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Development of a Calorimetric Facility for Measuring Excess Enthalpies at Temperatures of 20 to 80 °C and at Atmospheric Pressure.

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T-3356

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Golden, Colorado

Date 5/26/87

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Golden, Colorado

Date 5/27/87

Dr. A. J. Kidnay
Head of Chemical
Engineering and Petroleum
Refining Department

ABSTRACT

The overall objective of this project is to construct a calorimetric facility capable of measuring excess enthalpies with an error less than 1%.

A calorimetric facility utilizing commercial apparatus (LKB 2277calorimeter and two Isco metering pumps) as key components was built and tested on two systems: benzene-toluene and hexane-cyclohexane. The temperature range of the calorimeter is 20 to 80 °C, and the flow range for each stream is 0 to 20 ml/hr. The thermal output at present is limited to 4200 microwatts, but preliminary measurements indicate that it should be possible to operate the calorimeter outside this range.

After the benzene-toluene measurements were initiated it was discovered that the International Union of Pure and Applied Chemistry (IUPAC) recommends cyclohexane-hexane as the test system for flow calorimeters. Thus, only a limited amount of data were collected for benzene-toluene and the primary emphasis was placed on the cyclohexane-hexane measurements. The benzene-toluene data were compared to a smoothed equation generated from literature data, and our data were found to differ by less than ±2.5% from the equation. The primary data, cyclohexane-hexane, reproduced the IUPAC recommended equation with an error of

approximately ±1%. No flow rate dependence was found in the measurements.

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ACKNOWLEDGMENTS

I would like to thank the National Bureau of Standards and the State of Colorado for their funding support. I would also like to thank the Camille and Henry Dreyfus Foundation for the generous donation that allowed the purchase of the LKB calorimeter. Of course, I would like to thank Dr. A. J. Kidnay for his support and valuable guidance throughout this project. Finally, I would like to thank Dr. Richard Perkins for his invaluable assistance when the calorimeter malfunctioned at the start up of this project.

INTRODUCTION

Excess enthalpies or heats of mixing are important in completing energy balances that are used in designing process equipment. Excess enthalpy is the difference between the enthalpy of the actual solution and an ideal solution at the same temperature, pressure, and composition.

Heat of mixing has several features that it make it an interesting topic to study; heat of mixing represents the amount of non-ideality in a mixture, heat of mixing is used to correct different sets of enthalpy data to a common reference point, and heat of mixing can be used to determine if hydrogen bonding is present in a mixture.

The objective of this project is to build a calorimetric facility capable of measuring excess enthalpies with an error less than 1%.

The excess enthalpy was measured on two systems; benzene-toluene, and cyclohexane-hexane at 298.15 K and approximately 620 mm Hg. It was determined that the calorimetric facility is capable of measuring excess enthalpy data at 20 to 80 °C and pressures up to 2 atmospheres to within ±1%.

CALORIMETRIC FACILITY

This section is divided into three parts; the first discusses the process flow, the second the calorimeter operation, and the third the principles of heat flow measurement used by the LKB calorimeter.

A. Process Flow

The calorimetric facility was designed to minimize the amount of volume that exists between the pumps and the calorimeter. This was necessary for two reasons. First, the small volume minimizes temperature changes that would affect the flow rate and the stability of the calorimeter. Second, some of the liquids that will be used in the future are relatively expensive and hard to obtain in high purities and large quantities.

Figure 1.0 shows the equipment as it appears in the laboratory and Figure 2.0 is the process flow diagram. A detailed discussion of the calorimetric facility and an equipment list is in Appendix E.

The measurment begins with the pumping of the fluid using two ISCO LC-5000 precision metering pumps. These pumps have ranges of 0 to 400 ml/hr and 0 to 3700 psig. They are syringe pumps, and hence provide a pulse-free flow rate.

The fluid leaves the pumps and enters the filters,

Calorimetric Facility

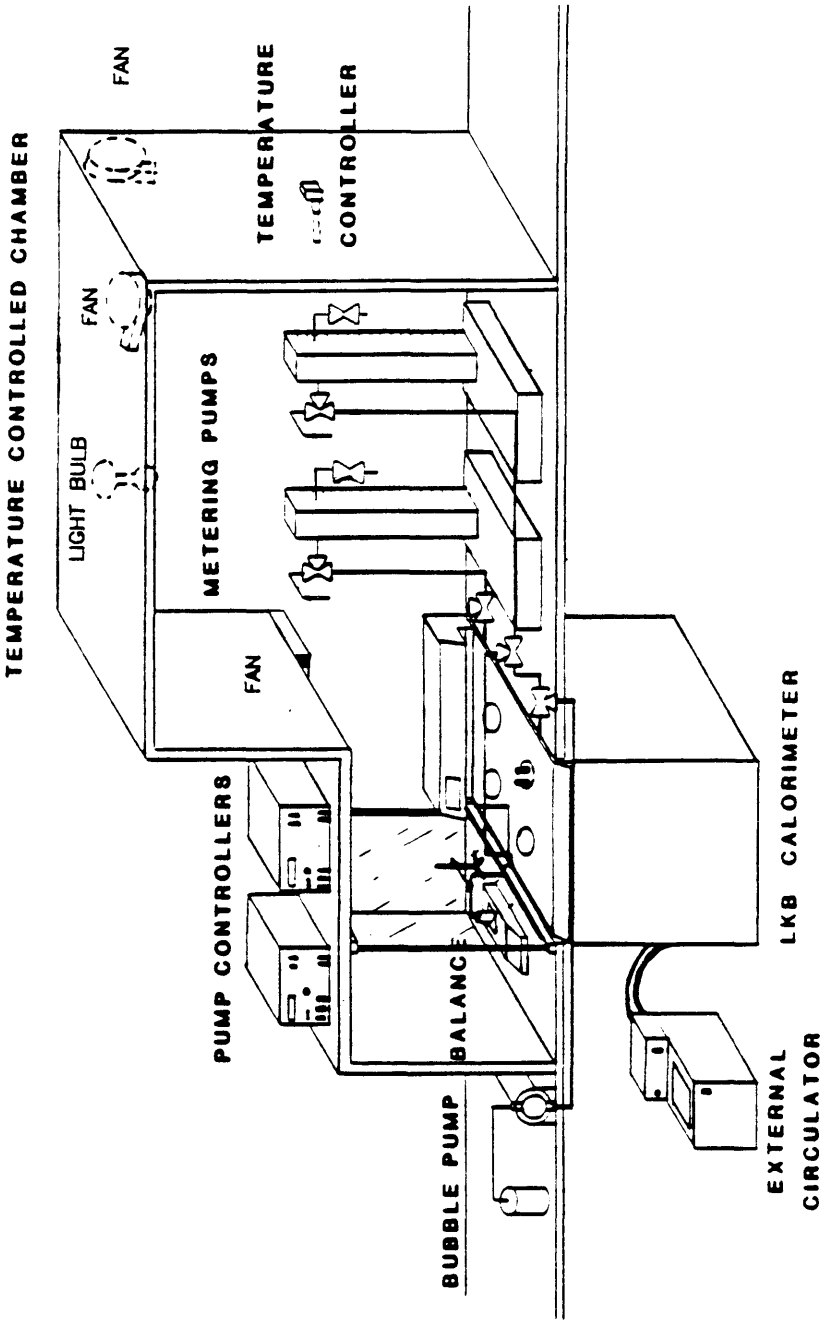

Figure 1.0

Process Flow Diagram

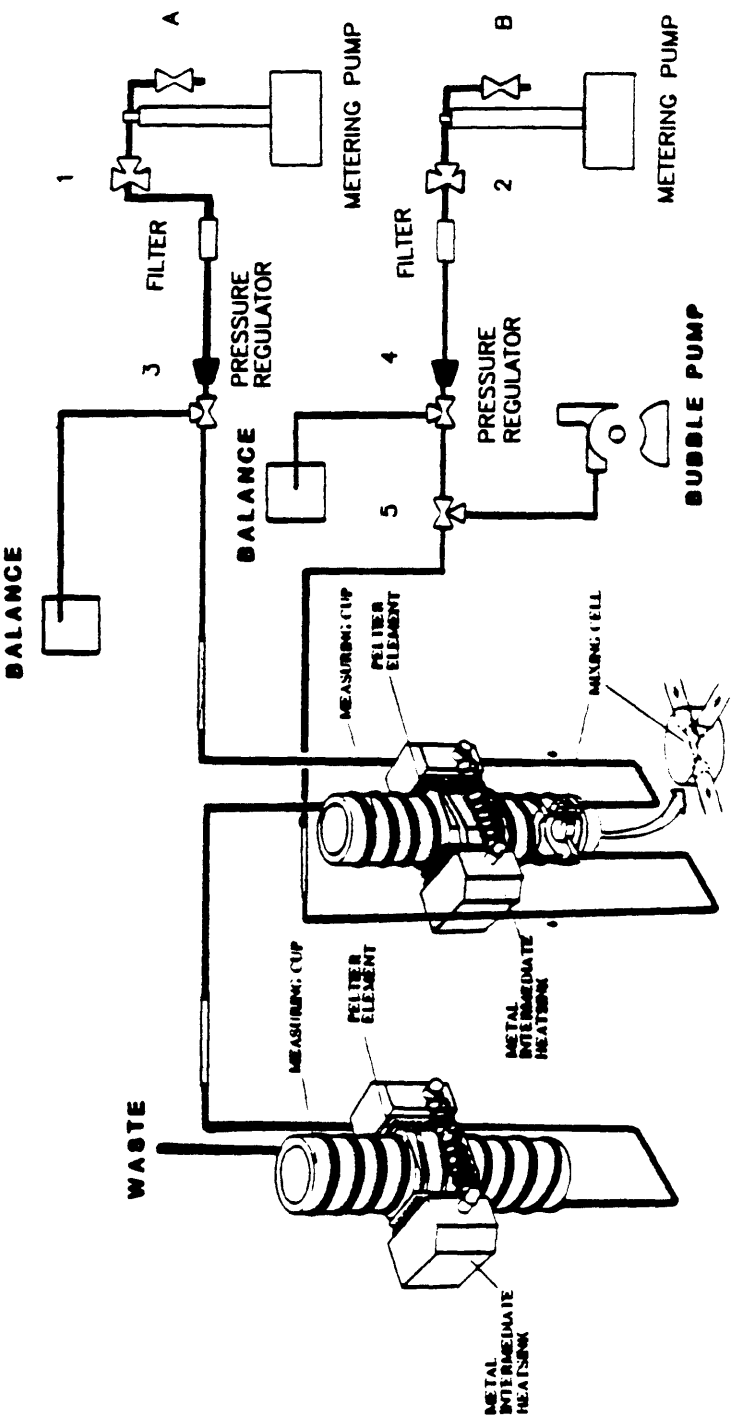

Figure 2.0

which remove any particles that could plug the 0.004 inch I.D. stainless steel tubing. After leaving the filter, the fluid enters a back pressure regulator which maintains 100 psig of back pressure on the pumps. This pressure is required so that the cylinder seals will seal properly. The pressure also helps stabilize the gears in the pumps thereby increasing the flow rate stability.

From the back pressure regulator the fluid can travel to the calorimeter or to the balance that measures the mass flow rate for each stream. The mass flow measurement technique is further discussed in Appendix H.

If the fluids flow to the calorimeter, both streams enter the measuring cell on the sample side as shown in Figure 2.0. The measuring cell is completely submerged in the calorimeter water bath, as shown in Figure 3.0. The fluids enter the measuring cell's gold tubing, which is in contact with the bath. The fluids then equilibrate to the bath temperature, meet at the bottom of the sample side measuring cup, and mix in a mixing tee. From the tee, the combined streams enter the measuring area where the heat of mixing flows to the thermoelectric detector (pel'tier element), then to the intermediate heat sink, and finally to the water bath. After leaving the measuring area, the stream exits the sample side of the cell and can go either

LKB 2277 Calorimeter

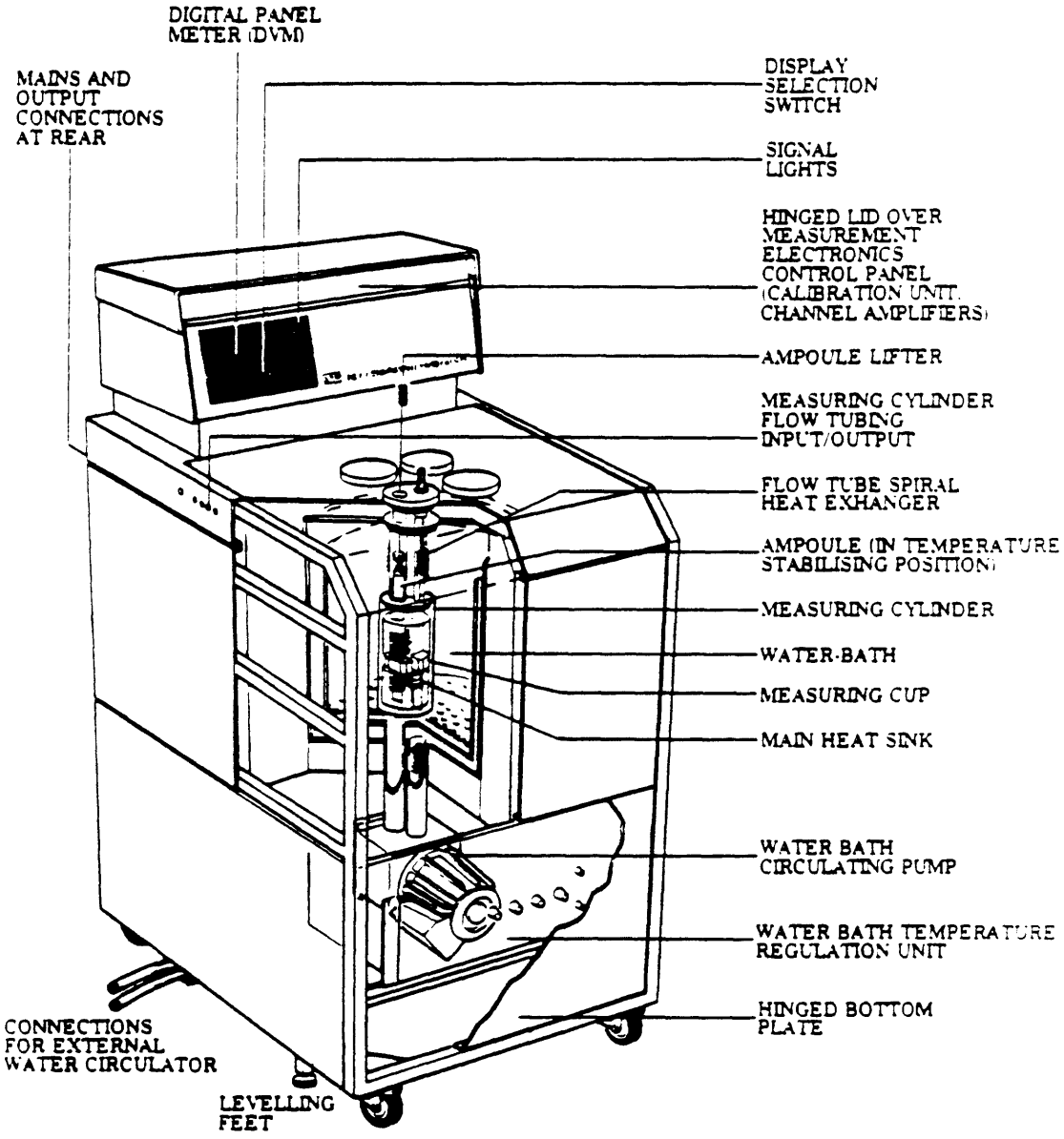

Figure 3.0

to waste or to the reference side of the cell. If the stream flows to the reference side, it follows the same path as previously mentioned. The purpose of sending the combined stream down the reference side is to subtract out all viscous heat effects and to stabilize the output, since the reference side will see all of the changes that the sample side will see except for the mixing effects. From the reference side the combined stream leaves to waste.

The top of the calorimeter, the pumps, and the balance are completely enclosed in a temperature controlled box, as shown in Figure 1.0. Temperature control is necessary to maintain a constant mass flow rate from the pumps, and to insure that the temperature never exceeds the 32 °C maximum operating temperature of the calorimeter's electronics. The balance used to measure the mass flow rate of the fluids is located to the left of the calorimeter, in a separate compartment completely isolated from the rest of the box so that no air currents will affect the balance readings. The box temperature is controlled by a Thermo-Regulator, a simple mechanical controller. The controller is connected to a 100 watt light bulb which acts as the heat source. The air is distributed and mixed by three fans carefully located in the box . One fan blows directly across the light bulb onto another fan, which, in turn, blows directly onto the

sensor, making the temperature response very fast. The temperature control is better than ±0.2 °C. The third fan helps distribute the air over the base of the calorimeter.

A third pump is located outside and to the left of the calorimeter box. This pump is used to remove bubbles and purge the system's contents (for complete details on bubble removal see Appendix G). This pump is not inside the box because precise temperature control is not necessary.

The entire lab is temperature controlled by an air conditioner and heater which maintains the temperature within 3°C over an eight hour period. Temperature control of the room is needed for two reasons. First, the electronics on the calorimeter are precision electronics and temperature fluctuation causes inconsistent performance. Second, the external water circulator can only control at a set rate, and thus large fast temperature fluctuations in the room may cause instability in the calorimeter bath temperature. The room temperature is usually kept between 19 and 22 °C.

B. Calorimeter Operation

The calorimetric facility is fairly easy to operate. Once the two fluids are completely degassed they are loaded into the pumps (this procedure is discussed in detail in Appendix F). Care must be taken in loading the fluids so

that no gas is left in the pumps, since bubbles in the fluid can cause unstable calorimeter output and poor results. Bubbles are a problem for two reasons; first, they cause partial blockage of the tubing, thus changing the flow rate, and second, perhaps most significant, is the heat effect due to vaporization and condensation inside a bubble.

The measuring cell is then completely rinsed with one of the two liquids, and a maximum flow rate is set. The calorimeter is then calibrated using the calibration heaters and adjustable amplifiers such that the reading on the calorimeter display is the same as the heater input.

The calorimeter is now ready to measure the excess enthalpy of the two fluids. The flow rate of each fluid is adjusted to give the desired mole fraction of the resulting stream. The flow rates can not exceed the rate at which all of the heat is dissipated through the thermoelectric detectors. Determining if the maximum flow has been exceeded can be done by keeping the same mole fraction, and checking to see if the excess enthalpy remains the same. Once a stable calorimeter output has been obtained the output is read from the display every two minutes for one hour, and then averaged.

Next, the fluids flow to a balance and into a flask designed to prevent evaporation of the liquids by placing a

layer of non-voaltile compound on top of the process fluids. The mass flow rates are measured approximately every three minutes for one hour, and then averaged. Mass flow rate measurements for each run are superior to pump calibrations since the reproducibility of the pumps over the entire cylinder volume is not good.

The excess enthalpy is then calculated as follows: (1)

$$H^e = \frac{\text{Calorimeter's output (microwatts)} * \frac{1E\text{-}6 \text{ watts}}{\text{microwatt}} * 3600 \frac{\text{sec}}{\text{hr}}}{\text{Flow rate (moles/hr)}}$$

H^e = kj/kmol.

