Received by OSTI
NOV 19 1990

AN AUTOMATED FLOW CALORIMETER FOR HEAT CAPACITY
AND
ENTHALPY MEASUREMENTS AT ELEVATED TEMPERATURES AND PRESSURES

Final Report
for Period March 1, 1987 - May 31, 1990

Victor F. Yesavage

Colorado School of Mines
Department of Chemical Engineering
and Petroleum Refining
Golden, CO 80401

August 31, 1990

Prepared for

THE U. S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-87ER13683

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, subcontractors, or their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights.

ABSTRACT

The need for highly accurate thermal property data for a broad range of new application fluids is well documented. To facilitate expansion of the current thermophysical database, an automated flow calorimeter was developed for the measurement of highly accurate isobaric heat capacities and enthalpies of fluids at elevated temperatures and pressures. The experimental technique utilizes traditional electrical power input, adiabatic flow calorimetry with a precision metering pump that eliminates the need for on-line flow rate monitoring. In addition, a complete automation system, greatly simplifies the operation of the apparatus and increases the rapidity of the measurement process.

The range over which the instrument was tested, was 300-600 K and 0-12 MPa, although the calorimeter should perform up to the original design goals of 700 K and 30 MPa. The new flow calorimeter was evaluated by measuring the mean, isobaric, specific heat capacities of liquid water and n-pentane. These experiments yielded an average deviation from the standard literature data of +0.02% and a total variation of 0.05%. Additional data analysis indicated that the overall measurement uncertainty was conservatively estimated as 0.2% with an anticipated precision of 0.1-0.15% at all operating conditions.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
MEASUREMENT PRINCIPLES	3
APPARATUS	3
Flow Loop	4
Pumping System	5
HPLC Valve	6
Pump Temperature Control	7
Pressure Measurement	8
Pressure Regulation	9
Preheaters	13
Calorimeter Cell	14
Calorimeter Working Heater	20
Calorimeter Thermometers	23
Vacuum System	24
SYSTEM AUTOMATION AND CONTROL	26
Automation Software	26
Automation Hardware	30
EXPERIMENTAL	36
EQUIPMENT EVALUATION AND EXPERIMENTAL RESULTS AND DISCUSSION	37
System Performance	37
Results and Discussion for Liquid Water	38
Error Analysis	43
Heat Leak Measurements	45
Results and Discussion for Liquid n-Pentane	48
CONCLUSIONS AND RECOMMENDATIONS	50
LITERATURE CITED	52
FIGURES	55
TABLES	82
PUBLICATIONS RESULTING FROM GRANT	86

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 calorimeter has been in operation making measurements on a range of fluids for the past twelve years (McConnell et al. 1984, Flanigan, 1986). Unfortunately, operational complexities have limited the use of this instrument. In general, the lack of skilled experimentalists has been a great impediment to continued operation of many flow calorimeters due to the exacting nature of the measurements (McGlashen, 1984).

In an attempt to eliminate this problem, we have built a new automated flow calorimeter and have completed 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 point. It is anticipated that this approach will make precision isobaric measurements routine.

The method of measurement is steady state flow calorimetry with electrical power input, which has been discussed extensively in the literature (e.g. Yesavage et al. 1967, Bier et al. 1974, Dreher 1979, Sandarusi 1990). 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 allow calculation of the mean isobaric

heat capacity via a first law analysis. Small corrections must be made to the data for Joule-Thomson effects (Miyazaki, 1973).

In general there are several difficulties with this measurement. Firstly, the calorimeter cell must be carefully designed to minimize heat leaks in or out of the system boundaries. Also, mass flow rate is typically difficult to measure with great accuracy in a recycle system (Yesavage, 1968, Miyazaki et al. 1980). Finally, great care must be expended in measuring the temperature rise precisely (McGlashen, 1984). 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.

Development work on all major calorimeter hardware and software components was completed. This includes the flow system, the measuring cell (calorimeter), and the automation electronics. In addition, a new copper cell was introduced, extending operation to higher flow rates and resulting in better system response and performance. Initial tests performed on the apparatus have shown the equipment to be working well with relatively few unexpected design flaws. Measurements of the isobaric heat capacity of water were performed for several different isotherms and isobars covering an operating range of 303-573K and 0-14 MPa. A number of isothermal measurements (323 K) was completed for liquid n-pentane at 323K and 3.5-10 MPa. The combined results for the two test fluids establish a maximum estimated uncertainty of 0.2% and a precision of 0.15% for the isobaric, mean, heat capacities determined with this calorimeter.

What follows is a discussion of the flow calorimeter including its automation hardware and software and the calorimeter evaluations and compari-

sons with literature data.

MEASUREMENT PRINCIPLES

The details of the measurement principles associated with flow calorimeters are presented in the PhD thesis of Sandarusi (Sandarusi, 1990). If zero heat leak is assumed, then the fundamental equation for mean isobaric specific heat capacity, as measured by an adiabatic flow calorimeter, is given as:

$$\bar{C}_p = [Q_{in}]/[\dot{m}]/[T_o - T_i] \quad (1)$$

where the three terms enclosed in brackets represent the three directly measured independent variables: electrical power input (Q_{in}), mass flow rate ($\dot{m}$), and the calorimeter temperature difference ($T_o - T_i$). The two intensive variables affecting the heat capacities, temperature and pressure, must also be determined. The electrical power input to the fluid from the resistance heater is calculated by:

$$Q_{in} = VI \quad (2)$$

where V is the voltage drop across the heater and I is the current input to the heater. Sandarusi (1990) discusses how minor corrections can be made for small temperature and pressure drops, to convert the mean heat capacity to a point value.

THE APPARATUS

The rationale that went into selecting the numerous components that were used in the calorimetric system are discussed in detail by Sandarusi (1990). The flow calorimeter system was composed of several individual subsystems in a closed flow loop. The layout of the apparatus is shown in Figure 1, illustrating the positions of all the major components that formed the complete calo-

rimeter system. These included the pumping system with its temperature and flow direction (HPLC valve) controllers, the preheaters, the pressure sensing and regulation (surge tank) systems, and the calorimeter cell itself with its attendant vacuum system. The figure does not include the automation electronics which are discussed in the following section. What follows is a description of all the major components along the flow path.

The Flow Loop:

The flow circuit itself was built mainly from stainless steel tubing (3.2 mm OD, 2.2 mm ID) using Swagelok fittings for all the connections. The loop was successfully tested to pressures in excess of 30 MPa with no leakage except for the occasional fitting failure. The total volume of the flow loop, excluding the surge tank and pump was approximately 250 ml. The total system volume was about 1 liter. The entire system was supported on an open Unistrut frame housing every calorimeter component including the automation system and control console. Only the pump and the external water bath were not mounted on this frame. The frame and pump were supported on wheels for portability. The flow loop had an adjustable pressure relief valve (Nupro SS-RL3S4- EP) (10-35 MPa), with a connecting blowout tank, to protect the pump and calorimeter from potentially damaging over-pressures (>30 MPa).

The water bath shown in Figure 1 was primarily used to regulate the temperature of the test fluid in the pump cylinders. This was necessary to facilitate the determination of the test fluid densities in the pump cylinders. The bath is also shown acting as a heat exchange medium for the moving fluid before it was recycled to the pump. To simplify the design, this portion of the loop has been temporarily eliminated, since the measurements made in this study only required the pump to be maintained at near ambient tempera-

tures. Other fluids may require substantially different pump cylinder temperatures (e.g. low boiling refrigerants). In these situations, the loop should be reinstalled to minimize the temperature load on the pump. A four meter, coiled, single pass, shell and tube heat exchanger (Parker DHTC-SS-4-Z), with 0.08 m^2 of surface, was used to cool the hot fluid exiting the calorimeter down to ambient temperature by counter-current heat exchange with house water.

The valves on the flow circuit allowed specific segments of the loop to be isolated, which was necessary in the calorimeter cleaning and filling procedures, and was occasionally needed during calorimeter operation. The valves also allowed the apparatus to be operated as an open loop system for flow rate calibrations and for limited, low pressure heat capacity measurements. The standard mode of operation though, required a closed circuit because of pressure regulation difficulties discussed later. As such, the on-off valves in the loop should always be positioned properly before the pump is activated.

Pumping System:

The pump used in the calorimeter flow circuit was a Ruska model 2248 dual piston (500cc/cylinder) metering pump with a manually adjusted, gear box transmission (type Quick Change, range WIII) providing 28 different flow rates ranging from 0.0833 to 18.667 ml/min. All wetted metal surfaces were machined out of 451 stainless steel to reduce corrosion and provide high strength. The pump has been successfully operated at pressures as high as 40 MPa. Mechanical power was supplied through the transmission and pump mechanism by a $3/4$ Hp (220V) synchronous motor. Each pump cylinder could also be manually driven by disengaging the transmission and turning the large handles on the spindle ends of the pistons. The motor speed was fixed by the power line frequency (60 Hz: 1800 rpm) and was thus independent of pump loading (pressure); theoretically

resulting in constant flow rates. The power line frequencies in the laboratory were found to be constant to 0.01% at any given time during a 24 hour period. This, in conjunction with the precision pump mechanism, resulted in volumetric flow rates accurate to 0.05% of the pump setting at pressures less than 10 MPa, satisfying most of the necessary design requirements for the flow system. A calibration study of the pump demonstrated however, a slight drop in flow rate at pressures greater than 10 MPa. This shift was probably the result of systematic errors in the mass flow calibration, which are discussed in Sandarusi (1990).

The reversible transmission box allowed operation of the pump in tandem and opposable modes. Tandem mode, where both pistons moved in the same direction, was used to fill the system with new fluid and was generally useful during manual pump operation. Opposable mode was always used when the calorimeter was operating. In this mode, one cylinder was refilling while the other was delivering fluid to the calorimeter, allowing continuous operation of the calorimeter pump. Automatic pump reversal occurred at the end of each pump stroke when the forward moving piston actuated its travel limit switch, providing completely unattended pump operation.

HPLC Valve:

Using a pump with two opposable pistons operating in a continuous and automatic manner, necessitated a fail-safe method of ensuring that the fluid flowed through the calorimeter system in the proper direction. Otherwise, reverse fluid flow could occur, rendering the subsequent measurements meaningless and possibly damaging the system. This was initially accomplished with a four check-valve (two valves/cylinder) manifold, but pump switch-over effects and concerns about cross-cylinder leakage led to their removal.

An electrically actuated, four port HPLC sampling valve (Valco EL40W) successfully replaced the check valves. An outline of the valve's operation is shown in Figure 2. This approach eliminated any chance of the fluid bypassing the calorimeter system and it guaranteed proper directional control of the fluid flow as long as the valve was positioned properly. The valve was rated to 35 MPa. To ensure proper positioning, an unused pole on the pump's main power relay, which set the direction of rotation of the pump motor, was tied to the external control logic of the valve, forcing the valve to toggle when the pump's motor and pistons switched direction. The valve position was fixed by the pump relay and was immune to any accidental switching. An override switch allowed the operator to disable automatic operation and manually position the valve with the main control switch. The override switch had to be set on automatic mode ("pump") when the calorimeter was operating or else proper directional control would be lost. A schematic of the required wiring is also shown in Figure 2. Filters (Valco ZUF2) were mounted on the two lines coming from the pump to protect the valve rotor from being damaged by particulates in the pump cylinders.

Pump Temperature Control:

Calorimetric determinations require that the mass flow rate through the calorimeter be known. The pump's calibrated volumetric flow rates were converted to a mass basis by multiplying by the fluid density in the pump cylinders. This in turn required that the temperature and pressure of the fluid in the cylinders be known and stable. The cylinder and fluid temperatures were maintained with cooling water that flowed through the pump cylinder jackets from an external temperature controlled bath (Precision Scientific "Tegal" model). Negligible temperature gradients were assumed to exist between the cylinder walls and fluid when the pistons were moving. This was confirmed

during the pump calibration process. The bath was stable to ± 0.05 K at temperatures ranging from 258 K to 373 K, potentially allowing a broad range of fluids to be studied, including low boiling or high viscosity systems. Water was generally used as the working fluid in the bath. Bath temperatures less than 274 K will require another fluid with a lower freezing point. The maximum temperature drift (0.05 K) in the bath corresponded to a shift in density of 0.01% for a typical liquid in the pump cylinder.

In addition, the pump mechanism and cylinders were enclosed in a plexiglass air bath controlled to ± 0.2 K with a Yellow Springs 63RC on/off controller. The air bath was used to insulate the pump cylinders from changes in room temperature. Unfortunately, the air bath was limited to an operating range of 295-310 K because there was no external heat sink except for the surrounding room. This in turn required that the ambient temperature be maintained at 5-10 K below the bath set point. This obviously presented a severe limitation on the operation of the bath. As such, the heat capacity measurements reported in this thesis were made with both the air and water baths set at a temperature of 303 K (30°C). Both the air and water baths are shown in Figure 1.

