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MASTER

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"AN IMPROVED INSTRUMENT FOR THE MEASUREMENT OF THE
THERMAL CONDUCTIVITY OF NON-ELECTROLYTE LIQUIDS"

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I. EXECUTIVE SUMMARY

In May of 1979 the Department of Energy allocated \$62,010.00 to support Contract DE-AC02-79ER10393 entitled: "An Improved Instrument for the Measurement of the Thermal Conductivity of Non-Electrolyte Liquids". The goal of the initial year, to design and construct such an instrument, has been successfully accomplished along with all the subgoals.

The funding for the second year (\$44,755.00) will enable the fruition of the first year's investment and labor. During the second year, we will test the apparatus against a known standard and measure the thermal conductivities of two coal-derived synthetic oils. These will be the first reported synthetic fuel thermal conductivities. Thermal conductivities data are mandatory for any heat transfer calculation.

II. INTRODUCTION

The report covers the first nine months of the research project: "An Improved Instrument for the Measurement of the Thermal Conductivity of Non-Electrolyte Liquids". The specific objective of the proposed work, currently being funded under Grant DE-AC02-79ER10393, is to design and construct an innovative transient hot wire thermal conductivity apparatus to measure the thermal conductivity of organic liquids at ambient conditions and at high temperatures and pressures.

During the first nine months, a thermal conductivity cell, precision temperature and pressure controlled environment, and a computerized data acquisition system, have been built and tested. The system is described in the main body of this report. The necessary computer software for data acquisition has been developed and experimental procedures have been established.

Preliminary experiments with liquid toluene at ambient condition have been conducted; these confirm the electronic circuitry and, more importantly, establish the proposed theoretical basis for thermal conductivity measurement as outlined in the addendum to the original proposal (CSM Proposal No. 933).

III. CURRENT STATUS AND FUTURE PLANS

Under the original proposal, the scope of the project is divided into three phases. During Phase I, the contractor is responsible for designing and constructing all components of the apparatus including electronic measuring and data logging circuits and the hot wire cell, itself. The estimated time of completion of this phase is twelve months. Currently, all of the components have been designed and constructed. These include the hot wire cell, precision temperature bath, pressure vessel, precision temperature and pressure measuring systems, electrical bridges and amplifiers, computerized data acquisition system and controlled environment for housing the equipment. A brief

description of the above devices, along with some photographs, are presented.

Preliminary measurements of the thermal conductivity of toluene at ambient condition, presented on Page 18, provide evidence which supports the theoretical basis for this study.

During the remaining period of Phase I, efforts will be directed towards the following tasks:

- A. Interfacing the system with the CSM main computer (DEC System 1091) for rapid real-time data transformation and analysis.
- B. Calibrating the hot wire cell with a platinum Resistance Thermometer with calibration traceable to the National Bureau of Standards.
- C. Investigating and minimizing random and systematic errors in electronic circuitry and measuring devices, estimating the overall error resulting from non-idealities in the physical system based on the mathematical model which is used for data analysis.

A renewal grant for the second year of the project has been requested and this second year will cover Phases II and III. During Phase II (anticipated to be four months in duration) liquid toluene will be extensively tested and the obtained values of thermal conductivity, over a wide temperature range, will be compared with Mani's (1971) data as an adequate confirmation of the apparatus. Any redesign or adjustments necessary to achieve agreement with Mani's results will be made during Phase II.

During Phase III, the thermal conductivities of two well-characterized synthetic oils (An SRC I naphtha and a Western Kentucky No. 11 distillate) will be studied.

The thermal conductivity determinations will be made over the temperature range of 100 to 500°F while the pressure range will be from 1 to 100 atmospheres.

IV. EXPERIMENTAL APPARATUS

A. Hot Wire Cell

The cell consists of two ceramic plates which are held parallel to each other by three adjustable stainless steel support rods as shown in Figure 1. At the center of each plate is a precision machined hole which houses a platinum cylinder. The platinum cylinder at the top is fixed while the one at the bottom is allowed to move vertically through the hole to compensate for thermal expansion. The hot wire is connected to these platinum cylinders at both ends using platinum taper pins and is suspended from the top plate. The average diameter of the wire is 1/2 mil. and its length can be adjusted from 13 to 15 cm. The support rods allow adjustments of the upper plate to ensure that the wire is in a vertical position.

The dimensions of the cell and wire were selected by simulating the experiment for various liquids and gases in order to minimize the differences between the real cell and the mathematical model used to determine the thermal conductivity. The materials used in construction are corrosion resistant to allow a wide variety of fluids to be tested. All of the cell components are stable over the range of interest.