C. Principle of Heat Flow Measurement

The calorimeter is designed to measure very small outputs of thermal energy, and as a result the temperature difference across the thermoelectric detector (Peltier elemtent) is also small, less than 1*E-6 °C. To enhance the accuracy of the measurement and minimize the effects not due to mixing, a differential or twin detector system is used, as shown in Figure 4.0. To eliminate viscous heat effects, if any are present, the combined stream from the sample side is run through the reference side. Therefore, the total power is that of the sample side less the power out of the reference side. This method gives much smoother base lines and better stability in the output than running the fluid

Differential Detector Method

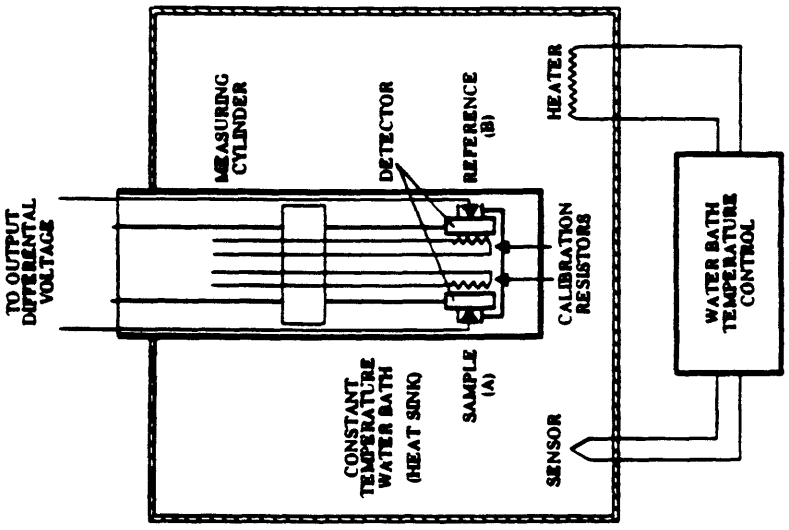

Figure 4.0

Basic Heat Flow Principle

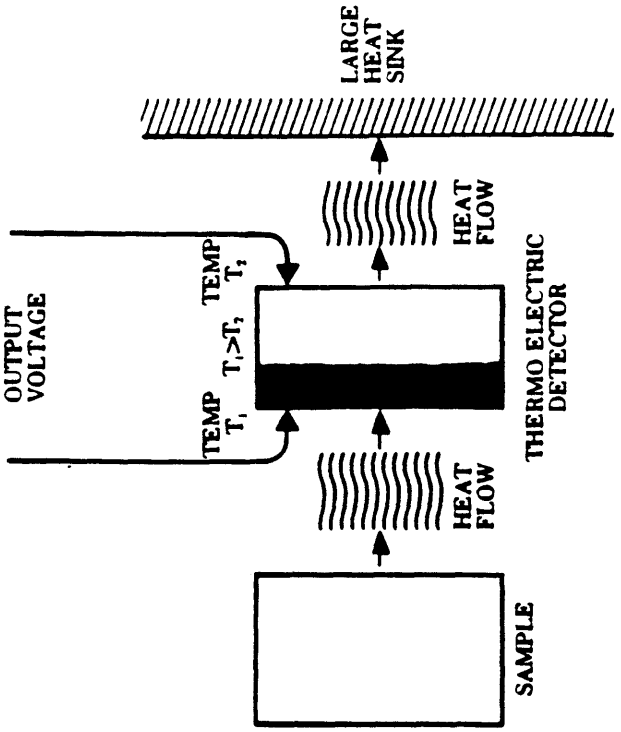

Figure 5.0

through just the sample side, which can also be done.

The measuring cell works as follows. The heat produced by the mixing of two fluids causes the temperature of the resulting fluid stream to change. This heat is transferred to the immediate surroundings, a thermoelectric detector, and is finally removed from the system when it flows into a large heat sink as shown in Figure 5.0. A voltage signal is produced from the thermoelectric detector which is proportional to the heat output from the system. The calorimeter is designed such that endothermic effects are just as reliably measured by the reverse heat flow.

The temperature gradient across the thermoelectric detector should remain very small as the output of the fluids increase past the 4200 microwatt range, since the system is designed for rapid heat transfer. This point however, needs further investigation.

EXPERIMENTAL RESULTS

This section is divided into two parts; the first discusses the heat of mixing results, and the second discusses flow effects on the measurements.

A. Heat of Mixing Results

At the start of this project, we were not aware that IUPAC recommends cyclohexane-hexane as the test system for flow calorimeters. Therefore we selected the benzene-toluene system was selected for study for several reasons. First, it has very low heat effects, making the excess enthalpy very easy to measure. Second, the liquids are readily available in high purities at low cost. Third, the liquids are easy to handle.

The benzene and toluene were both purchased from Aldrich Chemical Company, and had specified purities of 99.9+%. Data were taken over a range of approximately 0.20 to 0.85 mole fraction benzene at a temperature of 298.15 K and atmospheric pressure of approximately 620 mm of mercury. The excess enthalpy results are plotted on several graphs (the data are tabulated in Appendix A). Figure 6.0 is a plot of the measured data by itself. Figure 7.0 is a plot of the measured data along with three sets of literature data, whose authors claim less than 0.5% error (3, 4, 9).

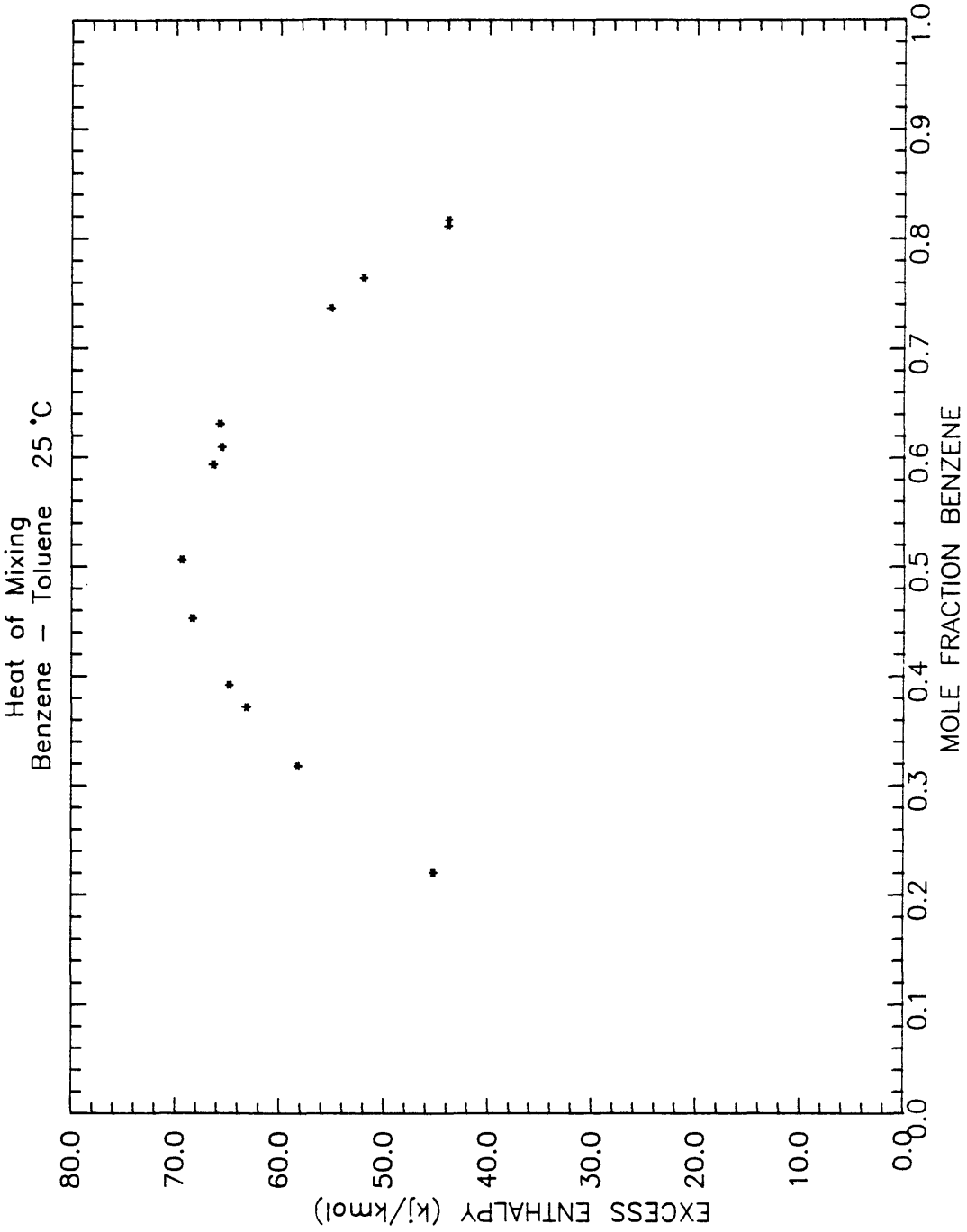
Heat of Mixing
Benzene – Toluene 25 °C
EXCESS ENTHALPY (kJ/kmol)
MOLE FRACTION BENZENE
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Figure 6.0

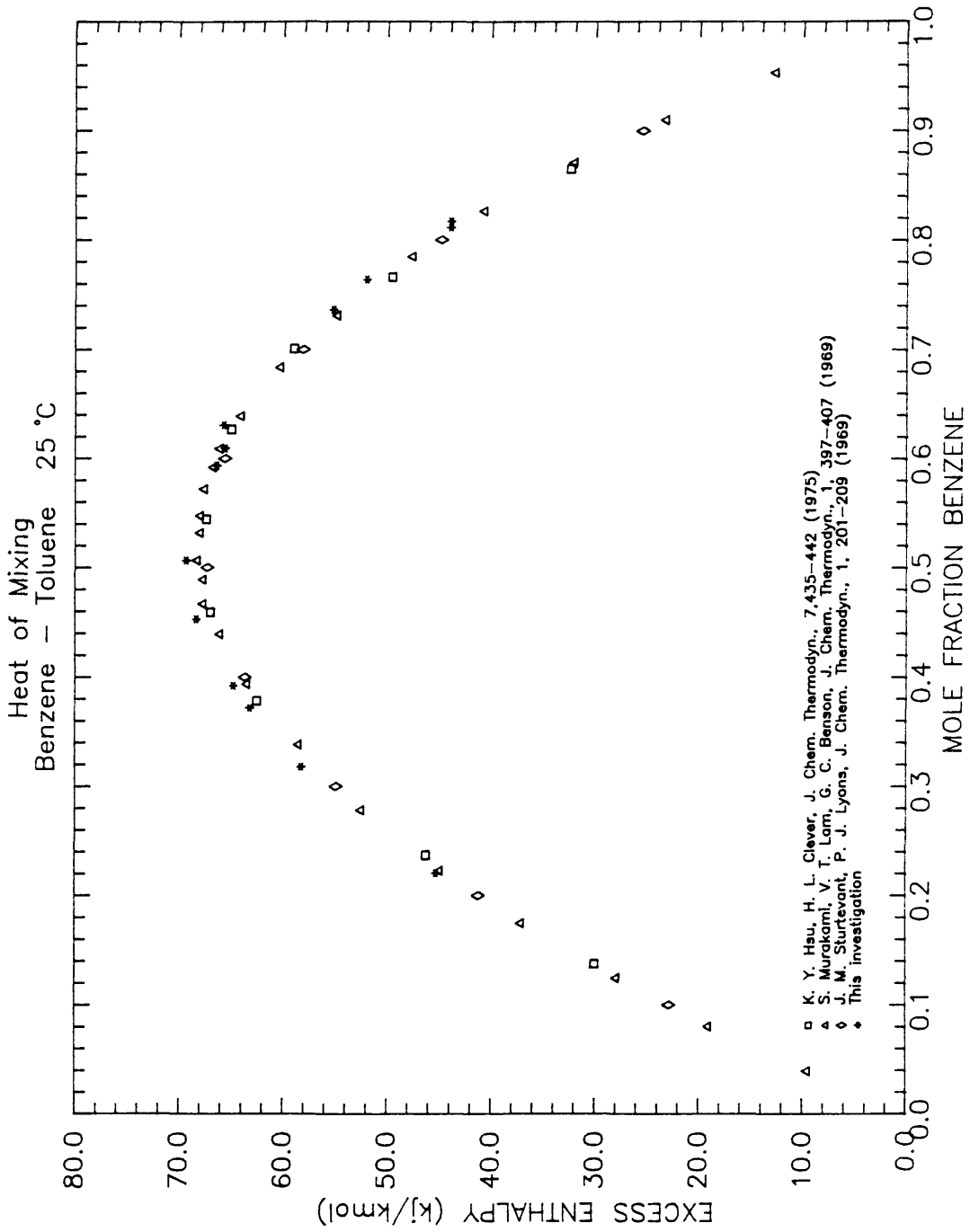
Heat of Mixing
Benzene – Toluene 25 °C
EXCESS ENTHALPY (kJ/kmol)
MOLE FRACTION BENZENE
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
K. Y. Hsu, H. L. Clever, J. Chem. Thermodyn., 7,435–442 (1975)
S. Murakami, V. T. Lam, G. C. Benson, J. Chem. Thermodyn., 1, 397–407 (1969)
J. M. Sturtevant, P. J. Lyons, J. Chem. Thermodyn., 1, 201–209 (1969)
This investigation

Figure 7.0

The data sets compare fairly well, but our results are consistently high.

The three sets of data were smoothed using an equation of the form: (2)

$H^e = X(1 - X)(A + B(1 - 2X) + C(1 - 2X)**2 + D(1 - 2X)**3)$

where X = mole fraction of benzene. The values obtained for the constants are; A = 272, B = -23.7, C = -5.65, and D = 10.1. Figure 8.0 is a plot showing the difference between the values generated by the smoothed equation and our measured values, referred to as residual. The inside and outside curves correspond to 1% and 2% differences, respectively. Almost all of the data fall near the negative 2% curve, suggesting a systematic or calibration error. Figure 9.0 is the same as Figure 8.0, but now all the data sets are shown for comparison. Almost all of the literature data fall within the 1% curve and are randomly scattered. The size of our error in the benzene-toluene data may possibly be attributed to three things. One, the hexadecane (the fluid in the collection flask on top of the benzene and toluene used to alleviate evaporation) is slightly soluble in both benzene and toluene; thus after about 25 to 30 minutes some of the liquid will begin to leak through the hexadecane layer and evaporate. This evaporation will cause the mass flow rate to be low and the excess enthalpy to be

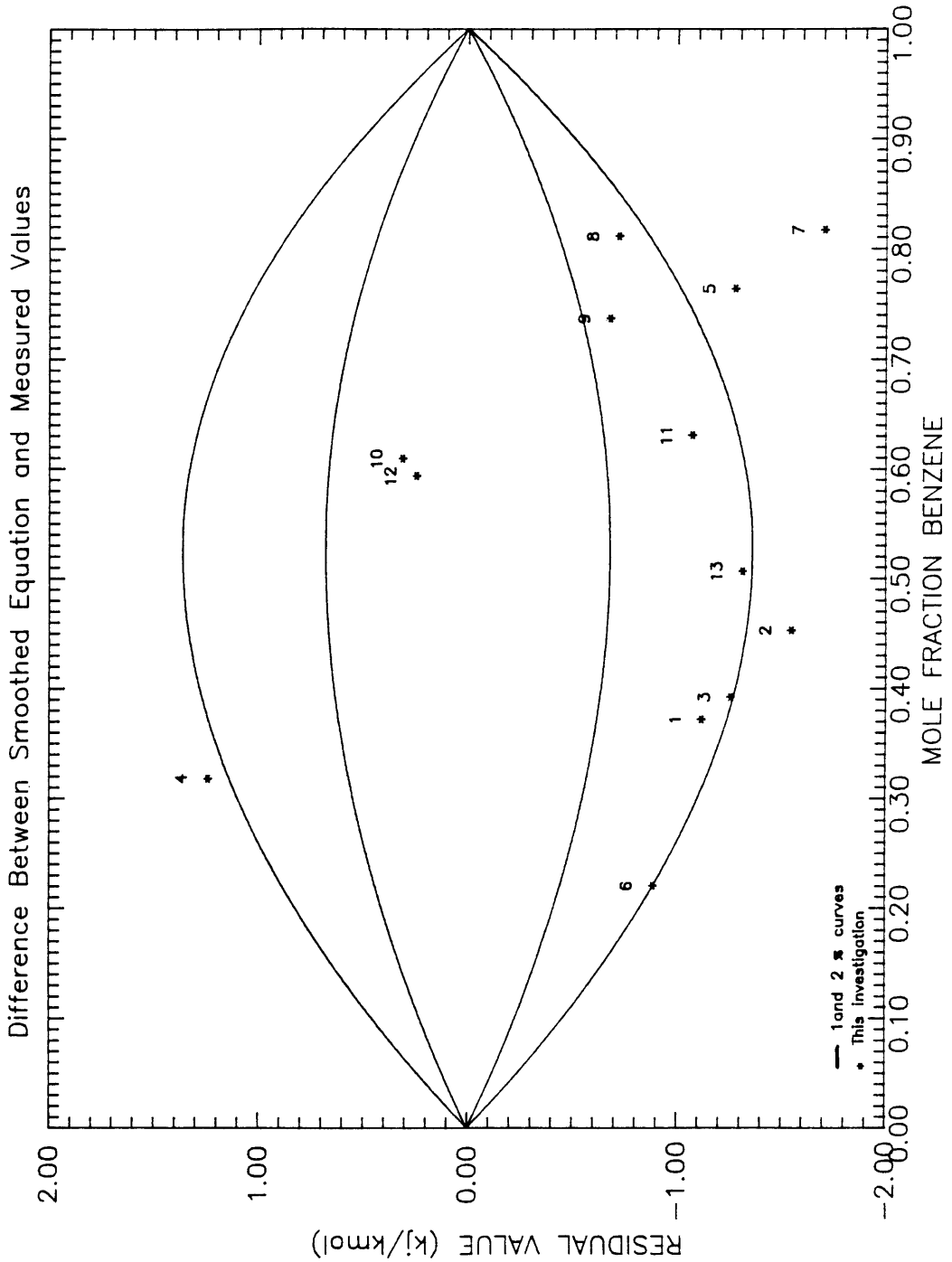
Difference Between Smoothed Equation and Measured Values
RESIDUAL VALUE (kJ/kmol)
2.00
1.00
0.00
−1.00
−2.00
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
MOLE FRACTION BENZENE
1 and 2 % curves
This investigation
1
2
3
4
5
6
7
8
9
10
11
12
13

Figure 8.0

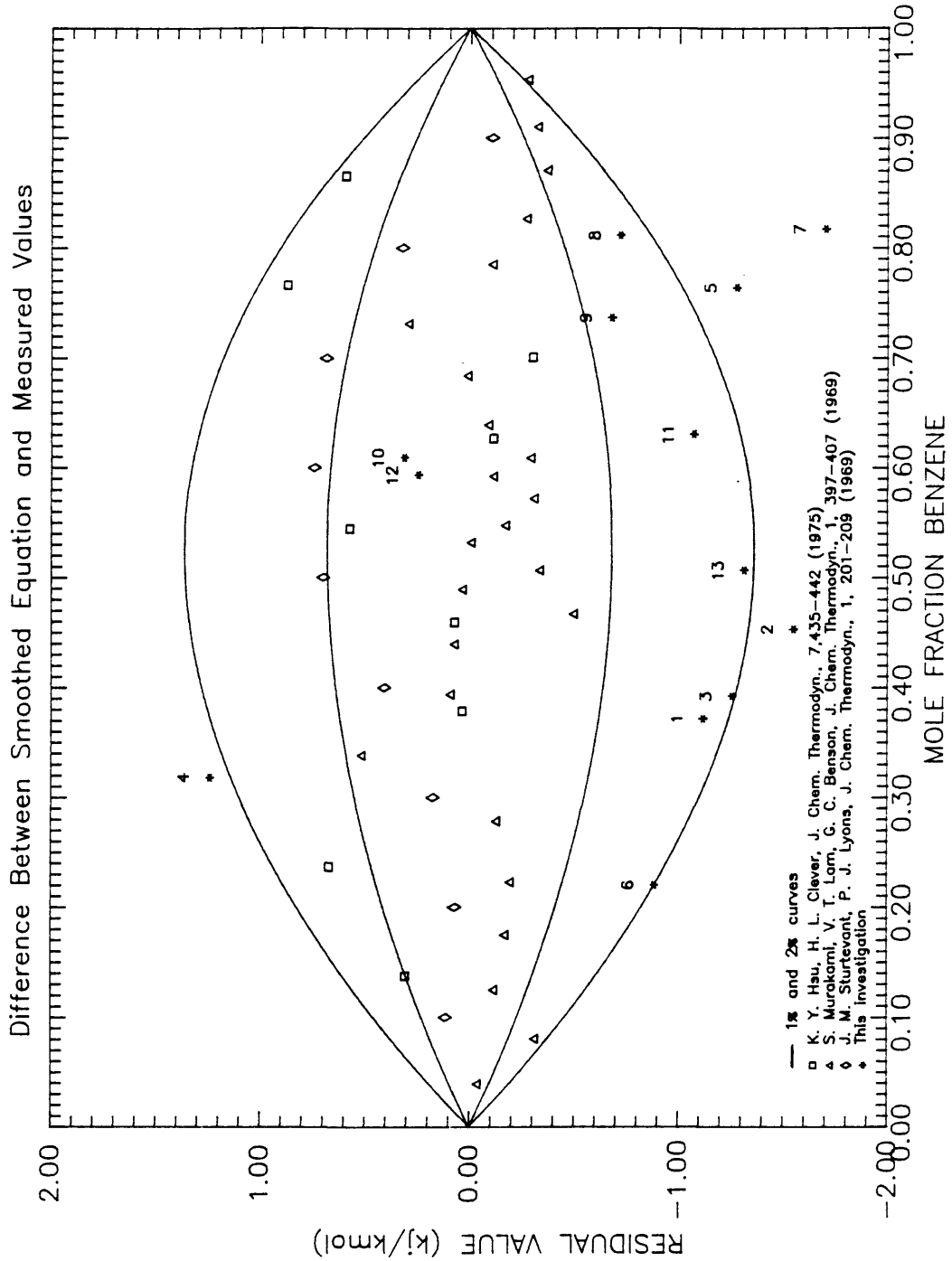
Difference Between Smoothed Equation and Measured Values
RESIDUAL VALUE (kJ/kmol)
MOLE FRACTION BENZENE
2.00
1.00
0.00
−1.00
−2.00
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1% and 2% curves
K. Y. Hsu, H. L. Clever, J. Chem. Thermodyn., 7,435–442 (1975)
S. Murakami, V. T. Lam, G. C. Benson, J. Chem. Thermodyn., 1, 397–407 (1969)
J. M. Sturtevant, P. J. Lyons, J. Chem. Thermodyn., 1, 201–209 (1969)
This investigation

Figure 9.0

high, which is exactly the results obtained. Two, the length of the experiment run was approximately 30 minutes. This time may have been inadequate for averaging the flow rate and calorimeter output, since the error decreased for the cyclohexane-hexane system when the data collection time was doubled. Three, it is possible that there was a systematic error in operating the equipment.

