International Journal of Thermophysics, Vol. 9, No. 6, 1988

An Automated Flow Calorimeter for Heat Capacity and Enthalpy Measurements[1]

J. A. Sandarusi[2] and V. F. Yesavage[2]

An automated flow calorimeter has been developed for the measurement of heat capacity and latent enthalpies of fluids at elevated temperatures (300–700 K) and pressure (< 30 MPa) with a design accuracy of 0.1%. The method of measurement is the traditional electrical power input flow calorimeter, utilizing a precision metering pump, which eliminates the need for flow-rate monitoring. The calorimeter cell uses a unique concentric coil design with passive metal radiation shields and active guard heaters to minimize heat leakage, eliminate the traditional constant-temperature bath, and facilitate easy component replacement. An additional feature of the instrument is a complete automation system, greatly simplifying operation of the apparatus. A novel multitasking software scheme allows a single microcomputer simultaneously to control all system temperatures, provide continuous monitoring and updates on system status, and log data. Preliminary results for liquid water mean heat capacities show the equipment to be performing satisfactorily, with data accuracies of better than ±0.3%. Minor equipment modifications and better thermometry are required to reduce systemic errors and to achieve the designed operational range.

KEY WORDS: calorimetry; flow calorimeter; heat capacity (isobaric); high pressure; high temperature.

1. INTRODUCTION

An extensive effort has been in progress in our laboratory to measure the thermophysical properties of industrially significant fluids for two decades. One area of particular interest has been the enthalpy of process fluids at high temperatures and pressures. To this end, a Freon boil-off flow

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Chemical Engineering and Petroleum Refining Department, Colorado School of Mines, Golden, Colorado 80401, U.S.A.

0195-928X/88/1100-0993$06.00/0

calorimeter has been in operation making measurements on a range of fluids for the past 10 years [1, 2]. Unfortunately, operational complexities have limited the use of this instrument. In general, the lack of skilled experimentalists has been a great impediment to the continued operation of many flow calorimeters due to the exacting nature of the measurements [3].

In an attempt to eliminate this problem, we have built a new automated flow calorimeter which is currently undergoing performance testing. The instrument was designed to measure heat capacities for both liquid and vapor phases and latent heats. The operational range of the instrument is 0–30 MPa and 300–700 K, although lower temperatures are possible with some modifications. The primary feature of the calorimeter is a microcomputer-based automation system which allows completely independent operation, requiring human intervention only to take data or change set points. It is anticipated that this approach will make precision isobaric measurements more routine.

The method of measurement is steady-state flow calorimetry with electrical power input, which has been discussed extensively in the literature (e.g., Refs. 4–6). This approach was selected because it is the most readily automated of all the flow calorimetry techniques. In brief, a measured amount of electrical power is input to a fluid with a known mass flow rate. Measurement of the resulting pressure change and temperature rise allows calculation of the mean isobaric heat capacity via a first-law analysis. Small corrections must be made to the data for Joule–Thomson effects [7].

In general, there are several difficulties with this measurement. First, the calorimeter cell must be carefully designed to minimize heat leaks in or out of the system boundaries. Second, the mass flow rate is typically difficult to measure with great accuracy in a recycle system [8, 9]. Finally, great care must be expended in measuring the temperature rise precisely [3]. The target accuracy for the new calorimeter is 0.1%. This is extremely difficult to achieve with this type of instrument, especially at high temperatures, where radiative heat losses become very significant. What follows is a discussion of the flow calorimeter and its automation hardware and software.

2. HARDWARE DESCRIPTION

2.1. Flow Circuit

Details of the flow system for the calorimeter are shown in Fig. 1. The primary components of the circuit are a Ruska dual-piston proportioning