Pressure Measurement:

In addition to temperature, the other variable needed to define the fluid densities in the pump cylinders was pressure. Each pump cylinder had an Omega, model PX300-5KGV, 0-345 MPa (5000 psi) strain gauge type, pressure transducer to monitor the internal cylinder pressure as shown in Figure 3. These transducers had a typical accuracy of ± 0.1 MPa. Transducer excitation was supplied by a HP 6214A DC power supply set at 10 volts.

Figure 3 also illustrates the pressure manifold where the calorimeter

inlet pressure and the pressure drop were measured. System pressure was determined with three Heise model 623, diaphragm type, pressure transducers. The three transducers separately covered the pressure ranges: 0-1.6 MPa, 0-6 MPa, and 0-4000 Psi (27.5 MPa) with a stated accuracy of 0.1% of full scale. The calibrations were checked and adjusted with a dead weight tester (DH model H5). The three manual valves on the manifold were used by the calorimeter operator to selectively isolate the transducers from pressures exceeding the transducer ratings.

The pressure drop across the calorimeter was monitored with a Validyne P378D variable reluctance, differential pressure transducer with rated accuracy of 0.5% (of full scale). The present transducer diaphragm has a measurement range of ± 0.138 MPa (20 psi); other ranges are possible with different diaphragms. The transducer was calibrated against the 1.6 MPa Heise transducer. A three way valve allowed the transducer to be manually zeroed during calorimeter operation, correcting the reading for transducer offsets due to high line pressures. The valve was also used to protect the transducer diaphragm from the very high calorimeter pressure drops that occasionally occurred when the system was accidentally vented at high pressure. In Figure 3 the normal valve position is depicted for differential pressure measurements. The sensor was zeroed with the valve in the opposite position. All four transducers were powered by a Lambda LDS-X-03 DC power supply set at 24 volts. The output signals were 0-30 mv, 0-10, and 0-5 volts DC for the Omega, Heise and Validyne transducers respectively. The transducer outputs were determined with the data acquisition system.

Pressure Regulation:

While not as critical as temperature regulation, good pressure control is necessary to make measurements in the two phase region and to minimize flow

rate fluctuations. Precise regulation in the vapor and liquid phases is not as important because pressure has only a modest effect on heat capacity, particularly in the liquid phase. Good pressure regulation in these regions was necessary more from an operational point of view, since fluctuating pressures can affect the control stability of the other system variables, especially in the vapor phase, where a liquid to vapor transition is required in the flow circuit.

For a variety of reasons, developing an automated pressure regulator proved to be difficult for this system. The two implemented designs were extensions of methods that had been used successfully in this laboratory in non-automated applications. The first of these, a set of stepper motor driven micrometering valves, was discarded shortly after construction because of concerns about plugging. In addition, it was found that pressure control with these valves was at best erratic since very slight flow rate fluctuations typically generated large pressure changes. This stemmed primarily from the large fluid capacitance of the flow loop and pump.

The second design, utilizing a back pressure regulator (Grove S-91XW), was moderately successful, having none of the valves' limitations. The control pressure of the regulator was loaded by a computer actuated, motorized pressure generator (HIP 87-6-5). The gearhead motor was a modification of the pressure generator that was added in this laboratory. An outline of the system is shown in Figure 4. The drive motor was operated in an on/off manner with a set of digital timers on the computer interface card. In contrast to valve-based regulators, back pressure regulators are inherently stable with regards to fluid pressure control and the probability of plugging is relatively small. Pressure regulation on the order of 0.1% was readily attained in this design when the automation system was to drive the motor.

The problem with using a back pressure regulator or a metering valve for pressure control is that an open flow loop is inherently required. Although advantageous because it allows venting of decomposition products, open loop pressure control is not readily applicable to this system because of the pump's large cylinder volumes and the periodic piston reversals.

Immediately before the pump pistons switched the original open loop system, the off-line cylinder would have refilled to its maximum volume (>500 cc) and the pressure in this cylinder would have been at near ambient (<0.1 MPa) conditions. Simultaneously, the cylinder delivering fluid to the calorimeter would have been nearly empty, with a cylinder pressure equal to that of the calorimeter, which may have been very high. At switch-over, which occurred at intervals of 30 to 120 minutes depending on the flow rate, the low pressure cylinder would have to be re-pressurized to the calorimeter operating pressure before fluid flow would restart. This pressurization time could be long because the total system volume was so big (about 1 liter) and the fluid compressibilities were non-zero. The time required for fluid flow to begin again depended on the flow rate and the phase state in the system, but at pressures higher than 1 MPa, it was long enough that an unrecoverable temperature upset would occur with every pump stroke reversal. This situation was clearly impractical since proper calorimeter operation required very tight temperature control, which in turn depended on constancy of flow. Although it would be possible to use a secondary pump to quickly pre-pressurize the off-line cylinder when necessary, the effort would potentially be excessively expensive and complex. As such, use of an open loop pressure control system was abandoned.

The remaining alternative was a non-vented closed loop system. This has traditionally entailed placement of one or more variable volume buffers into

the flow loop. To affect the system pressure, the buffers would have a pressure regulated, control fluid placed on one side of a movable partition and the system fluid on the other (Sirota and Mal'tsev 1959; Miyazaki 1973). Pressure equivalency between the control and system fluids would be limited only by the frictional losses in the partitioning mechanism. The application of this technique to the calorimeter system is shown in Figures 1 and 5. A 500 cc variable volume buffer (Y-Z Industries, Kwik Site) was placed downstream from the calorimeter. Nitrogen gas from an external cylinder was loaded manually through a valve manifold. A small disk shaped piston in the buffer separated the nitrogen from the test fluid. Because the piston was free to move, the calorimeter fluid pressure nearly matched the internal nitrogen pressure. The total pressure sensitivity of this system was limited by the resistance (friction) of the piston to movement. While it would be possible to automate the loading process and hence the pressure regulation, the current design has remained manual in operation because the preliminary measurements did not generally require dynamic pressure control. A high pressure, automatic, gas loading system also presented substantial safety hazards and additional operational complexity. Because a nitrogen cylinder was used as the pressure source, the calorimeter operating pressures were restricted to <14 MPa. Higher pressures than these were not necessary in the development phase of the calorimeter. Extending this system to higher pressure would require a compressor or pressure intensifier.

Overall performance of this system was adequate, with the system pressure typically fluctuating less than 1% over a complete pump stroke cycle. This level of control was more than satisfactory to make heat capacity measurements for liquid water. Nonetheless, there remained some operational peculiarities which will necessitate modification of the pressure regulation system

if the calorimeter is to be extended to low pressure vapor phase measurements. The presence of low pressure vapor in the system resulted in system-wide perturbations that were too large to allow steady state to be reestablished. One possible modification would be to place a second volume buffer in the flow loop upstream from the calorimeter (Miyazaki 1973). This second buffer would serve to diminish the size of the upset.

Preheaters:

The calorimeter fluid was brought to the desired operating temperature with a two stage preheat train consisting of a 500 watt main heater and 50 watt fine preheater. The layout of the preheat system is depicted in Figure 6. The main preheater was composed of a four meter long coil of tubing enclosed in an aluminum sand bath with a centrally placed 500 watt cartridge heater (Tempco HD05-0608N). Temperature sensing was provided with a stainless steel sheathed, 100 ohm, platinum resistance thermometer (Omega PR-11-4-100-.25-12.5-E) placed immediately adjacent to the coil in the sand. The fine preheater assembly consisted of an annular shell (13 mm) and tube (6 mm) design with a 50 watt cartridge heater (Watlow E3A50) immersed directly in the flowing fluid. Temperature measurement for the fine preheater was supplied with a 100 ohm, ceramic, mini-PRT (Minco S201PD), that was affixed (with ceramic cement) in a brass probe and positioned in the fluid stream immediately after the cartridge heater. AC power for both preheaters was supplied from the four channel, phase angle firing, triac power pack built for this study. The computer automation system provided the feedback control and also directly operated the triac power pack.

The main preheater supplied the majority of the fluid stream's heat. It was used to bring the cold test fluid to within 5-30 K of the calorimeter's inlet shield temperature. The main heater's set point temperature was adjusted

until the heat load on the downstream fine preheater was less than 75% of full power (50 watts). Achieving this at extreme heat loads required, because of the short heating coil, that the main heater's set point be as much as 100 K hotter than the inlet shield operating temperature. The fine preheater provided the remaining heat necessary to raise the fluid temperature to that of the inlet shield. Because the fluid could cool significantly as it passed through the top of the calorimeter vacuum chamber, a second mini-PRT, of identical design to the fine preheater control thermometer, was used to measure the fluid temperature immediately before the fluid entered the inlet calorimeter shield. This temperature drop was an inverse function of flow rate and directly related to the operating temperature. The temperature difference was negligible near ambient and was as large as 40 K at very high temperatures. To compensate for this drop, the fine preheater set point was adjusted to produce a fluid temperature at the inlet fluid thermometer which differed by less than 0.5 K from the inlet shield temperature.

Calorimeter Cell:

The most significant part of the entire apparatus is the calorimeter cell where heat capacity and enthalpy of vaporization measurements are made. The cell is shown in cross-section in Figure 7. The design followed the heat leak minimization scheme discussed earlier. This approach represents a very unique departure from the more traditional calorimeter designs. Foremost of which was the lack of an external constant temperature bath surrounding the calorimeter cell. This highly unorthodox approach was selected for several reasons. Firstly, there was a desire to eliminate many of the complex bath schemes that were used in the past (Grigor'ev et al. 1985; Dreher 1979; Lenoir et al. 1970). These systems generally required a variety of different bath

fluids for different temperature regimes. These fluids were often corrosive and/or generated noxious and possibly toxic fumes. Air baths, although having few of the above problems, are problematic in this application, because the temperature gradients in even the best ovens tend to be rather large ($>1K$). Eliminating the constant temperature bath also removed the design difficulties associated with developing a sealing mechanism for a high temperature vacuum chamber, since the vacuum system in this design would essentially be at ambient. In addition, baths, particularly liquid baths, often unnecessarily limit the maximum operating temperature of a flow calorimeter (e.g. Saitoh 1988). As a result, removing a high temperature bath from the calorimeter flow loop would in many respects greatly simplify the design and operation of any flow calorimeter, since a much smaller portion of the system would have to be maintained at high temperature. Any such simplification would inherently be of great benefit in an automated system.

An alternative to utilizing a constant temperature bath to regulate the environmental temperature around the thermodynamic system, would be to surround the actual calorimeter measurement cell with a set of metal shields actively maintained at the desired operating temperature within the enclosing vacuum chamber. This method had been successfully applied in several other calorimetric applications (Rogers and Sandarusi 1989; Kobayashi and Tashiro 1979) and was used as the basis for this design. The major problem with this approach, in contrast to fluid bath systems, was the possibility of large temperature gradients within the shield walls. The shields therefore had to be designed to keep these gradients small ($<0.5K$) if they were to function as an effective means of screening the calorimeter measurement cell from the surrounding environment.

As shown in Figure 7, the two shields used to accomplish this were com-

posed of machined, thick walled (9.7 mm), silvered, copper cylinders actively and precisely maintained at the inlet and outlet fluid temperatures by the automation system. Overall length of the assembled calorimeter was 38 cm with a total mass of 20 kg. The shields were individually heated with 4 meters of insulated heating wire tightly swagged into a helical groove cut along the exterior cylinder wall of each shield. The heating wire (1.6 mm OD) in each shield consisted of two nichrome wires insulated with MgO and sheathed in inconel (ARI 2HN-063B-13.0). The two nichrome wires were shorted at one end and were connected to a 100 volt DC power supply at the other end, resulting in a maximum heat duty of 60 watts for each of the 150 ohm heaters. Two removable copper caps (9.7 mm thick) were mounted on the ends of both shields, completing the separate inlet and outlet chambers/shells. These chambers contained and isolated the calorimeter cell components from the environment. The inlet shell and outlet shell were separated from each other with three small cross-section stainless steel posts used to suppress heat flow between the two chambers.

In addition, each shell had a tandem groove, cut next to the heater groove, in which stainless steel tubing (3.2 mm OD, 2.1 mm ID) was swagged. The calorimeter fluid flowed through this swaged tubing. Forcing the fluid under study to flow around the inlet and outlet shields served several purposes. Firstly, the moving fluid convectively minimized thermal gradients along the axis of the shell walls. Lastly, it allowed the inlet shield to act as a final temperature controller, buffering the fluid from minor shifts in the upstream preheater temperatures. This resulted in greater temperature stability at the inlet calorimeter thermometer. The four meter length of tubing wrapped around the inlet shield was sufficient to ensure a 0.05 K approach temperature. The temperature difference between the inlet shield and

inlet fluid, as measured by the inlet calorimeter thermometer, was generally small (<0.05 K) at most flow rates (>6 ml/min). This gradient was difficult to eliminate because it was inherent to the cell design. Fortunately, several tests have indicated that it has little or no affect on calorimeter performance.