At this stage in the investigation, we learned that IUPAC recommends cyclohexane-hexane as the test system for heat of mixing calorimeters. Therefore, the decision was made to stop work on benzene-toluene and go on to the new system.

The cyclohexane was purchased from Aldrich Chemical Company as HPLC grade, with a specified purity of 99.9+%. The hexane was also purchased from the Aldrich Chemical Company as HPLC grade, with a specified purity of 99.7%. The excess enthalpy data were taken at 298.15 K and an average atmospheric pressure of approximately 620 mm of mercury, and over a range of 0.2 to 0.9 mole fraction cyclohexane. The results are plotted on several graphs (the data are tabulated in Appendix B). Figure 10.0 is a plot of our data only, while Figure 11.0 adds the three sets of data recommended by IUPAC. As one can see, our data follow the shape of the IUPAC recommended data very well, and the

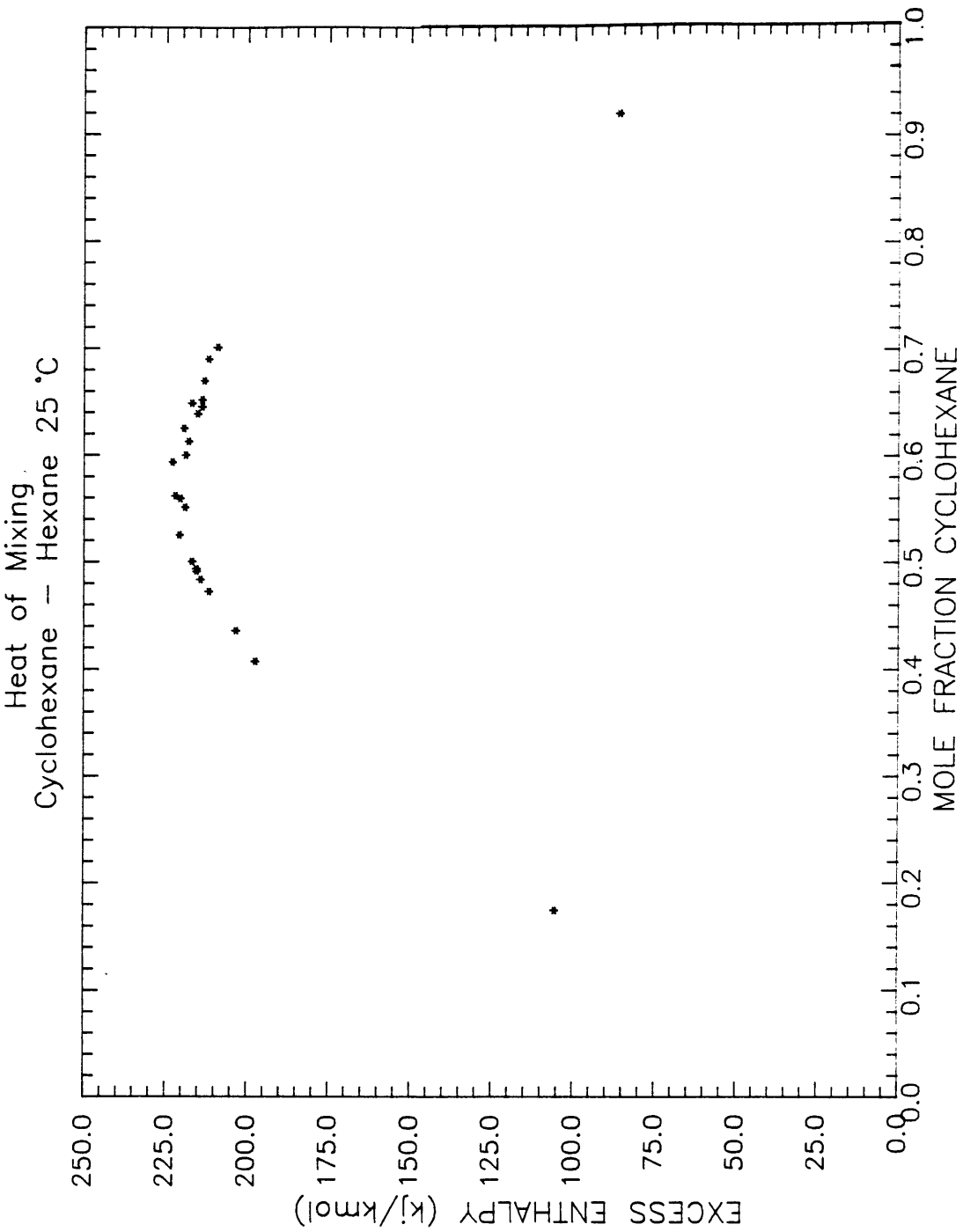
Heat of Mixing
Cyclohexane – Hexane 25 °C
EXCESS ENTHALPY (kJ/kmol)
MOLE FRACTION CYCLOHEXANE
250.0
225.0
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Figure 10.0

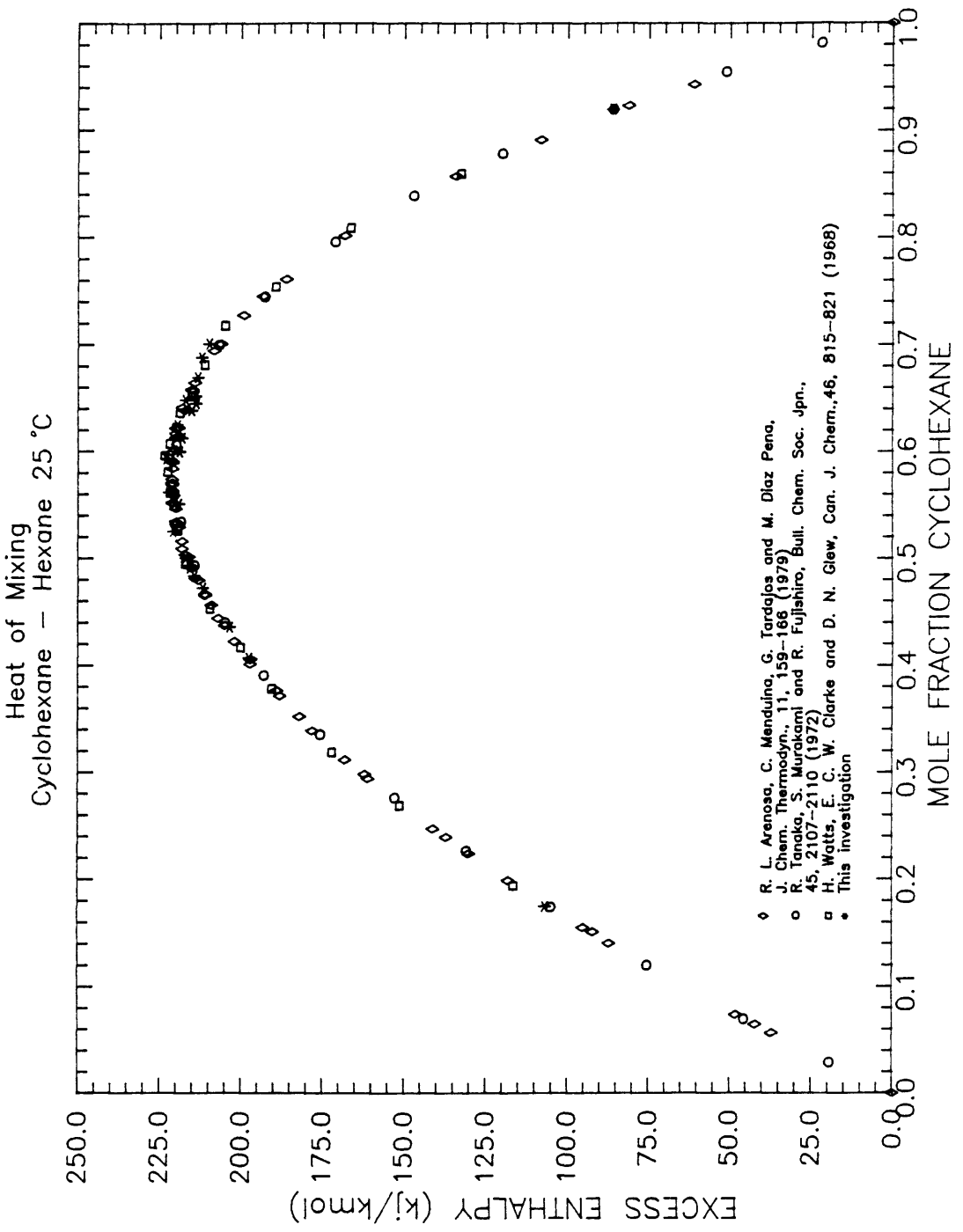
Heat of Mixing
Cyclohexane – Hexane 25 °C
EXCESS ENTHALPY (kJ/kmol)
MOLE FRACTION CYCLOHEXANE
250.0
225.0
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
◇ R. L. Arenosa, C. Mendulina, G. Tardajos and M. Diaz Pena, J. Chem. Thermodyn., 11, 159–166 (1979)
○ R. Tanaka, S. Murakami and R. Fujishiro, Bull. Chem. Soc. Jpn., 45, 2107–2110 (1972)
□ H. Watts, E. C. W. Clarke and D. N. Glew, Can. J. Chem.,46, 815–821 (1968)
• This investigation

Figure 11.0

agreement among all the data sets is good. IUPAC has recommended that all experimental measurements be compared to a smoothed equation of the same form as equation 1, where A = 866.10, B = -249.4, C = 97.0, and D = -31.81. The results of this comparison are plotted in Figures 12.0 and 13.0. Figure 12.0 is a plot of the difference between the smoothed equation and the results of this investigation. Figure 13.0 is the same plot as Figure 12.0, but with the IUPAC recommended data sets added for comparison. The solid curves represent 1% difference between the measured values and the smoothed equation. As one can see, most of our results fall within the 1% curve, with only four points falling outside. The data seem to be randomly scattered and follow no specific trend, suggesting that little or no systematic error is present.

B. Flow Effects

Since the flow rates show the most fluctuation out of all the measured values it is possible that the excess enthalpy might show some flow rate dependence. To check this, the residual is plotted against the cyclohexane, hexane, and total flow rate, in Figures 14.0, 15.0 and 16.0 respectively. Each data point is labeled in the order in which it was measured. All three figures show that the data is scattered randomly and no flow rate dependence exists.

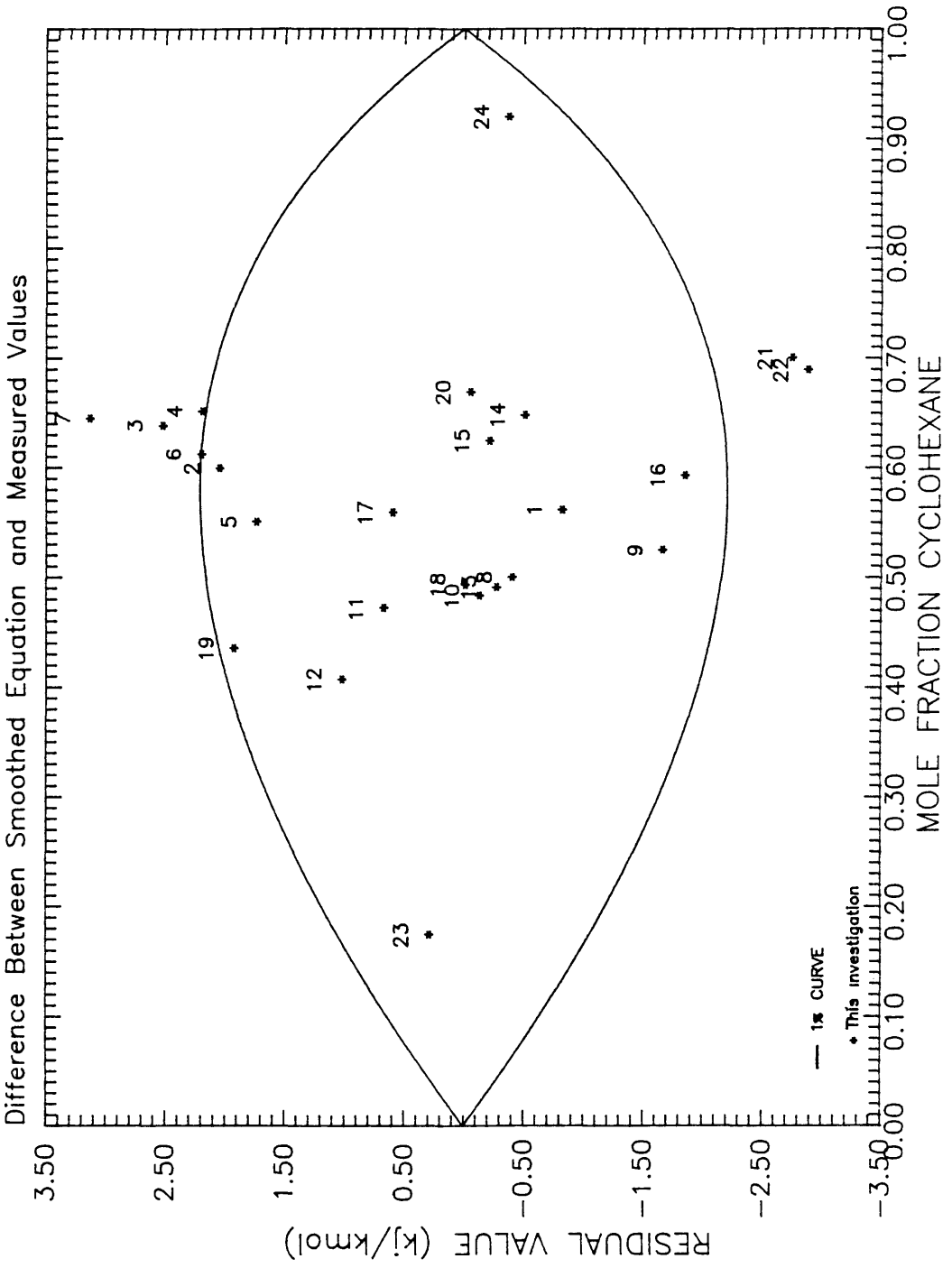
Difference Between Smoothed Equation and Measured Values
RESIDUAL VALUE (kJ/kmol)
MOLE FRACTION CYCLOHEXANE
3.50
2.50
1.50
0.50
-0.50
-1.50
-2.50
-3.50
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1% CURVE
This investigation

Figure 12.0

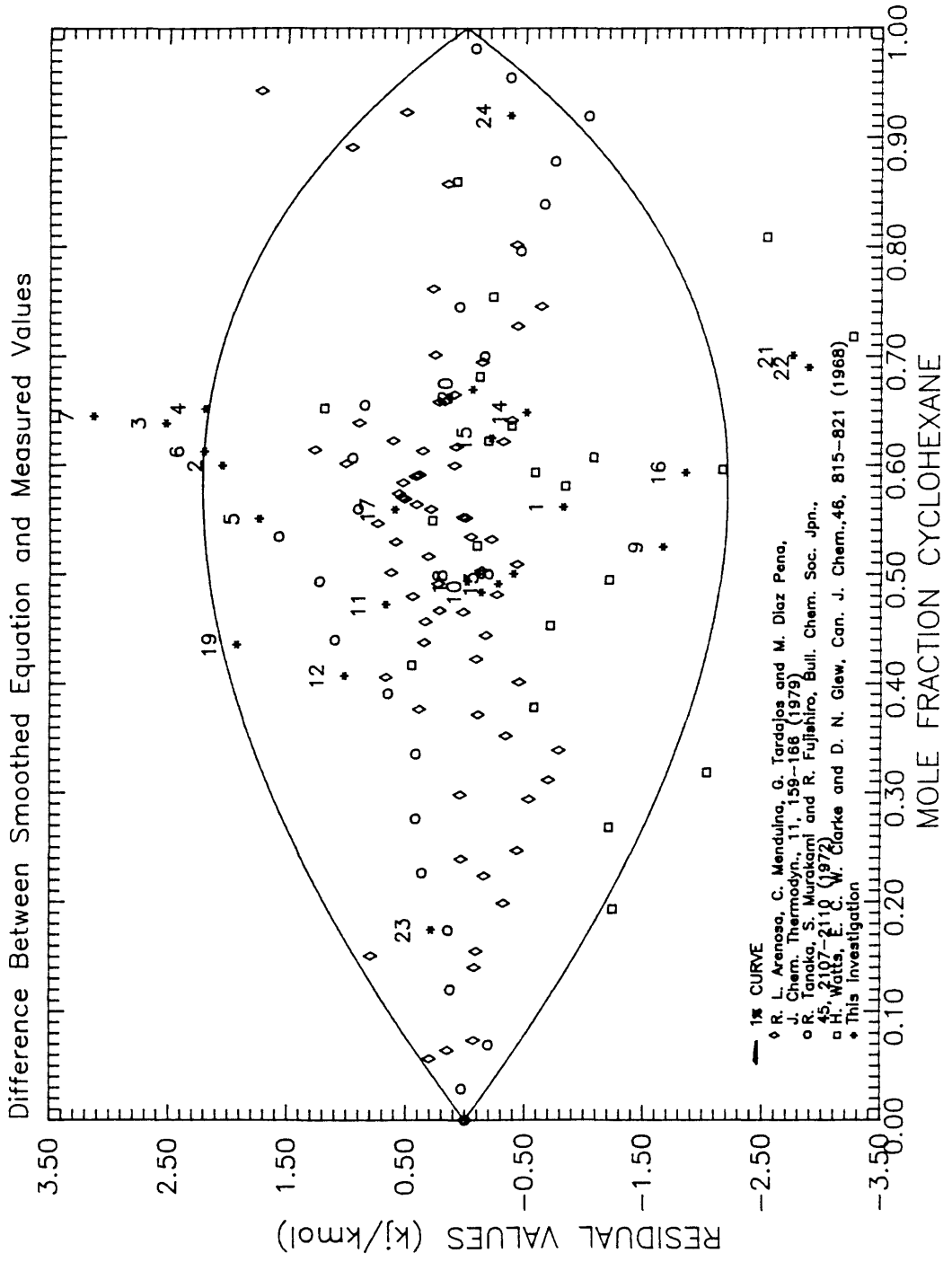
Difference Between Smoothed Equation and Measured Values
RESIDUAL VALUES (kJ/kmol)
MOLE FRACTION CYCLOHEXANE
3.50
2.50
1.50
0.50
−0.50
−1.50
−2.50
−3.50
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1% CURVE
◊ R. L. Arenosa, C. Mendulina, G. Tardajos and M. Diaz Pena, J. Chem. Thermodyn., 11, 159–168 (1979)
○ R. Tanaka, S. Murakami and R. Fujishiro, Bull. Chem. Soc. Jpn., 45, 2107–2110 (1972)
□ H. Watts, E. C. W. Clarke and D. N. Glew, Can. J. Chem.,46, 815–821 (1968)
* This investigation

