

ACHIEVING THERMAL EQUILIBRIUM BETWEEN
LIQUID AND VAPOR PHASES OF
A BOILING PURE
COMPONENT

By

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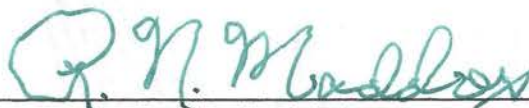
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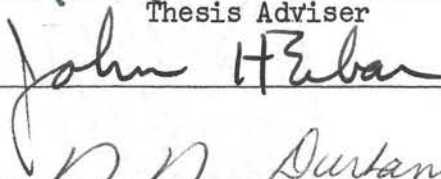
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Thesis Approved:



Thesis Adviser



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PREFACE

This study is concerned with the fact that at least some pure components have a tendency to superheat in the liquid phase when boiling in glassware. The proof of this phenomenon's existence and means for destroying the superheat are the primary areas of study.

I am indebted to Prof. R.N. Maddox for the advice and assistance he has provided while serving as my research adviser for this project. I would also like to thank the members of the Chemical Engineering Faculty for their assistance and advice.

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I especially wish to thank my parents, Mr. and Mrs V. Gail Fenderson, for their encouragement, confidence, and advice during my period of graduate study.

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LIST OF SYMBOLS

English Letters

A	Antione equation constant
B	Antione equation constant
C	Antione equation constant
d_a	Agitator diameter (ft.)
L/V	Ratio of liquid and vapor mass flow rates
rpm	Rotational rate (revolutions per minute)
Re_a	Agitator Reynold's number
t	Temperature ($^{\circ}\text{C}$)
T	Temperature ($^{\circ}\text{F}$)

Greek Letters

μ	Viscosity (lb./ft. min.)
ρ	Density (lb./ft. ³)

CHAPTER I

INTRODUCTION

The initial intent of this research was to explore a problem that several workers have reported in making tray efficiency studies. Burns (1), Hartman et al. (2), Liang and Smith (3), and Standart (4) have all noted measured vapor temperatures up to 4°C (7.2°F) lower than the calculated dew point temperature and up to 3°F lower than the measured liquid temperature for systems that should have been in equilibrium. The original intent of this study was to explore this phenomenon and attempt to determine the reason for this difference in the measured vapor and liquid temperatures.

The thermocouples to be used in this study were to be calibrated against the boiling points of several pure and research grade hydrocarbons. A distillation flask was set up and two thermocouples were inserted for calibration; one thermocouple was located in the liquid and one located in the vapor. During the calibration procedure, the liquid thermocouple was observed to have a significantly higher reading than the vapor thermocouple. This apparent difference between the temperatures of the vapor and liquid phases of a boiling pure component gave rise to this study.

CHAPTER II

EXPERIMENTAL APPARATUS

The basic experimental apparatus was a very simple one. It consisted of three basic parts: a one liter distilling flask with a heating mantle, a total condenser, and thermal measuring devices.

The distilling flask was equipped with three necks. Each neck had a ground glass $\text{F } 29/42$ female connector. These necks allowed the insertion of thermocouples, thermometers, and agitators into the flask. A three-way parallel connecting tube was joined to the center neck of the flask. One side of the connecting tube was used to convey hydrocarbon vapors to the condenser and return the condensed liquid to the flask. The other side of the connecting tube and one of the side necks were used for insertion of the thermal measuring devices. The third neck of the flask was used for agitator entry into the flask. When any of these openings was not in use, it was closed with a male $\text{F } 29/42$ ground glass plug.

The distilling flask was completely enclosed by an electric heating mantle, but only the bottom half of the mantle was used for heating. Power supply to the mantle was regulated by use of a Superior Electric Company type 116 powerstat.

The flask, connecting tube, and all other connections to the flask were insulated with glass wool to reduce any heat losses to the surroundings.

The total condenser was used to condense the hydrocarbon vapors and return the liquid to the distilling flask. The condenser was a glass, spiral tube type. The overall length of the condenser was 20 inches and was $2\frac{1}{2}$ inches in diameter. The spiral tube was $\frac{3}{8}$ inch in diameter. The condenser was water cooled, with the hydrocarbon vapors on the tube side. A sketch of the flask and condenser is shown in Figure 1.

Several thermal measuring devices were used in this study. The most basic were simple copper-constantan thermocouples with ice water reference junctions. Millivolt output readings from these and all other thermocouples used were made with a Leeds and Northrup model 755 type K-5 potentiometer with a Leeds and Northrup number 983401 DC Null Detector.

The liquid and vapor thermocouples were shielded to eliminate any radiation effects that might affect the thermocouple readings. This was done by suspending a short piece of $\frac{3}{4}$ inch electrical conduit around the thermocouple junctions. This is shown in Figure 2. Several layers of glass wool were placed between the heating mantle and the flask to eliminate any radiation from the heating mantle to the thermocouple junctions in the flask.

Two sets of differential thermocouples were also used. A differential thermocouple is simply a pair of junctions connected in series which measures the difference in temperature between the two junctions. This is possible because the junctions are connected in series with opposite polarity. Actually the simple thermocouple set up with an ice water reference junction is a differential thermocouple measuring the