Originally, the calorimeter shells were fabricated out of aluminum using a similar design scheme. Although somewhat successful, these shells were, for several reasons, eventually replaced with the present copper shields. The thermal conductivity of copper is significantly higher than that of aluminum, resulting in smaller shell temperature gradients. In addition, the larger thermal diffusivity of copper greatly improves the overall control response. Most importantly, the coefficient of expansion for copper nearly matches that of stainless steel. In contrast, aluminum has a much larger expansion coefficient. As a result of this mismatch, a tendency existed for the heater wire and fluid tubing to separate from their respective retaining grooves. The cause of this was the expansion and contraction of the aluminum shields induced by temperature cycling. Separation of the heating wire and the fluid tubing from the original aluminum calorimeter body resulted in eventual control failure. This difficulty was completely eliminated with the new copper shell. As a result, the heater wire and tubing remained in very good thermal contact with the copper calorimeter shields, yielding greatly improved responsivity and stability in the temperature control. This was especially true at the higher pump flow rate settings (>12 ml/min) where the previous aluminum calorimeter was not capable of operating with adequate temperature control.

A 100 ohm ceramic mini-PRT (Minco S201PD) was located at a point midway (longitudinally) along each shield's inner wall. The calibrated thermometers were used by the automation system to control the shield temperatures to an

estimated accuracy of ± 0.025 K. The massiveness of the calorimeter shields, coupled with the efficient insulation system, resulted in excellent control of the shield temperatures (± 1 mK). Blankets of glass cloth embossed with aluminum foil ("super-insulation") were wrapped around the calorimeter shields to further insulate the system from ambient and to reduce the shell heater loads. Less than 12 watts were required to maintain the entire calorimeter (2000 cm²) at 473 K, while less than 40 watts were needed at 700 K. The resulting low heat loss fluxes, in conjunction with the heavy copper walls, kept the shell temperature gradients small. Measurements at 473 K with several three junction, type J thermopiles measured temperature gradients of <0.1 K in the inlet shell and <0.05 K in the outlet shell. The gradient was larger in the inlet shell because of heat conduction to the vacuum chamber through the mounting posts on top of the inlet shell. As expected, these gradients increased as the fluid flow rates decreased. Less than 1 watt of heat transfer occurred between the two chambers when operating with a typical calorimeter temperature difference of 10 K. This small amount of leakage appeared to have little effect on the shield gradients. One modification to this design which should be considered in the future would be to place additional lengths of heating wire across the two exposed ends (inlet top and outlet bottom) of the assembled calorimeter. This would distribute the heat load more evenly along the shell surfaces and would result in even smaller temperature gradients.

Figure 7 also illustrates the details of the internal portions of the calorimeter. These internals form the actual calorimeter cell. Within the inlet chamber were two sets of passive shields formed from silvered copper cylinders and endcaps. The two shields enclosed the inlet thermowell, facilitating the accurate measurement of the inlet fluid temperature and isolating the inlet thermometer from the relatively large gradients in the inlet cham-

ber. The outlet chamber contained the calorimeter working heater and the outlet thermowell. The two layer, passive shielding system in the outlet chamber was similar in construction to the shields in the inlet chamber. The shields were designed to minimize heat losses from the calorimeter working heater and to eliminate the effect of temperature fluctuation in the outlet shield on the outlet temperature measurement. In both the inlet and outlet chambers, the passive shields were wrapped with fluid tubing to enhance the isolation of the enclosed components. The dimensions of these coils (4.8 mm OD tubing) were approximately 4 and 8 cm in diameter and with lengths of 8 and 14 cm respectively for the inlet and outlet sections. All of the exposed copper surfaces in the calorimeter, including the external calorimeter shells and the internal passive shields, were silvered to create low emissivity surfaces with good oxidation resistance.

Because the fluid could be incidentally heated as it crossed from the inlet chamber to the warmer outlet chamber, thus affecting the measurement accuracy, a method of shielding the fluid had to be developed. Figure 8 illustrates this design. It consisted of a brass tube inserted (snugly) into the extender fixture of the inlet shield. The primary effect of this was to lengthen the inlet shield surface, isolating the traversing fluid from the outlet shield. A piece of high temperature felt centered the fluid tubing in the brass tube, minimizing heat conduction to the fluid. A length of fiberglass tubing/insulation was wound around the fluid tube to further isolate it from inadvertent contact with other metal surfaces. This fixture also prevented the fluid from "seeing" ambient temperature (the vacuum chamber) in the space between the two shells. Finally, the connecting tube was constructed from 1.6 mm tubing to decrease the total surface area for heat transfer.

The limits of the thermodynamic system extended from the inlet thermo-

well to the outlet thermowell and excluded the calorimeter shells and most of the internal shielding. Because of space and other practical limitations, the pressure taps were located outside these limits. As a result, the measured pressure drops (<1 kpa: liquids, <20 kpa: vapor) were slightly larger than the actual values. However, since the effect of pressure on enthalpy is small, this difference should have little effect on the corrected isobaric heat capacities.

The implemented cell design, utilizing concentric layers of helical tubing coils on thin metal shields, was selected for its simplicity and because it facilitated easy modification and replacement of individual components. This was necessary because of the potential for component failure due to heater burn-out or due to plugging of the tubing by coke at high temperatures. Connections between components were made using fittings where possible and brazed joints everywhere else. This facilitated the easy assembly and disassembly of the calorimeter cell during the design and testing phases.

Calorimeter Working Heater:

A simple design philosophy was extended to the calorimeter working heater, where it was feared that frequent heater burnout would occur. This contrasts with the complex and expensive cell designs used by many previous workers (e.g. Yesavage 1968; Miyazaki 1973; Bier et al. 1974). Figure 9 shows the structure of the calorimeter heater and its capsule. The heater itself was composed of biaxial heater wire (ARI 2HN-063B-13.0) identical to that used in the calorimeter shields. The 90 cm length of heater wire was turned into two concentric helical coils that were placed in direct contact with the flowing fluid. This eliminated hot spots and thus minimized the potential for heat leaks (Rogers and Sandarusi 1989). The two nichrome wires in the inconel sheath were shorted together at both ends of the heater to form a parallel

circuit with a resistance of about 10 ohms. The low heater resistance was necessary to attain the required heat loads. The heater coil was enclosed in a small stainless steel capsule with welded endcaps. A simpler design utilizing brazed endcaps was used initially but eventually discarded because of leakage difficulties. The flow path in the capsule was designed to provide even heating of the fluid across the inlet and outlet traverses, minimizing temperature gradients along the capsule wall. The inlet and outlet fluid tubing were brazed into one endcap. The heater leads were fed through the opposite endcap. To further minimize heater losses, the electrical connections between the nichrome heating wire and the copper lead wires was made inside the capsule using two stainless steel tubes as feedthroughs.

Figure 10 presents a schematic of the circuit used to provide electrical power to the heater. It also shows the connections used by the automation system to control and measure the total power input to the calorimeter. A large 0-80 volt DC power supply (Kepco BOP-72M-5) was the source of the heaters current. The electric current input to the heater was determined by measuring the voltage drop across a calibrated, standard, current shunt (Otto Wolf model 13833/59; 0.1 nominal) placed in series with the calorimeter heater. The two heater voltage taps were connected outside the capsule, but as close as possible to the heater wire/copper lead junctions. The taps were used to determine the voltage drop across the heater. These two voltage measurements were made by the data acquisition system and allowed the power input to the heater to be accurately calculated (0.01%). The defining equation for the heater power is:

$$P_{htr} = I_{std} V_{htr} = V_{std} V_{htr} / R_{std} \quad (3)$$

where P, I, V and R respectively refer to power, current, voltage and resist-

ance and the subscripts "htr" and "std" refer to the heater and the standard resistor. The effect of locating the heater voltage taps outside the heater capsule was shown by calculation to be negligibly small. In addition, several measurements of stray thermal EMF's (< 1 mV) present on the power bus during calorimeter operation indicate that they had little affect ($< 0.01\%$) on the determinations and could be generally ignored (in contrast see: Grigor'ev et al. 1985). The heater voltage taps were also tied to the high impedance "sense" inputs of the Kepco power supply to provide better regulation of the heater power. Typical values for heater power stability after supply warm-up were 0.01-0.03%, depending on the output power levels.

Output voltages from the power supply were set by the computer through a 0-10 volt, 12 bit digital to analog converter whose output regulation was sufficient to have had no detectable effect on the power supply; even at low power outputs of 1-2 watts. The supply could also be set manually by disabling the DAC and using the built-in voltage reference. The supply gain was adjustable and was set approximately to a value of four, providing a maximum power supply output of 40 volts and 150 watts for a DAC input of 10 volts. A heater duty of 150 watts was sufficient to completely vaporize nearly all organic fluids at the highest pump flow rates. Because the present heater had such a low resistance (10 ohms), large currents ($I_{std}=1-2$ amps) had to be supplied to the heater in order to achieve the power output of 2-14 watts necessary for most heat capacity measurements. This created the potential of heating in the lead wires which could possibly affect the measurements. Large diameter (20 gauge) copper leads were used to minimize this.

Complete machine drawings of the calorimeter shells and working heater are located in Sandarusi (1990).

Calorimeter Thermometers:

The measurement of the temperature difference across the calorimeter is critical to the success of the apparatus. After a number of failures with a series of small commercial PRT's (e.g. Minco S215PA, Yellow Springs 138P), it was decided to build a set of precision, platinum, resistance thermometers which would ideally exhibit the long term calibration stabilities of the much larger standard platinum resistance thermometers (SPRT). They also should not have the self-heating problems in vacuum that characterized the commercial thermometers. These thermometers were built using a modification of an SPRT design found in the literature (Barber 1950). This design was selected because of its compactness and because it was easier to fabricate than the more traditional bifilar designs (Meyers 1932). The thermometer capsule is illustrated in Figure 11. An outline of the thermometer's construction follows; a more detailed description is available in the original reference. The sensor element consisted of 53 cm of 0.050 mm OD (0.002" dia), 99.999% pure platinum wire (California Fine Wire Co.) wound into a helical coil using a #62 (0.965 mm dia) drill bit as a winding mandrel. The resulting platinum wire coil was cleaned with nitric acid, an organic solvent (THF), and deionized water. It was then stretched to a length of 6 cm and inserted into a 7.0 cm length of 1.2 mm (ID), thin walled, Pyrex capillary tubing. A set of 0.15 mm (OD) platinum leads, bent into a U shape, were attached to each end of the sensor element by welding with an oxy-acetylene torch. A fine torch flame was used to fuse the lead/sensor wire junctions into the capillary tube ends. A final application of the torch was used to bend the element into a U shape. The 3.2 cm long element was then encapsulated into a larger 7 mm (OD) Pyrex sheath. The lead wires were sealed in Pyrex at one end of the sheath and a gas fill port was installed at the other. The coefficient of expansion of platinum

matches that of Pyrex, resulting in a hermetic seal at all temperatures (<900K). The capsule was filled through the fill/purge port with 99.999% pure nitrogen gas and then sealed after heating to 573K in an oxygen containing atmosphere to remove any combustibles (Berry 1982). The thermometer element was then annealed at 873K in a muffle furnace.

The resulting thermometers had a resistance of 26.5-27.0 ohms at the ice point with good overall calibration characteristics and excellent stability. The calibration process is discussed in Appendix A. The necessity of using a third order polynomial calibration curve rather than the true IPTS-68 function probably resulted from the sealing mechanism and other element imperfections (Actis and Crovini 1982). Thermal response times were comparable to other SPRT's (about 30 seconds) and self heating was undetectable. As a measure of the calibration stability, the ice points of the currently installed calorimeter thermometers were checked in an ice bath to determine the drift in R_0 after several major thermal cycles. These results are summarized in Figure 12 which shows the ice point shift of both thermometers. The seven discrete data points were randomly measured over a period of several months. The results indicate a random drift of less than 0.0002 ohms. This value corresponded to a calibration shift at the ice point of less than 2 mK. In addition, these shifts were probably attributable to difficulties associated with the ice point determination and may not indicate true calibration changes. The major limitations of this thermometer design were its relatively large size (4.5 cm long) and extreme fragility. In particular, the lead and sensor wire junctions tend to break easily with rough handling.