Figure 13.0

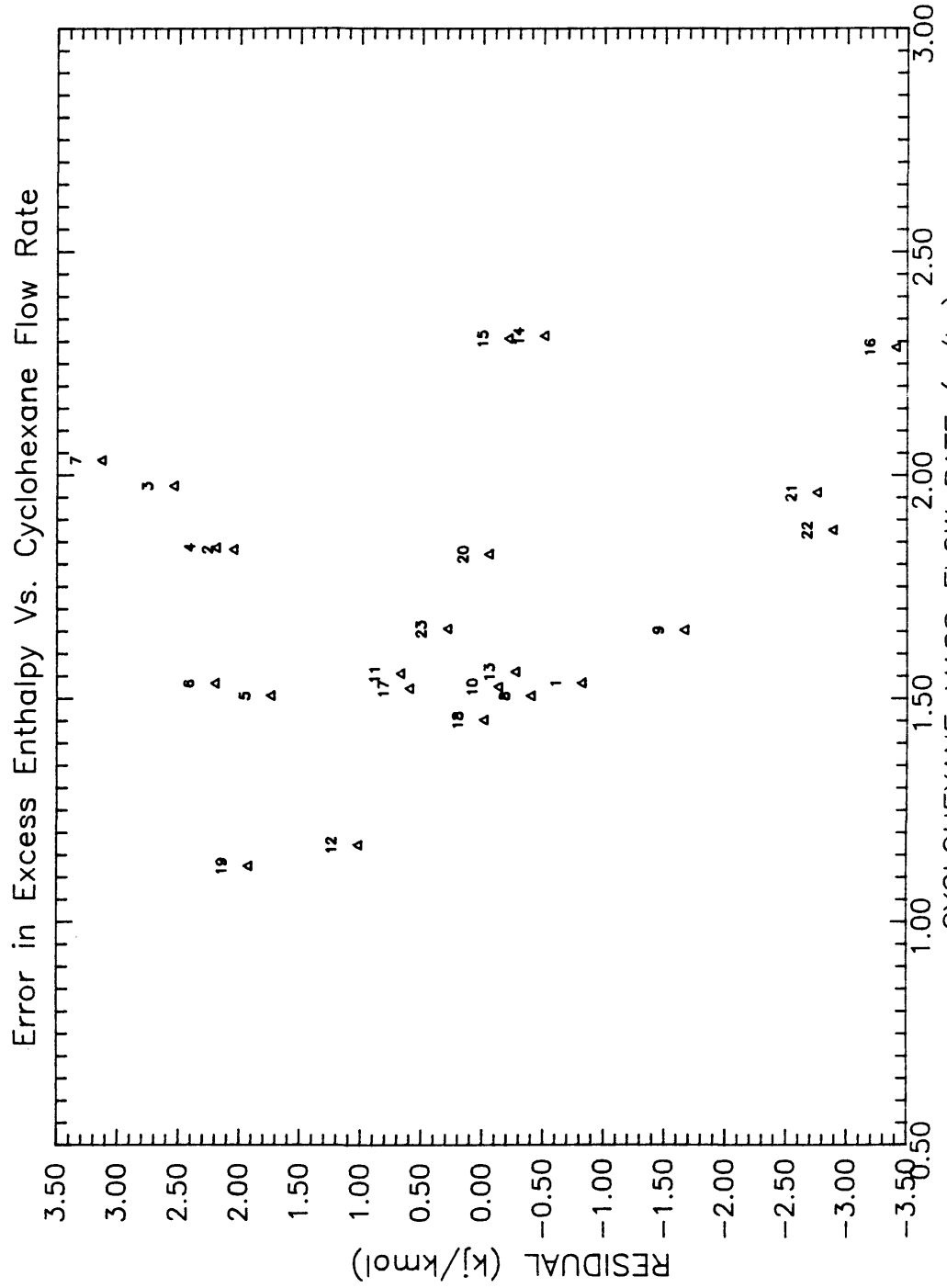
Error in Excess Enthalpy Vs. Cyclohexane Flow Rate
RESIDUAL (kJ/kmol)
CYCLOHEXANE MASS FLOW RATE (g/hr)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
0.50
1.00
1.50
2.00
2.50
3.00

Figure 14.0

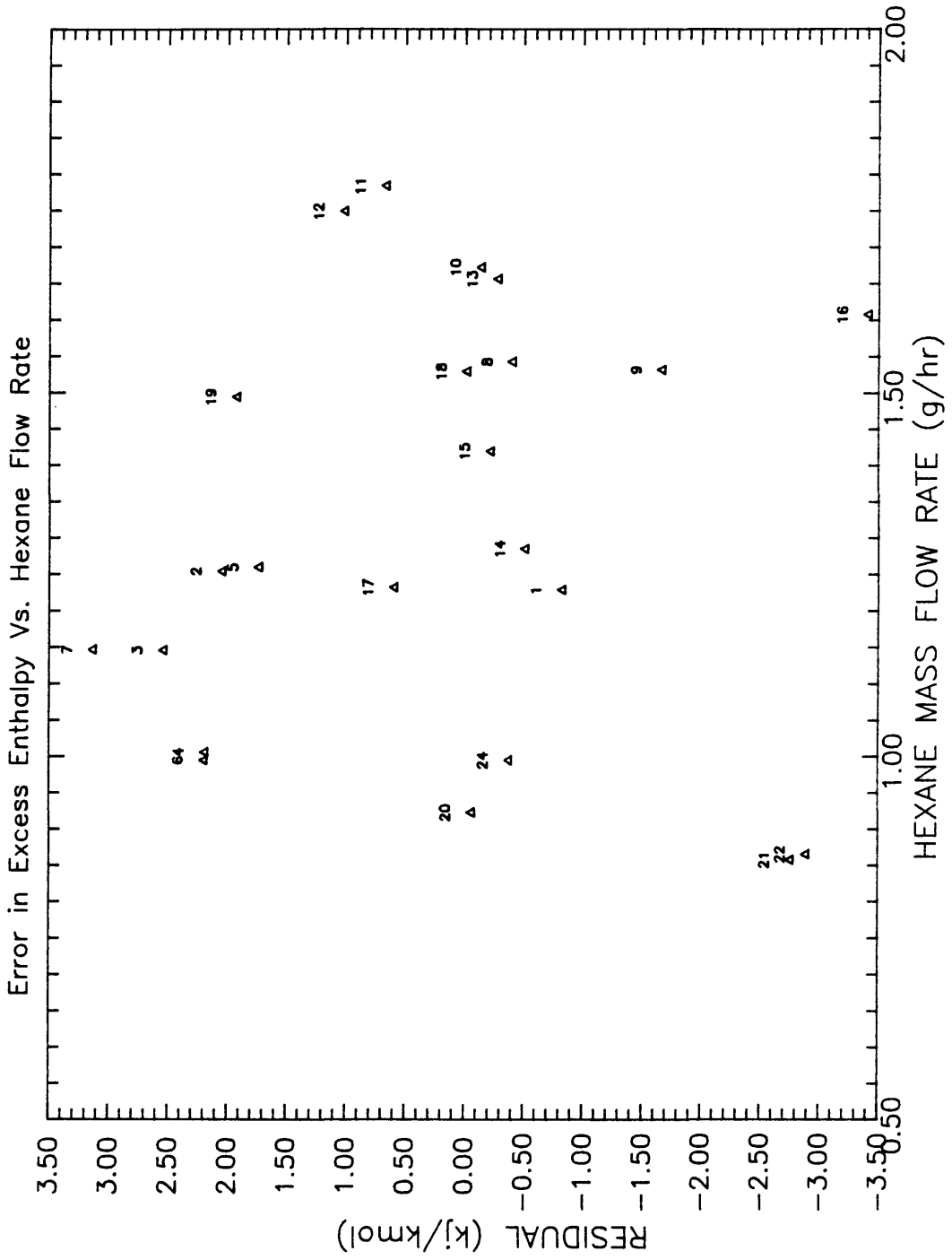
Error in Excess Enthalpy Vs. Hexane Flow Rate
RESIDUAL (kJ/kmol)
HEXANE MASS FLOW RATE (g/hr)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
0.50
1.00
1.50
2.00

Figure 15.0

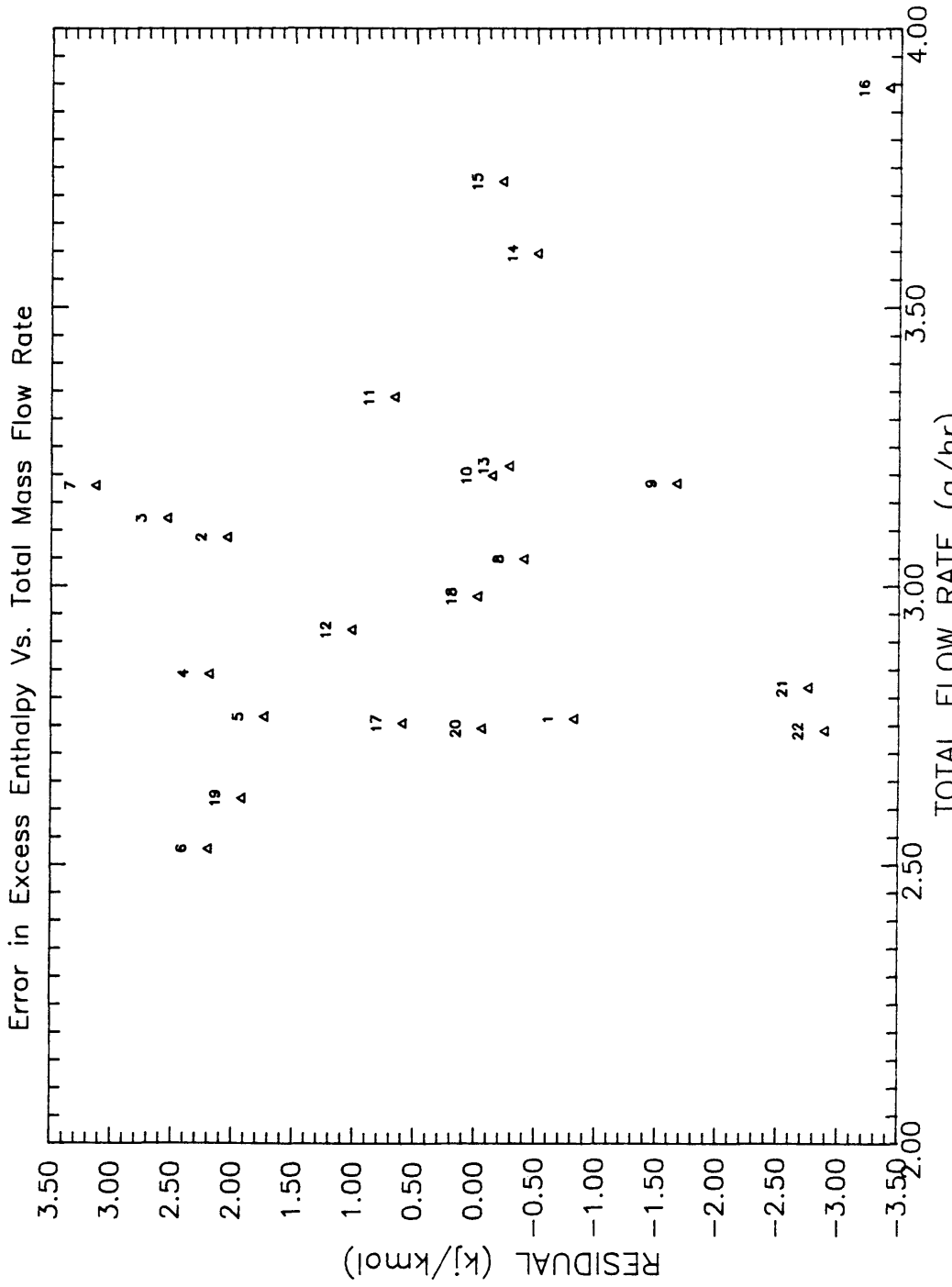
Error in Excess Enthalpy Vs. Total Mass Flow Rate
RESIDUAL (kJ/kmol)
TOTAL FLOW RATE (g/hr)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
2.00
2.50
3.00
3.50
4.00

Figure 16.0

CONCLUSIONS

The calorimetric facility works very well and is capable of reproducing the IUPAC recommended excess enthalpy data for the cyclohexane-hexane system to ±1%. The data seem to be scattered randomly, and show no sign of systematic error. Variations in the pump flow rates are believed to account for almost all of the error in the measured values, since this variable showed the most fluctuation. The temperature of the bath at which the measurements were made was 298.15 K, and was stable over the period of measurement to within 0.001 K. The calorimeter could always be calibrated with an error less than 0.30% using the calibration heaters in the measuring cell, and some of this calibration error may be attributed to unstable pump flow rates. The measured excess enthalpy values have no flow rate dependence.

The calorimetric facility was also capable of reproducing the benzene-toluene system to approximately ±2.5%. This error is high and may be attributed to several problems. Possibly the most significant problem was the lack of experience in operating the equipment, which did not seem to be the case for the cyclohexane-hexane system. Another possibility is that some of the benzene and toluene evaporated while making the mass flow measurements, since

hexadecane (the fluid used on top of benzene and toluene to alleviate evaporation) is slightly soluble in both fluids. Evaporation would cause the total mass flow rate to be low and the excess enthalpy values to be high, which is exactly the case.

It was virtually impossible to obtain data between 0 to 0.2 mole fraction and 0.9 to 1.0 mole fraction for either system, due to the greater instability in the pumps at the lower flow rates, and the fact that the calorimeter was limited to a total flow rate of approximately 14 ml/hr.

RECOMMENDATIONS

To increase the experimental accuracy several changes are suggested.

1. Replace the existing pumps with custom made pumps (the size of the piston should be reduced by at least one-half). The smaller piston would decrease the diameter effect (imperfect machining) of the cylinder wall at the lower flow rates, and would also increase the motor's speed, which will decrease the tendency for the pistons seals to stick to the walls of the cylinder, thus producing less fluctuations in the flow rate. Since the calorimeter can only handle flow rates to 20 ml/hr, the range of the pumps should be 0.00 to 20.00 ml/hr, with emphasis on the lower ranges. They should be able to produce stable and reproducible flow rates with a maximum deviation of 0.5% over the entire volume of the cylinder. The motor should be changed to a stepper motor for increased accuracy. If the Isco motor is used then the tachometer should be mounted directly to the shaft of the motor instead of through gears. This would enable the motor speed to be more accurately determined. At the flow rates of interest any small change in the direction of the pistons head can cause the piston to stick more than normal. It can also cause the flow rate to change by changing the volume in the cylinder. Therefore, the screw gear should be mounted

with two guiding rods to minimize the radial play. The Isco gear design could be used if all of the gears were made more rigid. The main drawback of the Isco pump is that the gears are sloppy and allow fluctuations in the flow rate at low pressures.

2. Improve the flow rate measurement apparatus. Two very accurate balances that weigh to 300 grams with a maximum error of 1 milligram are suggested. Note, theses balances could be eliminated if the pumps had excellent reproducibility.

3. Eliminate the teflon tubing in the calorimetric facility. A problem that often occurred throughout the experiment was penetration of air through the teflon tubing when the system was not in operation. Replacing the wooden face plate on the measuring cell with stainless steel will allow threaded connections to be used so the teflon tubing can be replaced with stainless steel. This feature would also allow the cell to operate at elevated pressures.

4. The entire system should be completely automated to allow more rapid and accurate data collection.

REFERENCES

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APPENDICES

APPENDIX A

Table 1.0
Excess Enthalpy Measurements for Benzene-Toluene

MOLE FRACTION CYCLOHEXANE	TOTAL MOLAR FLOW RATE (mol/hr)	CALORIMETER READING (μWATTS)	EXCESS ENTHALPY (kj/kmol)	RUN #
0.220	0.0784	986.1	45.28	7
0.318	0.0535	866.1	58.26	9
0.372	0.0517	907.6	63.18	12
0.392	0.0601	1082.1	64.83	10
0.453	0.0664	1262.0	68.37	11
0.506	0.0453	873.4	69.38	13
0.593	0.0538	991.9	66.40	1
0.609	0.0266	485.0	65.60	3
0.631	0.0537	980.8	65.74	2
0.736	0.0575	873.1	55.19	4
0.764	0.0843	1219.5	52.02	8
0.811	0.0788	962.1	43.93	5
0.817	0.0783	955.4	43.91	6

All the above data were taken at 25.00°C and approximately 620.0 mm Hg (Golden Colorado's average atmospheric pressure)

APPENDIX B

Table 2.0
Excess Enthalpy Measurements for Cyclohexane-Hexane

MOLE FRACTION CYCLOHEXANE	TOTAL MOLAR FLOW RATE (mol/hr)	CALORIMETER READING (μWATTS)	EXCESS ENTHALPY (kj/kmol)	RUN #
0.174	0.1130	3310.8	105.48	23
0.407	0.03421	1876.5	197.5	12
0.435	0.03070	1735.0	203.4	19
0.472	0.03918	2304.2	211.7	11
0.483	0.03753	2234.1	214.3	10
0.491	0.03775	2260.9	215.6	13
0.493	0.03440	2095.4	215.6	18
0.500	0.03579	2156.2	216.9	08
0.525	0.03741	2294.2	220.8	09
0.550	0.03251	1978.3	219.1	05
0.559	0.03237	1982.7	220.5	17
0.561	0.03247	2002.2	222.0	01
0.593	0.04582	2837.7	223.0	16
0.599	0.03633	2208.2	218.8	02
0.612	0.02976	1801.6	217.9	06
0.624	0.04386	2672.9	219.4	15
0.638	0.03676	2197.2	215.2	03
0.645	0.03746	2224.3	213.8	07
0.648	0.04237	2554.4	217.0	14
0.652	0.03349	1989.11	213.8	04
0.669	0.03235	1926.5	213.2	20
0.690	0.03233	1902.7	211.9	22
0.701	0.03325	1931.0	209.1	21
0.920	0.1433	3421.8	85.96	24

All the above data were taken at 25.00°C and approximately 620.0 mm Hg (Golden Colorado's average atmospheric pressure)

APPENDIX C

Table 3.0
Literature Survey of Previous Work on Benzene-Toluene

AUTHORS	RANGE	CALORIMETER TYPE	SOURCE	DATE
Hsu, K. Y. Clever, H. L.,	298.15 K	Beckman, flow	J. Chemical Thermodynamics 7, 435-442	1975
Pena, D. M., Menduina, C.	298.15 K	Isothermal dispalcement (Van Ness type)	An. Quim 69, 857-868	1973
Murakami, T., Lam, V. T., Benson, G. C.	298.15 K	Isothermal displacement (Van Ness type)	J. Chemical Thermodynamics 1, 397-401	1969
Sturtevant, J. M., Lyons, P. J.	298.15 K	Beckman, flow	J. Chemical Thermodynamics 1, 201-209	1969
Rastogi, R. P., Nath, J., Misra, J.	288.15-308.15 K	Batch	J. Phys. Chem. 71, 1277-1286	1967
Paz-Andrade, M. I.	293.55-313.16 K	Calvet, microcalorimeter	Acta Cient Compostelana 1, 117-130	1964
Mathieson, A. R., Thynne, J. C. J.	293.15 K	Batch	J. Chem. Soc. 3708-3713	1956

Table 3.0
Literature Survey of Previous Work on Benzene-Toluene

AUTHORS	RANGE	CALORIMETER TYPE	SOURCE	DATE
Canning, J., Cheesman, G. H.	297.48 K	Batch	J. Chem. Soc. 1230-1233	1955
Cheesman, G. H., Ladner, W. R.	279.45-337.65 K	Batch	Proc. R. Soc. London, Ser. A. 229, 387-395	1955

APPENDIX D

Table 4.0
Literature Survey of Previous Work on Cyclohexane-Hexane

AUTHORS	RANGE	CALORIMETER TYPE	SOURCE	DATE
Siddiqi, M.A., Lucas, K.	288.15-313.15 K 0.1-30 MPa	Flow	J. Chemical Thermodynamics 14(12), 1183-90	1982
De St. Romain, Huu Tra Van, Patterson, D.		Picker, Flow	J. Chemical Society, Faraday Transactions 1, 75(7), 1700-07	1979
Arenosa, R. L., Menduina, C., Tardajos, G., Diaz PEna, M.	298.15 K	Van Ness, Flow	J. Chemical Thermodynamics 11(2), 159-166	1979
Ferhat-Hamida, Z., Philippe, R., Merlin, J. C.	298.15 K	Differential Flow	J. Chim,Phys. Phys-Chim. Biol 76, 130-136	1979
Heintz, A., Lichtenthaler, R. N.	298.15 K 100 kPa	Flow	Ber. Bunsenges Phys. Chem. 83, 853-856	1979
Yanes, C., Pellicer, J.	298.15 K	Calvet, Batch	J. Chemical Thermodyncamics 11, 177-182	1979

Table 4.0
Literature Survey of Previous Work on Cyclohexane-Hexane

AUTHORS	RANGE	CALORIMETER TYPE	SOURCE	DATE
Christenson, J. J., Izatt, R.M., Eatough, D.J., Hansen, L.D.	289.15 K 1-136.9 atm	Flow	J. Chemical Thermodynamics 10(1), 25-34	1978
Chand, A., Fenby, D. V.	298.15 K	Larkin-McGalshan Flow	J. Chem. Eng. Data 22, 289-290	1977
Meyer, R., Giusti, G., Vincent, E. J., Meyer, M.	298.15 K	Picker, Flow	Thermochim. Acta 19, 153-160	1977
Christenen, J. J., Hansen, L. D., Eatough, D. J., Izatt, R. M.	298.15 K 200 kPa	Flow	Rev. Sci Instrum. 47, 6, 730-34	1976
Grolier, J.-P E.	298.15 K	Picker, Flow	Thermochim. Acta. 16, 27-38	1976
Letcher, T.M., Jerman, P.J.			J. S. Afr. Chem. Inst. 29(1), 55-62	1976
Romani, L., PAz Andrade, M. I.	298.15 K	Calvet	An. Quim 71(1), 3-6	1975