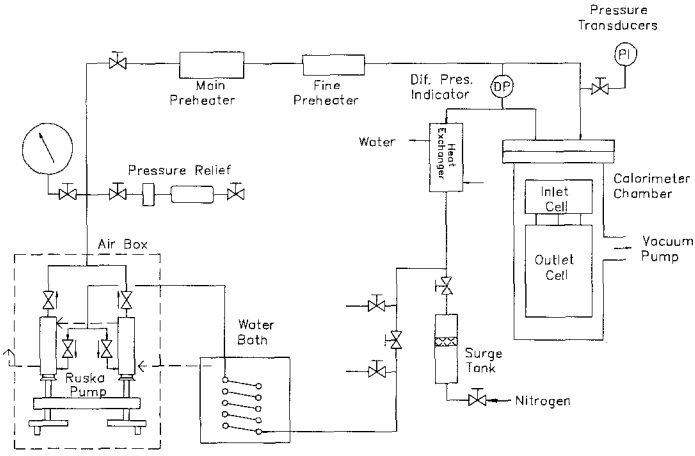

Fig. 1. Flow calorimeter process diagram.

pump, a two-stage fluid preheater, the calorimeter cell/vacuum chamber and attendant vacuum system, the pressure regulation system, and a water bath.

The Ruska pump is a continuous-flow metering pump with 500-cm^3 cylinders featuring very stable flow rates (better than 0.1%) over the 30 MPa pressure range. Constancy of flow is critical to our design since it eliminates the difficult task of high-accuracy flow measurement during instrument operation. Pump calibrations indicate that the volumetric flow rates are stable to 0.05%.

Fluid temperature in the cylinders is controlled by flowing water from the water bath (± 0.01 K) around the pump jackets. In addition, the pump mechanism and cylinders are enclosed in an air bath controlled to ± 0.1 K. Cylinder pressures are monitored with a set of 0- to 30-MPa 0.5% pressure transducers. Pressure and temperature measurements in the cylinders are necessary for calculation of the fluid density allowing volumetric flow rates to be converted to the required mass flows.

Fluid is heated to the operating temperature with two preheaters located immediately before the calorimeter vacuum chamber. They consist of helical coils of tubing in contact with external cartridge heaters. The first stage is a 500-W coarse heater followed by a second-stage 75-W fine heater. The preheaters are computer controlled via triac power packs and are designed to bring the system fluid to a maximum operating temperature of 700 K and to traverse the two-phase region.

Automating the pressure regulation system has proven to be difficult, due in part to the large volume of the pump cylinders and to the necessity

of repressurizing the downstream fluid after pump reversals. Currently, a manual method using a nitrogen-loaded surge tank with a floating disk piston separating the working fluid from the nitrogen is in use. Pressure control of ± 3 kPa is easily achieved with this method and minimal system upsets occur with pump switchovers. We are currently investigating the possibility of automating this method. Since precise pressure regulation is necessary primarily in the critical and two-phase regions [9], lack of an automated system should pose few problems outside of these regions.

2.2. Calorimeter Cell

The most significant part of the apparatus is the calorimeter cell, where heat capacity and heat of vaporization measurements are made. The cell design is shown in Fig. 2. The design is most similar to that of Powers and Miyazaki [7, 9], however, ours is simpler, permitting easier reassembly, and contains added and unique features to minimize heat losses. A unique feature of the design is the lack of an external constant-temperature bath. This was necessitated by concerns about vacuum maintenance at high temperatures and problems with precise temperature control in high-temperature air baths. Instead of an air bath to regulate the "ambient" cell temperature, the entire calorimeter cell itself is maintained at the desired operating temperature in vacuum with computer-controlled shields which form the exterior shell of the cell.

The two shields are composed of machined thick-walled aluminium cylinders actively and precisely maintained (± 3 mK) at the inlet and outlet fluid temperatures. Heat is added through metal-insulated heating elements wrapped around the shields. In addition, each shield is wrapped with tubing to minimize thermal gradients and to ensure that each shield is at the inlet/outlet fluid temperature. This is especially important for the inlet fluid since the shield buffers the fluid from temperature drift in the

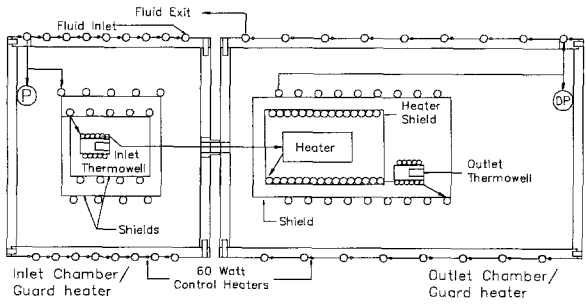

Fig. 2. Flow calorimeter cell details.