Vacuum System:

The calorimeter cell was enclosed in the vacuum chamber depicted in Figure 13. The removable portion of the chamber was fabricated from a 20.3 cm

OD (8"-11 gauge wall) by 44.5 cm long stainless steel tube with a bottom plate and a 25.4 cm (10") Conflat (Varian 954-5084) open-face flange welded on opposite ends of the tube. A 25.4 cm Conflat blank flange (Varian 954-5384), mounted onto the calorimeter frame, formed the chamber's top plate. The two flanges were mated together and sealed with a reusable viton O-ring (Varian 953-5085). A KF25 (HPS) stub connected the chamber to the two-stage, direct drive vacuum pump (Fisher Maxima D8) with an ultimate vacuum rating of 0.01 Pa (0.1 micron). The vacuum was monitored with a Granville Phillips Convectron (model 275) vacuum gauge. The present pumping system will readily attain a vacuum of <0.1 Pa assuming the calorimeter fittings don't leak. This corresponds to a Knudsen number of about 10, which should be sufficient to eliminate heat conduction and convection in the calorimeter cell (Rohsenow and Choi; 1961 Scott 1959).

The fluid tubing and wiring were brought into the vacuum chamber with three gland-type vacuum feedthroughs mounted on the vacuum chamber lid. The inlet and outlet fluid tubing and the two pressure taps passed through a Conax PL-18-A-8 sealed with a "Lava Seal" gland that will withstand high temperatures. Eight Kapton insulated power leads were made available to the calorimeter with the Conax MHM-125-A-4 fitting. These leads carried the power for the two calorimeter shields and the calorimeter working heater. The third Conax gland MHM-125-A-8 supplied the vacuum chamber with eight sensor cable assemblies, which were used to feed the various signals from the calorimeter cell to the data acquisition system. The cable assemblies, which are detailed in the figure, consisted of 3.2 mm OD by 15 cm stainless steel tubes, containing four, 22 gauge, insulated (magnet) copper wires per tube. The tube ends had vacuum epoxy applied as a sealant. The last two Conax fittings used teflon sealing glands.

The placement of the calorimeter cell in the chamber is also indicated in Figure 13. The calorimeter hung from three mounting posts (7.6 cm long) attached to the top plate. All calorimeter tubing and wiring connections were made in the space created by the posts above the inlet calorimeter chamber. The three posts were designed to present the smallest cross-sectional area for conductive heat transfer between the hot calorimeter cell and the chamber's top plate. Minor heat losses through the posts, in tandem with the hot fluid, produced only a modest rise in the temperature (<25 K) of the top plate and the Conax tubing fittings. The rest of the chamber remained cool at even the highest working calorimeter temperatures (700 K); a testament to the design of the calorimeter's insulation.

SYSTEM AUTOMATION AND CONTROL

Automation Software:

In developing the calorimeter's automation system, the primary consideration was that the controlled process variables be sampled by the data acquisition system at a sufficiently fast rate (twice the Nyquist frequency) to ensure good process regulation (Stephanopolous 1984). Sampling the process variables at too low a rate, would result in large instabilities, and potentially in the loss of system regulation. In addition to the control function, the automation system also had to make heat capacity measurements and provide the user with command and display facilities. The control hardware and software had to balance the needs of the user to input commands and to receive status reports from the system, with the needs of the control process for continuous and uninterrupted data sampling. That is, the control system could not be stopped for an extended period of time, while it was waiting for input (e.g. a new set point) from the user, if adequate regulation was to be main-

tained.

With this in mind, the design of the calorimeter's automation software was therefore intimately related to the form of the automation hardware. This resulted from the fact that automation systems which require process control capabilities, in addition to simple data logging, must, for the reasons discussed above, be inherently multi-tasking in nature. This concurrency of operating functions, as expressed in the necessary segregation of the user interface from the control and data logging tasks, can be achieved in various manners. These techniques are generally implemented in either the automation hardware or the control software. A comprehensive discussion of multi-tasking techniques is available elsewhere (Savitsky 1985).

The technique which was selected was a combination of the multiple processor and hardware interrupt techniques; offering a balance between the hardware complexity of the former with the software sophistication of the latter. A structural outline of this scheme is shown in Figure 14. A commercial multi-tasking scheduler called "Double Dos" (Softlogic Solutions) was used to effectively partition the microcomputer into two separate programming environments; each operating concurrently and independently in a time-shared manner. Double Dos exploited the computer's "clock ticks" to generate hardware interrupts for timing, and initiation of the process swaps.

The foreground process had control of the screen and served as the user interface, while the control process operated "quietly" in background, monitoring and driving the calorimeter hardware and electronics. Simultaneous calls to the operating system (MSDOS 3.2) or disk drives by both tasks were prioritized by the scheduler. Process priority was apportioned by the scheduler using a 2:1 time-priority assigned to the more important background control job. The primary responsibility of the background process was to monitor the

apparatus through the data acquisition system and to make the appropriate adjustments to the external control hardware that were necessary to maintain the system at the current set points. This process also collected, analyzed, and stored on disk all of the calorimeter data, including the mean isobaric heat capacities. With regards to process control, a simple, modified, proportional-integral-differential (PID), velocity algorithm (Stephanopolous 1984) was used by all four of the digital controllers in this program. The controller gains were arbitrarily set by experimentation and by no means represented an optimal set. They were however adequate, although the preheaters' performances may well be improved with a more rigorous tuning process (e.g. Ziegler-Nichols). Sharing access time to the data acquisition system among the many process variables (sensors) and controllers was accomplished with a simple round-robin prioritization scheme in the control code using sensor priorities that were adjustable at runtime from the foreground process (Savitsky 1985).

The second, lower priority process was resident in foreground and was used as the user/operator interface for a continuously updated display of the measured data points, current set points, and overall system status. The foreground task was also used as the medium to pass system commands to the background control task, to adjust the individual control parameters and set points, to enable or disable subsystems in the loop, and to change the measurement mode of the calorimeter system. This allowed the control task to be changed "on the fly" with no discernible slowing of the system controllers. Fluid flow rates and other measurement parameters were transferred from foreground to background to enable data processing in the control job. Conversely, data measured by the control program were passed to the foreground process for display and additional processing. The foreground process did not directly control any of the external hardware; that was left exclusively to the back-

ground process. The only exception to this was the valve used in the flow rate calibrations, which was toggled with a switching relay (#10) from the foreground process.

For this scheme to succeed, a method had to be developed to pass data and commands between the two processes, which occupied separate segments in the computer's memory. The technique which was ultimately implemented, required defining a duplicate set of variables in the control (Auto.pas) and user interface (Param.pas) processes. The variables used in common by both processes were defined as a shared set of data registers and command flags in each of the two programs. These two variable sets were forced to reside at identical locations in the computer's memory by absolute variable addressing. In this manner, both programs could simultaneously access and change a value in the shared variable set. A variable change initiated by one process was immediately detectable by the other process. These variables were stored in a third memory segment that was allocated with a simple "terminate and stay resident routine" (TSR). This routine was executed before Double Dos and the remaining two automation programs were loaded (Smith 1987). Other, generally more complicated inter-process communication techniques are also possible (Savitsky 1985).

Overall, this two-job strategy proved to be a highly successful mechanism for efficiently utilizing the automation hardware. While somewhat inefficient in its use of computer resources, this strategy proved to be nearly as fast as an equivalent interrupt driven system, while being much simpler to develop and modify. Partitioning the computer system resulted in smooth operation of the equipment with no freeze-up of the control system when operational or set point changes were executed. It ensured that each controlled unit received an adequate and nearly constant amount of computer time that was

independent of the size or scope of the foreground task. The rate of data transfer between the control task in background and the data acquisition hardware approached the maximum reading rates of the two DMM's. As such, any imperfections in the calorimeter's regulation and operation most probably did not result from software inadequacies, but from deficiencies in the design of the calorimeter flow loop and its individual components or from limitations in the automation hardware.

The system software was written exclusively in Pascal, which is a modern structured programming language well suited to the microcomputer environment and to this control strategy (Wold 1985; Cluley 1982). Both processes were implemented in "Turbo Pascal" (version 5.0) which is a fast, single pass compiler featuring a conveniently integrated environment with a native editor and dynamic debugger, absolute variable addressing, and Double Dos compatibility. It also offered complete access to the computer's internal hardware and operating system and its modular structure (units) allowed the ready development of sophisticated control programs not limited by the 64K memory barrier. The background process controlled the IEEE-488 bus and communicated with the data acquisition system through a set of Turbo linkable device driver routines purchased with the interface hardware (IOtech Personal488). The data entry and menuing system were developed using a set of commercial Turbo text and I/O utilities ("Techno Jocks"). A complete listing of all the software written for this study is located in Sandarusi (1990).

Automation Hardware:

With this software strategy in mind, there are a number of ways to implement the corresponding automation hardware. They differ mostly in the scope of the system and required accuracy of the measurements. Nonetheless, most calorimeter automation systems utilize similar hardware design strategies

(e.g. Rogers and Sandarusi 1989; Castro-Gomez 1987) as presented in the following outline. The entire process begins with the data acquisition system reading a signal from a selected sensor through a multiplexer. Because data acquisition resources are limited, a multiplexer is used to share the data acquisition module(s) with all of the system sensors. Several different types of data acquisition systems (e. g. Analog to Digital converters or AC bridges) can be utilized, depending on the required speed and accuracy. Since this calorimeter demanded very high accuracy, instead of high reading rates, moderately priced digital multimeters, capable of measuring resistances and voltages with a precision of 7 digits (approximately 21.5 bits), were used. The data is then fed to the system controller, usually a personal computer, which processes it and then takes the appropriate control response. The responses for this calorimeter primarily involved adjusting the output voltages of heater power supplies, but they could also take the form of triggering relays or motors, data logging, alarms, etc.

With regards to the automation system developed in this study, the electronics and all of the linkages necessary for automated control, data acquisition and system monitoring are shown in block diagram form in Figure 15. The heart of the system was an 8 MHz Kaypro 286i microcomputer which served as the system controller and operator interface. The microcomputer, via the automation software, communicated with and/or controlled various sensors, power supplies, relays, and multimeters in its role as system manager. A custom built computer interface card was installed on the computer's expansion bus, allowing the computer to directly command most of the control electronics (ElAbdalla and Abu-El- Haija 1988; Wikmark 1987). The interface card, which is not shown on the figure, has multiple digital I/O ports (six 8 bit parallel ports) and digital timer circuits (nine 16 bit multipurpose timers). The

interface card did not provide access or control over the IEEE-488 bus devices. A separate communication interface was used instead.

Data acquisition was performed with a Hewlett Packard (HP) 3457A and a Keithley 197 digital multimeter (DMM), which were used to monitor the system sensors and to feed the measured data via an IEEE-488 bus to the control computer. The IEEE-488 (also known as the GPIB or HPIB) bus is a commercial circuit board (IOtech "GPIB-488A") located in one of the computer's expansion slots. This is a powerful communication standard using an eight bit parallel data bus and featuring multilevel handshaking protocols and command lines. These combine to allow high speed data transfers (>100 kbaud) and provide ready access to and control of up to eight different (interfaced) instruments on the bus (LeVasseur 1982; Lesea and Zaks 1978). Most electronic instruments sold today come with an IEEE-488 interface option, which allows easy component replacement or expansion (by daisy-chaining) of the data acquisition system. The computer configured the DMM's for proper operation and it controlled the entire data acquisition process of DMM initiation and data recovery by issuing commands via software over the IEEE-488 bus.

The system sensors were primarily voltage-output pressure transducers and four wire, platinum resistance thermometers (PRT's). To improve software efficiency and data through-put, the HP DMM was devoted solely to reading the resistance/temperature sensors while the Keithley DMM monitored only the voltage sensors. This segregation resulted in faster reading rates because the meters were not required to switch measurement functions, which could greatly slow the DMM's. It also allowed the automation system to devote the faster HP 3457A, which ideally could make very rapid measurements (>50 individual readings/sec), to the time critical task of temperature control, where high sampling rates were essential for good system-wide temperature control. Realistic

reading rates for the HP3457A though, were generally slower because multiple samples, error filtering, and meter stabilization after channel switching, were required to complete a sensor reading. Typical reading rates were two to three sensor measurements per second. Measurement speeds for the slower Keithley 196 were generally half this value. These reading rates have proven to be sufficient for the present calorimeter, where both data acquisition (and logging) and control functions were shared by the same automation hardware.

Signals from the various sensors were routed to the proper multimeter with a computer driven, 32 channel, precision multiplexer using low thermal EMF mechanical (reed) relays. Semiconductor based multiplexers were not used because of concerns over signal integrity (Titus et al. 1979).

The automation electronics also included a twelve channel switching relay circuit. These relays provided the computer with the ability to activate and deactivate entire electrical systems. Its primary function was as a safety feature to ensure that no subsystem was active without direct computer intervention and to allow rapid equipment shutdown if execution of the operating software was terminated.