Table 4.0
Literature Survey of Previos Work on Cyclohexane-Hexane

AUTHORS	RANGE	CALORIMETER TYPE	SOURCE	DATE
Tanaka, R., D'Arcy	298 K	LKB, Flow	Thermochim. Acta 1, 163-175	1975
Mattingley, B. I., Handa, Y. P., Fenby, D. V.	298.15 K	Larkin-McGlashan Flow	J. Chemical Thermodynamics 7, 169-173	1975
Benson, G. C.	298.15 K	Picker, Flow	J. Chemical Thermodynamics (1), 19	1974
Lam, V. T., Picker, Patrick, Patterson, D., Tancrede, Pierre	298.15 K		J. Chemical Society, Faraday Transactions 2, 70(8), 1465-78	1974
Schroll Harsted, B., Sonnich-Thompson, E.	293.1-313.5 K	LKB Flow	J. Chemical Thermodynamics 6(6), 549-555	1974
Marsh, K. N.			Int. Data Ser., Selec. Data Mixtures. A, 1973, (1), 22	1974
Ahmed, Aklaq,	298.03 K		J. Chemical Society, Faraday Transactions 1, 69(2), 387-89	1973

Table 4.0
Literature Survey of Previous Work on Cyclohexane-Hexane

AUTHORS	RANGE	CALORIMETER TYPE	SOURCE	DATE
Arm, H., Bucher, P.	298.15 K	Batch	Chimia 27, 79-81	1973
Tanaka, R., Murakami, S., Fujishiro, R.	298.15 K	Van Ness, Dilution	Bull. Chem Soc. Jpn. 45, 2107-2110	1972
Gonzalez Posa, C., Nunez, L., Villar, E.	298.15 K		J. Chemical Thermodynamics 4(2), 275-287	1972
Paz Andrade, Maria I. Baluja, M. C., Nunez, L.	298.15 K		An. Quim 66(6), 949-54	1970
Dias d'Almedia,M., Fernandez-Garcia, J.G, Boissonas, Ch.,G.	298.15 K	Batch	Helv. Chim. Acta. 53, 1389-94	1970
Ewing, M. B., Marsh, K. N.	298.15-318.15 K	Van Ness	J. CHemical Thermodynamics 2, 295-296	1970
McGlashan, M. L., Stoeckli, H. F.	298.15 K	Flow	J. Chemical Thermodynamics 1(6), 589-94	1969
McGlashan, M. L., Stubley, D., Watts, H.	298.15-313.15 K	Flow	J. Chemical Thermodynamics 1, 390-393	1969

Table 4.0
Literature Survey of Previous Work on Cyclohexane-Hexane

AUTHORS	RANGE	CALORIMETER TYPE	SOURCE	DATE
Marsh, K. N., Stokes, R. H.	298.15 K		J. Chemical Thermodynamics 1, 223-225	1969
Murakami, S., Benson, G. C.	298.15 K	Van Ness	J. Chemical Themodynamics 1, 559-572	1969
Pouchly, J., Biro, J.	298.15 K	Calvet	J. Polymer Science 7, 463-466	1969
Sturtevant, J. M., Lyons, P. A.	298.15 K	Beckman, Flow	J. Chemical Thermodynamics 1, 201-209	1969
Watts, Harry., Clarke, Eustace C., Glew, D. N.	298.15 K	Larkin-McGlashan Batch	Can. J. Chem 46, 815-821	1968
Ridgway, K., Butler, P. A.	298.15 K	Batch	J. Chemical Engineering Data 12, 509-515	1967

APPENDIX E

EQUIPMENT DESCRIPTION

The calorimetric facility is composed of several primary components that will be given more thorough discussion. A complete list of the equipment, including manufacturer, is given in Table 5.0.

LKB Calorimeter

The LKB 2277 calorimeter consists of the following components:

A. Temperature control network.

B. Calibration unit

C. Amplifier board.

D. Flow-Mix cell.

A. Temperature Control Network

The temperature control network is shown in Figure 17.0. The temperature control system consists of five parts; the external water circulator, the preheater system, the fine heater system, the temperature regulation unit, and the digital temperature unit.

The external water circulator is used as the first stage of temperature control. It is completely separate from the bath and will maintain the water it circulates to

Table 5.0

PROCESS EQUIPMENT LIST

1. LKB 2277 Bioactivity Monitor. Multifunction calorimeter. LKB instruments, Inc. 9319 Gaither Rd., Gaithersberg, Maryland 20877.

2. Colora Circulating Bath. -10 - 90 degrees celsius. ±0.2 degrees celsius stability. Model WK3. LKB Instruments, Inc.

3. LKB FLow-Mix cell model 2277-204. Three modes of operation; Ampoule mode, Flow-through mode, and Flow-mix mode

4. Isco LC-5000 Precision Pump. 0-400 ml/hr, 0-3700 psi. Purchased on 10/86 from Isco, Inc. P.O. Box 5347 4700 Superior Street, Lincoln, Nebraska 68505.

5. Isco LC-5000 pump controllers.

6. Temperature controlled box.

7. Fisher balance. 0-30g/0-300g ±0.001g/0.01g. Series 7000, model 7303d. Fisher Scientific, 14 Inverness Dr. East, Building 148, 144 office, Englewood, Colorado 80112.

8. Cenco-DeKhotinsky Thermo Regulator. 0-300 degrees celsius, 0-300 watts controlled. Central Scientific Company. 1700 Irving Park Blvd. Chicago, Illinois.

9. General Electric 100 watt standard home light bulb.

10. Back pressure regulator. Part # U446 100 psig back pressure, Upchurch scientific, P.O. Box 1529 Oak Harbor, Washington 98277.

11. Biscuit Slim-Line fan. Model 87241. Woodstock New York. High Output fans. Redmond Co., Inc. Owosso, Michigan.

12. Pulsafeeder model LS-30 microflow micrometering pump. Stainless steel diaphragm. 50-500 ml/hr, 0-3000psig. Centennial Equipment Co., 15760 W. Sixth Ave., Golden, Colorado 80401.

13. Keithley model 191 Digital Multimeter. 5-1/2 digit resolution. EIL INstruments, INc. 98 Inca, Denver, Colorado 80223.

14. Wyles 24 volt DC power supply.

15. 24 volt DC solid state single-throw, single-pole relay.

16. Nupro inline filter housing. Model SS-2F-VCR-2 1/8 inch. Denver Valve & Fitting Co. 970 Simms St. Denver, Colorado 80215.

17. Nupro sintered filter element 0.5 micron. Model SS-2F.

18. Stainless steel tubing. 1/16" with 0.004" ID. Suppelco, Inc. 3110 Forest Oaks Dr. Suite 250 Houston, TX 77017.

19. Three way ball valves. 1/8". Denver Valve and Fitting.

Temperature Control Network

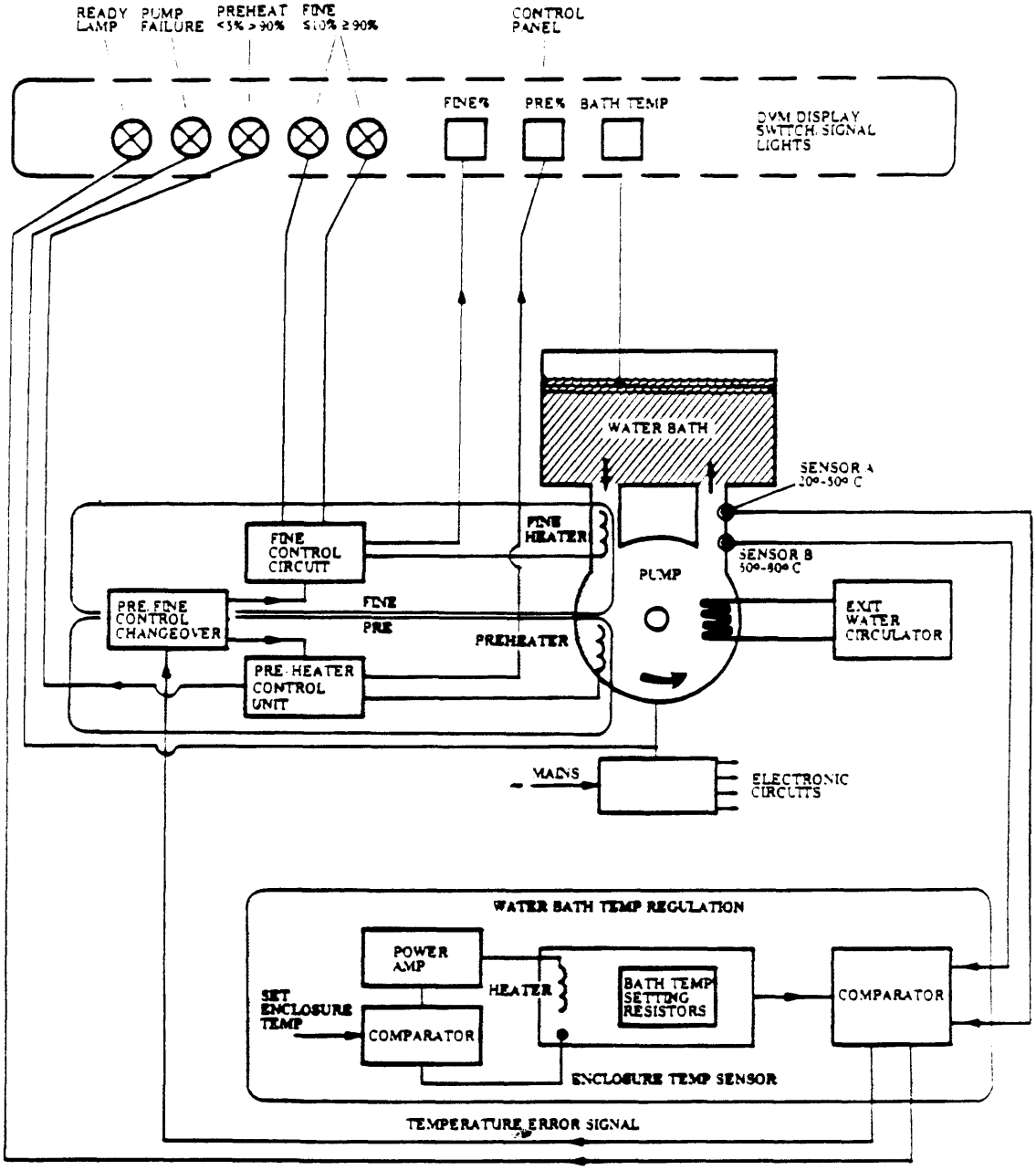


Figure 17.0

±0.4°C. By virtue of being separate, it keeps the pump assembly at a constant temperature allowing both the preheater and the fine heater to work at a predetermined power output. The external circulator bath is usually set at a temperature 3°C below the calorimeter bath temperature in order to act as a heat sink.

The preheater is a 100 watt foil heating element attached to the rear of the pump. The preheater designed to allow the fine heater to work at its optimum power level of approximately 40% of maximum power. If the preheater falls below 5% or rises above 90% of maximum power a warning light flashes to signal an adjustment may be necessary on the external circulator's temperature.

The fine heater is a 100 watt coil located at the pump inlet. The fine heater is designed to operate between 10% and 90% of maximum power. If the power level falls out of this range then a warning light will come on which suggests that an adjustment may be necessary on the external water circulator's temperature.

The temperature is set by series decade resistors located in the temperature regulation unit. This unit produces an output signal. The signal is compared with the signal out of the sensor (thermistor) located in the bath. If any difference exists between the two signals, an output

signal from the comparator circuit causes an appropriate change in the input power to the fine heater and preheater system.

Once the calorimeter water bath temperature has come to its set point, a ready light comes on. The ready light signals that the bath temperature has reached its set temperature. The stability of the bath is reported to be ±0.0002 °C for a minimum of 8 hours.

The temperature regulation unit is shown in Figure 18.0 (located on the front of the calorimeter, shown in Figure 3.0). This unit maintains the temperature in the bath and is also the main power supply to all of the calorimeter's electronics.

The switch labeled "Range" adjusts the temperature range of the bath; side "A" 20-50 degrees celsius and side "B" 50-80 degrees celsius. Switches labeled "A,B,C,D" set the resistance which adjusts the temperature of the water bath. The switches labeled "TPC 1" and "TPC 2" are check points for the temperature regulation unit if there is a problem with the bath temperature. Refer to LKB's service handbook for approximate values at all check points.

The digital temperature unit, shown in Figure 19.0, is located on top of the calorimeter in the electronics rack as shown in Figure 3.0. This unit controls all of the display

Temperature Regulation Unit

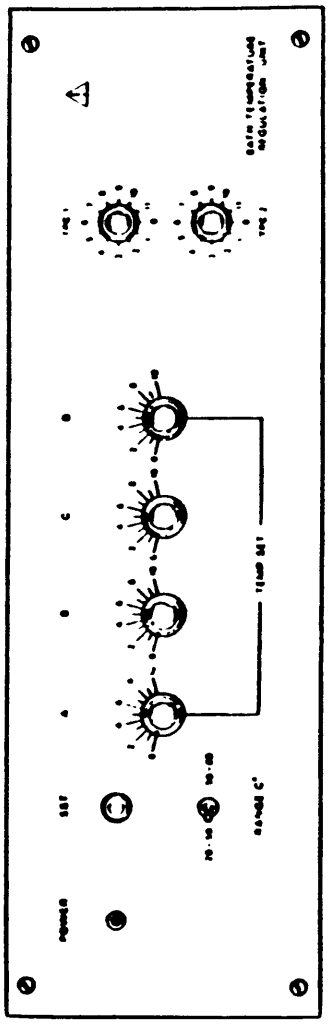


Figure 18.0

Electronics Rack

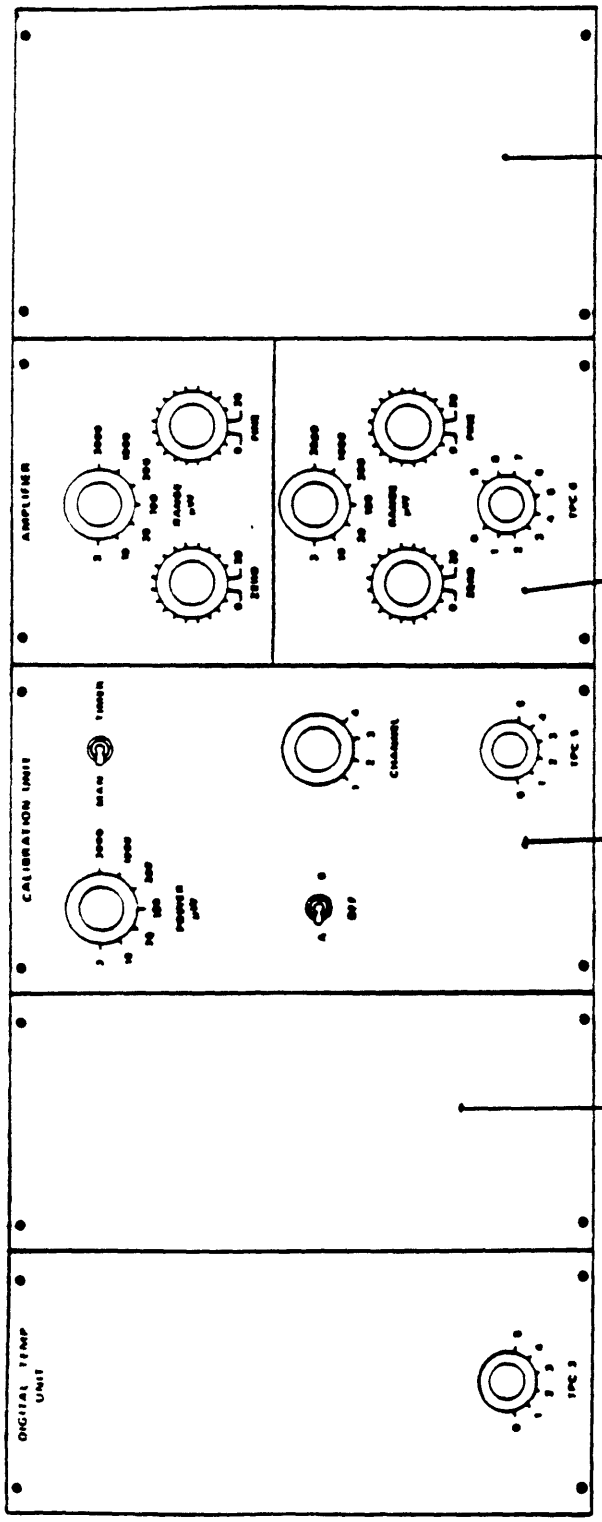


Figure 19.0

readings and analog to digital conversions. It also directs power to all sections of the calorimeter. The switch labeled "TPC 3" allows monitoring of the digital temperature unit.

B. Calibration Unit

The calibration unit, shown in Figure 19.0, is located on top of the calorimeter in the electronics rack. It is used to calibrate the measuring cell in any one of the three modes of operation of the cell. Setting a desired power level to the calibration heaters, located under the mixing tee of the measuring cell, allows the measuring cell to be calibrated. The calibration is done by adjusting the output from the calorimeter (the value read from the display), using the adjustable amplifiers, to correspond to the input power of the heaters.

The switch labeled "Power uW" is the power level switch and is adjustable from 3 to 3000 microwatts, allowing accurate calibration at several different levels of operation.

The "Channel" switch is a directional switch, meaning that the calorimeter can handle 4 different cells at one time, with only one calibration unit.

The switch labeled "man/timer" turns the calibration heaters on and off. The timer side is an option that does

not exist but was intended for timed calibration.

The "A/OFF/B" switch turns the calibration heaters on for either the flow-mix side "A", or the flow through side "B".

The switch labeled "TPC 5" is a check point for the calibration unit if there is a problem with that unit. "TPC 5" does not work due to an incapatibility with the newly replaced board and the existing calorimeter electronics.

C. Amplifier Board

The amplifier board, as shown in Figure 19.0, is located on top of the calorimeter in the electronics rack. The amplifier board is the most important board on the calorimeter. It reads the voltage output from the measuring cell and amplifies and filters the signal.

The board has two channels set up for two cells that can work simultaneously. Two more cells can be added if an additional amplifier board is obtained.

The switches labeled "Range" set the scale that the system will read. The smaller the scale, the more accurate the reading becomes. These switches also redefine the scale for the chart recorder hookup.

One of the modifications made to the calorimeter is the addition of direct voltage measurement of the measuring cell. The hookups are standard banana plugs located next to

the amplifier board. These plugs are connected directly to test point 5 (TP5) and ground (shown on the amplifier schematic, LKB Operation Manual, drawing 90013639). This is directly before both amplifiers and a series of voltage reducing resistors. Therefore, the voltage is not filtered but has the complete range of 0 to ±14mV. The advantage of this added feature is that it allows the calorimeter to work outside the 4200 uWatt range. The amplifiers are linear and checked (shown in the calibration section, Appendix F) such that the scale is approximately 2.64 E-4 volts/microwatt.

The potentiometers labeled "Zero" are the zero adjustment when there is no flow of heat in the measuring cell. These are 10 turn, potentiometers and are very sensitive to adjustments. The potentiometers labeled "Fine" are the adjustments to bring the calorimeter reading to that of the heaters when switched on. The switch labeled "TPC 6" is test point for the amplifier board if problems occur with that board.

D. Flow-Mix Measuring Cell

The flow-mix measuring cell is located on top of the calorimeter base as shown in Figure 3.0. The flow-mix cell is shown in Figure 20.0. The cell is capable of three modes of operation; ampoule mode, flow-through mode, and flow-mix mode. The flow-mix mode was used exclusively throughout

Flow-Mix Measuring Cell

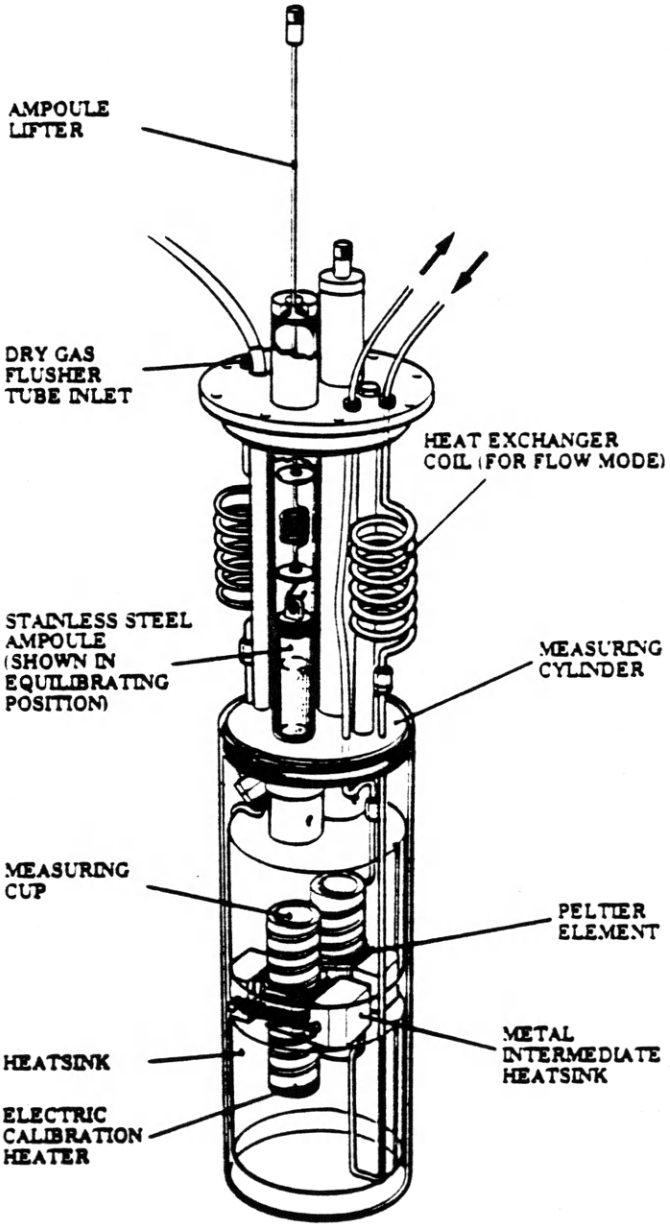


Figure 20.0

this investigation and therefore only this mode will be discussed. For information on the other two modes of operation refer to the LKB instruction manual.