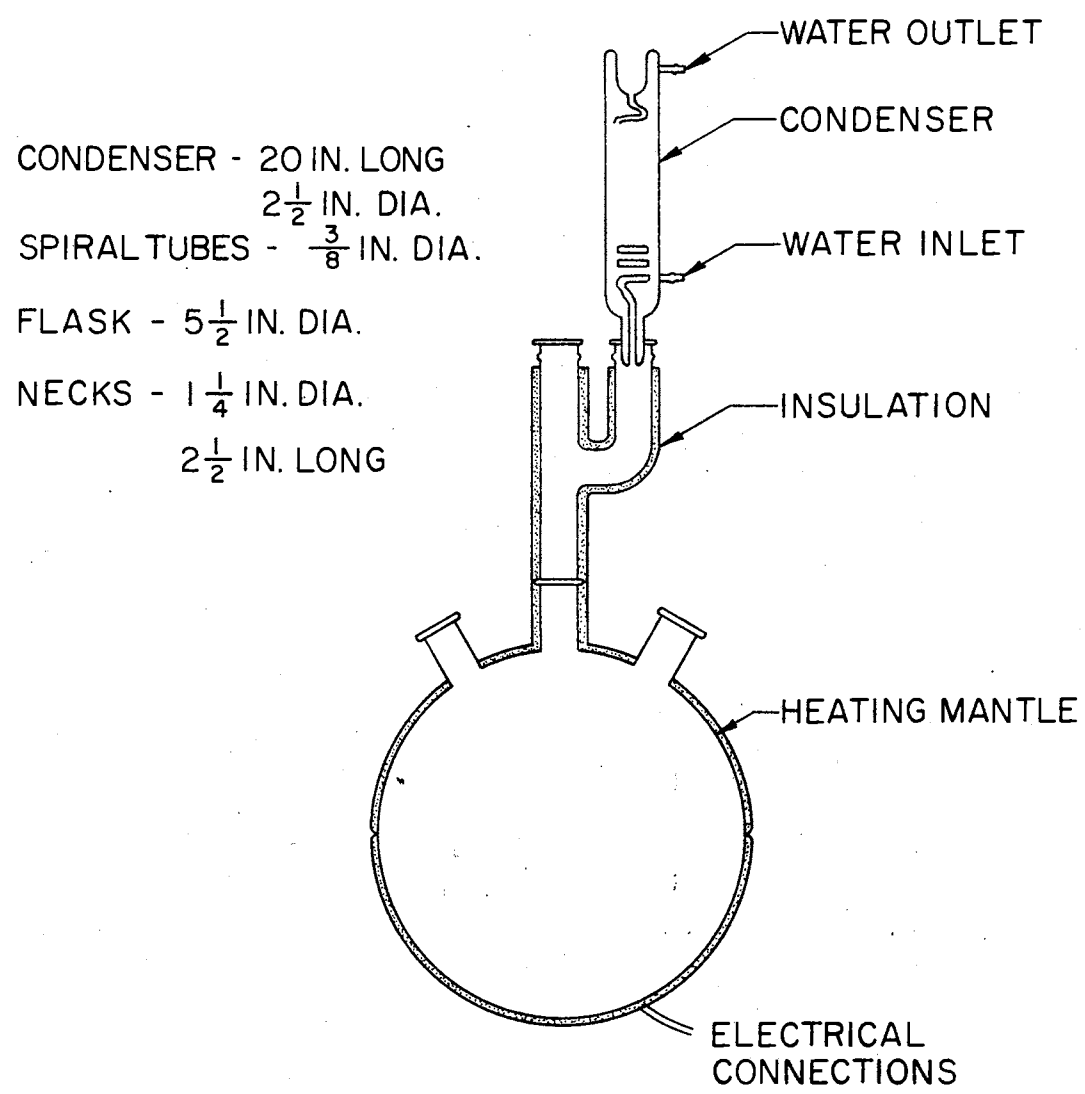


Figure 1. Experimental Apparatus

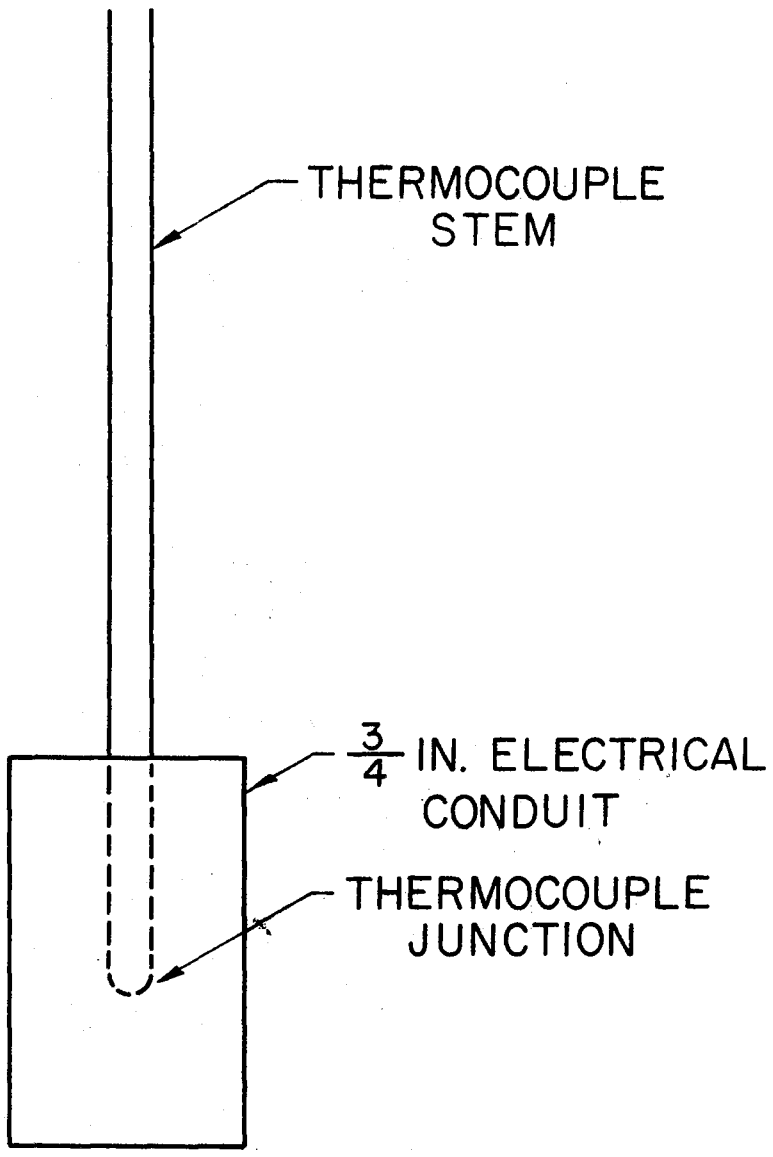


Figure 2. Thermocouple Junction Shielding

difference between the primary junction and the ice water junction. All junctions used in this study were copper-constantan.

The first differential thermocouple set is shown in Figure 3. The two junctions were positioned about $2\frac{1}{2}$ inches apart and secured to an 8 mm glass rod. The rod was about 24 inches long which allowed it to be raised or lowered so that both junctions could be positioned in the vapor or liquid phase or so one junction was in each phase. The copper lead from the top junction was coiled around the bottom of the rod so that it would pass through the liquid when the vapor-liquid thermocouple was in use. This was to eliminate any conduction losses from the vapor phase junction.

The second differential thermocouple set had two differential thermocouples. One set of junctions was positioned as in the first set on a similar rod. In addition to this set of junctions, another set of junctions was positioned on either side of the liquid junction with approximately one inch spacing between the junctions. This differential thermocouple was used to check for thermal currents in the liquid. These sets of differential thermocouples are shown in Figure 4.

A Beckmann differential thermometer was also used. This is a device for measuring very small temperature differences. The thermometer that was used was calibrated in 0.01°C increments so it allowed for very precise measurement of temperature differences. The Beckmann thermometer requires some knowledge of its construction before it can be successfully used. The thermometer is constructed in a manner such that the volume of mercury in the bulb may be regulated. This allows it to be used over a large temperature range though the temperature scale normally has only a six to ten degree span. The Beckmann thermometer was inserted through

the connecting tube and could be raised and lowered so that the thermometer bulb could be placed in either the liquid or vapor phase.

