Thermochimica Acta, 73 (1984) 117–129
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

AN ISOTHERMAL FLOW CALORIMETER DESIGNED FOR HIGH TEMPERATURE, HIGH PRESSURE OPERATION

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(Received 11 August 1983)

ABSTRACT

An isothermal flow calorimeter suitable for measuring either endothermic or exothermic heats of mixing from 373 to 673 K and from 0.1 to 40.5 MPa is described. 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^{-1} can be measured to an accuracy of $\pm 0.8\%$ at a constant temperature and pressure. The calorimeter was tested by measuring the heat of mixing of water–ethanol at 413 K and 1 MPa and was found to produce data in good agreement with previously measured 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 energy output of a controlled heater to balance the energy arising from the chemical reaction plus the energy 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 exchanged 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 temperatures and the temperature difference, if any, between the reaction zone and the surroundings is the same in both the calibration and run experiments.

An isothermal titration calorimeter [1], an isothermal titration microcalorimeter [2], an isothermal, high pressure, flow calorimeter [3] and an isothermal, elevated temperature, high pressure flow calorimeter [4] have been described. In addition, the application of isothermal calorimetry to the measurement of heats of reaction [5], of equilibrium constants for metal–ligand interaction and proton ionization [5], of heats of mixing [6,7] and of vapor–liquid equilibrium data [8] has been reported.

0040-6031/84/$03.00

This paper describes a novel method for the removal of energy from the reaction zone. This method is based on using a controlled heat leak path between the reaction zone and the surrounding container. Previous isothermal calorimeters described by us [1–4] have used a constant cooling Peltier device to remove energy from the reaction zone. This calorimeter retains all of the desirable operating characteristics and advantages of previous isothermal flow instruments [3,4] while offering the advantage of operating at temperatures up to 673 K, with the potential of operating at even higher temperatures. Binary heat-of-mixing data over the mole fraction range 0–1 can be produced at any temperature and pressure in the range of 373–673 K and 0.1–40.5 MPa, respectively. The data can be printed out in digital form and/or obtained as a strip chart recording.

The reason for the development of this instrument was to extend the temperature range (273–423 K) of the existing isothermal, isobaric, elevated temperature, high pressure flow calorimeter [4]. A versatile instrument was desired that, by only slight modification of the reaction chamber, could be used to measure energies arising from a wide variety of reactions under a wide range of reaction conditions. Many current problems in chemistry involve reactions at elevated temperatures and pressures such as (1) the chemistry in high temperature ocean vents, (2) corrosion problems in geothermal applications, in high temperature boilers and in heat exchangers and (3) super critical extraction involving hydrocarbons, alcohols, CO_2, etc. All tubing used in the calorimeter was Hastalloy C-273 to enable the unit to work under the extreme corrosive conditions that can arise at high temperatures, especially with aqueous solutions of inorganic salts and oxidizing agents.

The calorimeter has been tested by both electrical and heat of mixing (water–ethanol) calibrations at 413 K and 1 MPa. The data obtained were of approximately the same precision and accuracy ($\pm 0.8\%$) as those obtained from our isothermal flow calorimeters described previously [3,4].

APPARATUS

The calorimeter is very similar to the elevated temperature, high pressure, flow calorimeter described previously by us [4] and only a brief description will be given of those components that have not been changed extensively. The main changes are in the configuration and construction of the reaction vessel including the construction of a highly stable heat leak path. These modifications will be described in detail.

The main components of the calorimeter are the reaction vessel containing the isothermal cylinder and equilibration coil, the isothermal shields, the air bath, the flow circuit which contains the high pressure pumps and the isothermal control unit. A block diagram showing the main components of the unit is given in Fig. 1.

A reaction is initiated by starting the pumps and letting the reactants flow at a constant rate through the equilibration coil on the isothermal cylinder. A controlled heat leak path removes energy from the isothermal cylinder at a constant rate and discharges it to the reaction vessel bottom. The reaction vessel bottom is temperature controlled to ±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 (0–100 000 s^{-1}) supplied to the heater is measured and displayed in digital form and printed via Teletype. Energy effects due to the heat of mixing can be measured in the range 0.15–120 J min^{-1} with an accuracy of better than 0.8%. Two high pressure pumps coupled with a back pressure regulating valve allow the unit to be run at any pressure from 0.1 to 40.5 MPa. Any flow ratio of the two feed streams can be introduced into the equilibrium coil.