The cell is constructed of an outer aluminum shell with two inner aluminum blocks, above and below the measuring area, acting as main heat sinks. In between the two heat sinks are two sets of Peltier elements (thermoelectric detector) attached to intermediate heat sinks.

The flow system is constructed of 24 ct. 1 mm internal diameter gold tubing. The gold tubing is noncorrosive and also allows for fast heat transfer since the thermal conductivity of gold is higher than that of other metals.

The gold tubing starts under the face plate of the cell and coils approximately six times while in contact with the water bath, allowing the process fluid to come to thermal equilibrium before entering the measuring area.

The tubing next enters the actual measuring cylinder and traverses down the outside of the aluminum heat sinks to the bottom of the cell. From the bottom, the tubing heads back up towards the top through the center of the heat sinks. The two process fluid streams meet in a mixing tee at the bottom of side "A" ampoule measuring cup. After leaving the mixing tee, the combined stream is wrapped around the ampoule measuring cup, surrounded by an aluminum

block and located in the measuring area of the Peltier elements. Once the fluid leaves the measuring area, the combined fluid stream exits the measuring cylinder to waste or to the reference side.

It is advantageous, though not required, to send the waste fluid back through the reference side. If the fluid is sent down the reference side, the tubing traverses the same path as the flow-mix tubing but with only one stream. The advantage of this method is that once the system is calibrated for a flow rate it is good at all flow rates because the total power output is the power output from the sample side minus the power output from the references side. Since viscous heat affects occur on both sides the viscous heat affects are subtracted out by the reference side. This advantage is due to the twin detector system.

The measuring method of the twin detectors was designed for continuous monitoring of processes and reactions. Heat produced by the mixing process causes the fluid temperature to change. Heat is thus transferred from the fluid to the surrounding Peltier elements so that their temperature also changes. The heat is eventually removed from the system when it flows to a large heat sink.

The heat flow from the sample is measured by means of the voltage produced by the temperature gradient across the

Peltier elements. This voltage is calibrated against the power dissipated in a calibration heater.

Isco LC-5000 Pumps

The Isco pump is shown in Figure 21.0. This figure is shown for completeness in the discussion of the equipment. The pump controller is located to the left of the pump.

All of the switch and button functions are listed in Table 1-2, and 1-3 in the Isco pump manual and need no further discussion here. The Isco pumps are a single cylinder syringe type pump. That is, a screw gear moves the piston up through a stainless steel tube at a constant rate. The pump outlet pressure is read by a pressure transducer and fed back to the motor along with the tachometer's signal which control the motor's speed for accurate flow and pressure delivery.

Box Temperature Control

The calorimeter box is controlled by a mechanical temperature controller shown in Figure 22.0. The mechanical controller uses direct contacts to do the switching of the power to the light bulb. With standard line voltages the contacts are quickly pitted due to arcing and the controller will usually fail within a couple of months. To solve this problem a solid state relay powered by a 24 volt DC power

Isco LC-5000 Precision Metering Pump

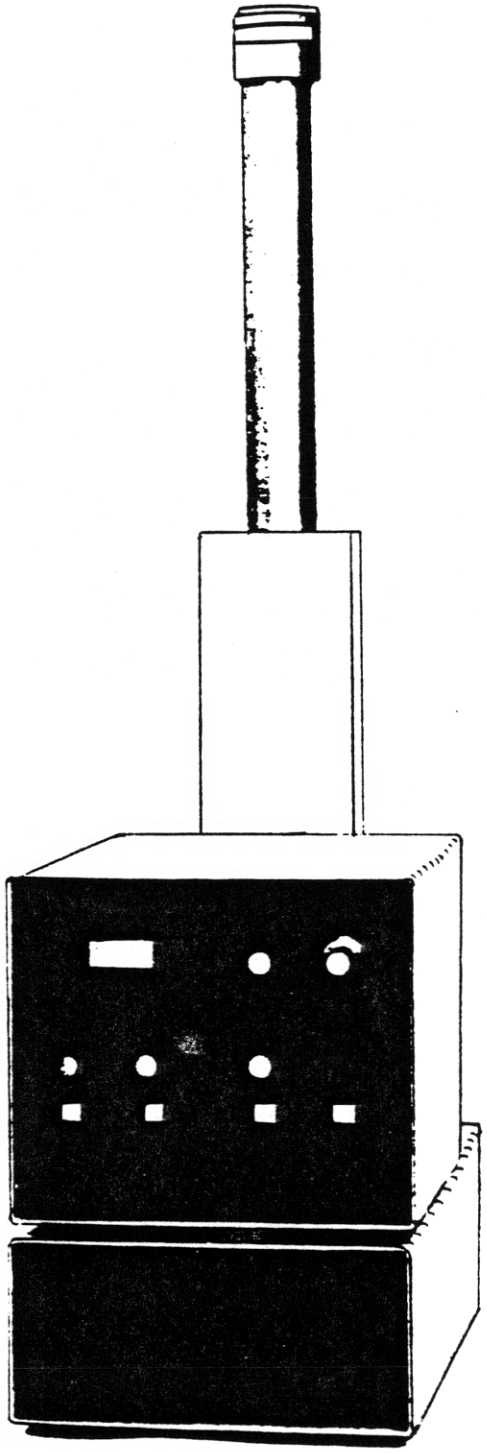


Figure 21.0

Box Temperature Control Scheme

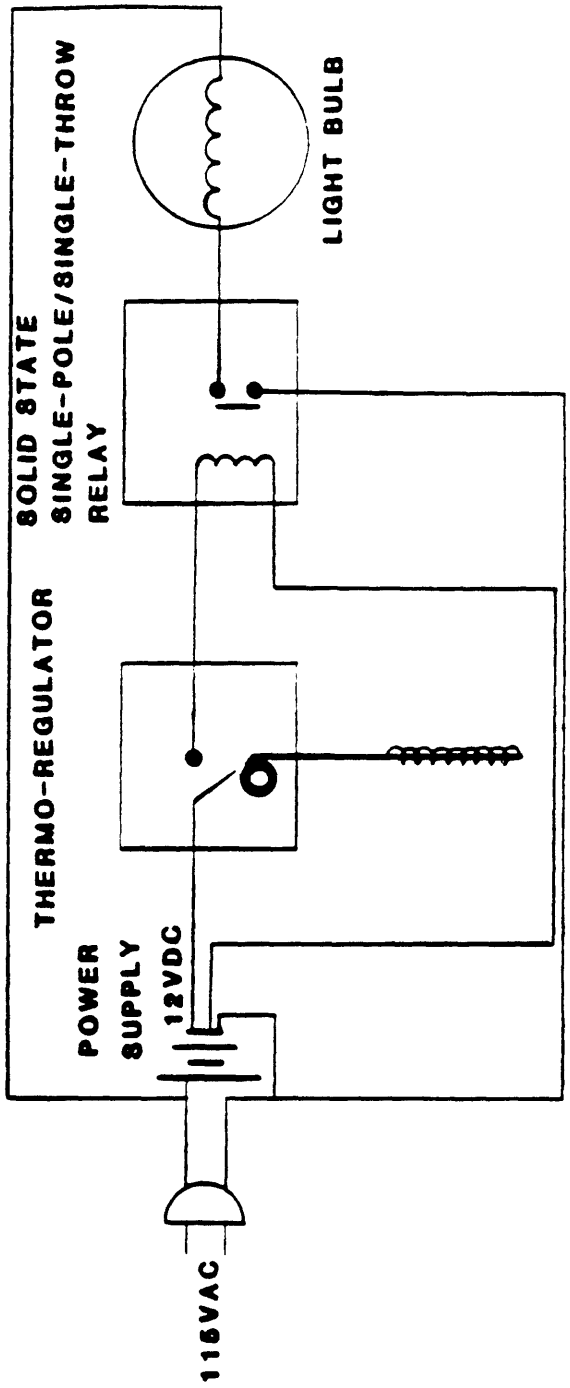


Figure 22.0

supply was designed to do the switching. This dropped the voltage across the controller contacts to 24 volts and almost completely eliminated all arcing.

APPENDIX F

EQUIPMENT TEST AND CALIBRATION

The components of the system that were tested or calibrated include the LKB bath, the measuring cell, the pumps, and the external water bath.

LKB Bath Water Bath

The calorimeter water bath was checked for set point and temperature stability. This was done using a Hewlett-Packard multimeter model 3457A and a platinum resistance thermometer which was calibrated by Yellow Springs Instrument Co. The accuracy of the PRT is ±0.0001 ohms, and resolution of the multimeter is ±0.000001 ohms.

The PRT was inserted in the bath through a mixing cell hole and placed approximately three fourths of the way from the top. The first experiment was to determine how good the short time temperature stability of the bath was at the bath temperature of 25.00°C. The temperature regulation unit was set at 3140 which corresponds to 25.001°C or 28.0807 ohms. The stability was checked by measuring the resistance approximately every 4 seconds (this corresponds to the fastest reading rate with the maximum accuracy that the multimeter can produce) for 26 minutes. Figure 23.0 is a graphical representation of the results. The graph shows

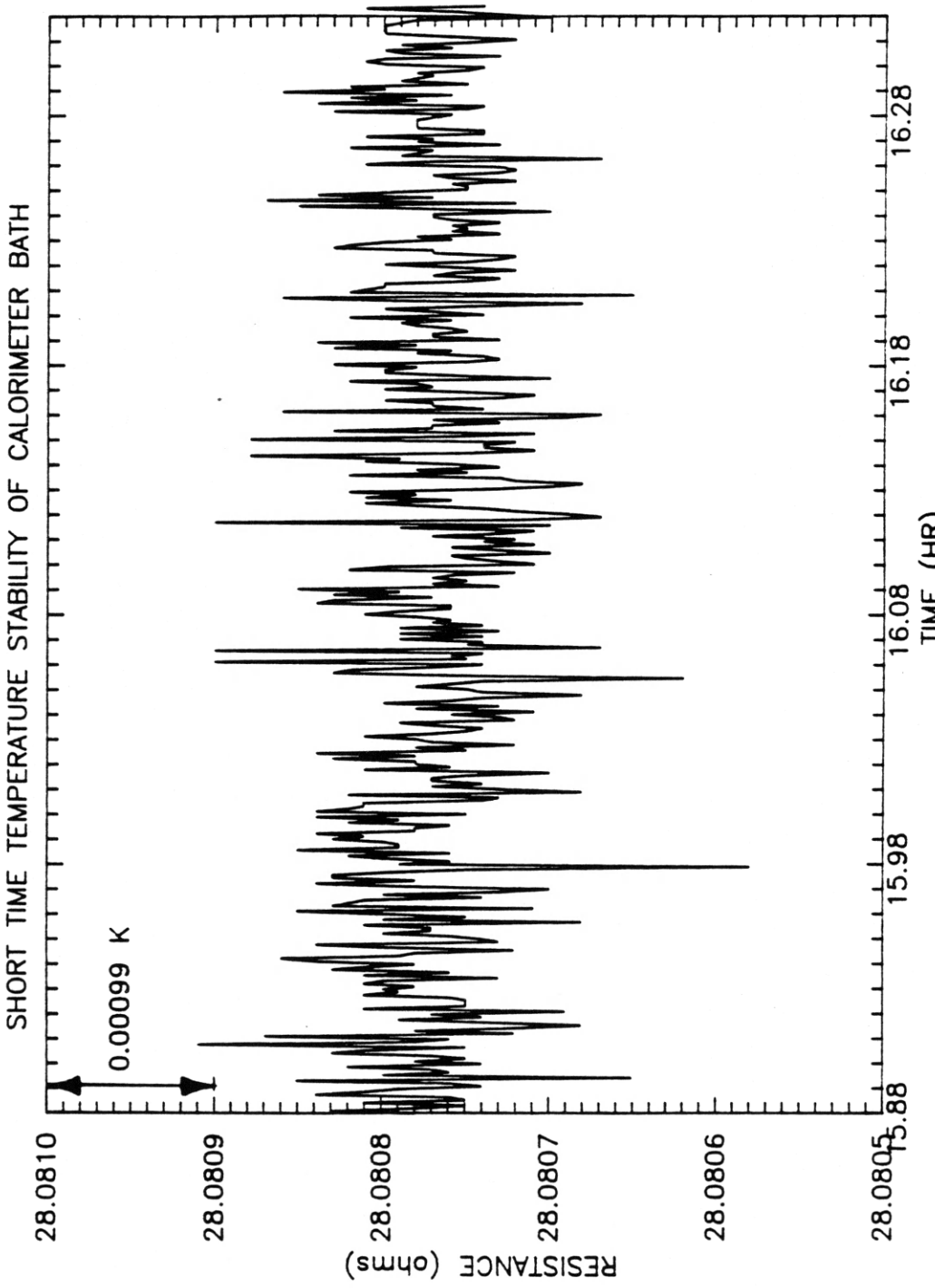

SHORT TIME TEMPERATURE STABILITY OF CALORIMETER BATH
0.00099 K
RESISTANCE (ohms)
28.0810
28.0809
28.0808
28.0807
28.0806
28.0805
15.88
15.98
16.08
16.18
16.28
TIME (HR)

Figure 23.0

that the bath is very stable (0.101 ohms corresponds to approximately 1.0000°C) with a fluctuation on the order of ±1 milli-Kelvin and a total deviation of less than 2 milli-Kelvin.

The next step was to check the long time stability. In this experiment the resistance was measured approximately every 4 seconds and the values were averaged over a 5 minute period for 33.5 hours. Figure 24.0 is a graphical representation of the results. Again, the deviation is on the order of 1 milli-Kelvin with a total deviation less than 2 milli-Kelvin.

Cell Calibration

To ensure that the 3000 microwatt calibration heater, provided by LKB is the value that it claims, was checked using the apparatus shown in Figure 25.0. This apparatus was also used to check the linearity of the amplifiers and voltage output of the thermoelectric detectors (Peltier elements).

The 3000 microwatt calibration heater was checked using a nylon rod with nichrome wire wrapped around the end (the wire acts as a heater when power is supplied to it) and placed in the sample side measuring cup. A H-P 12 vDC power supply is first connected to a 100 ohm standard resistor and then across the nichrome wire. The voltage drop is measured

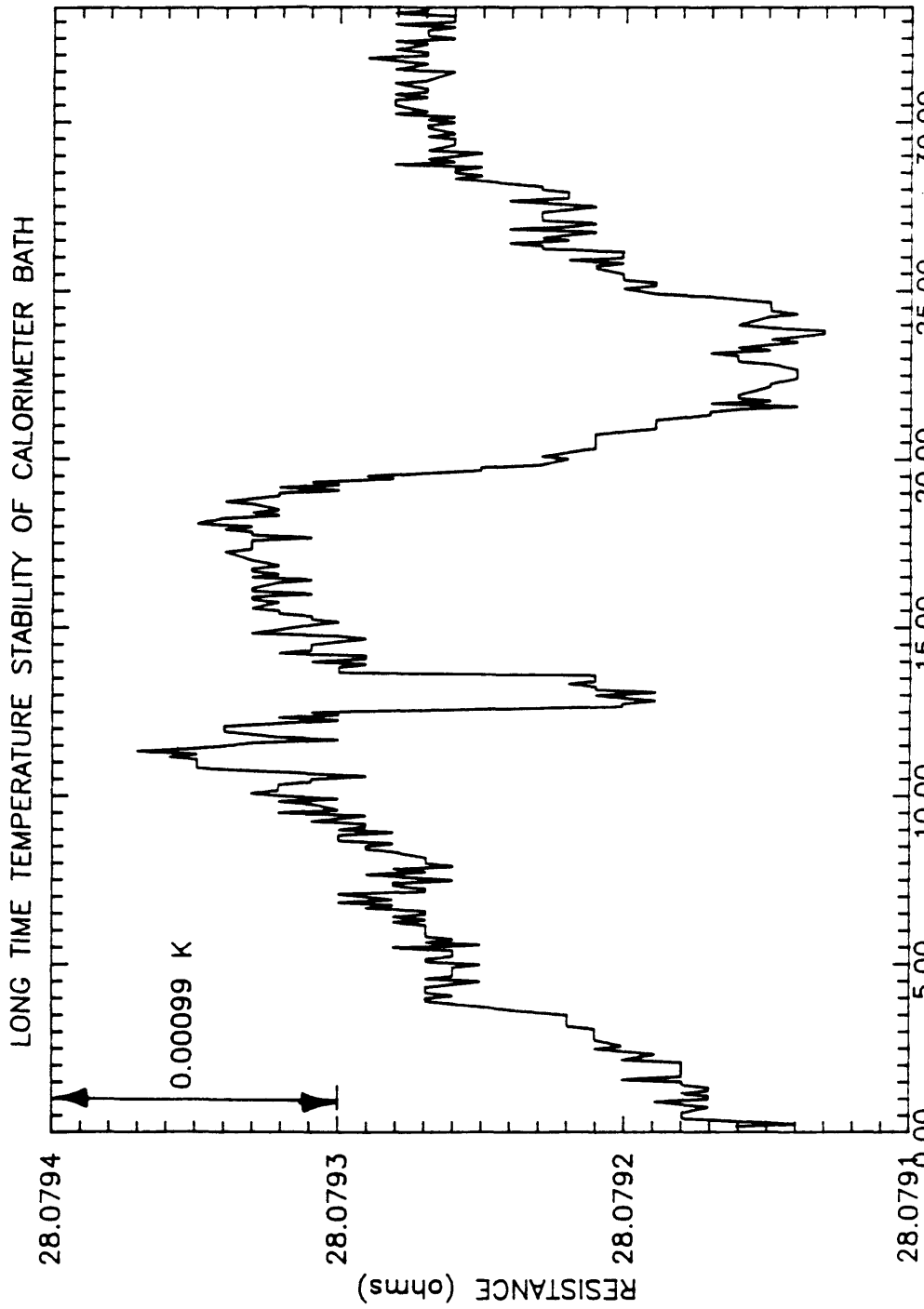

LONG TIME TEMPERATURE STABILITY OF CALORIMETER BATH
0.00099 K
RESISTANCE (ohms)
28.0794
28.0793
28.0792
28.0791
0.00
5.00
10.00
15.00
20.00
25.00
30.00
TIME (HR)

Figure 24.0

Calibration of Measurement Cell

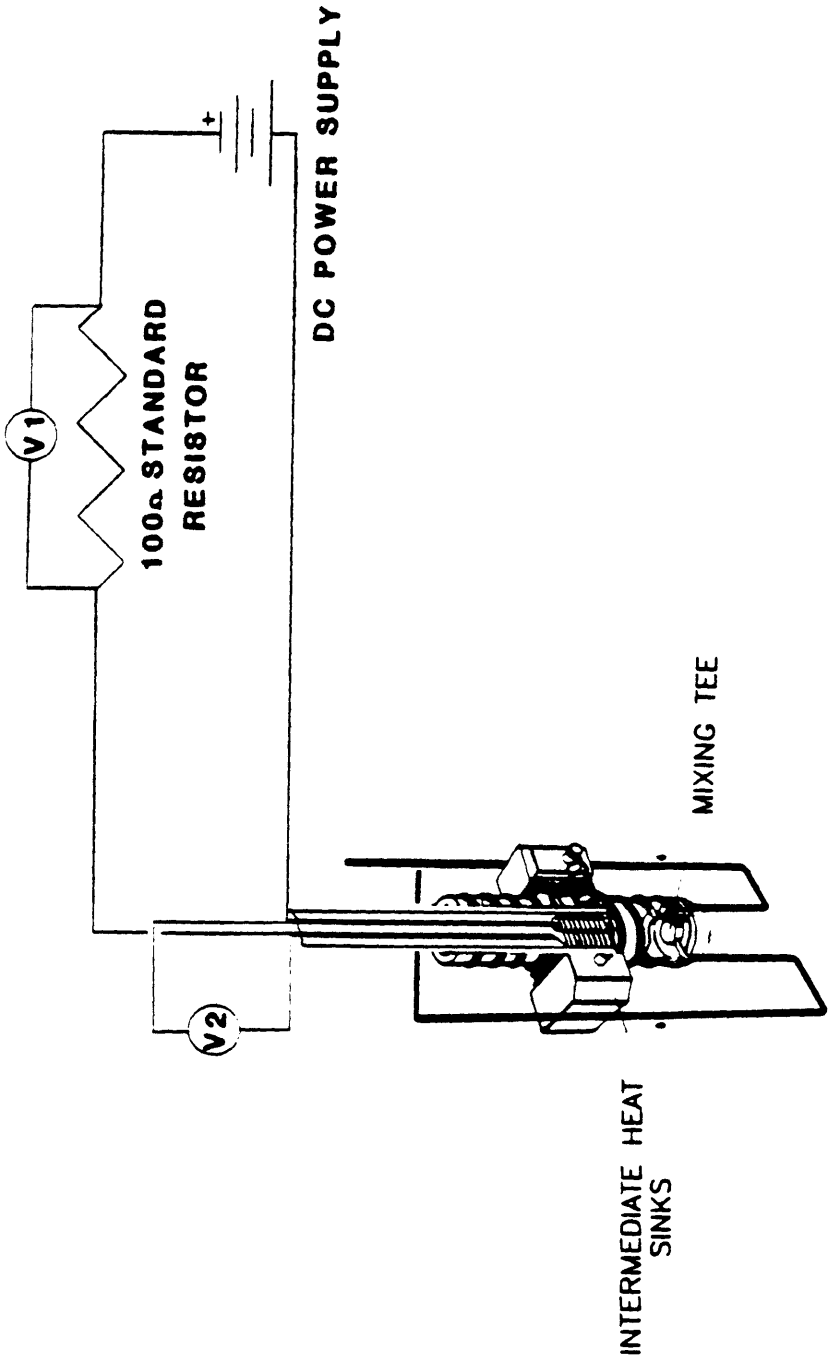


Figure 25.0

across the 100 ohm resistor to yield the current and the voltage drop across the resistor is measured so that the power input to the nichrome wire can be determined. By fixing the current and adjusting the voltage across the nichrome wire a set level of power can be input to the nichrome wire.