preheaters. The two shields are separated and capped, forming inlet/outlet chambers which isolate the cell internals from the ambient environment. Within the inlet chamber, two passive shields of silvered copper surround the inlet thermowell, facilitating accurate measurement of the inlet fluid temperature. The outlet chamber contains the calorimeter working heater and the outlet thermowell. A two-layer passive shielding system in the outlet chamber is designed to minimize heat losses from the calorimeter working heater to the environment and to eliminate the effects of outlet shield temperature fluctuation on the outlet thermometer.

Conductive heat transfer is eliminated by maintaining a 1 Pa or better vacuum around the cell in an enclosing vacuum chamber maintained at ambient temperature. Radiative heat transfer in the cell is minimized by eliminating gradients and by the use of passive shields. In addition, blankets of multilayer insulation minimize radiative losses from the calorimeter shields to ambient.

A cell design consisting of concentric helical tube coils on passive shields was selected to simplify component replacement due to coke plugging. Similarly, a simple capsule-type heater which is designed for easy replacement due to heater burnout is used to input heat to the working fluid.

Pressure taps are located as close as possible to the inlet and outlet thermowells. Inlet pressures are measured with three (1600-kPa, 6000-kPa, and 30-MPa) Heise pressure transducers with an accuracy of 0.1%. A Validyne differential pressure transducer measures the pressure drop across the system, which is typically less than 1 kPa. Inlet and outlet temperatures are measured with two small 100 Ω Minco ceramic-encapsulated platinum resistance thermometers (PRTs). In addition, a 10-junction Type J thermopile located between the outlet thermowell and the outlet shield is used to zero the temperature gradient in the outlet calorimeter section.

2.3. Automation Hardware

The system electronics and all of the linkages necessary for automated control and monitoring of the calorimeter components are shown in block diagram form in Fig. 3. The heart of the system is a Kaypro 286i microcomputer which serves as the system controller and operator interface. The microcomputer reads or actuates various sensors, power supplies, relays, and multimeters in its role as system manager. Data acquisition is accomplished with a Hewlett Packard (HP) 3457A and a Keithley 197 digital multimeter (DMM) which measure the system variables and feed the information via an IEEE-488 bus to the control computer. The sensors are primarily platinum resistance thermometers for temperature

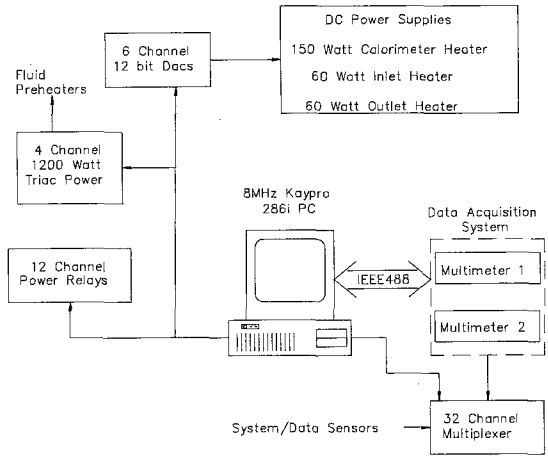

Fig. 3. Flow calorimeter automation hardware.

measurement and voltage output pressure transducers for pressure measurement. The HP DMM is used to read the resistance/temperature sensors, while the Keithley DMM is dedicated to the voltage-based sensors. The segregation of the DMMs speeds up throughput, allowing reading rates of two sensors per second per DMM [10]. The various sensors are routed to the multimeters with a computer-driven 32-channel precision multiplexer using low thermal EMF relays.

The two external preheaters are driven by a high-power four-channel (1.8 kW/channel) phase-angle firing triac power pack directly controlled by the microcomputer. Two 100-V/60-W DC power supplies are used to drive the two calorimeter shields. In addition, an 80-V/400-W DC amplifier powers the calorimeter heater capsule. All three DC power supplies are set with a six-channel 12-bit digital-to-analog converter (DAC) cricuit.