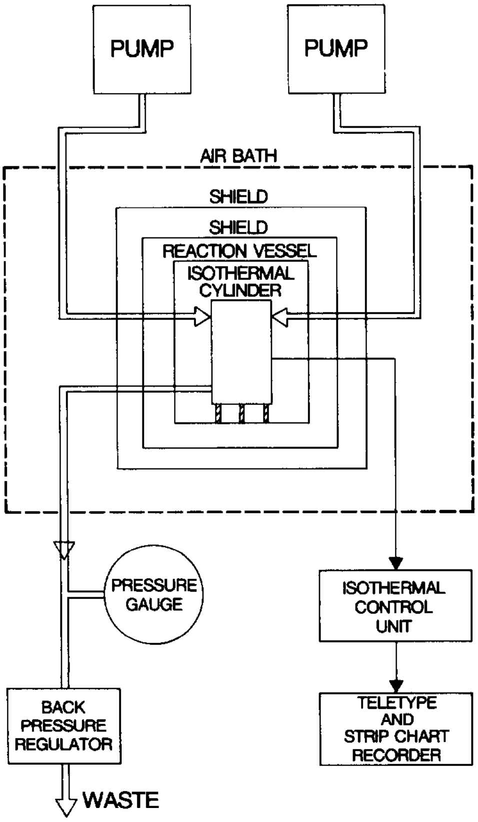

Fig. 1. A block diagram of the main components of the calorimeter. Electrical lines ———, Fluid lines ═══.

Reaction vessel and shields

The brass reaction vessel (9.5 cm i.d., 12.7 cm high) contains the isothermal cylinder and equilibration coil (Fig. 2). The isothermal cylinder consists of a nickel-coated copper cylinder (4.4 cm o.d., 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 0.476 cm o.d. (10-24) nickel plated brass 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 cut into its side three adjacent spiral grooves, each having 15 turns. The grooves accommodate the equilibration coil tubing and the wire for the calibration heater and the control heater. The equilibration coil is constructed of approximately 2 m of 0.159 cm o.d., 1.78 mm wall thickness, Hastalloy-C-273 tubing [9] coiled and silver soldered on the isothermal cylinder. All flow tubing used in the calorimeter was made of Hastalloy-C-273. 0.5, 2, and 20 Mohm thermistors [10] are cemented with ceramic adhesive in holes drilled in the bottom side

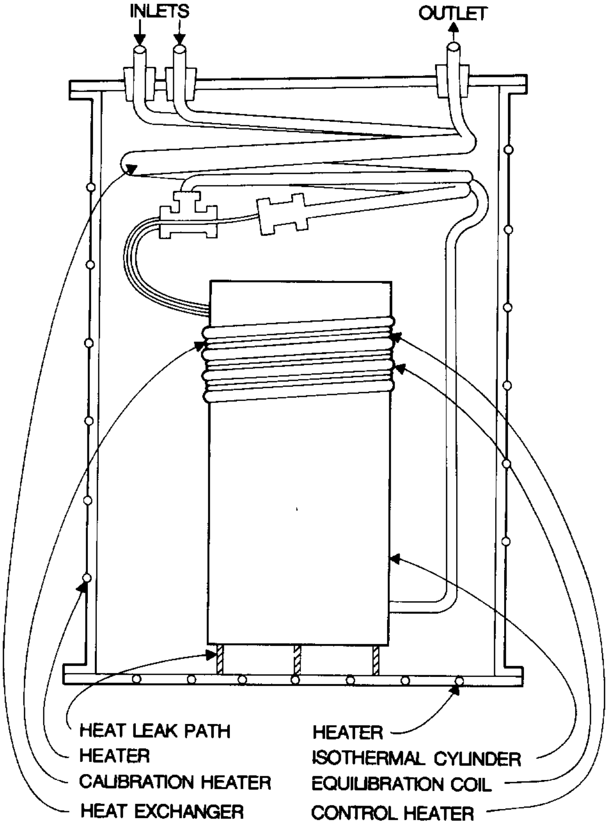

Fig. 2. Reaction vessel and contents.

of the isothermal cylinder. The thermistors are used to monitor continuously and control 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 1000 ohm Hy-Cal Engineering platinum resistance thermometer [11] for measuring the absolute temperature of the cylinder were also cemented into holes drilled in the bottom side of the isothermal cylinder.