Two different types of power supplies were used to provide the electrical power inputs to the five heaters in the calorimeter flow circuit. For a given temperature control application, a power supply was selected on the basis of the necessary control sensitivity and the heater duty. The first of these was the phase-angle firing, four channel, triac power pack, used by those heating applications which required large amounts of input power (up to 1900 watts/channel) and which did not need precise temperature control (>0.5 K). For this calorimeter, that meant the two fluid preheaters which used one triac channel apiece, leaving two channels for future use. The output power of each triac channel in the power pack was directly set via the computer's

interface card. The phase- angle firing mode for the individual triacs was selected to improve heater control and sensitivity and to eliminate the bump-bump power inputs that are characteristic of the traditional "burst of fire" modes used in industrial triac systems (Christopher and Holcombe 1988; Patterson et al. 1987). In phase-angle firing mode, a triac converts the power pack's input line voltage (60 Hz, 120 volts) to a 60 Hz output with an RMS (root mean square) voltage that theoretically can be adjusted to any arbitrary value (by the computer) in the range 2-115 volts. The triac varies the effective output voltage by allowing only a controlled fraction of each half-sine-soid of the input voltage to pass through to the load (Smith 1980). The power pack and its operating principle is discussed in greater detail in Sandarusi (1990).

Triac power packs are a very cost effective method of delivering large amounts of electrical power to resistive loads. Unfortunately, the resulting power regulation levels are often not adequate for applications requiring exceptional temperature control (<5 mK). In addition, it is very difficult to accurately determine the amount of AC power input to the load. Finally, the oscillating AC voltages can introduce spurious noise into the measurement of high accuracy sensors. For these reasons, DC power supplies, instead of the AC triac power pack, were used to drive the three precision temperature control applications in the calorimeter cell, including the two calorimeter shields (inlet and outlet) and the main calorimeter heater. The three separate DC power supplies were configured as large operational (inverting) amplifiers with adjustable gains presently set at 10 for the two shield supplies (Kepco Ptr-100-0.6) and 4 for the calorimeter heater supply (Kepco BOP72-5M). As amplifiers, the regulated output voltages could be adjusted by connecting smaller, signal level voltages to the corresponding control inputs of each

power supply. A computer controlled, six channel, 0-10 volt (DC), 12 bit, digital to analog converter (DAC) was used by the automation system to provide these control voltages. Three of the DAC channels were used by the DC power supplies, three remain available.

Many of the electronic components used in the calorimeter's automation system were built in-house to meet performance specifications not readily found in commercial systems, and to minimize cost. These components were also built with multiple and redundant channels to allow for future system expansion or modification if necessary, and to minimize downtime due to single channel failure. They included the 6 channel DAC, the 32 channel multiplexer, the 4 channel triac power pack, and the 12 channel power relay system. In addition, all of these units were directly controlled by the microcomputer via the digital interface card designed and built in this laboratory. The remaining automation components, the DMM's, the GPIB bus, and the micro-computer, were purchased commercially and were not modified in any way. A detailed description of the working logic and schematics for all of these electronic components is available in Sandarusi (1990).

Figures 16 and 17 detail the heater control loops for the main and fine preheaters, and the inlet and outlet calorimeter shields and their integration into the automation system. All four controllers were simple feedback loops consisting of a sensor, controller, and power supply/actuator. The temperature sensors in all four cases were four lead, 100 ohm PRT's read by the HP DMM through the multiplexer. A typical control sequence consisted of the control computer selecting a multiplexer channel, executing a DMM trigger and read cycle (through the IEEE-488 bus), and then adjusting the corresponding heater's power supply. Channel assignments for the multiplexers, triacs, and DAC's are shown in the figures for all four control zones. The open ended control

loop for the main calorimeter heater is also shown in Figure 17.

Application of this control system to the calorimeter shields resulted in very good temperature regulation with stabilities of ± 0.001 K readily attained at all operating temperatures (up to 700 K). Achieving shield temperatures with these regulation levels required that the temperature of the fluid flowing into the calorimeter (inlet shield) be reasonably stable (± 1 K) with no sudden temperature shifts. This in turn meant that the preheater temperatures must also be stable. This presented no particular difficulty and typical regulation levels of ± 0.5 K were attained at even the highest temperatures. These small preheater drifts were readily accommodated by the inlet calorimeter shield. Unfortunately, measurements requiring fluid vaporization at low pressure in any one of the preheaters resulted in a significant loss of temperature regulation in the preheaters, and consequently in the inlet calorimeter shield.

EXPERIMENTAL

The details of the experimental procedure are presented in Sandarusi (1990). This includes both the operation of the computer, as well as the system itself. The purities and preparation procedures for the two fluids used in the calorimeter's evaluation process are discussed below.

A Millipore "Milli-Q" purification system, which deionized and filtered particulates and organics from ordinary house water, was used to produce the water used in the calorimeter. This system provided water which was equivalent to triply distilled, deionized water. Electrolyte removal was such that the resulting water had an electrical conductance of 15-18 Mohm/cm. The estimated water purities were in excess of 99.99 mole percent. Dissolved atmospheric gases were removed by bubbling helium through the water for several hours

before the water was loaded into the flow circuit and pump.

Prior to loading, the air in the calorimeter system was evacuated with a vacuum pump. Small amounts of the sample water were then flashed into the system to dilute and flush out the remaining air. The procedure was repeated several times to ensure that no air was left in the system. The sample was loaded into the system by the manual withdrawal of the pistons from the pump cylinders. The loading procedure was designed to guarantee that no air remained in the calorimeter's closed flow loop. The presence of air in the water negatively affected the operation of the calorimeter and the resulting data quality.

The normal pentane used in this calorimeter was supplied by Baker Chemicals ("Resi-Analyzed") and was determined by gas chromatography to have a purity of about 99.9 mole percent. The remaining contaminants were found (by GC-MS) to be primarily the two isomers of n-pentane: 2,2-dimethylpropane and 2-methylbutane. The n-pentane sample was degassed by boiling for a short period of time (<1 min) under vacuum. An airless loading procedure, identical to that for water, was used to fill the calorimeter with n-pentane.

EQUIPMENT EVALUATION AND EXPERIMENTAL RESULTS AND DISCUSSION

The overall performance of the calorimeter hardware and system is presented in this section. In addition, the results of the mean heat capacity determinations for liquid water and n-pentane are tabulated and discussed. The discussion includes an analysis of the systematic measurement errors and uncertainties.

System Performance:

As a prelude to operating the calorimeter, calibration studies were performed on the pressure transducers, the pumping system, and on the main calorimeter thermometers. The results are discussed in detail in Sandarusi (1990) and only a summary of these calibrations is presented here. The pressure transducers and the current shunt (0.1 ohm standard resistor) used in the calorimeter power measurement were found to be operating well, introducing no significant systematic error into their respective measurements. The pressure transducers were highly stable and exhibited no deviation from the manufacturer's stated 0.1% accuracy rating. The resistance of the current shunt (0.099993 ohms) was essentially invariant, with an uncertainty of less than 0.01%.

The final design of the calorimeter system as a whole performed very well with the resulting mean heat capacity measurements approaching the original target accuracy of 0.1%. Problems with earlier incarnations of the system, and in particular the calorimeter cell, proved especially vexing and greatly hampered (and extended) the completion of the project. Of particular difficulty were the calorimeter thermometers, fluid leaks in the cell and vacuum chamber, and a large and unaccountable heat leak into the calorimeter system. The automation system, in tandem with the other system components, performed very well, allowing easy and rapid measurement of fluid heat capacities over a broad range of conditions. Temperature regulation was exceptional, excluding the system wide upsets resulting from pump piston reversals. The occasional failures of the automation system were generally not fatal and as such allowed mostly unattended operation of the system.

Results and Discussion for Liquid Water:

The mean heat capacity measurements for liquid water are presented in Table 1. The data are listed in chronological order with a run number included

for reference purposes. The breaks in the table indicate points in time during the calorimeter operation when the calorimeter cell was disassembled for repair or modification. This procedure usually resulted in a slight shift in the calorimeter measurements, and as a result in the individual data sets separated by a disassembly. All the necessary data for calculating the mean heat capacities were incorporated into the table. These include the inlet pressure (P_{in}), the mass flow rate ($\dot{m}$), the calorimeter inlet (T_{in}), outlet (T_{out}) and differential temperatures (DT), and the power input to the calorimeter heater (Q_{in}). The mean temperature ($\bar{T}$) listed in the table was the average of the calorimeter inlet and outlet temperatures. This mean temperature represents a good estimate of the temperature corresponding to the true differential heat capacity (not the mean value). This results from the fact that for nearly all of the measurements, the isobaric heat capacities were not strong functions of temperature and did not exhibit large data curvature along the measured isobars.

Although the data were not truly isobaric, the calorimeter pressure drops were always small enough (<0.001 MPa) to have no effect on the measurements. For example, the expected temperature drop stemming from Joule-Thomson cooling of liquid water at 323.1 K was on the order of 0.5 mK for a typical pressure loss of 0.001 MPa (NBS/NRC 1985). This value was essentially insignificant considering the 10 K temperature difference used in most of the experiments. As a result, the heat capacity data listed in the table were virtually identical to the true isobaric values. Because the pressure drops and corrections were so uniformly small, the measured pressure drops were not listed in the tables for the sake of brevity.

As has been previously discussed, the measured mean heat capacities for water were compared against two primary literature references. The first of

these was a computer program (NBS/NRC 1985) based on the equation of state for water developed by Haar et al. (1984). This Fortran program was used to predict all of the mean heat capacities at temperatures in excess of 373 K. At lower temperatures (<373 K), the low pressure (1 atm) but high accuracy data of Osborne et al. (1939) were used. If necessary, pressure corrections estimated by the above computer program were applied to Osborne's data. The results of these comparisons are presented in Table 1. Of particular note is the fact that the literature values listed in Table 1 are the mean isobaric heat capacities and not point estimates of the true differential values. In addition, to maximize the comparability of the measured data, the tabulated experimental values were not in any way corrected for pressure or temperature effects. This eliminated the effect of the any potential correction errors on the evaluation process.

The water data covered a wide range of operating pressures (0.08-11.56 MPa) and temperatures (303-573 K). The cumulative statistics for the entire water data set were a mean error of 0.02% and a standard deviation of 0.05%. In these situations, the term error refers to the deviation from the corresponding standard literature data. While these two statistics indicate that the calorimeter had attained the desired accuracy of 0.1%, they are probably low, since the complete data set was skewed towards experiments in the lower temperature range of 320-330 K, where data are believed to be more accurate. At these temperatures, the calorimeter has historically performed well and the literature values were very well defined (0.01%). The concentration of measurements in this temperature range resulted from the repeated use of these temperatures as a reference point to quickly and conveniently test the success of a particular cell design or modification. As a consequence, the data must be more selectively analyzed to illustrate the effect of the various independ-

ent variables on the overall experimental uncertainty (P,T and flow rate).

The first of these variables is the effect of pressure which is illustrated in Figures 18 and 19. Figure 18 presents the results of an isothermal study (323.1 K) covering the pressure range 0-11 MPa. The variation in the data appears to be approximately linear (as is the predictive model) with a mean error of 0.02% and a standard deviation of 0.02%. The presence of a slightly larger pressure effect (slope) in the measured heat capacities is consistent with the previously observed tendency of the pump flow rates to decrease slightly with increased pressure. This discrepancy though may not be indicative of any failure of the calorimeter since the difference between the two data sets was so small. A scatter plot of the relative errors for the data of Figure 18 and for two additional sets of isothermal data is presented in Figure 19. Once again, pressure appears to have little impact on the performance of the calorimeter, with the total mean error for these three separate data sets being essentially 0.0%. Of particular interest in Figure 23 is the fact that the lack of pressure functionality was observed over the entire temperature range of 323.1-567.9 K. As a result, it can be concluded that pressure appears to affect the data quality very little, and the calorimeter presents an ideal means of accurately determining the relationship between pressure and isobaric heat capacities.

The data of Figure 19 reveal an additional feature of the calorimeter behavior; namely the reproducibility of the calorimeter. During the evaluation process, the calorimeter cell occasionally required disassembly for repair or modification. As was mentioned earlier, this often caused the measurements to shift somewhat. For example, in Figure 23 the average error in the low pressure experiments of the 323.1 K isotherm was approximately +0.05%, while that of the 328.2 isotherm reversed sign to a value of -0.06%. The major difference

between these two data sets was that they were separated by several calorimeter cell disassemblies. In contrast, the calorimeter had a typical measurement precision of better than 0.05% if the calorimeter cell remained untouched during a measurement series. A clearer measure of long term reproducibility, including the effect of cell disassembly, is given in Figure 24. The data in this figure were all determined at nearly identical operating conditions and at several widely separated points in time. Multiple cell reassemblies separate the individual data sets presented in Figure 20. The measurement conditions for these data were 323 and 328 K and 0.1 MPa, with a pump flow rate setting of 16 ml/min and a calorimeter temperature difference of about 10 K. The mean error of this data set with respect to the corresponding literature values was 0.01%. Not enough data were available to make a similar analysis at higher temperatures, but there were indications that the precision decreased slightly to a value of about $\pm 0.1\%$ at these conditions.