In addition to the basic parts of the apparatus, two modifications were made. A liquid agitator was added, and a reflux head to take a vapor product was added.

The agitator was a one inch diameter paddle type agitator. The agitator shaft passed through a seal in one of the side necks of the flask. A Fisher Scientific Company variable speed, type CRGL-2, 115 volt motor was used to drive the agitator. Rotational speeds from about 45 to 2500 rpm were possible with this motor. At low rotational rates, a stopwatch and simple timing of the rotation rate was used. At higher rates, an Electronic Brazing Company Stroboscope model 510 AL was used for determining rotational rates. When the stroboscope was used, the surroundings were darkened in order to achieve better visual resolution.

In converting the flask to a simple distilling apparatus, the total condenser was replaced by a magnetically controlled reflux head. This modification allowed a vapor product to be withdrawn. The purpose of taking a vapor product was to check for possible effects of small amounts of low boiling impurities in the liquid charge. Since there could be only very small volumes of these impurities in the charge, the reflux head was necessary rather than taking a total vapor product with no reflux. The reflux head operated by condensing the vapors and either returning the condensate to the flask or to a product collection vessel. This was controlled by an electromagnet which influenced the position of a small, moveable funnel. When the magnet was on, the funnel was held in a position directing the liquid condensate to the product collection vessel. When the magnet was off, the funnel returned to a position

which returned the condensate to the flask. The magnet was regulated by a Flexopulse timer. This timer was a cyclic on-off timer, which could be set to give on-off cycles ranging from 5 seconds on and 120 seconds off to 120 seconds on and 5 seconds off. The use of the timer allowed almost any liquid and vapor mass flow rate ratios within the reflux head, L/V ratio, to be achieved.

