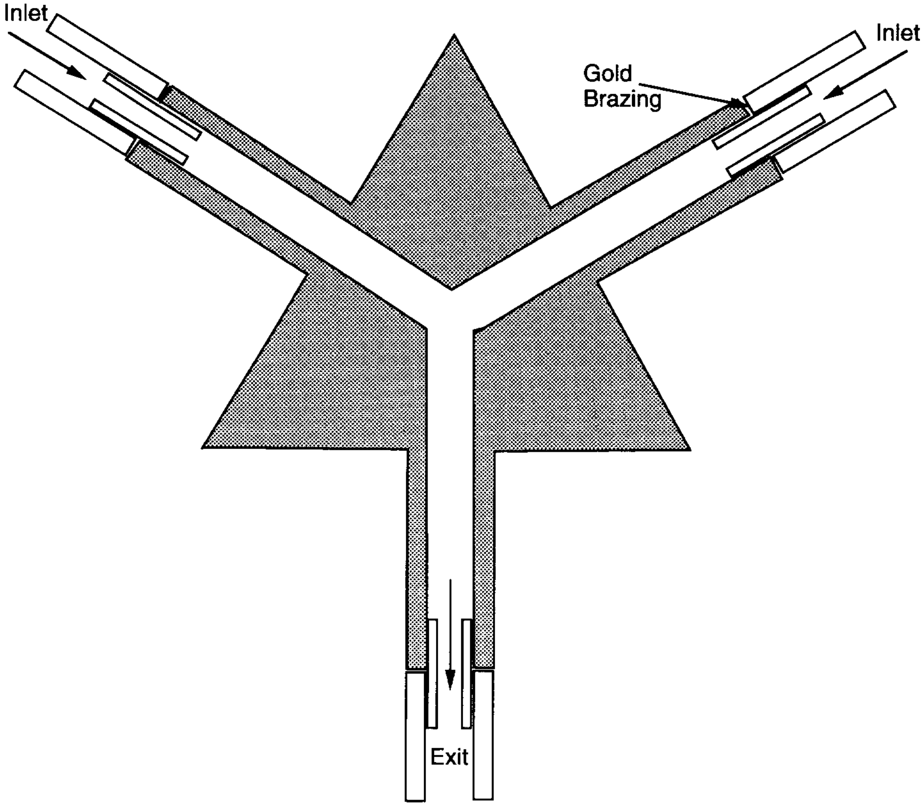

Fig. 3. Triangular mixing chamber. Shaded areas are platinum–10% iridium alloy. Clear areas are platinum–10% rhodium tubing.

and maintains the 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 (1–25 000 s^{-1}) supplied to the heater is measured, displayed in digital form, and recorded. Two high-pressure pumps coupled with a back-pressure regulator allow the calorimeter to be run at any pressure from 0.1 to 20.0 MPa. The flow rates of the two feed streams are controlled by the Macintosh SE computer.

2.1. Reaction vessel

The reaction vessel (Fig. 2) consists of a stainless steel container enclosing the isothermal cylinder and equilibration coil. A Peltier thermoelectric cooler (Borg-Warner # 140-7) is in contact with the top of the stainless steel container to facilitate transfer of heat from the cooler to the oil bath. The container is fitted with an O-ring seal to prevent leaks and the lid is attached by stainless steel screws. The unit is suspended 25 cm below the mount situated on the top of the oil bath by four stainless steel rods. The copper cylinder is 1.75 cm OD, 9.4 cm high, with a wall thickness of 0.24 cm. The top of the cylinder is closed and is 0.64 cm thick. Two 0.16 cm diameter holes drilled through the side near the top accommodate two control thermistors. The cylinder has one spiral groove machined into its side, having 22 turns. The groove accommodates the equilibration coil tubing. Clad wires used for the calibration heater and the control heater are wound onto the cylinder between the equilibration coils. The equilibration coil is 110 cm of 1.59 mm OD, 0.40 mm wall thickness platinum–10% rhodium tubing (Engelhard, NJ). Before entering the reaction vessel, the reactants are equilibrated to the bath temperature in 1.40 m of platinum–10% rhodium tubing.