The calibration and control heaters each consisted of 1.8 m of Omegaclad wire No. 304-K-MO-040 (0.102 cm o.d.) [12] having a resistance of approximately 90 ohm and are silver soldered in the spiral grooves cut in the side of the isothermal cylinder. A heater, comprised of a 0.61 m length of Omegaclad wire No. 304-K-MO-062 (0.157 cm o.d.) having a resistance of approximately 10 ohm, is silver soldered in a spiral groove cut in the bottom of the reaction vessel. Three thermistors (0.5, 2 and 20 Mohm) are cemented on the bottom of the reaction vessel. The heater and the appropriate thermistor depending on the temperature range to be investigated are connected to a Hart Scientific Model 370 iso-therm precision temperature controller [13]. The temperature of the bottom of the reaction vessel is controlled to ± 0.0005 K. 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 plated brass screws connecting the bottoms of the two vessels. The size, number, and length of bolts were designed to give a heat leak rate of approximately 1 J s^{-1} with a temperature difference of 1 K.

After entering the reaction vessel and before entering the coil, the reactants are equilibrated with the products from the coil in a countercurrent heat exchanger. This exchanger consists of 0.30 m lengths of the inlet and exit tubing which are wired together, so that the two inlet streams run countercurrent to the exit stream. The two tubes containing the reactants are brought together as shown in Fig. 3. The tube diameter of one stream is reduced from 0.159 to 0.0813 cm. The smaller tube is fitted inside the larger tube and the two reactant streams run coaxially for approximately 1/4 turn of the equilibration coil before the smaller inlet tube ends and mixing begins. Three thermistors (0.5, 2, and 20 Mohm) are cemented and a 1.2 m length of Omegaclad wire No. 304-K-MO-062 having a resistance of approximately 20 ohm is silver soldered to the outside surface of the reaction vessel. The heater and appropriate thermistor are connected to a Hart Scientific Model 3701 iso-therm precision temperature controller and the temperature is controlled at the same temperature as the isothermal cylinder. The bottom and the sides of the reaction vessel are controlled at different temperatures and are insulated from each other by an asbestos gasket.

The thermal shields consist of two brass cans surrounding the reaction vessel as shown in Fig. 4. The inner shield has a 0.60 m length of Omegaclad wire No. 308-K-MO-125 (0.3175 cm o.d.) having a resistance of approxi-

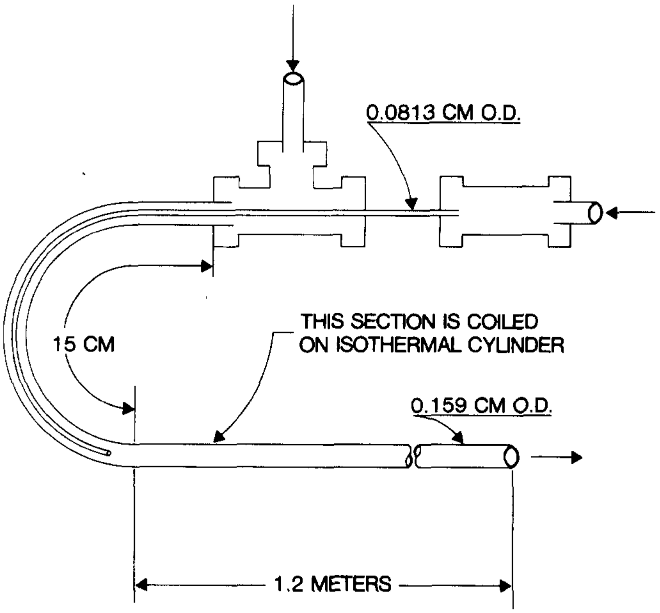

Fig. 3. Components of equilibration coil including inlet connectors.

mately 30 ohm and three thermistors (0.5, 2, and 20 Mohm) attached to its outside surface. The heater and thermistor are connected to a Hart Scientific Model 3701 iso-therm precision temperature controller. The outer shield is