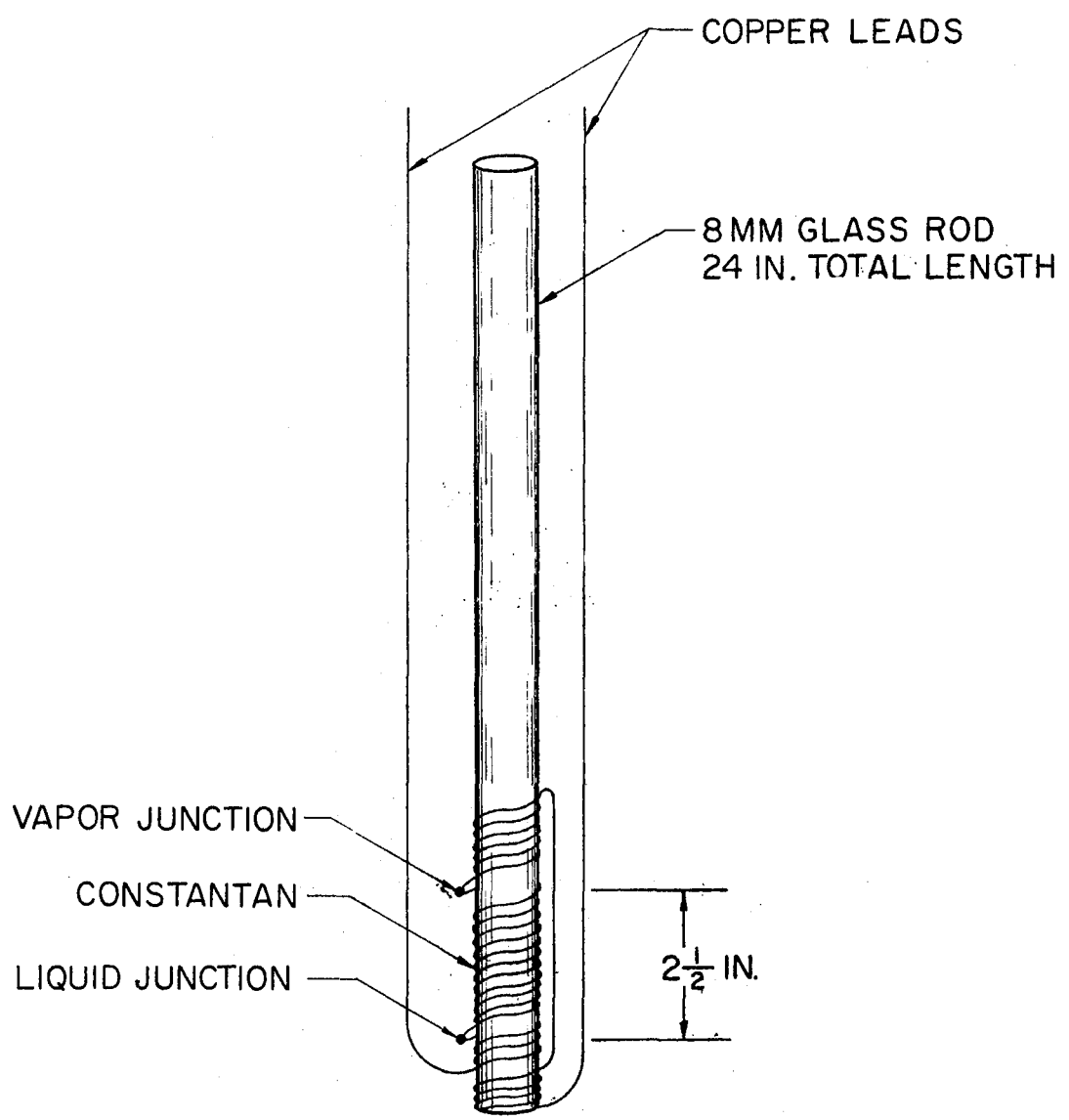


Figure 3. Differential Thermocouple

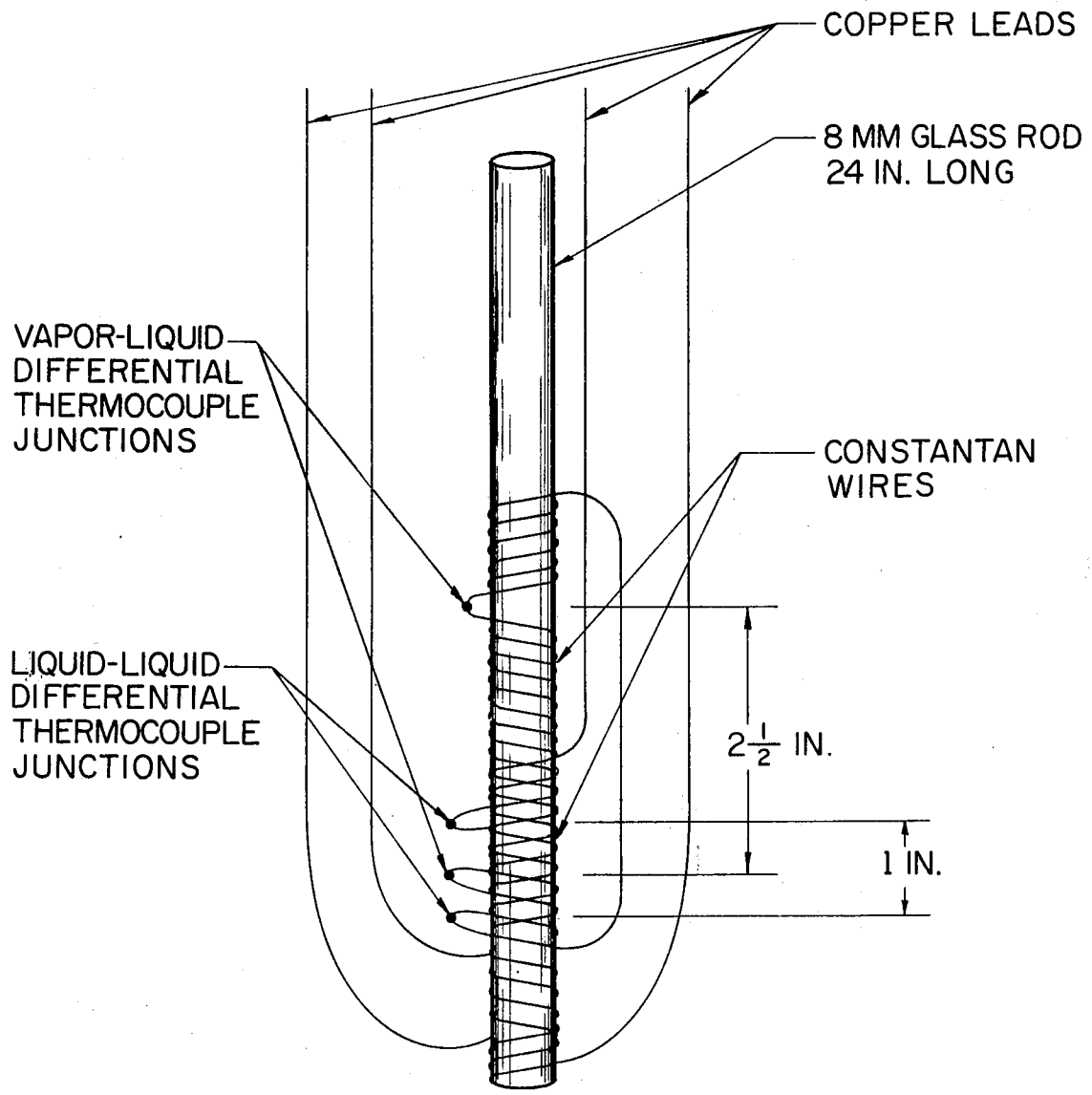


Figure 4. Second Differential Thermocouples

CHAPTER III

EXPERIMENTAL PROCEDURE

A liquid charge to the one liter flask of 700 to 900 milliliters was necessary to give a sufficient volume of liquid reservoir in the flask at all times. Smaller volumes of liquid would require that the liquid thermocouple be positioned either too close to the vapor-liquid interface where it would sometimes would not be totally immersed in the liquid or too close to the flask wall where it could be affected by thermal gradients near the wall. Boiling chips were always added with the liquid charge to provide adequate nucleation sites.

After the liquid charge was made to the system, heat input was initiated. A gradual heating of the system was better so that the initiation of boiling could be better controlled, and a heat flux near the minimum required for moderate boiling could be utilized. This heat flux, of course varied depending on the boiling point and the heat of vaporization of the component.

The heating up period usually took from one to three hours. The thermocouples were monitored and readings allowed to become stable before any readings were recorded.

After the system had come to a stable state, readings were begun. Depending on the type of measurements to be taken, somewhat different procedures were used.

When simple thermocouples were in use, care was taken to insure that the junctions were not too close to the system boundaries. Care was also taken to insure that the ice water reference junction was actually at 32°F . This was accomplished by using a large volume of crushed ice and distilled water in a Dewar flask. The use of distilled water was particularly important. The available tap water was especially high in mineral salts and could make as much as 2°F difference in the thermocouple readings. Precautions were also taken to eliminate any current induction in the thermocouple lead wires. A very significant current could be induced because of the very small potentials generated by the thermocouples. The steps that were used were making sure that the leads were short as possible and securing the leads to some solid support to limit movement. The potentiometer was also periodically checked to see that it was in proper operating condition. These checks, for which instructions were given in the potentiometer manual, included checking the standard cell, the calibration between scales, and the current standardization.

When using differential thermocouples, the precautions were similar to those for the simple thermocouples. The differential thermocouples were checked initially to see that both junctions produced equal potentials at the same temperature. This check was most easily made by placing the differential thermocouple in an ice water mixture or the vapor of a boiling liquid and measuring the potential. There should be no net potential when both junctions are at the same temperature. Induced currents were even more important with the differential thermocouples since the readings being taken were smaller in magnitude. Care was also taken when using differential thermocouples in the positioning

of the junctions so that each one was in the proper phase. If the vapor junction was too close to the vapor-liquid interface, the liquid could be splashed onto the junction when the bubbles broke the surface. If the liquid junction was too close to the interface, there was the possibility that the junction was not totally immersed in the liquid at all times. The problem of junction location was not normally a great one since the achievement of any sort of stable readings under conditions of improper junction location was virtually impossible.

The Beckmann thermometer presented more problems in its preparation for use than in its use. The volume of the mercury in the thermometer bulb must have been properly regulated before it could be used. To do this, the thermometer had to be brought to approximately the temperature of use, normally one or two degrees greater than the maximum temperature of application. At this point the volume of mercury was established. This was done by breaking the column of mercury just above the temperature scale. The excess volume was then channeled into an excess mercury reservoir. This mercury could be returned to the thermometer bulb at any time that it was needed. After the mercury volume in the bulb had been properly regulated, the thermometer was ready for use. In this study, the Beckmann thermometer was inserted into the system through a seal in one side of the connecting tube and the center neck of the flask. It was possible to move the position of the thermometer bulb into either the vapor or liquid phase. The Beckmann thermometer was placed in the phase to be checked and allowed to remain for ten minutes then the scale reading was recorded. The bulb was then moved into the other phase and allowed ten minutes to reach a new reading. Normally only a minute or two was required to reach a stable reading, but the additional time

was allowed to make sure there were no fluctuations. This procedure was repeated several times to check the consistency of the readings.