The completed cell is shown in Plate 1. This cell has been tested to 500°F and is performing well. The wire tensioning mechanism adjusts for expansions of the wire and support rods at high temperatures. The platinum pins allow a broken cell wire to be quickly replaced and are,

HOT WIRE CELL THERMAL CONDUCTIVITY INSTRUMENT

FIGURE 1: HOT WIRE CELL

in addition, reusable. It does not appear that the delicate nature of the fine platinum wire will present problems with this cell.

PLATE 1
HOT WIRE CELL

B. Pressure Controlled Environment

The cell pressure system layout is shown in Figure 2. The system has been designed and constructed to operate to 200 atmospheres.

The pressure system is protected with a rupture disk assembly.

The pressure vessel is a 1 liter stainless steel flanged vessel designed for 350 atmospheres at 300°C. The vessel has a support ring on which the hot wire cell rests. Two high pressure electrical leads are mounted through the vessel lid. All valves, fittings, and tubing utilized in the pressure system are stainless steel.

All valves and gauges, as well as the electrical control components for the temperature bath, are mounted on a 1/8 inch thick aluminum control panel which is shown in Plate 2. This panel also functions to protect operating personnel in case of an accident. The micro-computer and related electronics will be mounted on this control panel when interfacing with the school's central computer is completed.

A vacuum system is provided for degassing liquid samples to minimize the effects of dissolved gases on the thermal conductivity measurements and to reduce the chance of oxidation of the liquid samples. The tubing throughout most of the pressure system is 1/4 inch to facilitate the handling of viscous liquids. Smaller diameter 1/8 inch tubing is used from the in-line trap to the gauges since liquids will not be permitted in the gauges. Two Heise gauges, for precise pressure measurements, are used. The ranges of pressure measurements are 1 to 34 atmospheres for the low pressure gauge and 1 to 200 atmospheres for the high pressure gauge, resulting in the maximum sensitivity in pressure measurements over the desired range. The pressure and vacuum systems are vented outside the building for safety.

TUBING LAYOUT THERMAL CONDUCTIVITY INSTRUMENT

FIGURE 2: TUBING LAYOUT

PLATE 2
INSTRUMENT PANEL

The pressure system has been pressure tested to 200 atmospheres with nitrogen. Liquids and gases have been piped through the cell pressure vessel. The system functions well and no major problems are anticipated.

C. Temperature Controlled Environment

The temperature controlled bath consists of a double-walled vessel with 4 inches of fiberglass insulation between the inner and outer walls. This bath is shown in Plate 3. The bath fluid is well mixed to provide a uniform temperature throughout the bath. The outer vessel is vapor sealed. The lids to the temperature bath and the cell pressure vessel are rigidly mounted through 3/4 inch threaded rods to a heavy structural steel frame. To gain access to the bath and pressure vessel, the bath vessels are lowered with a small hand winch attached to the support frame. This design allows tubing and electrical connections to be permanent.

The bath is initially brought to temperature with four 2000 watt electrical heaters. When the operating temperature is reached, three of these heaters are turned off and the fourth heater, which is adjustable, is set to nearly balance heat losses from the bath. The temperature is then controlled with a Bayley Precision Controller which is accurate to $\pm .001^{\circ}\text{C}$ of the set point. The Bayley Controller drives a 250 watt tubular heater. For low temperatures, where heat losses are not sufficient to allow the controller to operate at a reasonable power level, a cooling water coil is provided. This coil also serves to cool the bath quickly from high temperatures.

PLATE 3

OVERALL VIEW OF THE TEMPERATURE
BATH AND THE PRESSURE VESSEL

The bath fluid used is Dowtherm G which is very stable at high temperatures. Since Dowtherm G is flammable, an inert nitrogen blanket is maintained over the bath during operation. The bath fluid expands significantly over the designed temperature range so an overflow vessel is provided to maintain a constant fluid level in the bath. The safe operating temperature of the bath is limited to 500°F since this is near the boiling point of Dowtherm.

The bath has been tested to 500°F. No high temperature related problems were encountered. The temperature control of the bath has been tested at various temperatures by measuring the resistance of the hot wire cell in place in the pressure vessel with a 5-1/2 digit multimeter. A slow drift of the controller set point has been detected. Since the time frame of a typical thermal conductivity measurement is less than 10 seconds, the drift will have no effect. Continued testing is underway to correct the drift problem and to assure that the temperature is constant throughout the bath.