While pressure appears to have little influence on the data quality, temperature is potentially a much more significant variable. This derives from the fact that isobaric heat capacities are generally a much stronger function of temperature than pressure everywhere except near phase boundaries and in the critical region. More importantly, radiative heat transfer increases as the fourth power of absolute temperature, implying that any heat loss should dramatically increase with the temperature. As before, two graphs are used to illustrate the effect of temperature. In Figure 21, nine data points covering a temperature range of 323-523 K along the 6.03 MPa isobar are shown. The data appear to agree well with their corresponding predictions and the overall temperature behavior is excellent. One can conclude that the calorimeter appears to accurately measure mean heat capacities over a broad range of temperatures and pressures with a slight decrease in performance at elevated

conditions.

The maximum operating temperature at which experiments were performed in this study was 573 K. This relatively low maximum temperature was a consequence of the 14 MPa limitation of the pressure regulation system, rather than from any fundamental problem in the calorimeter design. This resulted from the fact that only liquid phase measurements could be made due to the high heat of vaporization. 700 K may well represent a realistic upper temperature limit for the calorimeter, although the overall error could increase substantially at these untested high temperatures.

Of additional concern is the impact of the calorimeter differential temperatures on the measurements. For most of the data points listed in Table 1, the temperature differences were set at approximately 10 K. This temperature difference was selected because it presented a reasonable balance between the need to minimize measurement uncertainty in the temperature by increasing the total difference, while simultaneously moderating the driving force for heat transfer by decreasing the difference as much as possible. The relationship between the calorimeter temperature difference and the heat capacity measurement is shown in Figure 23. Measurements at two different calorimeter inlet temperatures (468 K (6.03 MPa) and 318 K (0.1 MPa)) were completed using temperature differences of 5, 10, and 15 K. In both cases, little variation in the data was apparent.

Error Analysis:

The estimated error in the calorimeter temperature difference was difficult to quantify because of the imprecise nature of the calibration procedure and as such, the value eventually assigned was somewhat arbitrary. A value of 10 mK was assumed based on past experience with these and other PRT's. This corresponded to an error of 7 mK in the individual temperature measurements

(inlet and outlet) which is a realistic estimate of the uncertainty given the imperfect natures of the sensing element and the calibration. The effect of measurement error was assumed to be negligible (<1 mK) in comparison with the calibration error, because of the high accuracy of the data acquisition system (HP 3457A DVM).

To estimate the overall measurement uncertainty, the defining relation for mean heat capacity needs to be recast from the form of Eq. (1) into the following adiabatic expression:

$$\bar{C}_p = (V_{htr} V_{std}) / (R_{std} \rho q \Delta T) \quad (4)$$

The new form merely restates the mass flow rate in terms of density (ρ) and volumetric flow rates (q), and it expands the expression for the calorimeter power input (Q_{in}) into its measurable constituents, including the voltage drops across the calorimeter heater and current shunt and the absolute resistance of the current shunt. The standard resistor was calibrated to an accuracy of better than 0.01%. The accuracy of the two voltage measurements was limited by the DVM calibration, thermal EMF's (negligible) in the heater circuit, and any drift in the main power supply used by the heater. The power measurement was typically stable to 0.01% over the course of a measurement cycle, while the DVM itself had a precision of 0.001%. These individual uncertainties lead to an estimated accuracy of better than 0.01% for the two required voltage determinations. The uncertainty of the combined total calorimeter power measurement was thus on the order of 0.01%; implying that the uncertainty of this variable (assuming no heat losses) was insignificant. The mass flow rate accuracy was dependent on both the densities in the pump cylinder and on the precision of the volumetric flow rate from the pump. As was noted earlier, the

pump calibration had substantially demonstrated that the volumetric flow rate uncertainty was on the order of $<0.1\%$. The liquid water densities were very well defined ($>0.001\%$) at the temperatures and pressures of the pump cylinders, while the temperature of the pump cylinders did not drift sufficiently to alter the density estimates ($<0.01\%$). The effect of pressure measurement error in the pump cylinder was considered negligible. The estimated error for the calorimeter temperature difference was on the order of 10 mK or 0.1% for a typical fixed gradient of 10 K. At lower temperature differences, the error correspondingly increases. If all of the above experimental uncertainties are applied to Eq. (5) through a simple propagation of errors approach, the overall measurement accuracy for the mean, isobaric, specific heat capacity can be estimated as $<0.15\%$. This value readily accommodates the scatter in the tabulated water data over the entire measurement range. In many respects, this level of uncertainty is overly conservative, particularly at the lower temperatures and pressures where the two primary measurement (T and $\dot{m}$) uncertainties are diminished. At these conditions, the errors in temperature and mass flow rate were approximately 5 mK and 0.05% respectively, resulting in a total uncertainty of 0.08% . Nonetheless, 0.15% represents a very reasonable estimate of the calorimeter's performance over its entire operating range; especially when one considers that the literature data against which the higher temperature comparisons were made had an accuracy of only 0.2% .

Heat Leak Measurements:

The above error analysis ignored the effect of absolute and differential pressure uncertainty, which were assumed to have little impact on liquid heat capacities. The analysis also assumed that the calorimeter cell was operated adiabatically, with no uncontrolled heat leak. As a result, 0.15% can be considered a conservative estimate of the total potential error, or rather as

the total adiabatic uncertainty. A heat loss represents a systematic error in the calorimeter design. To establish the existence of any heat leaks in the calorimeter, several experiments were performed whereby mean heat capacities were measured as a function of mass flow rate. The rationale for this is illustrated in Eq. (5) which demonstrates that the effect of a heat leak decreases at higher mass flow rates, assuming that the heat loss term is at least bounded at infinite flow rate.

$$\lim_{\dot{m} \rightarrow \infty} \left[\bar{C}_p = \frac{(Q_{in})}{\dot{m}(T_o - T_i)} - \frac{(Q_{lst})}{\dot{m}(T_o - T_i)} \right] = \frac{Q_{in}}{\dot{m}(T_o - T_i)} \quad (5)$$

The flow rates selected for study typically ranged from 8 ml/min to the maximum pump setting of 18.667 ml/min. Figures 24 and 25 illustrate the results of several such experiments at two different temperature levels. The dashed lines in Figure 25 are first order least squares regressions of the heat capacity data with respect to the inverse of mass flow rate. The regression lines were omitted for clarity from Figure 24 due to the large number of data points. In both figures, the variation between apparent heat capacity and the inverse flow rate was roughly linear as expected from Eq. 6, with the measured values decreasing with increased flow or heat load. Linearity is implicit in Eq. 6 if one assumes that the heat leak is constant, with the value of the loss fixed by the calorimeter temperature and not by the flow rate. For the lower temperature data set (323 and 328 K), the variation was weak and effectively disappeared at the highest flow rates. The heat leak appeared to increase somewhat for the two data sets at 473 K as evidenced by the greater variation (slope) of the data. The slope and intercept of a first order regression of the heat capacity data versus inverse flow rate can be utilized to estimate the heat loss and the true heat capacity. Applying

regression analysis to the data set of Figure 24 results in an estimated average heat loss of 0.005 watts. This is equivalent to an error of less than 0.05% at the two highest flow rates (power inputs >11 watts). With regards to the data of Figure 25, the heat loss is about 0.006 watts (0.05%) at 3.45 MPa, while the estimated heat loss for the 6.03 isobar is 0.015 watts (0.12%). This last value of 0.12% is somewhat anomalous given much of the previous experience with the equipment. An additional advantage of the above heat loss analysis is that it provides a means of correcting the heat capacity data if necessary. As a result, the heat leak test should be performed routinely if the greatest accuracy is desired. It appears that in most cases the heat leak effect is negligible and can be easily compensated for by operating at the highest pump settings.

Nonetheless, all of these data clearly indicate the presence of a small heat leak in the current calorimeter cell. This heat loss must necessarily degrade the data quality from the previously estimated adiabatic uncertainty of 0.15%. For water, the heat leak appears to be on the order of 0.15% or less. A value of 0.15% for the heat leak probably represents an upper bound for this error and past experience seems to suggest that it is generally significantly smaller, especially at lower operating temperatures. Incorporating the heat leak into the estimated adiabatic uncertainty results in a total error estimate for the water measurements of 0.2%. This value is somewhat arbitrary but it is identical to the uncertainty of the literature data against which the experimental data were compared. As such, it is probably an acceptable estimate of the total measurement uncertainty at all temperatures and pressures for the liquid water isobaric heat capacity determinations. While this figure (0.2%) for the total measurement uncertainty appears to be excessive given the excellent overall agreement of the data with the litera-

ture, it is the author's opinion that 0.2% is a more realistic estimate of the equipment's capabilities than the value 0.05% which was suggested by the mean deviation of the water data.

Results and Discussion for Liquid n-Pentane:

For most organic systems, the specific heat capacities and the liquid densities are much smaller than those of liquid water. As a result, much less power must be input to the calorimeter heater to achieve comparable temperature increases with these lower heat capacity flux ([Picture]) fluids. Consequently, the effect of a heat leak is much greater for these fluids, since the heat transfer rate is essentially independent of the fluid and is fixed by the absolute calorimeter temperature. For example, the heater duty for an n-pentane measurement utilizing a 10 K temperature difference is only 40% of that for a equivalent volume of liquid water. A 0.015 watt heat leak would now result in a 0.25% error in the data. To further investigate this potential, heat capacity measurements were performed on liquid n-pentane. The limited results of this study are presented in Table 2. The nine data points (versus 68 for water) were essentially isothermal (323 K) and were selected to emphasize the effect of pressure and flow rate on n-pentane mean heat capacities.

In Figure 26, the three data points determined at a pump setting of 16 ml/min (0.17 g/s) were plotted against several different sets of literature data to illustrate the effect of pressure. Minor adjustments were made to the original data of Kharin et al. (1985) and Peng and Stiel (1974) to compensate for deviations from 323.1 K. The total enthalpy data of Lenoir et al. (1970) were regressed and then differentiated at 323.1 K and 3.45 MPa. The data point of Messerly et al. (1967) was an estimate of the saturated heat capacity at 323.1 K (0.155 MPa) calculated by extrapolating the original saturated data set from a high temperature of 303 K. The second estimate of the saturated

heat capacity at 323.1 K (0.155 MPa) was derived from a data fit developed in a recent literature review (Grigor'ev et al. 1989). The curve presented in this plot was a cubic spline fit of Kharin's three points and Grigor'ev's estimate of the saturated heat capacity. The reported uncertainty in these four points was less than 0.4%. These data also illustrate the tremendous variation in the literature with regards to data quality, even for fluids as simple as n-pentane.

The errors reported in Table 2 were relative to the curve in Figure 26. In all cases, the experimental deviations were small ($<0.1\%$) and well within the uncertainty of the original data. The mean error for this set was 0.04% with a standard deviation of 0.08% . As expected, no dramatic variation in data quality was apparent with pressure in the three measurements plotted in this figure. To further investigate calorimeter performance, a heat leak experiment was performed at 323.1 K and 3.45 MPa, utilizing several different flow rates as before. The results are depicted in Figure 27. In contrast with the results of the water studies, the data now indicate no apparent relationship between heat capacity and flow rate. Instead, the data are randomly distributed about a mean value of 2.4187 J/gK with an astounding spread of less than 0.05% . This behavior implies that no significant heat losses occurred at these conditions.

While these data (n-pentane) are in many respects too limited (narrow temperature range) to draw many meaningful conclusions about the calorimeter's capabilities, they do appear to indicate that the calorimeter performs equally well with a low heat capacity flux fluid as it does with a fluid like water. This is enhanced by the low overall error (0.04%) for these admittedly limited data in tandem with the negligible heat leak apparent at these measurement conditions. More measurements with n-pentane are required to further justify this conclusion. A total measurement uncertainty of 0.15% for n-pentane is

probably justified.

CONCLUSIONS AND RECOMMENDATIONS

In conclusion, the new adiabatic flow calorimeter has been shown to accurately measure mean, isobaric heat capacities for liquids at elevated temperatures and pressures. The apparatus was successfully tested and operated at pressures of up to 12 MPa and over a temperature range of 300-600 K with water as the primary test fluid. The mean error of the water measurements was +0.02%, indicating that the calorimeter is approaching the target accuracy of 0.1%.

