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AN ISOTHERMAL FLOW CALORIMETER FOR HIGH TEMPERATURE AQUEOUS SOLUTIONS

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ABSTRACT

An isothermal flow calorimeter suitable for measuring heats of reaction in aqueous solutions from 373 to 773 K and from 0.1 to 40.5 MPa is described. Chemical and corrosion resistance was obtained by using only tantalum metal 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^{-1} can be measured to an accuracy of ±1.0% at constant temperature and pressure. The calorimeter was tested by measuring the heat of mixing of water–ethanol at 373 K and 1 MPa and of hexane–toluene at 413 K and 10.50 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], an isothermal, elevated temperature, high pressure flow calorimeter [4] and an isother-

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mal flow calorimeter designed for high temperature, high pressure operation [5] have been described. In addition, the application of isothermal calorimetry to the measurement of heats of reaction [6], of equilibrium constants for metal–ligand interaction and proton ionization [6], of heats of mixing [7,8], and of vapor–liquid equilibrium data [9] has been reported.

This paper describes a calorimeter suitable for use with high temperature aqueous solutions containing inorganic salts and 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 instruments [3–5] while offering the advantage of operating at temperatures up to 773 K with the potential of operating at even higher temperatures. Energy effects can be measured at any temperature and pressure in the ranges 373–773 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.

This instrument was developed to increase the resistance to chemical attack and to extend the temperature range (273–573 K) of the existing isothermal, isobaric, elevated temperature, high pressure flow calorimeter [4,5]. 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) chemistry in high temperature ocean vents, (2) corrosion problems in geothermal applications, in high temperature boilers and in heat exchangers, and (3) supercritical extraction involving hydrocarbons, alcohols, CO_2, etc. All tubing used in the calorimeter was made of tantalum 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 calibrations (water–ethanol at 373 K and 1 MPa and hexane–toluene at 413 K and 10.50 MPa). The data obtained were of approximately the same precision and accuracy (±1.0%) as those obtained from our isothermal flow calorimeters described previously [3–5].

APPARATUS

The calorimeter is very similar to the elevated temperature, high pressure flow calorimeter described previously by us [5] 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 and the removal of the unit from an air bath environment to one of free standing in the laboratory.

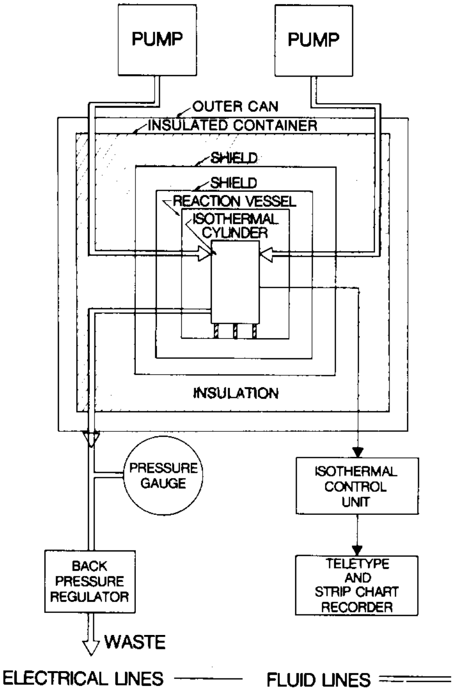

Fig. 1. A block diagram of the main components of the calorimeter.

The main components of the calorimeter are the reaction vessel containing the isothermal cylinder and equilibration coil, the isothermal shields and insulating container, 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 equilibrium 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 at ±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 (0–100000 s^{-1}) supplied to the heater is measured and displayed in digital form and recorded on a Commodore computer. Energy effects due to the heat of mixing can be measured in the range 0.15–120 J min^{-1} with an error of less than 1.0%. 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.

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 cut into its side three adjacent spiral grooves, each having 15 turns. The grooves accommodate the equilibration coil tubing and the clad wire used for the calibration heater and the control heater. The equilibration coil is constructed of approximately 2 m of 0.159 cm OD, 1.78 mm wall thickness, tantalum tubing (Superior Tube Co., Norristown, PA) coiled and silver-soldered on the isothermal cylinder. All flow tubing used in the calorimeter was made of tantalum. One 2-Mohm and two 20-Mohm thermistors (Ther-