The first step in the calibration procedure is to calibrate the calorimeter using the 3000 microwatt calibration heater provided by LKB (described in the calorimetric facility section). Then using the apparatus shown in Figure 25.0 adjust the voltage and current to give 3000 microwatts of power to the nichrome wire and record the output of the calorimeter. A comparison of the values obtained by the two methods of calibration are listed in Table 6.0. All of the calibration measurements differ by less than 3 microwatts. Therefore, the LKB calibration heaters are correct and used for all calibrations.

The linearity of the amplifiers were checked to ensure that the calibration was good at all levels of operation. The voltage to microwatt response was also checked simultaneously. This was done using the same apparatus as shown in Figure 25.0 and the same technique as described in the calorimetric facility. A H-P multimeter was also connected to the output of the measuring cell (shown in

Table 6.0

3000 Microwatt Calibration Heater Check

V1 VOLTS	V2 VOLTS	WATTS MEASURED	WATTS CALORIMETER
2.406001	0.124702	3000.28	2999
2.406008	0.124700	3000.29	2998
2.406000	0.124702	3000.33	3000
2.406001	0.124700	3000.28	3000
2.406495	0.124775	3002.78	3001

drawing no. 90013639 of the LKB service handbook) to read the voltage output. A known amount of power is supplied to the nichrome wire and the calorimeter output and measuring cell voltage output are recorded. The results are listed in in Table 7.0. As one can see the amplifiers are linear and the voltage to microwatt response is 0.000265026 mV/microwatt.

Pump Calibration

The pumps were also calibrated, but the calibrations were not used because better accuracy could be obtained by measuring the mass flow rate for each run. Figure 26.0 is a typical plot showing the stability in the pump flow rate. As one can see the instability in the flow rate is greater than 1% of the average flow rate.

External Water Bath Calibration

The external water circulator calibration (Table 8.0) was provided by LKB and provided here for completeness. The 298 K (25°C) value has been adjusted slightly from the published value. The decade resistor should be set at 3140 for a bath temperature of 25.00°C.

Isothermal Check

Another major check on the calorimeter was to determine if the heat of mixing experiment takes place isothermally

Table 7.0

Measuring Cell Calibration

CALORIMETER READING µWATTS	MULTIMETER READING milli-volts	CONVERSION FACTOR mV/µWATT
57	0.015009	0.000263316
318	0.084258	0.000264962
323	0.085020	0.000263220
344	0.091981	0.000267387
345	0.092034	0.000266765
1028	0.273016	0.000265580
1034	0.274980	0.000265938
1036	0.275026	0.000265469
3012	0.797157	0.000264660
3014	0.799462	0.000265250
3027	0.802017	0.000264954
3038	0.804313	0.000264751
3900	1.0310201	0.000264364
3905	1.0320012	0.000264277
4087	1.0810210	0.000264502

Average value for conversion factor = 0.000265026 mV/µWATT
Standard deviation = 0.000001457 mV/µWATT

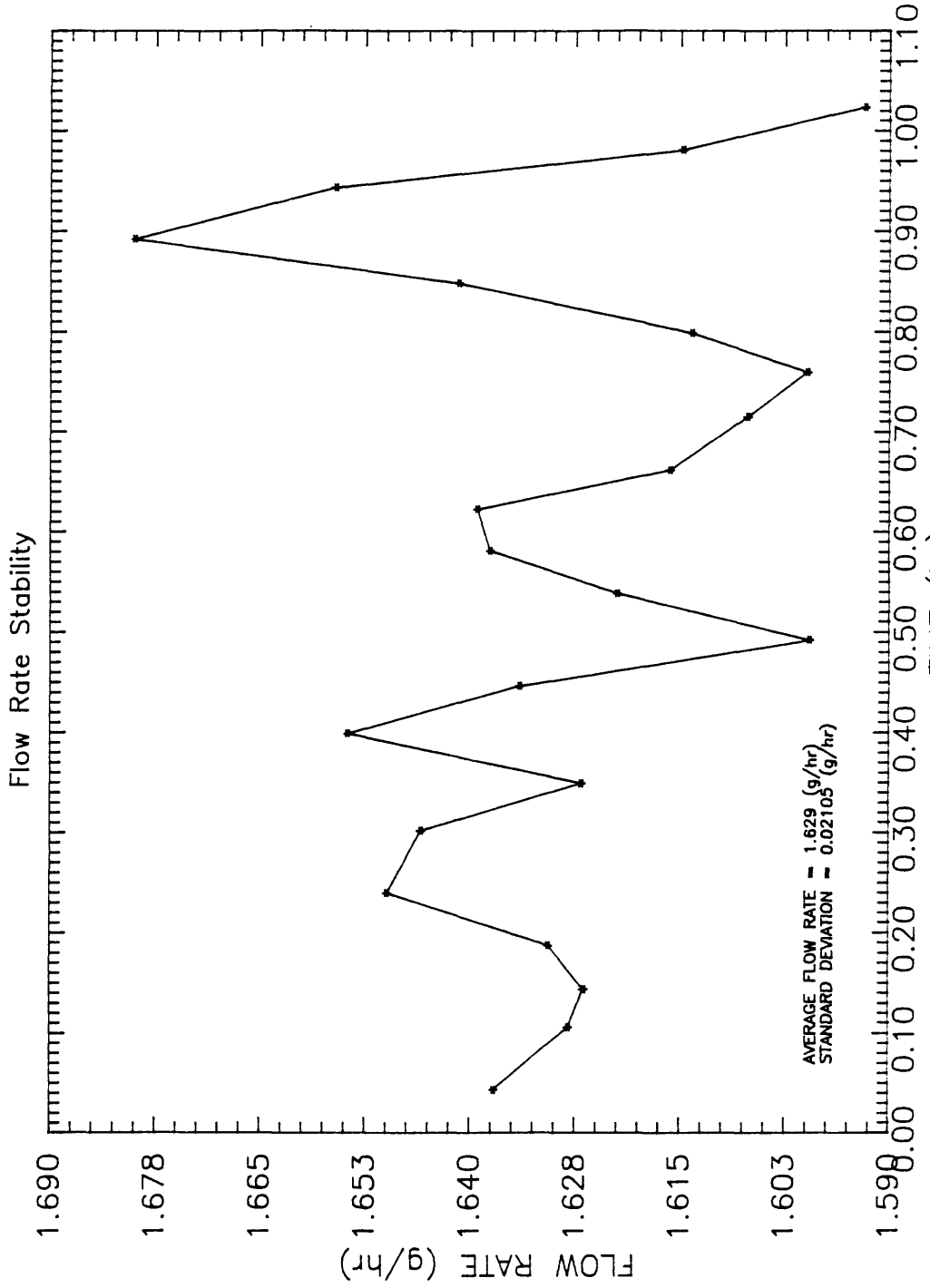

Flow Rate Stability
FLOW RATE (g/hr)
1.690
1.678
1.665
1.653
1.640
1.628
1.615
1.603
1.590
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
TIME (hr)
AVERAGE FLOW RATE = 1.629 (g/hr)
STANDARD DEVIATION = 0.02105 (g/hr)

Figure 26.0

Table 8.0

LKB Bath and External Bath Settings

BATH TEMP °C	DECADE SET OHM/10	CIRC TEMP °C	BATH TEMP °C	DECADE SET OHM/10	CIRC TEMP °C
20.00	3925	16.5	50.00	6615	47.5
21.00	3754	17.5	51.00	6348	48.5
22.00	3591	18.5	52.00	6093	49.5
23.00	3436	19.5	53.00	5849	51.0
24.00	3289	21.0	54.00	5616	52.0
25.00	3140	22.0	55.00	5394	53.0
26.00	3015	23.0	56.00	5182	54.0
27.00	2888	24.0	57.00	4979	55.0
28.00	2767	25.0	58.00	4785	56.0
29.00	2651	26.0	59.00	4599	57.0
30.00	2532	27.0	60.00	4421	58.0
31.00	2436	28.0	61.00	4252	59.0
32.00	2337	29.0	62.00	4089	60.0
33.00	2241	30.0	63.00	3934	61.0
34.00	2150	31.0	64.00	3785	62.0
35.00	2063	32.0	65.00	3642	63.0
36.00	1981	33.0	66.00	3506	64.0
37.00	1902	34.5	67.00	3375	65.0
38.00	1826	35.5	68.00	3250	66.0
39.00	1754	36.5	69.00	3130	67.0
40.00	1685	37.5	70.00	3015	69.0
41.00	1619	38.5	71.00	2904	69.0
42.00	1556	37.5	72.00	2789	70.0
43.00	1496	40.5	73.00	2697	71.5
44.00	1439	41.5	74.00	2600	72.5
45.00	1384	42.5	75.00	2507	73.5
46.00	1331	43.5	76.00	2417	74.5
47.00	1231	44.5	77.00	2331	75.5
48.00	1232	45.5	78.00	2249	77.5
49.00	1186	46.5	79.00	2170	77.5

(as the equipment manufacture suggests). This experiment was performed by placing the PRT down in the sample side measuring cup. Once the PRT reached thermal equilibrium with the bath, the 3000 microwatt calibration heater was turned on and the temperature was measured. Figure 27.0 is a graphical representation of the results. Figure 27.0 clearly shows that the temperature rise due to 3000 microwatts of power is insignificant for heat of mixing measurements, since the temperature rise is less than 0.03°C.

There are a few problems associated with the above mentioned method. Unfortunately, this is the only place in the apparatus that the temperature can be checked. This brings up the following points: first, the PRT is in glass and generally requires the end to be submerged at least 6 inches in the measuring fluid. The measuring area of the calorimeter is less than 2.00 cm and therefore approximately 25 cm's are exposed to the bath temperature of 25.00°C and approximately 25 cm's are exposed to calorimeter box temperature of 29°C . This exposure allows for conduction of heat into and out of the measuring area. This is why there is a positive slope on the graph, but it should be the same as the starting slope though this is not shown.

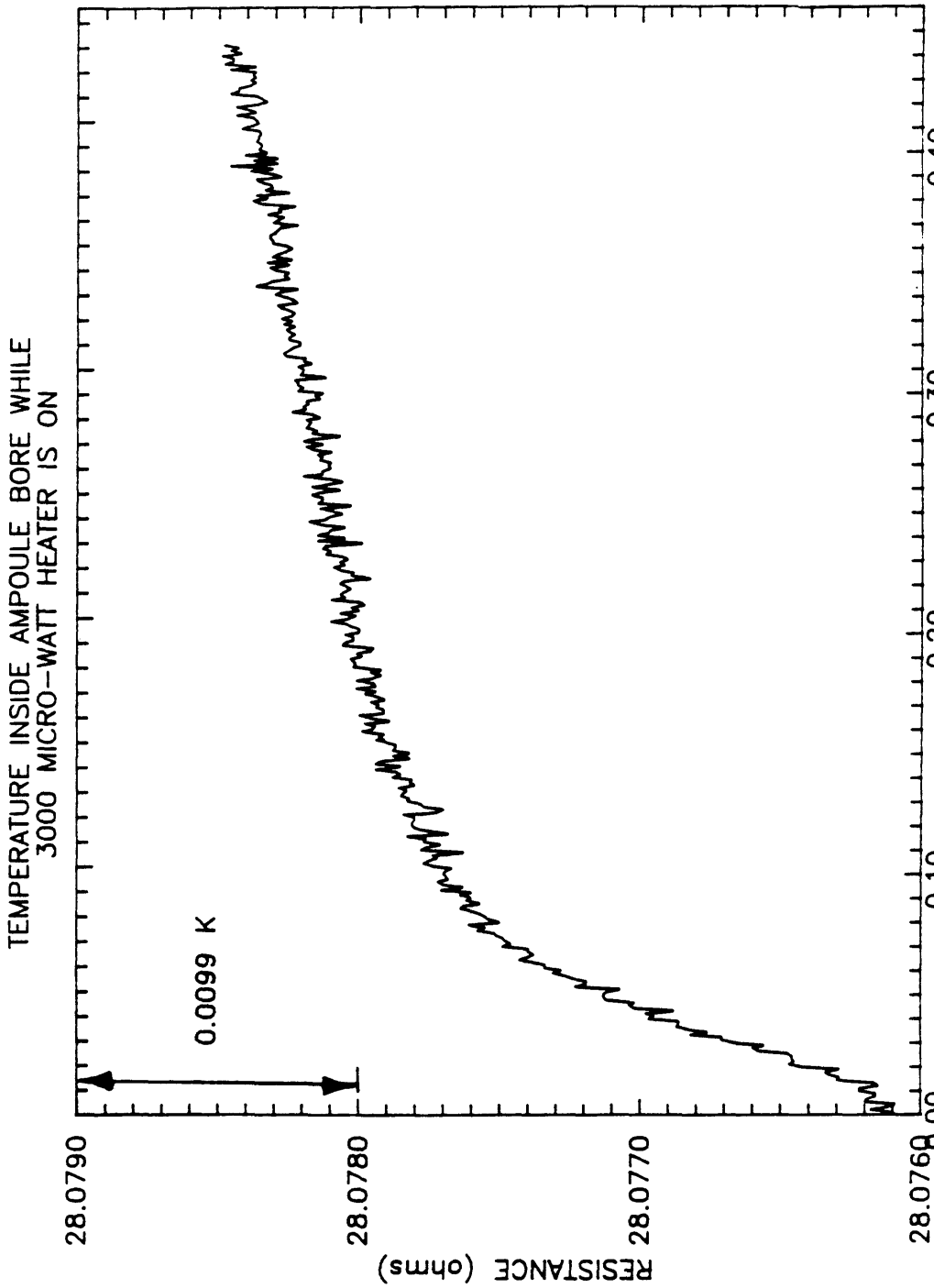

TEMPERATURE INSIDE AMPOULE BORE WHILE
3000 MICRO-WATT HEATER IS ON
0.0099 K
28.0790
28.0780
28.0770
28.0760
RESISTANCE (ohms)
0.00
0.10
0.20
0.30
0.40
TIME (hr)

Figure 27.0

APPENDIX G

EXPERIMENTAL PROCEDURE

This section describes the procedure used in operating the equipment. This is also the prescribed method for future users.

I. Pump Loading

Figure 2.0 shows the process control network.

1. Rinse the pump cylinders with a mild solvent such as acetone or ethanol. For complete details on pump operation refer to the Isco pump manual.

2. Reset the pistons to the full position, such that a vacuum can be pulled on the entire cylinder.

3. Hook up a vacuum pump as shown in Figure 28.0.

4. Switch valves #1, and #2 to the closed position. Turn off power to the pumps and start the vacuum pump.

5. Continue pulling a vacuum on the pumps cylinder for at least one half hour. This step is done because it will leave the cylinders clean and dry, since there is approximately 15 ml of dead volume that can never be removed by flushing.

6. Replace the vacuum hose with a nitrogen line.

7. Open valves #1, and #2 to the fill position.

8. Purge the pump cylinders with nitrogen for 10-20 minutes. This step is done to insure that the pump cylinders and fill lines are completely dry.

9. Rinse the pump with a small amount of desired liquid. This means, fill the pump with 40-50 ml of the desired liquid and run the pump in the fill

Vacuum System

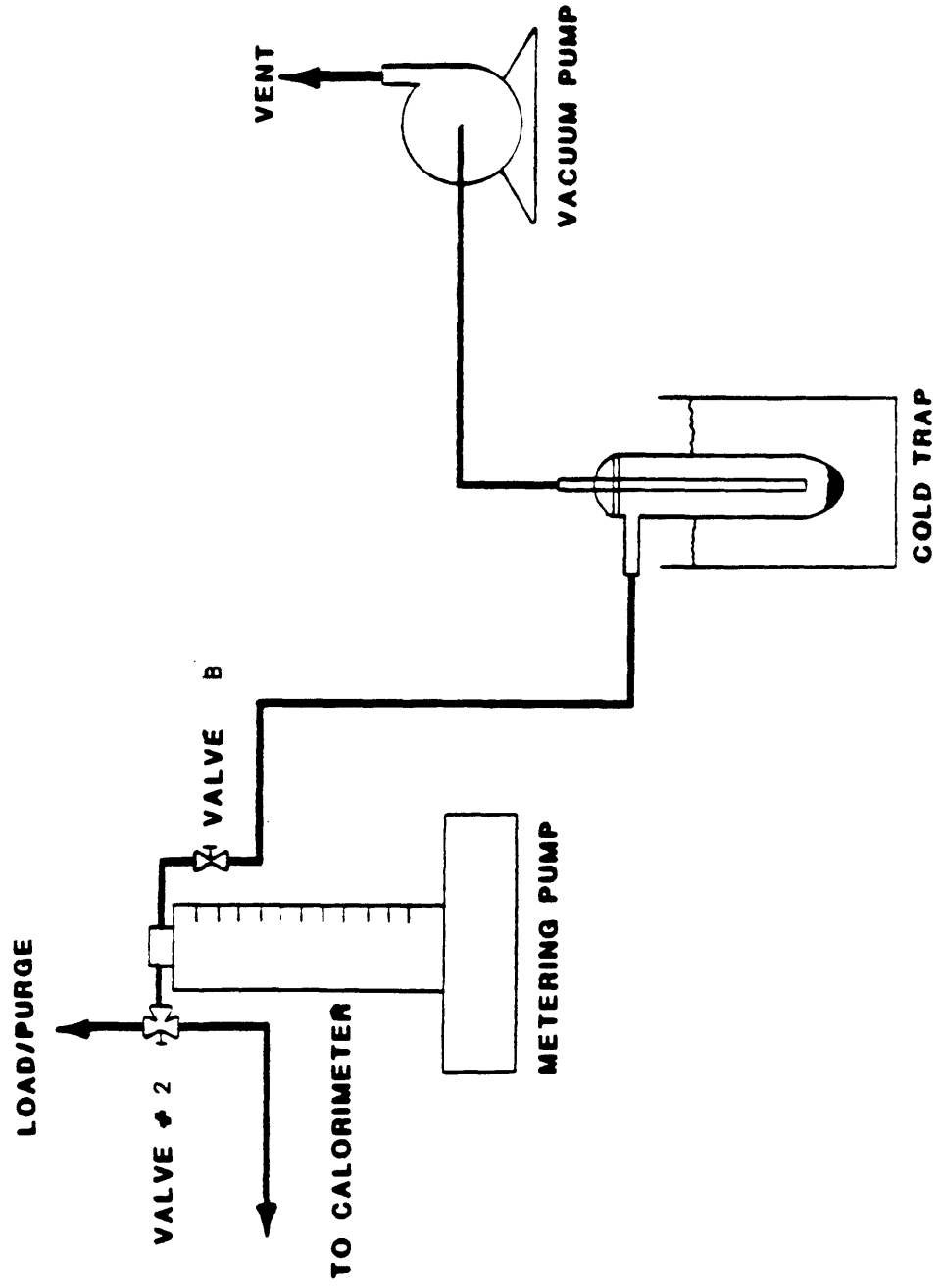


Figure 28.0

mode until the cylinder reaches the full mark. Next, displace this liquid by running the pump in the purge mode until the empty cylinder light comes on. Discard this liquid. Repeat this step several times.