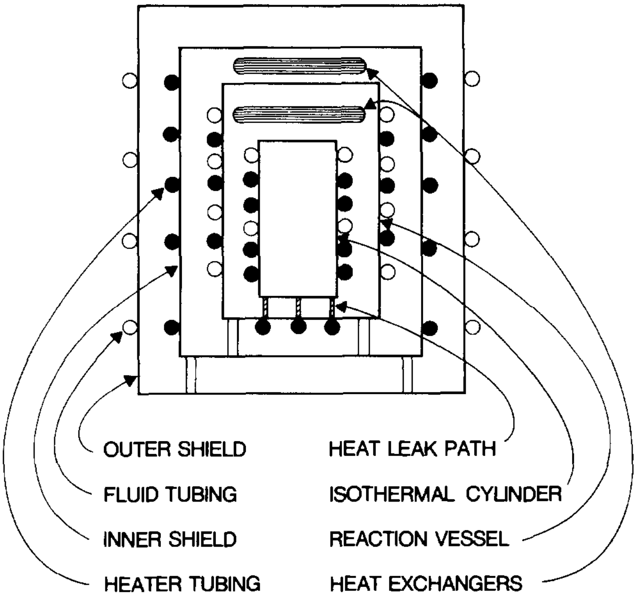

Fig. 4. Schematic representation of reaction vessel and thermal shields showing configuration of flow lines and heaters.

not temperature controlled, but is allowed to assume a steady state temperature between that of the inner shield and the air bath. A thermal path is provided from the reaction vessel through the shields to the air bath through three 0.476 cm o.d. stainless steel bolts and spacers connecting the reaction vessel to the first shield and the first shield to the second shield as shown in Fig. 4. The bolt circles are rotated 60° between the two shields.

Chromel–alumel thermocouples were cemented with ceramic adhesive to the bottom and sides of the reaction vessel and to the two shields. These thermocouples were used to monitor the temperatures of these various surfaces and to aid in setting the temperatures of the various surfaces. 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 673 K.

Flow circuit

A schematic diagram of the fluid circuit is shown in Fig. 1. Three different pump systems, a Waters model 6000 series [14], a Varian, Inc. 8700 series [15], and an ISCO, Inc. Model 314 series [16] can be used in the operation of the unit.

The Waters pumps and a model 660 solvent programmer were used for all the calibration runs reported here. This system has been described [3,5]. The unit can be run in either the variable or fixed mode. In the variable mode, the programmer provides a means of changing continuously the flow delivery rate of each pump according to a preselected program and this mode can be used to scan the entire mole fraction range to get an approximate heat of mixing curve. In the fixed mode, the flow rate of each pump is set and remains constant during the run. The fixed mode was used for all the runs reported here. The flow rates of the pump were measured for each run made.

The pressure in the system was controlled by a back pressure regulator [17] placed in the exit line from the reaction vessel and used in conjunction with a pressure regulator [18]. Pressure was monitored with a 0–14 MPa Heise gauge [19]. The control gas to the back pressure regulator was supplied by a compressed nitrogen gas cylinder. The available pressure in the gas cylinder limited the pressures attainable by this arrangement to less than 14 MPa. Pressure fluctuations in the flow line were less than ±14 kPa at the highest pressure (14 MPa) as indicated by repeated observations of the Heise gauge with no noticeable fluctuations at low pressures. The two inlet streams are equilibrated to the temperature of the isothermal cylinder by (1) passing through 2 m of tubing attached to the outside surface of the outer shield, (2) passing through a 0.30 m long countercurrent heat exchanger in contact with the exit stream, (3) passing through 1.2 m of tubing silver soldered to the outside surface of the reaction vessel and (4) passing through another 0.30 m long countercurrent heat exchanger. The exchangers are described in the section on reaction vessel and shields. In the entire flow circuit the fluids come in contact with only Hastalloy-C-273 tubing and stainless steel fittings.