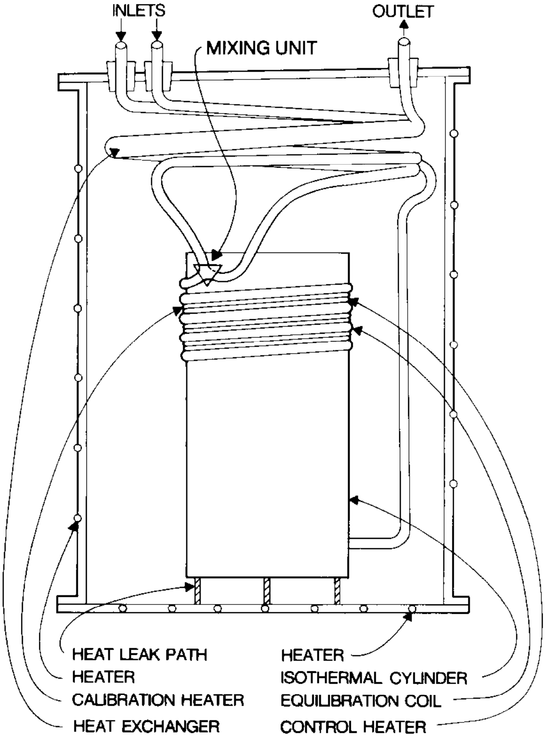

Fig. 2. Reaction vessel and contents.

mometrics, Inc., Edison, NJ) are cemented with ceramic adhesive in holes drilled in the bottom of the isothermal cylinder. The thermistors are used to continuously monitor 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 (Santa Fe Springs, CO) platinum resistance thermometer for measuring the absolute temperature of the cylinder were also cemented into holes drilled in the bottom 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 OD) (Omega Engineering, Inc., Stamford, CT) having a resistance of approximately 90 ohm, silver-soldered in the spiral grooves cut in the side of the isothermal cylinder. A heater comprised of a 0.56 m length of Omegaclad wire No. 304-K-MO-062 (0.157 cm OD) having a resistance of approximately 13 ohm is silver-soldered in a spiral groove cut in the bottom of the reaction vessel. Three thermistors (one 2- and two 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 (Provo, UT) Model 3701 iso-therm precision temperature controller. 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 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 in a triangular shaped mixing chamber as shown in Fig. 3. The two inlet tubes and the exit tube from the mixing chamber were electron-beam welded into the tantalum mixing chamber. The mixing chamber is silver-soldered against the side of the isothermal cylinder. Three thermistors (one 2- and two 20-Mohm) are cemented and at 1.2 m length of Omegaclad wire No. 304-K-MO-062 having a resistance of approximately 26 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 nickel cans surrounding the reaction vessel as shown in Fig. 3. The inner shield has a 1.8 m length of Omegaclad

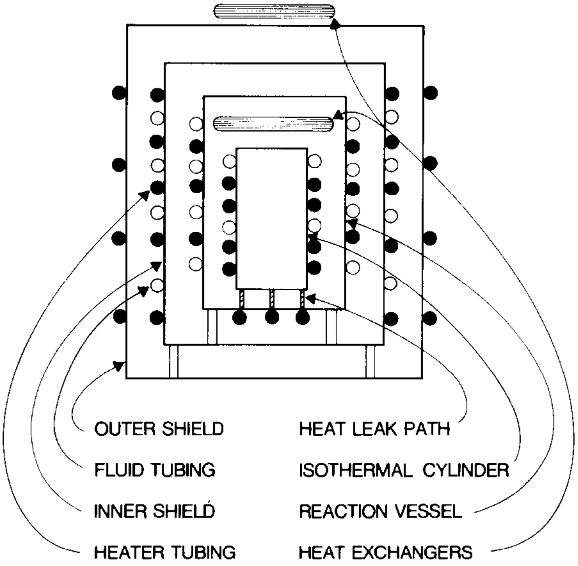

Fig. 3. Schematic of reaction vessel and thermal shields showing configuration of flow lines and heaters.

wire No. 308-K-MO-062 having a resistance of approximately 36 ohm and three thermistors (one 2- and two 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 not temperature controlled, but is allowed to assume a steady state temperature between that of the inner shield and the surrounding insulation. A thermal path is provided from the reaction vessel through the shields to the insulation through three 0.635 cm OD nickel bolts and spacers connecting the reaction vessel to the first shield and the first shield to the second shield as shown in Fig. 3. 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 773 K.