The mixing chamber, shown in Fig. 3, was machined from a piece of solid platinum–10% iridium alloy. The mixing chamber is in the shape of an equilateral triangle with the sides being 7 mm and having a thickness of 2 mm. Protruding from the center of each side is a cylinder 1.59 mm in diameter and 2.5 mm in length. Holes 0.80 mm in diameter were drilled through the center of the cylinders into the triangle to form a Y where the fluids mix. The two inlet tubes and the exit tube from the mixing chamber were gold-brazed to the protruding cylinders of the mixing chamber so that the opening of the tubes lines up with the drilled holes. The platinum–10% rhodium tubing was only available in 36 cm lengths. Therefore, the pieces had to be joined to form the required length of tubing. This was accomplished by gold-brazing two 1.59 mm OD tubes over a 0.80 mm OD platinum–10% rhodium inner tube to form a joint as shown in Fig. 3. With an inner platinum–10% rhodium sleeve, the corrosive solutions contact only platinum and gold metals at elevated temperatures. A stainless steel outer sleeve (not shown) was connected to the outside of the joint to support and protect the soft gold union. All flow tubing used in the calorimeter is made of platinum–10% rhodium tubing and the total length is about 9 m. Two thermistors (Thermometrics, Inc., Edison, NJ) with resistances of 50 and 500 kΩ, respectively at 25°C are attached with Thermalbond 4952 thermally conductive epoxy (Thermalloy, Inc., Dallas, TX) in the holes drilled in the side near the top of the isothermal cylinder. The thermistors are used to monitor and control continuously the cylinder at a constant temperature.

The calibration and control heaters each consist of approximately 110 cm of Omegaclad wire No. 304-K-MO-040 (0.106 cm OD) (Omega Engineering, Inc., Stamford, CT) having a resistance of approximately 60 Ω (at 25°C) coiled on the side of the isothermal cylinder.

2.2. *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, similar to those described by Busey et al. [4], are used for delivery of fluids to the calorimeter. Each pump has a capacity of 500 ml with a flow rate adjustable from 0.1 to 400 ml h^{-1}. Solutions under study are contained in the Teflon bags inside the pushers. 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 and bottom. Each pusher has an adapter 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 onto the adapter. The lower end of each Teflon bag is heat-shrunk around a plug machined from solid Teflon.

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 0–3000 psi 3D Instruments Inc. (Huntington Beach, CA) pressure gauge. The control gas to the back-pressure regulator is supplied by a compressed nitrogen gas cylinder. Pressure fluctuations are less than ±0.5% of the system pressure as indicated by repeated observations of the pressure gauge. In the entire flow circuit, the fluids come in contact only with Teflon bags, platinum alloys, gold, and Monel valves which are located at the exits from the pushers. The flow circuit inside the calorimeter consists of only platinum–10% rhodium tubing, the platinum–10% iridium mixing chamber, and gold to connect the tubing to the mixing chamber. Thus, the fluid contacts only platinum and gold metals when at a temperature above ambient.

2.3. Oil bath

Vegetable oil was used instead of water in the Hart Model 5007 constant-temperature bath to thermostat the calorimeter insert. The reaction vessel and accompanying lines are immersed in the oil bath, whose temperature is controlled to ±0.001°C. The absolute temperature of the Hart 5007 constant temperature bath was set with a Hart Scientific (Pleasant Grove, UT) 1006 digital thermometer which is traceable to IPTS-68.

2.4. Isothermal control unit

The isothermal cylinder and attached equilibration coil (Fig. 2) are held at a constant temperature (as indicated by a thermistor sensor attached to the cylinder)

Table 1
Heats of mixing (H_m) for ethanol and water at 348.15 K and 1.52 MPa

Flow/(ml min^{-1})	x(EtOH)	H_m/(J mol^{-1}) Literature [a]	H_m/(J mol^{-1}) This study [b]	n [c]	Δ [d]	Δ/%
0.42	0.1667	-116 ± 2	-115 ± 7	3	1	1
0.50	0.2308	-42 ± 2	-42 ± 3	4	0	0
0.58	0.2857	21 ± 2	19 ± 2	4	−2	9
0.75	0.3750	70 ± 2	68 ± 4	4	−2	3
0.32	0.5454	108 ± 2	106 ± 4	4	−2	2

[a] Literature values were obtained using Eq. (2) in Ref. [5]. [b] Average of duplicate runs. [c] Number of duplicate runs. [d] $\Delta = H_m$(this study) − H_m(literature).

by maintaining the Peltier cooler at a constant cooling rate while varying the heat input to the isothermal cylinder with the control heater. The control circuit is very similar to those described previously [1-3] and is available either as a Tronac 550 isothermal control unit or as a Hart Scientific 3704 isothermal control unit. The present unit uses a Tronac 550 isothermal control unit.