The range of operating flow rates is determined by the type of fluids being investigated in the calorimeter. A small difference in temperature between the entering and exit fluids can cause an error in the determination of the heat of mixing. We have found in other calorimeters [3,4] using standard systems (i.e., hexane–cyclohexane) that for flow rates above 6 $\text{cm}^3\ \text{min}^{-1}$, the fluid leaving the isothermal cylinder is not completely equilibrated to the temperature of the cylinder. The flow rate at which nonequilibration occurs depends on the properties (i.e., viscosity, density, etc.) of the fluids in question. This effect can easily be determined by measuring the heat of mixing at progressively higher total flow rates. When the measured heat becomes dependent on the flow rate nonequilibration is occurring. By making runs at flow rates lower than the one for which breakthrough occurs, equilibration can be assumed to occur.

Air bath

The air bath consists of a Blue M Electric Company Mechanical Convection Ultra-Temp Model BFD-20F-4 Oven [20]. The reaction vessel, shields, and accompanying lines are suspended in the air bath. The air bath is capable of operating over the temperature range 298–973 K.

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) by maintaining the heat leak path at a constant cooling rate while varying the energy input to the isothermal cylinder with the control heater. The control circuit is very similar to those described previously [1] and is available as a Tronac model 550 isothermal control unit [21] or as a Hart Scientific Model 3704 iso-therm isothermal control unit [13]. The present unit uses a Hart 3704 iso-therm unit. The frequency of pulses supplied to the heater (0–100000 s^{-1}) is displayed in digital form and printed via teletype and is also recorded on a strip chart recorder.

PROCEDURE

The unit consisting of the reaction vessel and shields (Fig. 4) is placed in the air bath and the controllers are adjusted to the unit is operating at the desired temperature. The controlled cylinder and reaction vessel side are set at the same temperature. The bottom of the reaction vessel is set at a temperature approximately 1.0 K lower than the cylinder temperature. The wall of the inner shield is set at a temperature approximately 5 K lower than the reaction and vessel bottom temperature. The reaction vessel side 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 controlled plate, and the correct wall temperature has been obtained. The air bath temperature is set approximately 10 K lower than the controlled cylinder temperature. A temperature gradient is thus provided for the heat generated in the equilibration coil to be transferred to the air bath by conduction.

The pumps are charged with the reactants and the flow lines purged by first running one pump, then the other. A run consists of first running one pump at the total flow rate chosen for the reaction to determine a base line heater pulse rate. Then, both pumps are run at their respective flow rates and the reaction steady state heater pulse rate determined, followed by the other pump being run at the total flow rate and the base line 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 the calibration heater. For most runs only an electrical calibration is made with a chemical calibration being made periodically to confirm the electrical calibration.

PERFORMANCE

Chemical calibrations were made earlier of the low temperature version of the calorimeter using the systems $HClO_4$–NaOH, $HClO_4$–tris(hydroxymethyl)aminomethane and *n*-hexane–cyclohexane at 298 K [3] and of the elevated temperature calorimeter using the systems *n*-hexane–cyclohexane at 298 K and water–ethanol at 383 K [4]. These calibration runs showed that the calorimeters were capable of producing accurate measurements at a wide range of flow rates and concentrations. To test the performance of the present calorimeter, heat of mixing measurements were made on the system water–ethanol at 413 K and compared with values previously measured by us for this system [4]. Our previous measurements for the water–ethanol system at 413 K have been found to be in error due to the flow rate for one component being calculated from the measured total flow rate and the flow rate of the other component without the correction for the change in volume upon mixing being taken into account. The corrected values together with the original values are reported in Table 1. A comparison of the heat of mixing values for the water–ethanol system determined with the present calorimeter compared with the correct values reported in Table 1 are given in Table 2 and show agreement to ±0.8% or better through most of the range.

TABLE 1

Corrected heat of mixing data for water–ethanol system at 413 K and 1 MPa

Values reported earlier [a]		Corrected values [b]	
Mole fraction water	Heat of mixing (J mol^{-1})	Mole fraction water	Heat of mixing (J mol^{-1})
0.2063	596	0.2356	574
0.2208	589	0.2461	570
0.3620	812	0.3928	773
0.4813	876	0.5093	829
0.5751	860	0.5982	814
0.5777	851	0.6005	805
0.6826	756	0.6716	744
0.7516	657	0.7406	647
0.7887	578	0.7769	570
0.8088	545	0.7983	538
0.8544	440	0.8458	435
0.9216	221	0.9141	219
0.9236	217	0.9161	216
0.9378	192	0.9318	191
0.9416	193	0.9355	191

[a] Rev. Sci. Instrum., 52 (1981) 1226.