Flow circuit

A schematic diagram of the fluid circuit is shown in Fig. 1. Three different pump systems, a Waters Associates (Milford, MA) model 6000 series, a Varian, Inc. (Palo Alto, CA) 8700 series, and an ISCO, Inc. (Lincoln, NE) Model 314 series can be used in the operation of the unit. The ISCO pumps were used for all the calibration runs reported here. This system has been described previously [5]. All runs were made in the fixed mode, where the flow rate of each pump is set and remains constant during the run. The flow rates of the pump were measured for each run made.

The pressure in the system was controlled by a back pressure regulator (Grove Valve and Regulator Co., Oakland, CA, model S-91XW, Teflon diaphragm) placed in the exit line from the reaction vessel and used in conjunction with a pressure regulator (Grove Valve and Regulator Co., Oakland, CA, model 15-LHX). Pressure was monitored with a 0–14 MPa Heise Co. (Newton, CT) gauge. 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 a 0.30 m long countercurrent heat exchanger in contact with the exit stream, (2) passing through 2 m of tubing attached to the outside surface of the inner shield, (3) passing through 1.2 m of tubing attached to the outside surface of the reaction vessel, and (4) passing through another 0.30 m long countercurrent heat exchanger contained in the reaction vessel. The exchangers are described in the section on Reation Vessel and Shields. In the entire flow circuit the fluids come in contact with only tantalum tubing, Hastalloy-C-273 pump barrels and stainless-steel fittings. The entire flow circuit between the pumps and the back pressure regulator consists of only tantalum tubing and the tantalum mixing chamber in which the tubing is electron-beam welded. This means that the fluid only contacts tantalum tubing when at a temperature above ambient.

The range of operating flow rate 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 flow calorimeters [3,4] using standard systems (i.e., hexane–cyclohexane) that for flow rates above 6 cm^3 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.

Insulated container

The insulated container consists of a 38 cm OD stainless-steel cylinder 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 (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 [1–5] and is available as a Tronac model 550 isothermal control unit (Tronac, Inc., Orem, UT) or as a Hart Scientific Model 3704 iso-therm isothermal control unit. The present unit uses a Hart 3704 iso-therm unit. The frequency of pulses supplied to the heater (0–100000 s^{-1}) is displayed on a Commodore 64 computer and is recorded on floppy disk at the completion of each run.

PROCEDURE

All the controllers are adjusted so 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 vessel bottom 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 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 pumps are charged with the reactants and the flow lines purged by first running one pump, then the other. A run consists, first, of running one pump at the total flow rate 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 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 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 on 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 on the elevated temperature calorimeter using the system *n*-hexane–cyclohexane at 298 K [4] and water–ethanol at 383 [4] and 413 K [5]. These calibration runs showed that the calorimeters were capable of producing accurate measurements over 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 373 K and 1 MPa and hexane–toluene at 413 K and 10.50 MPa and compared with values measured previously by us for these systems. A comparison of the heat of mixing values for the water–ethanol system and for the hexane–toluene system determined with the present calorimeter compared with previously determined values [10,11] are given in Table 1 and show agreement to ±1.0% or better through most of the range. No values of heats of mixing for the ethanol–water and hexane–toluene systems have been measured at temperatures above 413 K. The results obtained indicate that the instrument is capable of producing heat-of-mixing data over a wide concentration range at temperatures up to 413 K and beyond, with the only limitation being the temperature limits of the materials of construction. This upper temperature limit is presently approximately 773 K and is determined by the thermistors and wire used in the unit.

TABLE 1

Measured heat of mixing data for water–ethanol systems at 373 K and 1 MPa and hexane–toluene system at 413 K and 10.50 MPa

Mole fraction	Heat of mixing ($J\ mol^{-1}$)		Δ [b]
	This study	Previous study [a]	
Water–ethanol [c]			
0.0301	−16.3	−16.4	−0.1
0.5493	470.2	474.3	−4.1
Hexane–toluene [d]			
0.2000	291.8	291.7	+0.1
0.4000	413.9	420.5	−6.6
0.4998	433.8	429.1	+4.7
0.7280	329.5	323.9	+5.6

[a] Ref. 10.

[b] Δ = heat of mixing this study − heat of mixing from ref. 10.

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

[d] Specification of materials: hexane, Phillips Petroleum, > 99 mol% pure; toluene, Phillips Petroleum, > 99 mol% pure.

DISCUSSION

By combining the principles of isothermal flow calorimetry, with the chemical resistance of tantalum metal an instrument 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 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.

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