Several of the electronic subassemblies were built in-house to meet performance specification not readily found in commercial systems and to allow for future system expansion if necessary. These include the 6-channel DAC, the 32-channel multiplexer, and the 4-channel triac power packs. A 12-channel power relay system was also built to allow the computer to turn on/off critical components. All of the these units are directly controlled by the microcomputer via an interface designed in our laboratory.

3. AUTOMATION SOFTWARE

A novel software scheme designed to control and monitor the apparatus was just recently implemented, a structural outline of which is

shown in Fig. 4. The control code effectively partitions the microcomputer into background and foreground jobs, each performing a different task. The first job has top priority and is resident in the background. Its primary duty is to control the equipment at the current set points by driving all of the computer external electronic hardware. The background job monitors the apparatus through the data acquisition system and makes appropriate control adjustments to maintain the system. Currently a modified proportional-integral-differential (PID) velocity algorithm [11] is used by the digital controllers in this program. The second job is in the foreground and is used primarily as the user/operator interface and system status display. In addition, the foreground job passes various control commands adjusting the operation of the control task in the background. Conversely, data measured by the control program are sent to the foreground process. Partitioning of the computer system allows for smooth operation of the equipment with no system freeze-up on set-point changes and ensures that each controlled unit receives an adequate and nearly constant amount of control time independent of the foreground task. It also allows real-time data analysis to occur in the foreground with little effect on the background efficiency. In order to pass data and commands between the two processes, an identical set of variables sharing the same memory locations is defined in the two separate computer programs. A variable change initiated by one process is immediately detected by the other.

In the future, an expert system shell may also be placed in this foreground job to make the calorimeter "smart," allowing automatic data analysis and decisions as to the next data-point selection. Currently, an operator is required to select the data-point set and the operator must decide when a measurement is complete, allowing the system to move to the next set point. The current system software is written exclusively in Pascal, which allows absolute variable addressing. The multitasking scheduler is a commercial package called Double Dos.

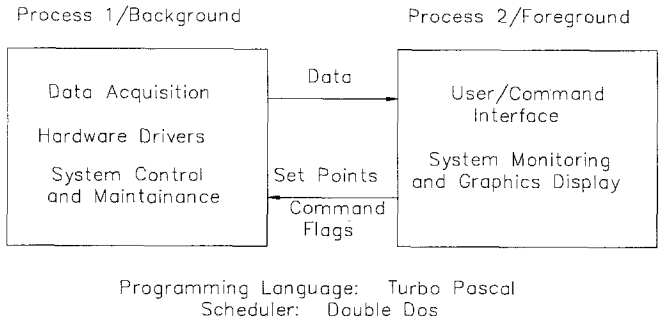

Fig. 4. Flow calorimeter automation software outline.

4. CALORIMETER EVALUATION

In general, the majority of the components in the system have worked well. This includes the data acquisition system and associated electronics and the automation software. In particular, the control system has performed very well, with the critical calorimeter shield temperatures easily controlled to the target values of ± 3 mK. A minor problem concerns leaks in the calorimeter cell, limiting the effective range of the calorimeter to temperatures and pressures lower than the designed capabilities. The leaks stem primarily from poorly brazed joints in the cell. Leakage problems should be eliminated shortly with careful mofification of the cell.

To judge the performance of the apparatus, water was run as a test fluid. Mean heat capacities were determined for liquid water at pressures up to 3500 kPa and a temperature range of 328–479 K. Results of the test runs are shown in Table I. Data errors are less than 0.3% and are typically between 0.1 and 0.2%. Although these errors are greater than the target value of 0.1%, we are nonetheless encouraged considering that the apparatus has been operational for only several months.