When the agitator was installed, it presented no significant new problems. The only additional measurement that was required was the rotational rate of the agitator. At low rates, the speed of the agitator was determined by simply counting the revolutions during a period of time, determined with a stopwatch. At higher rates, the rotational speed was determined with a stroboscope. This instrument operates by utilizing a flashing light at a specified periodic rate. To use the instrument, the light is shined on a cyclic operation, such as rotation. When the rate of the flashing light and the cyclic operation are equal, the cycle seems to be frozen. Care was taken to see that the rotational rate that was determined was the same as that recorded by the stroboscope. If the stroboscope and the cyclic operation were a harmonic of each other, the cycle would appear to freeze but the stroboscope would not indicate the true cycle rate. This was avoided by completely darkening the surroundings so that visual resolution was better; making a series of runs by starting at low rates and increasing the rate slightly from one run to the next was also better. All other measurements were made in the manner previously described.

The purpose of using a reflux head was to monitor the thermocouple readings as a small amount of product was withdrawn. The product withdraw rate was required to be slow since only a small amount of product was to be taken. A charge of 900 milliliters was used in order to maximize the total amount of low boiling impurity that could be taken as a vapor product. Heat input was the same as that used with

the total condenser. A somewhat greater heating up period was required in order for the reflux head to reach the system temperature and function properly. There was a vapor thermocouple installed in the reflux head with the junction positioned at the point that the vapors entered the reflux condenser. When the vapor thermocouple registered approximately the same reading as the liquid thermocouple and was stable, the system was ready to begin product withdrawal. The product rate could be varied by changing the settings on the Flexopule timer. A timer setting to regulate the electromagnet to 15 seconds on and 60 seconds off was used. This gave a product rate that was small enough to check for the possible impurity effects. By using a water cooled, volumetrically calibrated collection vessel, the total product volume collected in addition to the liquid, vapor, and differential vapor-liquid thermocouple readings could be recorded.

CHAPTER IV

RESULTS AND DISCUSSION OF RESULTS

Initially two thermocouples were used. One was positioned in the vapor phase by inserting it through the connecting tube and the center neck of the flask, and the other inserted through one of the side necks into the liquid phase. Toluene was charged to the flask and allowed to begin boiling. The original intent at this point was merely to calibrate the two thermocouples. After the toluene had been boiling a sufficient length of time that equilibrium should have existed, readings were taken. These readings showed a significant difference in the two thermocouple readings. In order to check the possibility that the thermocouples were producing different potentials for the same temperature, the positions of the thermocouples were exchanged. The vapor thermocouple was lowered into the liquid, and the liquid thermocouple was raised into the vapor. The readings are given in Table I. The millivolt--temperature conversions were made using a standard thermocouple conversion table (5). These readings indicate vapor readings of 229.14°F for thermocouple 1 and 229.28°F for thermocouple 2. The corresponding liquid temperatures are 230.15°F for thermocouple 1 and 230.57°F for thermocouple 2. These readings, although not identical, were close enough to indicate that neither thermocouple was faulty. Thermocouple 1 showed a 1.01°F difference in the liquid and vapor temperatures, and

thermocouple 2 showed a 1.29°F difference. This indicated that the liquid and vapor thermocouples were not at the same temperature.

TABLE I
READINGS FOR TOLUENE BOILING AT 734.6 mm Hg

	Vapor (mV)	$^{\circ}\text{F}$	Liquid (mV)	$^{\circ}\text{F}$
TC1	4.7259	229.14	4.7587	230.15
TC2	4.7296	229.28	4.7639	230.57

With the thought that there could be temperature effects induced by the position in the distilling flask, the two thermocouples were reversed. This had no effect on the thermocouple readings. The vapor thermocouple produced the same potential regardless of where it was positioned in the vapor phase. The liquid thermocouple readings were the same unless the junction was positioned very close to the heated flask wall or the vapor-liquid interface.

All work was done in glassware, and a mixture of $\frac{1}{4}$ inch Berl saddles and 4 mm glass beads had been used as boiling chips. In order to check the possibility that there were insufficient nucleation sites for boiling, the $\frac{1}{4}$ inch saddles and 4 mm beads were replaced by crushed saddles and 1 mm beads. Approximately the same total volume of boiling chips was used; this should have provided many more nucleation sites. This change of boiling chips had no effect on the liquid or vapor thermocouple readings.

Originally the thermocouples were not shielded from radiation as shown in Figure 2. The temperature difference seemed to indicate that there might have been some radiation effects in the thermocouple readings. This seemed to be logical at this point since radiation from the vapor thermocouple to the surroundings would lower its reading somewhat, and the liquid thermocouple could have been receiving radiation from the heating mantle increasing its reading. In order to eliminate these possible effects, the thermocouples were shielded as shown in Figure 2. Several layers of glass wool were also used to shield the heating mantle. With these changes made, the readings still did not change from those in Table I. This indicated that there were no radiation effects influencing the vapor or liquid thermocouple readings.

The toluene was then replaced by 800 milliliters of normal heptane. This allowed the behavior of another of another component to be checked.

A Beckmann differential thermometer was also used to replace the thermocouples at this time. The Beckmann thermometer was calibrated in 0.01°C increments. The thermometer bulb was positioned in the vapor and boiling was initiated. When sufficient time for steady state had elapsed, the thermometer reading was taken and recorded. The actual magnitude of the Beckmann thermometer reading has no significance, but rather the difference in readings is important. After the vapor reading was made, the thermometer bulb was lowered into the liquid and the liquid reading was taken and recorded. Table II gives the results of the use of the Beckmann thermometer with boiling normal heptane. This shows a 1.25°C (2.25°F) difference in the vapor and liquid temperatures. The thermometer scale was inverted so that the lower reading actually corresponds to a higher temperature.

TABLE II
BECKMANN DIFFERENTIAL THERMOMETER
READINGS FOR n-HEPTANE

Phase	Thermometer Reading
Vapor	1.27 °C
Liquid	0.02
Vapor	1.27
Liquid	0.02
Vapor	1.27
Liquid	0.02

A differential thermocouple was used next. The first one used was like that illustrated in Figure 3. First the differential thermocouple was positioned in the liquid phase of the boiling normal heptane. This produced a potential of 0.0001 millivolts. The differential thermocouple was then raised slightly so that one of the junctions was in the vapor and the other was still in the liquid. This produced a potential difference of 0.0529 millivolts. The differential thermocouple was then raised more so that both junctions were in the vapor phase. The potential produced with both junctions in the vapor phase was 0.0008 millivolts. These readings correspond to 0.00°, 2.34°, and 0.03°F respectively as shown in Table III. This showed negligible temperature variations within a phase with potentials so small that they are very likely the result of slightly different potential outputs from the two junctions. The vapor and liquid difference was a very significant 2.34°F for this case, with the liquid temperature greater.