3. Procedure

The reaction vessel is immersed in the oil bath and the isothermal control unit is adjusted to maintain the vessel at the oil bath temperature. The two reactants are placed into two Teflon bags (Fig. 1, inset 1). The pumps are filled with distilled water which is pumped into the pushers to expel the reactants into the calorimeter. The measurements are made in a steady-state, fixed composition mode. The experimental determination consists of running one pump to determine a baseline heater pulse rate or the number of pulses required to balance the heat leak and maintain the cylinder isothermal when no reaction occurs. Next, the second pump is started and after an equilibration period the heater pulse rate is determined for the mixing solutions. The difference in the heater pulse rates before and during

Table 2
Heats of dilution (H_{dil}) of 3.222 M NaCl at 323.15 K and 0.34 MPa

Flow/ (ml min^{-1})	m_f [a]/ (mol kg^{-1})	H_{dil}/(J mol^{-1}) Literature [b]	H_{dil}/(J mol^{-1}) This study [c]	Δ [d]	Δ/%
1.50	0.6034	265 ± 8	268 ± 16	−3	−0.84
1.50	0.9111	259 ± 4	259 ± 10	0	−0.15
1.50	1.3800	209 ± 3	207 ± 7	2	1.09
1.50	2.100	109 ± 2	108 ± 4	1	0.85

[a] Final concentration in mol kg^{-1}. [b] Values are averages calculated by us from data in Ref. [6]. Uncertainties were calculated or estimated by us from these data. [c] Average of duplicate runs. [d] $\Delta = H_m$(this study) $- H_m$(literature).

Table 3
Heats of dilution (H_{dil}) of 3.222 M NaCl at 348.15 K and 0.34 MPa

Flow/ (ml min^{-1})	m_f [a]/ (mol kg^{-1})	H_{dil}/(J mol^{-1}) Literature [b]	H_{dil}/(J mol^{-1}) This study [c]	Δ [d]	Δ/%
1.50	0.6034	−712 ± 20	−732 ± 16	20	−2.8
1.50	0.9111	−551 ± 18	−556 ± 11	5	−2.2
1.50	1.3800	−396 ± 14	−390 ± 7	6	−1.7
1.50	2.100	−228 ± 8	−225 ± 5	3	−1.8

[a] Final concentration in mol kg^{-1}. [b] Values are averages calculated by us from data in Ref. [6]. Uncertainties were calculated or estimated by us from these data. [c] Average of duplicate runs. [d] $\Delta = H_m$(this study) $- H_m$(literature).

reaction is a measure of the heat of reaction. Electrical calibration is performed by adding power to the calibration heater from a d.c. power source. The amount of electrical power is obtained by measuring the potential drop across the calibration heater and across a 10 Ω standard resistor in series with the heater.

4. Performance

To test the performance of the present calorimeter, heats of mixing of ethanol with water were determined at 348.15 K and 1.52 MPa. Pure ethanol (100%) from Midwest Grain Product Company was used without further purification. The distilled, deionized water was boiled to expel carbon dioxide before use. Table 1 gives the calorimetric data obtained and literature values from Ott et al. [5]. The agreement with the literature data is excellent.

The heats of dilution of aqueous sodium chloride were measured at 323.15 (0.34 MPa), 348.15 (0.34 MPa), 372.85 (6.6 MPa) and 398.15 K (1.03 MPa). The solutions used in the measurements were made by dissolving appropriate amounts of salt in distilled water. The sodium chloride used was Aldrich ACS reagent (99+%). The water used was deionized using a fixed-bed cation exchange column. Measurements were made at concentrations and temperatures used by other workers. The results were compared with literature values [4,6,7]. The dilution enthalpies of NaCl(aq) taken at 323.15 K and 0.34 MPa and shown in Table 2 are in excellent agreement with the experimental results of Messikomer and Wood [6]. At 348.15 K and 0.34 MPa, the agreement between Messikomer and Wood [6] and our data is good, as shown in Table 3. At 372.85 K and 6.6 MPa, data for the heat of dilution of NaCl(aq) were collected at several flow rates. The results are compared with Busey et al. [4] and given in Table 4. Reasonable agreement was obtained for data collected at all flow rates. Table 5 contains data for the dilution of NaCl(aq)

Table 4
Heats of dilution (H_{dil}) of 1.000 M NaCl at 372.85 K and 6.6 MPa

Flow/ (ml min^{-1})	m_f [a]/ (mol kg^{-1})	H_{dil}/(J mol^{-1}) Literature [b]	H_{dil}/(J mol^{-1}) This study [c]	Δ [d]	Δ/%
1.00	0.1641	-1239 ± 21	-1250 ± 85	−11	0.9
1.00	0.2465	-1000 ± 18	-1034 ± 57	−35	3.4
1.00	0.3292	-832 ± 7	-861 ± 43	−30	3.5
1.00	0.4953	-556 ± 6	-582 ± 28	−26	4.6
1.00	0.7465	-258 ± 3	-261 ± 19	−3	1.1
0.59	0.1641	-1239 ± 21	-1266 ± 144	−27	2.2
0.66	0.2465	-1000 ± 18	-973 ± 86	27	−2.7
0.74	0.3292	-832 ± 7	-816 ± 57	16	−1.9

[a] Final concentration in mol kg^{-1}. [b] Values are averages calculated by us from data in Ref. [4]. Uncertainties were calculated or estimated by us from these data. [c] Average of duplicate runs. [d] $\Delta = H_m(\text{this study}) - H_m(\text{literature})$.