With regards to the overall system hardware, the performance was in general satisfactory. This was especially true for the integrated automation system which has greatly simplified the operation of what is a very complex apparatus. The two-task control scheme, while somewhat novel and inefficient, represents an extremely simple and effective solution to the problem of balancing the many control requirements. The use of the high performance pump has also simplified the design of the apparatus while simultaneously improving the data quality substantially. The calorimeter thermometers built for this study greatly facilitated the accurate measurement of the calorimeter temperature difference while eliminating most of the problems previously experienced with small PRT's. As a result, the measurement uncertainty was substantially reduced. Finally, the successful implementation of a unique bath-less calorimeter design, utilizing actively controlled shields to define the local calorimeter temperature environment, represents a significant improvement in the design of this class of calorimeter.

Mean heat capacity studies using water and n-pentane as test fluids indicate that the total measurement uncertainty is on the order of 0.2% with

an anticipated reproducibility 0.1-0.15%. This uncertainty value is due to adiabatic measurement error (0.15%) and to an uncontrolled heat loss. The heat leak was generally very small but increased with temperature having an estimated upper bound of 0.01 watts. In all cases the above errors are conservative estimates and are probably valid only at extreme operating conditions. Typical measurement errors may be as small as 0.05-0.1% at milder temperatures. The more limited experiments performed with n-pentane were not as conclusive as the extensive water measurements, but the apparent lack of a heat leak in conjunction with very small errors for all of the data suggest that at least comparable accuracies can be achieved for low heat capacity flux fluids.

In light of these results, the calorimeter can be considered a success. In many respects, the design innovations implemented in this calorimeter are useful contributions to the field of flow calorimetry. The resulting apparatus was easy to use and produced data as good as or better than the best flow calorimeters of this type. These apparent successes are tempered by the failure to achieve all of the design goals, especially the inability to obtain complete pressure regulation.

The calorimeter is presently being used in a National Science Foundation sponsored program to obtain measurements, especially in the critical region, for n-pentane, methanol, acetone and their mixtures.

LITERATURE CITED

Actis, A. and Crovini, L. 1982. "Interpolating Equations for Industrial Platinum Resistance Thermometers in the Temperature Range -200 to +420°C". In Temperature, Its Measurement and Control in Science and Industry, Ed. in Chief J. F. Schooley, v. 5, part 2, 819-827. American Institute of Physics, New York.

Barber, C. R. 1950. "Platinum Resistance Thermometers of Small Dimensions". Rev. Sci. Instruments. 27 (February): 47-49.

Berry, R. J. 1982. "Oxidation, Stability, and Insulation Characteristics of Rosemount Standard Platinum Resistance Thermometers". In Temperature, Its Measurement and Control in Science and Industry, Ed. in Chief J. F. Schooley, v.5, part 2, 753-762. American Institute of Physics, New York.

Bier, K.; Ernst, G.; and Maurer, G. 1974. "Flow Apparatus for Measuring the Heat Capacity and the Joule-Thomson Coefficient of Gases". J. Chem Thermodynamics. 6: 1027-1037.

Castro-Gomez, R. C. 1987. "A Thermoelectric Total Enthalpy Flow Calorimeter: Its Application to Binary Mixtures of Chlorofluoromethanes". Ph.D. diss., Texas A. M. University, College Station, TX.

Christopher, G. and Holcombe, J. A. 1988. "Computer-Controlled Heating of a Graphite Filament for Use in Thermal Desorption Studies". Analytical Instrumentation. 17 (3): 235-253.

Cluley, J. C. 1982. Minicomputer and Microprocessor Interfacing. New York: Crane Russak and Co.

Dreher, Ingo. 1979. "Experimental Determination of the Isobaric Specific Heat Capacity of Propan-2-ol up to Pressures of 30 MPa and Temperatures of 573 K". J. Chem. Thermodynamics 11: 993-1103.

ElAbdalla, A. M. and Abu-El-Haija. A. I. 1988. "Personal Computer Flexible Multichannel Interface for Data Acquisition of Low-Frequency Signals". IEEE Trans. on Instrumentation and Measurement. 37 (4): 510-514.

Flanigan, D. A. 1986. "Enthalpy Measurements and Predictions for the Pure Components m-Cresol, Quinoline, Tetralin and the Constituent Binary Mixtures in the Temperature Range 291 to 675 K and at Pressures to 10 MPa". Ph.D. diss., Colo. Sch. of Mines, Golden, CO.

Grigor'ev, B. A.; Gerasimov, A. A.; Kharin, V.; and Rastorguev, Y. 1985. "Heat Capacity of n-Pentane in the Liquid and Vapour Phases Including the Critical Regions". High Temperatures - High Pressures. 17: 317-324.

Grigor'ev, B. A.; Rastorguev, Yu. L.; Kurumov, D. S.; Gerasimov, Kharin, V. E.; and Plotnikov, S. A. 1989. "Thermodynamic Properties of n-Pentane". Unpublished (Grozny Pet. Inst., Revolution St. 21, 364902: Grozny, USSR).

- Haar, L.; Gallagher, J. S.; and Kell, G. S. 1984. NBS/NRC Steam Tables. Washington D.C.: Hemisphere Publishing Co.
- Kharin, V. E.; Grigor'ev, B. A.; Gerasimov, A. A.; and Rastorguyev, Y. L. 1985. "Experimental Study of the Liquid Heat Capacity of n-Pentane at 293-697 K and Pressures up to 60 MPa". Isvest. Vysshikh. Ucheb. Zavedenii Neft. i. Gas. 28 (10): 54-7.
- Kobayashi, Y. and Tashiro, M. 1979. "Experimental Investigation of Isobaric Specific Heat of Water Substance up to 573 K and 90 MPa". In Water and Steam Their Properties and Current Industrial Applications. Ed J. Straub and K. Scheffler, 205-210. New York: Pergamon Press.
- Lenoir, J. M.; Robinson, D. R. and Hipkin, H. G. 1970. "Flow Calorimeter and Measurement of the Enthalpy of n-Pentane". J. of Chem. and Eng. Data. 15 (1): 23-26.
- Lesea, A.; Zaks, A. 1978. Microprocessor Interfacing Techniques. Berkeley, CA: Sybex.
- LeVasseur, Dan. 1982. "A Microprocessor Based Interface for the IEEE-488 Bus". Chapter Two in Microprocessors Applications Handbook. Ed. D. F. Stout. New York: McGraw-Hill.
- McConnell, J.R.; Fleckenstein, R.R.; Kidnay, A.J.; and Yesavage, V. F. 1984. "A Boil-off Calorimeter for the Measurement of the Enthalpy of Coal-Derived Liquids." Ind. Eng. Chem. Process Des. Dev. 23: 267-271.
- McGlashan, M. L. 1984. "Current Trends in Precise Calorimetry". Thermochimica Acta. 72: 55-70.
- Messerly, J. F.; Guthrie, G. B.; Todd, S. S.; and Finke, H. L. 1967. J. of Chem. Eng. Data. 12 (3): 338-346.
- Meyers, C. H. 1932. "Coiled Filament Resistance Thermometers". J. Res. Nat. Bur. Stand. 9: 807-813.
- Miyazaki, Takaya. 1973. "Design, Development and Evaluation of a High-Accuracy Recycle-flow Multipurpose Calorimeter". Ph.D. diss., Univ. of Michigan, Ann Arbor, MI.
- Miyazaki, T.; Hejmadi, A. V.; and Powers, J. E. 1980. "A New High-Pressure Recycle- Flow Calorimeter and Results of Determinations with Ethane". J. Chem. Thermodynamics. 12: 105-124.
- NBS/NRC. 1985. Steam tables computer program.
- Osborne, N. S. 1930. "Calorimetry of Fluids". Natl. Bur. Stand., J. of Res. 4: 609-29.
- Patterson, W. I.; Kamal, M. R.; and Gomes, V. G. 1987. "Time Proportioning Computer Control of Resistive Heating". Analytical Instrumentation. 16 (4): 447-466.
- Peng, Ding-yu and Stiel, L. I. 1974. "Heat Capacity of Liquid n-Pentane at

Elevated Pressures". AIChE Symposium Series. 70 (No. 140): 63-69.

Rogers, P. S. Z. and Sandarusi, J. A. 1989. "A Completely Automated Flow, Heat Capacity Calorimeter for Use at High Temperatures and Pressures". Submitted to Review of Scientific Instruments.

Rohsenow, W. M. and Choi, H. 1961. Heat, Mass, and Momentum Transfer. Englewood Cliffs, NJ: Prentice-Hall.

Saitoh, A.; Sato, H.; and Watanabe, K. 1988. "A New Apparatus for the Measurement of Heat Capacity at Constant Pressure of Liquid Refrigerants". Paper presented at "The Tenth Symposium on Thermophysical Properties", June 20-23. NBS: Gaithersburg, MD.

Sandarusi, J. A. 1990. "An Automated Flow Calorimeter for the Determination of Isobaric Heat Capacity and Enthalpy at Elevated Temperatures and Pressures" Ph.D. Thesis, Colorado School of Mines, Golden, CO.

Savitsky, S. R. 1985. Real-Time Microprocessor Systems. New York: Van Nostrand and Reinhold.

Scott, R. B. 1959. Cryogenic Engineering. Princeton, NJ: Van Nostrand.

Sirota, A. M. and Mal'Tsev, B. K. 1959. "Experimental Investigation of the Heat Capacity of Water at 10-500°C and 500 kbar/cm³". Teploenergetika. 6 (9): 7-15.

Smith, J. T. 1987. Getting the Most from Turbo Pascal. New York: McGraw-Hill.

Smith, R. J. 1980. Electronics: Circuits and Devices. 2nd ed. New York: John Wiley and Sons.

Stephanopoulos George. 1984. Chemical Process Control. New York: Prentice Hall.

Titus, J. A.; Titus, C.A.; Rony, P. R.; and Larsen, D. G. 1979. Microcomputer-Analog Converter Software and Hardware Interfacing. Indianapolis, IN: Howard W. Sams and Co.

Wikmark, Gunnar. 1984. "A Versatile Computer Interface for Experiment Control and Data Acquisition". Analytical Instrumentation. 13 (2): 145-157.

Wold, Ivar. 1985. "Choosing a Micro-Computer Programming Language for Industrial Applications". Advances in Instrumentation. vol. 40 (part 2) Paper #85-0778: 941-947.

Yesavage, V. F.; Mather, A. E.; Katz, D. L.; and Power, J. E. 1967. "Enthalpies of Fluids at Elevated Pressures and Low Temperatures". Industrial and Engineering Chemistry. 59 (11): 35-52.

Yesavage, V. F. 1968. "The Measurement and Prediction of the Enthalpy of Fluid Mixtures Under Pressure". Ph.D. diss., Univ. of Michigan, Ann Arbor, MI.

FIGURE 1: The Calorimeter Flow Loop.

FIGURE 2: Schematic of the Four-Port High Pressure Liquid Chromatography Valve Used to Regulate the Direction of Fluid Flow.

FIGURE 3: The Pressure Manifold Layout for the Pump and the Calorimeter Inlet and Differential Pressure Transducers.

FIGURE 4: The Original, Automated, Pressure Control Scheme Using a Back Pressure Regulator and an Open Flow Loop.

FIGURE 5: The Current Manual Pressure Regulation Scheme Utilizing a Closed Flow Loop.

Note: All heated surfaces and lines are thermally insulated
All thermometers are 100 ohm platinum RTD's, $\alpha=0.385$

FIGURE 6: The Design and Layout of the Calorimeter Preheaters in the Flow Loop.

FIGURE 7: The Two Chambered Calorimeter Measurement Cell for Isobaric Heat Capacity Determinations.

FIGURE 8: The Shielding Scheme Used to Isolate the Inlet Fluid from the Hotter Outlet Chamber.

FIGURE 9: The Calorimeter Working Heater Capsule.

FIGURE 10: The Calorimeter Heater Power Bus and Connections to the Kepco DC Supply and Standard Resistor.

FIGURE 11: The Capsule-Type Calorimeter Thermometers Based on a Design of Barber (1950).

FIGURE 12: The Drift in the Ice Points (273.15 K) of the Two Main Calorimeter Thermometers as Determined Over the Period of Several Months.

FIGURE 13: The Calorimeter Vacuum Chamber and Insulation System.

Programming Language: Turbo Pascal
Two Process Scheduler: "Double Dos"

FIGURE 14: Outline of the Two-Task Control Scheme and Automation Software.

FIGURE 15: Outline of the Calorimeter Automation Hardware and Data Acquisition System.

FIGURE 16: The Feedback Control Loops for the Automated Preheaters.

FIGURE 17: The Feedback Control Loops for the Calorimeter Shields and Heater.