TABLE III
DIFFERENTIAL THERMOCOUPLE
READINGS FOR n-HEPTANE

Phase	Thermocouple Reading	
Liquid and liquid	0.0001 mV	0.00 °F
Liquid and vapor	0.0529	2.34
Vapor and vapor	0.0008	0.03

With several indications of a difference in the vapor and liquid temperatures, an obvious question was, which phase was at the correct boiling point temperature? In order to evaluate this question, constants for the Antoine vapor pressure equation were obtained from Lange (6) and API 44 (7). From this equation, a boiling point of 228.98°F was calculated for toluene at a pressure of 734.6 mm Hg. As was shown in Table I, the standard millivolt-temperature conversion table (5) indicated a vapor temperature of 229°F for both thermocouples and a liquid temperature of 230°F for both. These calculations and measurements indicated that the vapor phase was the more nearly correct reading for the boiling point temperature of a pure component.

Since the reduction in size of the boiling chips had no apparent effect on the vapor-liquid temperature difference, and also since the above calculations tended to indicate that the vapor phase reading was the more nearly correct, an agitator was installed in the distilling flask. The first agitator that was used was a large paddle type agitator approximately 2½ inches in diameter. This agitator was on a ground glass shaft that passed through a ground glass seal in one of the

side necks of the flask. The rate of rotation of this agitator was limited to fairly low rates by the ground glass seal. A different set of differential thermocouples was also installed. This set was like that shown in Figure 4. A liquid thermocouple was also installed. At low rotation rates that could be obtained with this agitator, there was no apparent change in any of the thermocouple readings.

The problems associated with the ground glass seal in the first agitator prompted the replacement of it with one that could be operated at higher rotational rates. The one installed was the one described in Chapter II. A liquid type seal was used to allow rotational rates up to 2500 rpm. With this modification made, research grade normal heptane was again charged to the flask. The heat input was adjusted to maintain a moderate boiling rate with no agitation. When sufficient time for steady state had been allowed, the differential thermocouple reading was monitored as rapid agitation was initiated. Immediately there was a drop in the differential thermocouple reading. This was an indication that the agitation reduced the vapor-liquid temperature difference. The heat input was stopped and the system allowed to cool. Again boiling was started with the same heat input as the previous case. This time the liquid thermocouple was monitored as agitation was started. The liquid thermocouple reading showed the same characteristics as the differential thermocouple had shown. This seemed to indicate that the agitation caused a reduction in the liquid temperature.

The apparent positive results that had been achieved in reducing the vapor-liquid temperature difference by agitation prompted a more thorough investigation. The liquid and vapor-liquid differential thermo-

couple readings for agitation rates from 0 to 2480 rpm were made for the heat input used above. These results are shown in Figure 5 and Table VI in Appendix B.

The data in Table VI show that as the agitation rate increased above approximately 200 rpm there was a definite downward trend in the vapor-liquid differential thermocouple readings. The liquid thermocouple also, in general, showed a downward trend. The exceptions were results of ambient pressure variations. No pressure control was used on the system since primary interest was on vapor-liquid differential readings which are, at most, only slightly affected by pressure variations.

The plot of the data in Table VI shown in Figure 5 showed the decreasing trend in the temperature difference with increasing agitator Reynold's number. The narrow range of Reynold's numbers about a median of approximately 10,000 contains a discontinuity. This range contained an apparent transition region in which no steady readings could be obtained. At the highest agitation rate, the vapor-liquid temperature difference had been reduced to 0.05°F . This was approximately the limit of the reliability of the differential thermocouple, but it appeared that slightly greater agitation rate would reduce the difference to 0.

The next check that was made was on the effect of heat flux on the vapor-liquid temperature difference. This was accomplished by varying the heat input to the system at a constant agitation rate. Pure grade normal pentane was used as the liquid charge for these runs. The results are given in Table VII in Appendix B and Figure 6. This showed that as the rate of heat input to the system increased, as indicated by the increasing wattage reading, the difference in the vapor and liquid temperature increases.

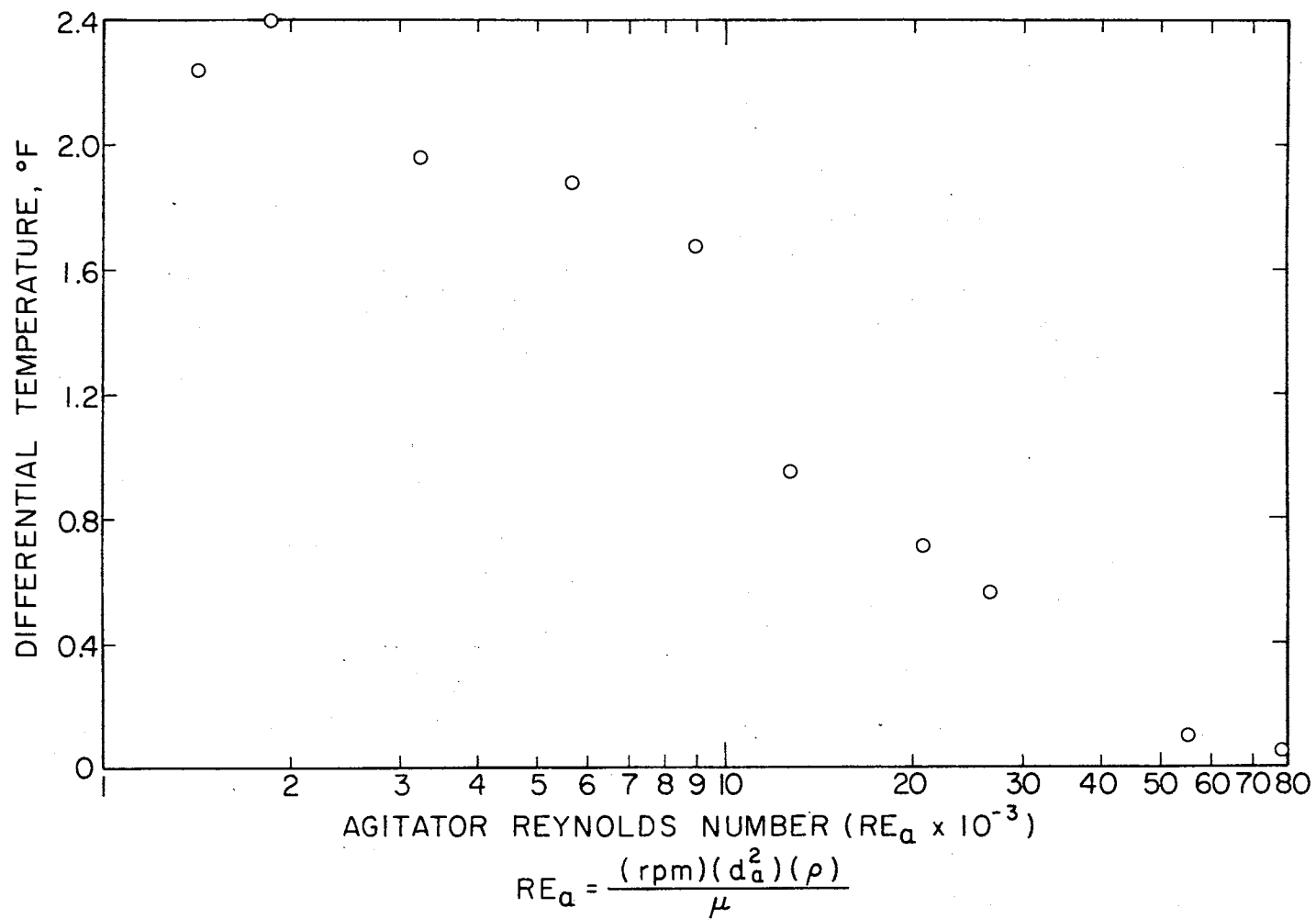


Figure 5. Differential Thermocouple Reading vs Agitator Reynold's Number for n-Heptane