Table 5
Heats of dilution (H_{dil}) of 1.022 M NaCl at 398.15 K and 1.03 MPa

Flow/ (ml min^{-1})	m_f [a]/ (mol kg^{-1})	H_{dil}/(J mol^{-1}) Literature [b]	H_{dil}/(J mol^{-1}) This study [c]	Δ [d]	Δ/%
1.00	0.0901	-2389 ± 50	-2290 ± 157	99	−4
1.00	0.1643	-1956 ± 36	-1972 ± 187	−16	0.8
1.00	0.4677	-994 ± 14	-982 ± 30	12	−1.2
1.10	0.0901	-2389 ± 50	-2372 ± 142	17	−0.7
1.20	0.1642	-1956 ± 36	-2015 ± 72	−60	3

[a] Final concentration in mol kg^{-1}. [b] Values are averages calculated by us from data in Ref. [7]. Uncertainties were calculated or estimated by us from these data. [c] Average of duplicate runs. [d] $\Delta = H_m$(this study) $- H_m$(literature).

at 398.15 K and 1.03 MPa which are compared with values from Archer [7]. These data were also collected at various flow rates. The agreement is good.

When small heats are measured, the relative error increases. The uncertainty of the experimental results obtained from the present calorimeter is 0.014 J min^{-1} with a 95% confidence level. This uncertainty of 0.014 J min^{-1} leads to 1% or less error when measuring heats of 1.4 J min^{-1} or greater but the percent error becomes larger when measuring smaller heats. For example, it is 7% when measuring a heat of 0.20 J min^{-1}.

Data are collected in a fairly small range of flow rates from 0.5 to 1.5 ml min^{-1}. Total flow conditions have been varied from 0.5 to 1.5 ml min^{-1}. The results are independent of flow rate.

The calibration heater is designed to provide an evenly distributed source of heat over the entire length of the isothermal cylinder. It is expected that the major portion of the mixing or reactions heats will occur near the mixing chamber. The flow of the fluids carries the heat not yet absorbed along the equilibration coil. The placement of the calibration heater may not mimic a fast reaction but it is adequate for the reaction heats and dilution heats studied and the range of flows used. Obtaining the same ΔH value using different flow rates also shows that the current configuration is satisfactory.

5. Discussion

By combining the principles of isothermal calorimetry with the chemical resistance of platinum alloys to corrosive 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 primary advantage of this calorimeter over a previously described calorimeter insert [8] is in the placement of the calibration heater. Gruszkiewicz et al. [8] observed a systematic 3.5% error due to the fact that the calibration heater covered only half of the surface where mixing occurs. This was not the case with the calorimeter insert described by Ott et al. [2] in which the calibration heater extended the length of the mixing zone, but the control heater covered a different area of the isothermal cylinder. The calibration heater in the present calorimeter is located in such a way that it lies parallel to the mixing coil along the entire length of the isothermal cylinder. Therefore, the calibration heater and the mixing coil are affected in the same manner by the heat leaks which result from hot or cold spots along the surface of the cylinder. The control heater also extends the length of the isothermal cylinder resulting in smaller thermal gradients than would exist if the control heater is in a different location.

The use of platinum alloys to construct both the tubing and mixing chamber in order to minimize corrosion has allowed us to use HCl and other corrosive solutions in measuring heats of reaction regularly without ill effects. This has resulted in a greater output in the number of data points collected as compared to similar calorimeters constructed of stainless steel or Hastelloy-C tubing due to low maintenance requirements.

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References

[1] J.J. Christensen, L.D. Hansen, D.J. Eatough, R.M. Izatt and R.M. Hart, Rev. Sci. Instrum., 47 (1976) 730.
[2] J.B. Ott, C.E. Stouffer, G.V. Cornett, B.F. Woodfield, R.C. Wirthlin, J.J. Christensen and U.K. Deiters, J. Chem. Thermodyn., 18 (1986) 1.
[3] J.L. Oscarson, X. Chen, S.E. Gillespie and R.M. Izatt, Thermochim. Acta, 185 (1991) 51.
[4] R.H. Busey, H.F. Holmes and R.M. Mesmer, J. Chem. Thermodyn., 16 (1984) 343.
[5] J.B. Ott, G.V. Cornett, C.E. Stouffer, B.F. Woodfield, C. Guanquan and J.J. Christensen, J. Chem. Thermodyn., 18 (1986) 867.
[6] E.E. Messikomer and R.H. Wood, J. Chem. Thermodyn., 7 (1975) 119.
[7] D.G. Archer, J. Solution Chem., 15 (1986) 727.
[8] M.S. Gruszkiewicz, J.T. Sipowska, J.B. Ott and R.C. Graham, J. Chem. Thermodyn., 24 (1992) 1027.