FIGURE 18: The Specific Heat Capacity of Water as a Function of Pressure at 323.1 K. [Runs 25-36]

FIGURE 19: The Effect of Pressure on Measurement Error for the Specific Heat Capacity of Water. [Runs 23-36, 55-56]

FIGURE 20: Measurement Scatter in the Low Pressure Water Heat Capacity Determinations at 323 and 328 K.

FIGURE 21: The Specific Heat Capacity of Water as a Function of Temperature at 6.03 MPa. [Runs 31, 37-41, 45, 52-53]

FIGURE 22: The Effect of Temperature on Measurement Error for the Specific Heat Capacity of Water.
[Runs 19-22,31,37-45,52-56]

FIGURE 23: The Effect of Calorimeter Temperature Differences on Measurement Error for the Specific Heat Capacity of Water. [Runs 45-47, 57-59]

FIGURE 24: The Effect of Calorimeter Mass Flow Rate on the Determination of Water Specific Heat Capacities at 323 and 328K. [Runs 1-2, 10-18, 60-67]

FIGURE 25: The Effect of Calorimeter Mass Flow Rate on the Determination of Water Heat Capacities at 473 K. [Runs 3-7, 45, 48, 51]

FIGURE 26: The Specific Heat Capacity of n-Pentane Along the 323.1 K Isotherm. [Runs 68, 69, 75]

FIGURE 27: The Effect of Mass Flow Rate on the Determination of the Specific Heat Capacity of n-Pentane at 323.1 K. [Runs 69-74]

TABLE I

Mean, Isobaric, Specific, Heat Capacity Measurements for Water

Run	P (MPa)	m (g/s)	T _{out} (K)	T _{in} (K)	$\bar{T}$ (K)	ΔT (K)	Q _{in} (Watts)	C _p ^{exp} (J/g·K)	C _p ^{lit} (J/g·K)	Deviation (%)
1	0.14	0.2655	333.385	323.267	328.326	10.118	11.238	4.1834	4.1826	0.02
2	0.11	0.1328	333.292	323.224	328.258	10.068	5.594	4.1855	4.1826	0.07
3	3.45	0.2659	477.720	468.134	472.927	9.586	11.417	4.4795	4.4774	0.05
4	3.45	0.1330	477.428	467.892	472.660	9.536	5.681	4.4807	4.4757	0.11
5	3.45	0.3102	477.874	468.265	473.069	9.609	13.345	4.4769	4.4782	-0.03
6	3.45	0.2659	477.723	468.127	472.925	9.596	11.424	4.4774	4.4774	0.00
7	3.45	0.1330	477.432	467.890	472.661	9.542	5.685	4.4811	4.4761	0.11
8	0.08	0.2659	333.284	323.119	328.202	10.165	11.313	4.1855	4.1826	0.07
9	0.07	0.1329	334.181	323.087	328.634	11.093	6.169	4.1830	4.1826	0.01
10	0.08	0.2659	333.258	323.085	328.172	10.173	11.312	4.1822	4.1826	-0.01
11	0.08	0.1330	333.243	323.059	328.151	10.184	5.664	4.1834	4.1826	0.02
12	0.08	0.0665	333.167	323.020	328.093	10.147	2.822	4.1847	4.1826	0.05
13	0.08	0.1773	333.351	323.069	328.210	10.282	7.625	4.1839	4.1826	0.03
14	0.08	0.2321	332.734	323.079	327.907	9.655	9.371	4.1826	4.1826	0.00
15	0.08	0.2659	333.249	323.088	328.169	10.161	11.298	4.1818	4.1826	-0.02
16	0.08	0.3102	333.263	323.090	328.176	10.173	13.196	4.1818	4.1826	-0.02
17	0.08	0.0665	333.032	323.012	328.022	10.020	2.787	4.1851	4.1826	0.06
18	0.08	0.2659	333.264	323.088	328.176	10.176	11.313	4.1814	4.1826	-0.03
19	0.08	0.2213	318.279	308.093	313.186	10.186	9.424	4.1814	4.1788	0.06
20	0.08	0.2213	328.252	318.077	323.164	10.175	9.414	4.1818	4.1809	0.02
21	0.12	0.2213	353.202	343.072	348.137	10.130	9.394	4.1914	4.1927	-0.03
22	0.21	0.2213	378.102	368.060	373.081	10.042	9.366	4.2148	4.2153	-0.01

TABLE 1 (Continued)

Run	P (MPa)	m (g/s)	T _{out} (K)	T _{in} (K)	T̄ (K)	ΔT (K)	Q _{in} (Watts)	C _p ^{exp} (J/g·K)	C _p ^{lit} (J/g·K)	Deviation (%)
23	0.10	0.2659	333.300	323.096	328.198	10.204	11.340	4.1797	4.1826	-0.07
24	3.68	0.2663	333.295	323.097	328.196	10.198	11.331	4.1726	4.1747	-0.05
25	0.08	0.2655	328.162	318.162	323.162	10.000	11.106	4.1830	4.1809	0.05
26	1.00	0.2656	328.173	318.165	323.169	10.008	11.114	4.1809	4.1788	0.05
27	2.00	0.2657	328.173	318.165	323.169	10.008	11.112	4.1784	4.1767	0.04
28	3.04	0.2659	328.175	318.165	323.170	10.010	11.113	4.1759	4.1742	0.04
29	4.00	0.2660	328.177	318.169	323.173	10.007	11.108	4.1734	4.1721	0.03
30	4.96	0.2661	328.173	318.164	323.168	10.009	11.109	4.1709	4.1701	0.02
31	6.03	0.2662	328.180	318.164	323.172	10.015	11.112	4.1680	4.1675	0.01
32	7.00	0.2663	328.182	318.164	323.173	10.018	11.111	4.1646	4.1654	-0.02
33	8.00	0.2664	328.180	318.166	323.173	10.015	11.110	4.1638	4.1634	0.01
34	8.96	0.2666	328.182	318.168	323.175	10.014	11.108	4.1613	4.1613	0.00
35	10.03	0.2667	328.186	318.170	323.178	10.016	11.109	4.1592	4.1587	0.01
36	11.00	0.2668	328.188	318.170	323.179	10.018	11.110	4.1571	4.1567	0.01
37	6.03	0.2662	353.253	343.262	348.258	9.991	11.123	4.1822	4.1801	0.05
38	6.07	0.2662	377.163	368.315	372.739	8.848	9.907	4.2061	4.2027	0.08
39	6.00	0.2662	403.138	393.315	398.226	9.823	11.083	4.2387	4.2425	-0.09
40	6.00	0.2662	427.982	418.314	423.148	9.668	11.045	4.2919	4.2944	-0.06
41	6.00	0.2662	452.907	443.298	448.102	9.610	11.164	4.3639	4.3643	-0.01
42	0.10	0.2659	328.123	318.134	323.128	9.989	11.103	4.1805	4.1809	-0.01
43	0.10	0.2659	308.151	298.107	303.129	10.044	11.161	4.1793	4.1788	0.01
44	0.08	0.2659	328.187	318.165	323.176	10.022	11.141	4.1809	4.1809	0.00
45	6.03	0.2662	477.927	468.329	473.128	9.598	11.405	4.4640	4.4635	0.01
46	6.03	0.2662	473.328	468.319	470.824	5.009	5.939	4.4539	4.4527	0.03
47	6.03	0.2662	483.278	468.335	475.807	14.943	17.817	4.4790	4.4774	0.04
48	6.03	0.3106	477.961	468.342	473.152	9.619	13.332	4.4627	4.4635	-0.02
49	6.03	0.2218	477.865	468.274	473.069	9.590	9.501	4.4661	4.4635	0.06

TABLE 1 (Continued)

Run	P (MPa)	$\dot{m}$ (g/s)	T _{out} (K)	T _{in} (K)	$\bar{T}$ (K)	ΔT (K)	Q _{in} (Watts)	C _p ^{exp} (J/g·K)	C _p ^{lit} (J/g·K)	Deviation (%)
50	6.03	0.1775	477.806	468.239	473.023	9.567	7.588	4.4686	4.4631	0.12
51	6.07	0.1331	478.131	468.163	473.147	9.968	5.930	4.4698	4.4635	0.14
52	6.04	0.2662	503.046	493.240	498.143	9.806	12.041	4.6130	4.6097	0.07
53	6.03	0.2662	528.102	518.186	523.144	9.916	12.759	4.8337	4.8299	0.08
54	8.00	0.2664	553.059	543.054	548.056	10.005	13.711	5.1439	5.1426	0.02
55	10.17	0.2667	577.941	567.963	572.952	9.978	15.069	5.6626	5.6656	-0.05
56	11.56	0.2669	578.020	567.938	572.979	10.082	15.069	5.6011	5.6040	-0.05
57	0.08	0.2655	323.130	318.138	320.634	4.992	5.547	4.1843	4.1801	0.10
58	0.08	0.2655	328.182	318.139	323.160	10.043	11.150	4.1814	4.1809	0.01
59	0.08	0.2655	333.781	318.048	325.915	15.733	17.472	4.1822	4.1818	0.01
60	0.08	0.1328	328.112	318.130	323.121	9.982	5.542	4.1826	4.1809	0.04
61	0.08	0.2655	328.173	318.145	323.159	10.028	11.134	4.1814	4.1809	0.01
62	0.08	0.2213	328.202	318.164	323.183	10.038	9.289	4.1822	4.1809	0.03
63	0.08	0.1328	328.118	318.135	323.126	9.983	5.544	4.1834	4.1809	0.06
64	0.08	0.1770	328.163	318.143	323.153	10.019	7.418	4.1826	4.1809	0.04
65	0.08	0.2655	328.184	318.148	323.166	10.037	11.143	4.1818	4.1809	0.02
66	0.08	0.3098	328.193	318.143	323.168	10.050	13.013	4.1801	4.1809	-0.02
67	0.08	0.3098	328.191	318.143	323.167	10.048	13.013	4.1814	4.1809	0.01

Note: The error values are relative to the data of Osborne et al. (1936) and the predictions of NBS-NRC steam table program (1985).

P: Inlet Pressure. $\dot{m}$: Mass Flow Rate. T_{out}: Outlet Temp. T_{in}: Inlet Temp.

$\bar{T}$: Mean Temp. ΔT : Temperature Difference. Q_{in}: Heater Power.

C_p^{exp}: Experimental Heat Capacity. C_p^{lit}: Literature Heat Capacity.

C_p^{exp}=Q_{in}/($\dot{m} \Delta T$); Deviation=100*(C_p^{exp}-C_p^{lit})/C_p^{lit}.

TABLE 2

Mean, Isobaric, Specific, Heat Capacity Measurements for n-Pentane

Run	P (MPa)	$\dot{m}$ (g/s)	T _{out} (K)	T _{in} (K)	$\bar{T}$ (K)	ΔT (K)	Q _{in} (Watts)	C _p ^{exp} (J/g·K)	C _p ^{lit} (J/g·K)	Deviation (%)
68	5.36	0.1675	327.769	318.145	322.957	9.624	3.864	2.3995	2.4020	-0.10
69	3.45	0.1668	328.102	318.136	323.119	9.966	4.021	2.4187	2.4181	0.03
70	3.45	0.0834	328.043	318.093	323.068	9.950	2.008	2.4187	2.4181	0.03
71	3.45	0.1946	327.976	318.148	323.062	9.828	4.628	2.4196	2.4181	0.06
72	3.45	0.1112	328.103	318.115	323.109	9.988	2.686	2.4183	2.4181	0.01
73	3.45	0.1390	328.133	318.135	323.134	9.998	3.361	2.4183	2.4181	0.01
74	3.45	0.1668	328.098	318.134	323.116	9.964	4.021	2.4191	2.4181	0.04
75	9.99	0.1689	327.977	318.129	323.053	9.848	3.971	2.3881	2.3881	0.00
76	9.86	0.0844	327.966	318.091	323.029	9.875	1.993	2.3902	2.3886	0.07

Note: Error values are based on the data of Kharin et al. (1985).

P: Inlet Pressure. $\dot{m}$: Mass Flow Rate. T_{out}: Outlet Temp. T_{in}: Inlet Temp. $\bar{T}$: Mean Temp. ΔT : Temperature Difference. Q_{in}: Heater Power.C_p^{exp}: Experimental Heat Capacity. C_p^{lit}: Literature Heat Capacity.C_p^{exp} = Q_{in} / ($\dot{m} \Delta T$); Deviation = 100 * (C_p^{exp} - C_p^{lit}) / C_p^{lit}.

PUBLICATIONS RESULTING FROM GRANT

Sandarusi, J. A. and Yesavage, V. F. 1988. "An automated Flow Calorimeter for Heat Capacity and Enthalpy Measurements," International Journal of Thermophysics 9: 993-1002.

A second paper is currently under preparation.

END

DATE FILMED

12 / 10 / 90