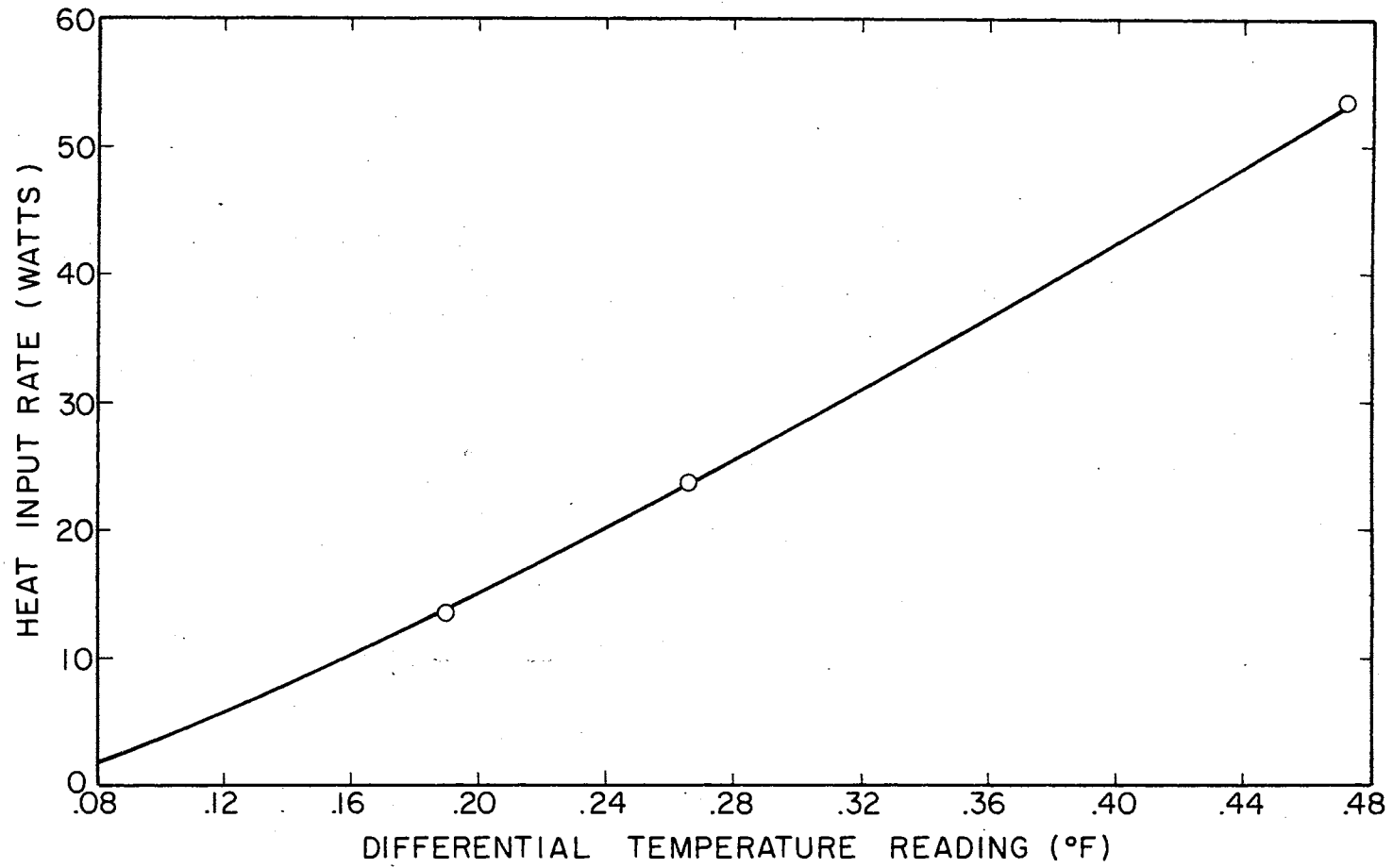


Figure 6. Variation of Liquid-Vapor Temperature Difference for n-Pentane at $Re_a = 6820$

With the heat flux influence effects shown above, an effort to utilize the minimum possible heat input to achieve boiling was made. A long, slow heating period to the boiling point was used. The data for this are shown in Table VIII in Appendix B and Figure 7. The increasing heat inputs shown in the last column of Table VIII and at the slash marks on Figure 7 were made at times when the liquid temperature appeared to be leveling off. The liquid used for this test was research grade normal heptane. As boiling began, the liquid temperature dropped slightly and began a non-periodic cycling of about 0.1°F . This cycling appeared to be a liquid superheating and then a sudden decrease in the liquid temperature as a release of vapor bubbles. The vapor-liquid differential thermocouple reading was, of course, of no meaning during the heating up period. Upon boiling, however, the differential thermocouple reading varied but averaged about 0.035 millivolts or 1.4°F . With the unstable boiling condition, the differential would jump to as much as 3°F at times. Some check on the low heat flux boiling of water also showed extreme difficulty in achieving stable differential thermocouple readings.

All of the experimental runs to this point had been made with toluene, normal heptane, and normal pentane. Some runs had been made with other components, as with water above, but these were for behavioral interest only and no data had been taken. No comparison of the behavior of different components under similar operating conditions had been made. Vapor-liquid temperature differences for five components were obtained. These differences were obtained for moderate boiling rates with no agitation; the results are given in Table IV. The readings for a homologous series such as the aromatics, benzene and toluene, or the