D. Power Supply Arrangement

Electrical power is provided through three 20 amp/110 volt circuits and two 30 amp/220 volt circuits as shown in Figure 3. The 220 volt power is used for the main bath heaters and the room air conditioner. All power going to the bath is shut off with a single switch. For safety, as well as a crude indication of bath temperature, an Omega thermocouple limit switch is used to cut main heater power if the set point is exceeded. The remaining two 110 volt circuits feed the electric room heaters, mixer, vacuum pump mixer, viscous liquid heater and instrument electronics.

ELECTRICAL LAYOUT THERMAL CONDUCTIVITY INSTRUMENT

FIGURE 3: ELECTRICAL LAYOUT

E. Precision Temperature and Pressure Measurement

The temperature of the bath and test fluid is measured with a Leeds and Northrup platinum resistance thermometer. The thermometer is nulled with a matching Mueller Bridge and null detector combination. Both the Mueller Bridge and platinum resistance thermometer are furnished with a report of calibration traceable to the National Bureau of Standards. This combination allows temperatures to be measured to $.002^{\circ}\text{C}$ accuracy over a range of -183°C to 650°C . The Mueller Bridge is currently 8 months overdue but should be available for cell wire calibration in early February. The platinum resistance thermometer and null detector have been received.

The pressure of the test fluids is measured with two Heise gauges. The gauges will be calibrated against a dead weight tester before thermal conductivity data are collected. The low range gauge measures from 1 to 34 atmospheres within 0.034 atmospheres. The high range gauge measures from 1 to 200 atmospheres to within 0.204 atmospheres.

V. COMPUTER CONTROL AND DATA ACQUISITION

A. Control

The OPAMP unbalanced bridge in the lower central part of Figure 4 shows the circuit used both to provide known power to the hot wire and simultaneously to measure the change in resistance of the wire. The voltage $v_i(t)$ is a staircase voltage which increases as the square root of time. By balancing the bridge before the staircase is applied, the power dissipated in the cell becomes independent of hot wire resistance to first order, and for resistance changes limited to 1% the power will increase linearly in time within 0.0025%.

FIGURE 4: ELECTRONIC CIRCUITRY

The OPAMP bridge has twice the sensitivity of a conventional bridge and does not require either source or detector to be floating. Effects of offset voltage are the same as they would be with an ordinary bridge followed by the OPAMP.

The bridge OPAMP is a DATEL AM-490-2 unit, which has very high gain and very low offset-voltage temperature drift and noise. The time constants at the non-inverting and inverting inputs were adjusted to be equal in order to produce a flat bridge frequency response and, thus, eliminate transients resulting from the steps of the staircase.

The staircase $v_i(t)$ is produced by KEPCO Operational Power Supply OPS15-1.5B and Digital Programmer SN500-121. The AIM65 microcomputer updates the digital input to the Programmer periodically. Response time of the programmer-power supply system is well within a millisecond. A filter system to smooth the staircase output has not yet been designed.

Computer control is accomplished by a program written in machine-language, which allows rapid response. On-board AIM65 timers provide quartz crystal accuracy of the experiment timing. The computer generates 16-bit accurate square roots and rounds them for the 12-bit input of the programmer. Square roots are loaded into a table before the experiment is begun and do not need to be calculated while the experiment is in progress. This easily allows steps to be as short as one millisecond. The control part of the program provides for the experimenter to apply a constant voltage $v_i(t)$ to the bridge for a short time of order of milliseconds and to read the bridge output $v_o(t)$; in this way, the bridge can be balanced in the absence of contaminating thermal effects.

B. Data Acquisition

Output $v_o(t)$ from the bridge is amplified by the other DATEL AM-490-A OPAMP, which is configured as a precision gain-of-100 preamplifier. High-frequency response of this circuit is purposely destroyed to reduce noise in the signal. The time constant is chosen to be 0.25 millisecond, which allows response to one millisecond steps.

The Analog Devices ADC 1130 Analog-to-Digital Converter digitizes the amplified bridge output. This A/D is a 14 bit device which has a conversion time of 25 microseconds. Because the AIM65 microcomputer has only 16 input/output port pins, it was necessary to provide another R6522 port for control of and data transfer from the A/D. Addresses hexadecimal 9000 - 900F were chosen for the port because they were especially easy to decode from signals present on the AIM65 board.

Data acquisition is accomplished by another part of the machine-language program. The program reads a square root value from the table and loads it into the latches of the SN 500-121 Programmer. It then reads hot wire resistance-change data from the A/D and stores them in the table address from which it obtained the square root value. Only then does it strobe the Programmer, so that a voltage $v_i(t)$ proportional to the new square root value will be applied to the bridge. Thus, the data is always acquired after the system has had a maximum amount of time for transients to die out. The table, which initially contains the square root values, is gradually converted to a data table as the experiment progresses.