We currently belive that most of the error can be ascribed to difficulties in measuring the temperature rise in the calorimeter. Ceramic encapsulated mini-PRTs are currently in use. These thermometers have proven to be unreliable, with large vacuum-induced self-heating problems

Table I. Preliminary Results for the Mean Heat Capacity of Liquid Water[a]

Average temp. (K)	Pressure (kPa)	Mean heat capacity		Error (%)
		Experimental ($J \cdot g^{-1} \cdot K^{-1}$)	Literature [15] ($J \cdot g^{-1} \cdot K^{-1}$)	
328.1	72.4	4.1843	4.1818	+0.06
328.1	988.7	4.1822	4.1797	+0.06
328.3	1008.9	4.1789	4.1797	−0.02
328.3	3472.0	4.1676	4.1780	−0.16
348.5	996.5	4.1830	4.1881	−0.12
378.1	772.2	4.2320	4.2224	+0.23
395.9	776.3	4.2647	4.2538	+0.26
398.0	772.2	4.2618	4.2559	+0.14
417.9	772.9	4.3040	4.2978	+0.15
424.8	987.4	4.3107	4.3141	−0.08
432.7	774.6	4.3413	4.3367	+0.11
449.6	986.3	4.3941	4.3903	+0.09
479.5	2110.0	4.5155	4.5192	−0.06

[a] Flow rate = 8.000 ml · min^{-1}; temperature rise = 10°C.

and significant short-term calibration drift [12]. We are currently investigating the feasibility of replacing these thermometers either with a calibrated thermopile (Type T) [7, 13] or with capsule-type primary standard PRTs [5, 6, 14]. We feel that either of the above approaches will greatly diminish the relative errors, allowing the apparatus to approach the target accuracy of 0.1%.

In addition to thermometry problems, temperature gradients in the calorimeter shields may prove to be larger than anticipated, resulting in heat leaks. This will be particularly important at very high temperatures, where radiative heat transfer dominates. As such, an accuracy of 0.1% may be unrealistically low for very high-temperature measurements. Some design changes in the cell are being implemented to minimize these gradients and any potential heat leaks. Several experiments are planned where shield gradients will be measured utilizing thermocouples.

5. CONCLUSIONS

The new flow calorimeter and its automation system have been shown to work successfully, with relative errors approaching the design specifications. Some remaining problems must be resolved before the apparatus can make high-accuracy measurements at the highest temperatures and pressures. Nonetheless, the current success of the instrument represents a significant improvement over past calorimeters of its type and it should do much to improve the current data base of heat capacities and enthalpies. Upon completion of system modifications and testing with water, measurements will be made on methanol and *n*-butane.

ACKNOWLEDGMENTS

The authors would like to thank the U.S. Department of Energy for their support of this work under agreement DE-FG02-87ER13683, the National Science Foundation for Grant CBT-8611630, and the Phillips Petroleum Company for providing Mr. Sandarusi with a Phillips Fellowship.

REFERENCES

1. J. McConnell, R. Fleckenstein, A. Kidnay, and V. Yesavage, *I & EC Proc. Des. Dev.* **23**:267 (1984).
2. D. Flanigan, Ph.D. thesis (Colorado School of Mines, Golden, (1986).
3. M. L. McGlashan, *Thermochim. Acta* **72**:55 (1984).
4. V. Yesavage, A. Mather, D. Katz, and J. Powers, *I & EC* **59**:35 (1967).
5. K. Bier, G. Ernst, and G. Maurer, *J. Chem. Thermo.* **6**:102 (1974).

6. I. Dreher, *J. Chem. Thermo.* **11**:993 (1979).
7. T. Miyazaki, Ph.D. thesis (University of Michigan, Ann Arbor, 1973).
8. V. Yesavage, Ph.D. thesis (University of Michigan, Ann Arbor, 1968).
9. T. Miyazaki, A. Hejmadi, and J. Powers, *J. Chem. Thermo.* **12**:105 (1980).
10. W. Cash, E. Stansbury, C. Moore, and C. Brooks, *Rev. Sci. Instr.* **52**:895 (1981).
11. G. Stephanopolous, *Chemical Process Control* (Prentice Hall, Englewood Cliffs, N.J., 1984), pp. 635–637.
12. B. Mangum, *J. Res. NBS* **89**:305 (1984).
13. A. Furtado, Ph.D. thesis (University of Michigan, Ann Arbor, 1973).
14. C. Barber, *J. Sci. Instr.* **27**:47 (1950).
15. NBS/NRC, Properties of Steam, computer program (1985).