The fill lines should now be full of liquid. This step helps insure that the pump cylinders are clean and also free of bubbles.

10. Fill the pumps with the desired liquid.

11. Again hook up the vacuum pump as before.

12. Switch valves #1, and #2 to the closed position and pull a vacuum on the system until approximately 5-10 ml of liquid has collected in the cold trap. This procedure is used to degass the process liquids. If a high boiling point liquid is used the following method which is equally proficient may be used in most cases.

Place the bottle holding the liquid on a stir plate with a stir bar in the bottle as shown in Figure 29.0. Place a two hole stopper in the bottle with a helium line in one hole. Attach a screen filter to the line. The filter will help disperse the helium into many small bubbles, thus increasing its ability to remove dissolved gases. Make sure the helium line is at the bottom of the bottle. Turn on the helium and the stirrer plate so that there is good mixing (note: do not stir too vigorously as this causes gases to be pulled backed into the liquid by the vortex). The helium will remove the dissolved gases in the liquid if purging is done for a reasonable amount of time. When filling the pumps, make sure that the liquid stays in a helium environment. This can be done by applying helium to the bottle while filling the pump.

13. Open valves #1, and #2 to load/purge position. Purge a small amount of liquid. Switch the pump settings to the pump position at 400 ml/hr and begin pumping the liquid out the purge/fill line.

14. Once all of the gas is removed from the pump, if there is any, switch valves #1,2 to the pump position while the pump is pumping. Hopefully, this procedure will eliminate all of the dissolved

Degassing of Liquid

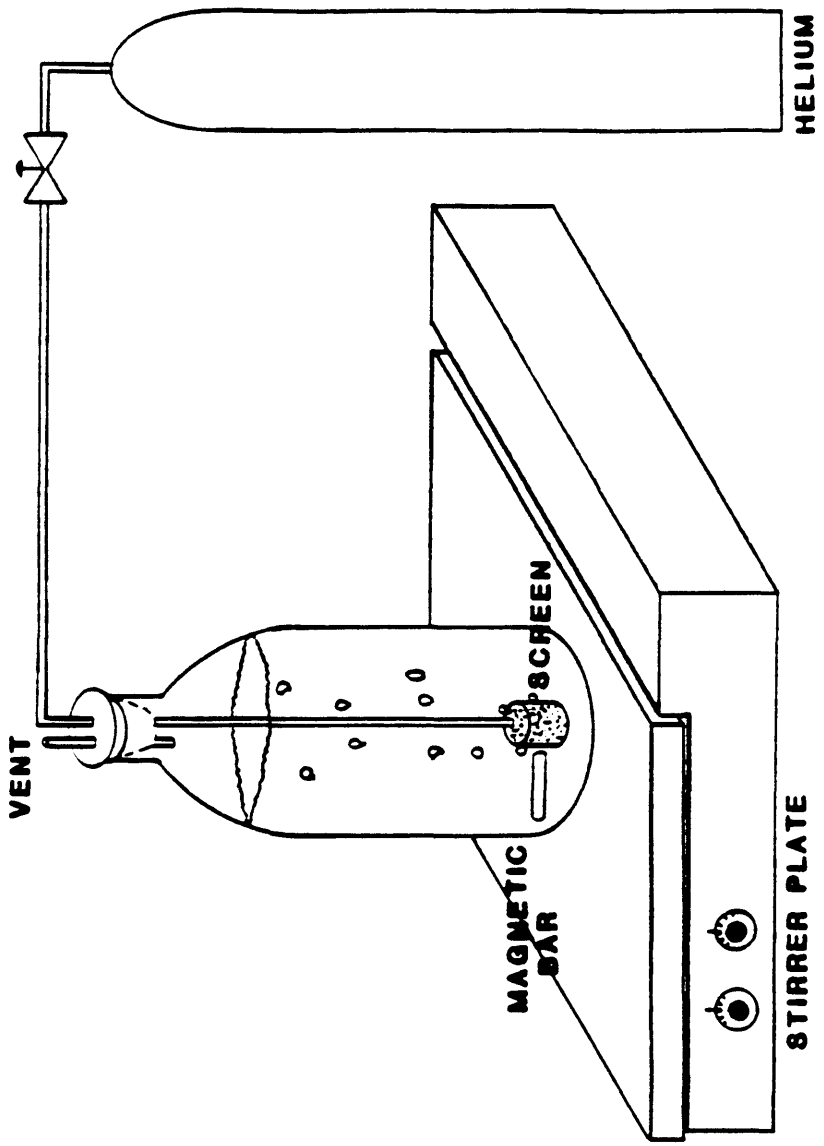


Figure 29.0

and other gasses from the pump cylinders, if it does not there is a section called bubble removal that is described in the trouble shooting section.

II. Calorimeter Operation

1. Figure 18.0 (found in the Description of equipment section, Appendix E)is a drawing of the decade resistor box. The decade resistor box is used to set set the bath temperature. Its range is 20-80 degrees centigrade. The LKB bath temperature is set by first setting the range to either 20-50 or 50-80 degrees centigrade. Next, set the temperature by adjusting switches a, b, c, d to the corresponding values for the desired temperature found in Table 8.0.

2. To control the bath temperature the external water bath must be correctly set. The external bath acts as a heat sink, therefore the temperature is usually set 2-3 degrees centigrade below the calorimeters bath temperature.

   Table 8.0 lists the suggested setting for the external bath temperature(these values are rough estimates and depend upon room temperature and the fine control setting).

   If the fine heater or preheater are not balanced correctly then a fine adjustment must be made to the external bath control (see description of equipment section for explanation of the bath control system.). Once the bath temperature is at its set point the ready light will come on.

III. Calibration of the Flow-Mix Measuring Cylinder

1. This must be done for each new system that is being run to insure that no leaks exist in the cylinder and flow rates are not too high such that it creates an error in the measurement.

   Starting with pump #1, turn valve #2 to the calorimeter position, valve #1 to the measuring position, and valve #5 to the bubble removal position.

2. Using the bubble pump, purge the bubble line through the measuring line with the same liquid which exists in pump #1 until no bubbles remain in

that line. This will prevent the introduction of bubbles into the measuring cell.

3. Once the line is rinsed, turn valve #2 to the calorimeter position and set the bubble pump to a setting less than 40 ml/hr.

4. Set pump #1 flow rate to 15 ml/hr. Let pump #1 and the bubble pump run for approximately one hour. This will insure that only one liquid exists in the tubing and cell and will allow for correct calibration of the cell. If a small amount of another liquid other than the desired calibration liquid exists in the cell or in the tubing before the cell it can cause the calibration to be significantly off.

5. Now, the system contains only one liquid and the system can be calibrated. Because the exit line of the measuring side is sent to the reference side all viscous heat effects are taken into account and the calibration is good at all flow rates (this may not be necessary in most cases).

6. Turn off the bubble pump and turn valve #4 to the off position.

7. Set pump #1's flow rate to the maximum combined flow rate of each fluid. This will help speed up the calibration procedure.

8. Once the pump's flow rate has stabilized (this is evident by a constant pump pressure and a stable base line from the calorimeter), the system is ready for calibration.

   Turn the "man/timer" switch on the calibration unit to the "timer" side as shown in Figure 19.0. Turn switch #1 on the calorimeter to "Channel 2". Turn the "A/B" switch on the calibration unit to the side "A" (The calibration is done on side "A" because this is the side where the actual measurement is taking place. Side "B" is the reference side). Adjust the zero pod on channel 2 which is located on the LKB's amplifier so that the calorimeter reads 0 microwatts.

9. If the liquids of interest have a high enthalpy of mixing then a decision must be made as to which

scale the calibration should be made for. All of the liquids in this investigation were calibrated on either the 1000 or 3000 microwatt scale.

Set the calibration level with the "Power" switch on the calibration unit. Switch the "Man/Timer" switch to the "Man" (manual) side (this will turn on the calibration heaters).

10. To make sure that this is the actual zero, and the flow rates are not too high, turn off pump #1 and let it set for one half hour or until no change occurs in the calorimeters output. This will allow for the flow rate to come to a halt and the system to come to thermal equilibrium.

11. Repeat step #9.

12. Once a steady zero value is obtained turn pump #1 back on and continue this procedure.

13. Once the system has reached a steady-state value at its set flow rate (This usually takes 20-40 minutes), adjust this value to read the calibration value by adjusting the fine-pod adjustment located on the amplifier board. This adjustment is very sensitive and takes several attempts.

14. Turn the "Man/Timer" switch back to the timer position which turns off the heaters and repeat steps 11 and 12 until there is no change in both end point values. This step usually requires 3-5 times to complete.

15. If the heat effects of the system being run exceed 4200 uWatts then the above steps can be ignored. A multimeter with at least 6-1/2 digit resolution must be used here connected as previously mentioned to the banana plugs located on the electronics rack. The system has already been calibrated using a HP multimeter model 3457A, see calibration section for more information.

IV. Measurement Procedure

1. Turn valves #3, and 4 to the calorimeter position and valve #5 to the pump position.

2. Set the pumps to the desired flow rates.

3. Once the flow rates stabilize, which is demonstrated by a constant calorimeter reading, take the calorimeter reading every three minutes for at least ten readings (more readings may be required depending on the stability of the output). This will allow a means of some statistical evaluation of each point. If the value never stabilizes refer to the trouble shooting section on possible problems and solutions.

4. Switch valves #3, 4 to the measuring position.

Mass Flow Rate Measurement

A. For a liquid with a density >0.77 g/ml and non-reactive with Hexadecane (silicone oil can be substituted in place of hexadecane where appropriate).

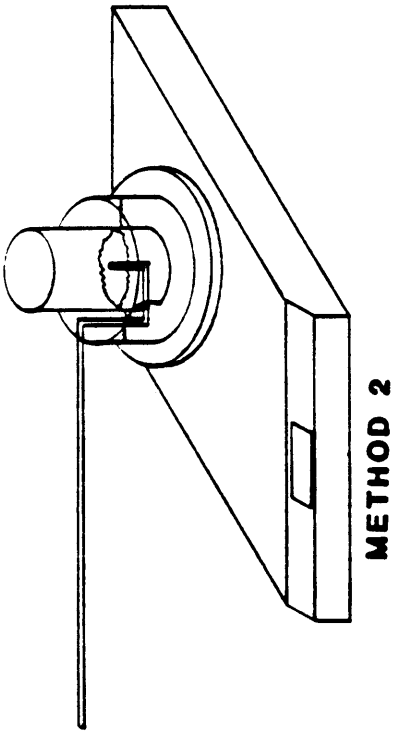
1. Put approximately 20 ml of the liquid being measured in a flask as shown in Figure 30.0 method 1.

2. Put approximately a 2-3 mm layer of hexadecane on top of the measuring liquid. The hexadecane has such a low vapor pressure that it will not allow a path for any significant evaporation.

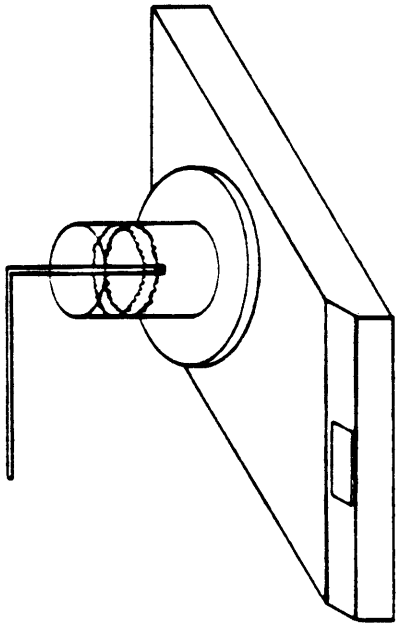
3. Place the vial on the balance and place the tubing in the liquid. Be sure not to let the tubing touch any part of the flask as this will affect the flow rates reading (The clamp keeps the tube from vibrating and and touching the flask).

4. Let the balance stabilize for a minute or so and then begin recording mass and time at three minute intervals for at least 30 minutes.

Flow Rate Determination



METHOD 2



METHOD 1

Figure 30.0

B. For liquids with a density less than 0.77 g/ml and not soluble in water or hexadecane.

1. Assemble the apparatus as shown in Figure 30.0, method 2.

2. Fill the cup to the 50 ml mark on the cup with water (or hexadecane). On top of the water place approximately 10 ml of hexadecane.

3. Using a syringe evacuate the air in the cylinder, thus filling it with liquid. Carefully remove the syringe and adjust the flask and tubing such that the tubing is not touching any part of the flask or beaker.

4. Start flow into the measuring apparatus and let run for 5-10 minutes before beginning run. This should allow enough time for the system to come to a pseudo vapor-liquid-equilibrium in the top of the cup.

5. Do the same as mentioned in the previous step 4.

V. Pump Control Box

1. The pump box is controlled by a network as shown in Figure 22.0. The temperature settings are relative so the desired temperature is found by trial and error. Since no specific temperature is needed 29.2°C (112.84 ohms) was found to be a good temperature for the size of heater element installed.

2. The temperature can be adjusted by adjusting the regulator.

3. The temperature is sensed in the middle of the box and read by a multimeter.

APPENDIX H

TROUBLE SHOOTING

A. Unstable calorimeter reading.

1. Bubbles.
2. Leaky measuring cell.
3. Pump problems.

B. Can not bring measuring cell into calibration limits.

1. Leaky measuring cell.
2. Bad amplifier
3. Bad peltier element.

C. Flow rates varying.

1. Unstable box Temperature.
2. Pump problems.
3. Leak in tubing connections.
4. Dirt or fragments in tubing.

D. Enthalpy of mixing values are too low for exothermic effects and too low for endothermic effects.

E. Enthalpy of mixing values are too high for exothermic effects and too high for endothermic effects.

F. Balance causing flow rates to vary.

1. Vibrations causing unstable reading.

G. Unstable bath temperature in the calorimeter.

1. Water level is too low or dirty.
2. Water level in external circulator is low or dirty.

3. Room temperature is fluctuating beyond systems capability to control.

H. Unstable box temperature.

1. Room temperature is too close to the box's set point.

2. The contact points on the controller are pitted or have enormous amounts of carbon deposit.

3. The relay is going bad.

I. Pump Problems.

1. Unstable flow rate.

2. Unstable back pressure.

3. Pump switching directions while pumping or purging.

SOLUTIONS

I. Bubbles

A. De-gas liquid as described in pump loading step 13.

B. 1. Shut off pump #2.

2. Open valve #5 of the bubble pump. Turn valve #4 to the bubble line position. Turn valve #3 to the measuring position.

3. Flush the bubble line with a low surface tension liquid such as ethanol or a surfactant using the bubble pump.

4. Once the line has been flushed set pump #1 flow rate to 15 ml/hour.

5. Turn valve #5 to the calorimeter position and valve #4 to the measuring position.

6. Let this configuration run for 1 minute then switch valve #4 back to the measuring position and valve #3 to the calorimeter position.

7. Repeat steps 6 and 7 10 - 20 times. This should remove any bubbles that are attached to the tubing wall, if not use another low surface tension fluid and repeat the above steps.

C. Do not turn off pumps. Keep liquid flowing in the tubing at all times. This should be done because the teflon tubing that connects the stainless tubing to the calorimeter is aerobic.

II. Leaky Measuring Cell

A. 1. Disconnect the cable from the cell to the amplifier board. Carefully remove the cell from the bath (make sure to remove directly upward without side to side movement as this may cause damage to the gold tubing). Place the cell on a counter top and dry the cell. Push down on the top of the cell. The top of the cell and the tubing section should give way slightly into the aluminum shell and expose a steel split-o-ring. With a knife or a small pick remove the split-o-ring. With the ring removed the outer aluminum shell can be removed. Dry the inside of the measuring cell with nitrogen. The black o-ring seal is located right below the steel split-o-ring. Place a small amount of seal grease around the O-ring (be careful not leave too much grease exposed to the bath as this will cause the bath water to become cloudy and thus changed).

2. Check the seals around the tubing and face plate. If there is a leak around the tubing (this is best checked by using a helium leak tester) seal it with a sealant that is not water soluble.

3. Condensation can occur into the cell during semi humid periods if left open to the atmosphere. This problem will cause the same symptoms as a leaky cell. This problem is taken care of by blowing the cell out with dry nitrogen down the ampoule cells and the air line. This step should be performed on a

regular basis as preventative maintenance.

III. Pump Problems

A. 1. Back pressure of 50 psig is required to seal the seal on the pumps piston. The back pressure also makes the gears become rigid and helps stabilizes the flow.

2. Back pressure can be applied by three methods if feasible: first a back pressure regulator, secondly using a length of very small internal diameter tubing, and thirdly by a packed column. A metering valve is not recommended as it will pressurize up and relieve thus causing instability in the flow.

B. 1. Pump instability can be caused by a worn gear or the tachometer brushes may be dirty. For these problems refer to the Isco service department.

2. Dirt inside the cylinder and worn seals can cause unstable back pressure and flow rate. Refer to the Isco service book for instructions on cleaning the cylinder and replacing the seals.

C. Unstable temperature in the pump box can also cause unstable flow rates because the pumps deliver a constant volumetric flow rate. This can be solved by keeping the temperature swing of the pump box to a minimum.

D. If the pump is switching back and forth on its own (switching gear directions) an adjustment needs to be made to the proximity sensor. The sensor simply senses presence of a specific gear which in turn tells the pump which direction it is pumping. Sometimes grease builds up on this sensor and cleaning the gear and the sensor will take care of the problem.

IV. Faulty Amplifier

A. 1. If the amplifier goes bad as suggested by meaningless readings on the calorimeter there

are two options. The first option is to call LKB and have the board replaced. The second option is to use a nanovolt meter to read directly the cell voltage. The amplifier is not a must use item, it only amplifies the signal to a convenient level and fine tunes the end points to make the calibration easier. Since the amplifiers are linear a volt meter can be used with a little calibration and checking. In fact the range can be expanded over the display limits that the LKB uses as long as all heat transfer is accounted for.

V. Faulty Peltier Elements

A. To replace the peltier elements remove the shell of the measuring cylinder. This is done by pushing down on the top of the cylinder and removing the exposed split ring. This will allow the shell to slide off.

2. Remove the heat shield tape.

3. Remove both springs that hold the intermediate heat sinks together. This now allows the heat sinks to move.

4. Remove the intermediate heat sinks.

5. Detach the lead wires to the peltier element.

6. Remove the peltier element and the heat transfer grease.

7. Apply new heat transfer grease to the new peltier element and replace the element to the intermediate heat sink (be careful to realign the element as closely as possible to the one removed).

8. Replace the springs and heat tape.

9. If the bottom spring fell out of the main heat sink block replace and put cylinder back together as it was.

VI. Unstable Box Temperature

A. The room temperature is too close to the box's temperature. To avoid this predicament lower the room temperature or raise the boxes temperature. Remember that electronics exist in the box and therefore it is recommended for best results not to operate above 35 degrees centigrade.

B. The power supply to the temperature control network could be going out. This can be replaced with a 24 volt DC power supply.

C. If the heater element is sticking on or off the contacts on the controller could be damaged or the relay could be going out.

1. Replace the contacts or carefully file the deposits off of the contacts.

2. Replace the solid state 24 volt DC relay. This part can also be replaced with a non-solid-state relay but will not last as long.

VII. Leaky Tube Connections

A. Replace or tighten tubing connections.

VIII. Dirt Or Fragment In Tubing

A. Replace the tubing.

IX. Enthalpy of Mixing Values Are Too High for Exothermic Effects and Too Low for Endothermic Effects.

A. Lower the flow rates. The flow rates are too high and complete mixing and/or heat transfer is not taking place before leaving the measuring area.

B. Lower the flow rates. The flow rates are too fast and the fluid entering the measuring cell is above the bath temperature.

X. Enthalpy of Mixing Values are Too Low for Exothermic affects and Too Low High Endothermic Effects.

A. Possible evaporation of fluid is taking place while making flow rate measurements.

XI. Balance Problems

A. If the flow rate is fluctuating or below what it should be there is the possibility that fluid is evaporating from the measuring apparatus. This can be solved by placing a non reactive low vapor pressure fluid on top of the measuring fluid.

B. 1. To get rid of an unstable balance make sure that the tubing is clamped tightly right next to the balance.

2. Do not let the fluid fall into the measuring apparatus. Make sure that the end of the tubing is under the measuring fluid.

XII. Water Bath Problems

A. Fill water baths with 18 mega ohm deionized water only. Do not add any inhibitor as LKB suggests. The inhibitor is not needed when using deionized water and it only clouds the water more rapidly. For information on changing the water in the baths refer to the LKB service handbook.

XIII. Room Temperature Problems

A. If the room temperature is fluctuating beyond the LKB's capability to control, check to see if the air conditioning is functioning properly.

B. Lower the room temperature. This will keep the room from getting above or near the box's temperature. This will also cause the heater to turn on, thus better temperature control of the room.