This control and Data Acquisition System works well and, from a preliminary analysis, produces reliable data. Its success has, in fact, pointed to the need for an efficient mechanism to transfer the massive amounts of data produced to the School's central computer. Data analysis, plotting, etc. are much more efficiently done there. A program has been written which allows the AIM65 microcomputer to be a terminal of the central computer. This program is currently being debugged.

An overall view of the micro-computer, digital to analog convertor, power supply and recorder is shown on Plate 4. Plate 5 displays an open view of the bridge circuit, Op-Amps, A/D Convertor and the input port.

VI. CONTROLLED ENVIRONMENT FOR HOUSING THE EQUIPMENT

Many of the electronic components and measuring devices (i.e., Mueller Bridge and Null Detector) are sensitive to the temperature variation at which they are exposed to. In order to minimize any temperature fluctuations, a partitioned housing area was built, as shown on Plate 6. A thermostatically controlled air conditioner and a forced air heater are used for temperature control. Tests have shown a controlled temperature around the apparatus front panel to within $\pm 0.5^{\circ}\text{C}$.

VII. PRELIMINARY RESULTS - A THERMAL CONDUCTIVITY EXPERIMENT USING LIQUID TOLUENE

In order to test the electronic circuitry and the validity of the proposed theory, a ramp power was generated by the micro-computer (i.e., Rockwell AIM65) in digital form and was input to the bridge as an analog staircase function. The platinum wire cell was immersed in a steel container filled with commercial grade toluene. The temperature rise of the wire caused by the ramp perturbation resulted in an imbalance

PLATE 4
OVERALL VIEW OF THE
ELECTRONIC COMPONENTS

PLATE 5
OPEN VIEW OF THE BRIDGE CIRCUIT,
OP-AMPS, A/D CONVERTOR AND INPUT
PORT

PLATE 6
CONTROLLED TEMPERATURE HOUSING

in the bridge. This imbalance was amplified with precision amplifiers and was fed back to the computer where it was stored on magnetic tape. For a typical experiment, 1000 values of voltage imbalance were recorded over a 5 second period. Bridge imbalance values were then converted to temperature rise of the platinum wire.

From the theoretical model of the transient hot wire subjected to a ramp heat input, it is expected that a plot of (temperature/time) vs. $\ln(\text{time})$ would give a straight line with slope proportional to the value of thermal conductivity. Such a plot is presented in Figure 5. Figure 5 shows that the data points appear to form a straight line after an initial short time scatter. The thermal conductivity of toluene at ambient condition, obtained from this data, is 118.7 (mw/m.k.) compared to 129.1 (mw/m.k.) reported by Mani. This agreement is considered to be good, since many approximations are made for arriving at a value of thermal conductivity. These approximations arise from the impurities such as dissolved gases in the toluene, temperature-resistance coefficient of the platinum wire, short time transient response of the bridge circuit, deviation from verticality of the wire, lead resistance and their contribution to the bridge imbalance equation, magnetically induced vibrations, and film resistance at the wire surface caused by the existence of impurities. Other contributions to the error in thermal conductivity measurement arise from the deviation of the ideal source model from the physical system, which are discussed in the following section. All of these potential sources of differences are being thoroughly analyzed.

VIII. ANALYSIS OF APPROXIMATIONS TO THE IDEAL LINE SOURCE MODEL

The ideal line source model only approximates the response of the actual cell. A variety of factors which might effect the temperature response of the wire must be considered. These factors include non-uniform wire radius, finite heat capacity of the wire, the effect of bounded media, knudsen effect, axial conduction, free

Figure 5 : SAMPLE RUN - THERMAL CONDUCTIVITY OF TOLUENE AT AMBIENT

convection, radiation and, finally, truncation errors. Careful design and construction of the cell and its housing, along with controlled fluid condition and correct heat input levels, can minimize or eliminate any contributions from these effects to the apparent thermal conductivity. An extensive study of the nature and contributions of these approximations have been completed. A paper entitled: "Mathematical Modeling and Approximations of a Vertical Transient Hot Wire Subjected to a Time Variant Perturbation for Thermal Conductivity Measurements", is being prepared. Current cell design and experimental plans and parameters are based on the results of a computer simulation which utilizes the theoretical basis of this paper.

IX. ERROR ANALYSIS

Monte Carlo error analysis of the hot wire cell data is currently under way. Sensitivity analysis of the cell modeling equation indicates that the rate of change of power input to the cell wire, the measurement of wire temperature changes, time since start of the experiment and the wire resistance must be carefully measured for an accurate determination of thermal conductivity. This error analysis is continuing in order to determine the accuracy of resulting thermal conductivity measurements based upon the accuracy of the measuring equipment and the method of data analysis.