[b] Calculated flow rate corrected for volume of mixing—see Performance section in text.

TABLE 2

Measured heat of mixing data for water–ethanol system[a] at 413 K and 1 MPa

Mole fraction water	Heat of mixing (J mol^{-1})		
	This study	Table 1 [b]	Δ [c]
0.1757	459	432	27
0.2287	572	542	30
0.2992	672	667	5
0.3368	740	721	19
0.3657	754	756	−2
0.3873	772	778	−6
0.4380	810	817	−7
0.4825	839	836	3
0.5287	830	838	−8
0.6109	729	801	−9
0.6565	759	758	1
0.7177	676	675	1
0.7888	540	546	−6
0.8299	446	456	−10
0.8908	299	307	−8

[a] Specification of materials: ethanol, USD anhydrous reagent quality, U.S. Industrial Chemical Co.; water, distilled and deionized.

[b] Values of heat of mixing were calculated from smoothing equation applied to corrected values in Table 1.

[c] Δ = heat of mixing this study − heat of mixing (Table 1).

The heat of mixing values measured in this study have been combined with the corrected values from Table 1 and are reported in Table 3. The values of the coefficients A_n in the equation

$$H^E(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{n=0}^{C} A_n(1-2x)^n \tag{1}$$

were found by a least squared curve-fitting program and are given in Table 3

TABLE 3

Summary of heat of mixing data for water–ethanol system at 413 K and 1 MPa

Mole fraction water	Heat of mixing, H^E, (J mol^{-1})	
	Measured [a]	Calculated [b,c]
0.1757	459	445
0.2287	572	555
0.2356	574	568
0.2461	570	587
0.2992	672	675
0.3368	740	727
0.3657	754	760
0.3873	772	781
0.3928	773	786
0.4380	810	817
0.4825	839	833
0.5093	829	836
0.5287	830	834
0.5982	814	805
0.6005	805	803
0.6109	792	795
0.6565	759	752
0.6716	744	735
0.7177	676	670
0.7406	647	633
0.7769	570	567
0.7888	540	543
0.7983	538	524
0.8299	446	455
0.8458	435	419
0.8908	299	308
0.9141	219	246
0.9161	216	241
0.9318	191	198
0.9355	191	188

[a] Values of heat of mixing measured in this study (Table 2) and in a previous study (Table 1).

[b] Calculated using eqn. (1). Values of A_n in eqn. (1) are $A(0) = 3341.47$, $A(1) = -121.712$ and $A(2) = -447.599$.

[c] Standard deviation between measured values and calculated values is 11.0.

together with standard deviation, s. Values of H^E (calculated) reported in Table 3 were calculated from eqn. (1). The fit of the two sets of data is very satisfactory as indicated by the low value of 11 for the standard deviation. The instrument was tested using the water–ethanol system to 623 K and was found to perform well over the entire temperature range. No values of heats of mixing for this system have been measured at temperatures above 413 K. These results demonstrate that the instrument is capable of producing heat-of-mixing data over a wide concentration range at temperatures up to 623 K and beyond with the only limitation being the temperature limits of the materials of construction. This upper temperature limit is presently approximately 673 K and is determined by the wire used in the unit.

DISCUSSION

By combining the principles of isothermal calorimetry, flow calorimetry, environmental control using an air bath and multiple shields and a controlled heat leak path, an instrument has been developed that can measure heats of mixing at constant temperature and pressure 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 involving nonaqueous solvents and concentrated solutions which may undergo large heat capacity changes. In addition, no correction is necessary for heat exchange between the calorimeter and its environment. 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.

ACKNOWLEDGMENTS

The authors appreciate the financial support of the U.S. Department of Energy Contract No. DE-AC02-82ER13024 and the Electric Power Research Institute Contract No. RP 2160-2 which made this work possible. Helpful discussions with Dr. Delbert J. Eatough, Dr. Lee D. Hansen, and Mr. Roger M. Hart are acknowledged.

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18 Grove Valve and Regulator Co., Oakland, CA, U.S.A., model 15-LHX.
19 Heise Co., Newton, CT, U.S.A.
20 Blue M Electric Company, Blue Island, IL, U.S.A.
21 Tronac, Inc., Orem, UT, U.S.A.