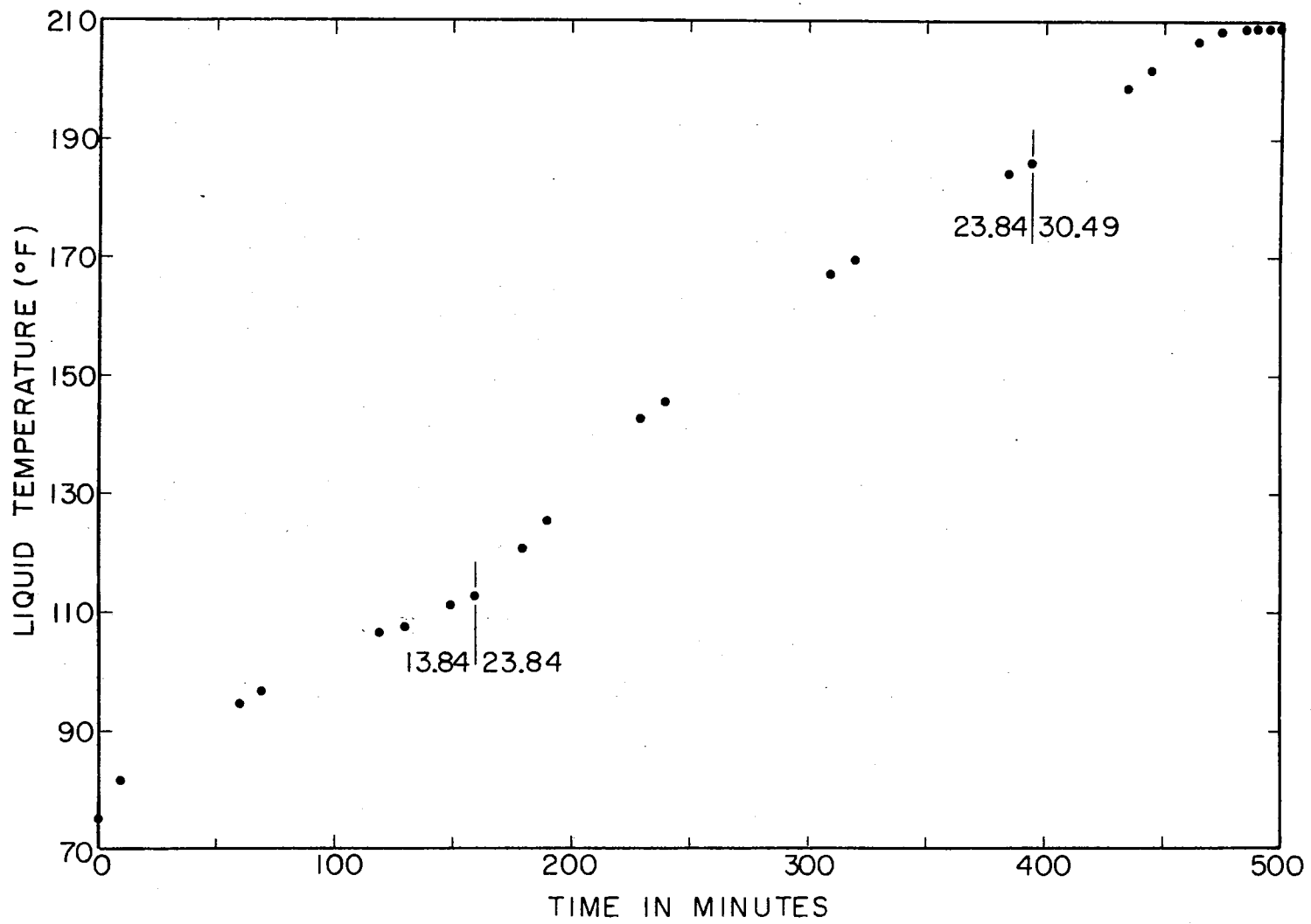


Figure 7. Liquid Thermocouple Reading vs Time from Start Up to Boiling

paraffins, normal heptane and normal pentane, are seen to increase with boiling temperature; but there are inconsistencies between the aromatics and paraffins. The water cannot really be compared to any of the other components because of its polar character and extremely high latent heat of vaporization. This may account for the difficulty in achieving stable readings with water. This and previous results tended to indicate that the phenomenon causing the liquid superheating was a complex one and probably dependent on several physical properties.

TABLE IV

THERMOCOUPLE DIFFERENTIALS FOR PURE
COMPONENTS WITH NO AGITATION

Component	Thermocouple (mV)	Differential (°F)
n-Pentane	0.0195	0.85
n-Heptane	0.0485	1.94
Benzene	0.0200	0.80
Toluene	0.0327	1.26
Water	0.0281	1.12

One possible explanation for the vapor-liquid temperature difference was that a very small amount of a low boiling impurity existed in each of the components even though each was a research or pure grade liquid. To check this possibility, the flask was converted to a simple distilling apparatus by replacing the total condenser with a magnetically controlled reflux head described in Chapter II. A relatively im-

pure charge of normal heptane was used in order to maximize any light component effect. The vapor thermocouple was monitored as a vapor product was taken at a very slow rate. Enough product was taken to insure that all light components would have been removed. The results are given in Table V. The results indicated that the vapor temperature does not change as product is withdrawn. If any light component had been present, the vapor temperature would have had a steady increase of one to two degrees as the product was withdrawn. The vapor temperature did vary slightly, but there was no steady change, and the maximum difference in any two readings was 0.38°F . This indicated that no low boiling component effects were present even though the charge had been the relatively impure normal heptane.

A check was also made with water boiling in an open beaker. This was done to evaluate the possibility of pressure gradients existing within the experimental apparatus. The differential thermocouple was used to check the vapor-liquid temperature difference. This was a fairly difficult test because of the extreme difficulty in insuring that the vapor junction was in a saturated vapor phase and was not affected by entrained liquid as the bubbles broke the surface of the liquid. Also, as the liquid vaporized, the volume was reduced to the point that the liquid junction was not totally immersed in the liquid. This condition required the runs to be of short duration. The differential thermocouple reading for this check averaged about 0.0322 millivolts or 1.29°F . This showed that there were no pressure gradient effects influencing the vapor-liquid temperature difference.

TABLE V

VAPOR THERMOCOUPLE READINGS FOR 4°C BOILING POINT
RANGE n-HEPTANE WITH $L/V = 0.8$

Time (min)	Product (ml)	Thermocouple Reading (mV)	Thermocouple Reading ($^{\circ}\text{F}$)
0	0	4.1470	206.62
15	5.5	4.1470	206.62
30	14.0	4.1475	206.81
45	21.5	4.1480	207.00
60	29.0	4.1475	206.81
75	36.5	4.1479	206.96
90	45.0	4.1480	207.00
105	54.0	4.1479	206.96

CHAPTER V

CONCLUSIONS

The results of this study indicated that a temperature difference between the liquid and vapor phases of the boiling pure components that were studied did exist. The results and vapor pressure calculations indicated that the liquid phase superheated and that the vapor phase was the more nearly correct temperature for the boiling point of the component. The vapor-liquid temperature difference was shown to be significantly decreased by sufficient agitation of the liquid phase. This decrease of the liquid temperature appeared to be a result of the added kinetic energy input to the liquid. The agitated liquid appeared to tear the vapor bubbles from the nucleation site. In order to generate a bubble at a nucleation site, there must be a surface temperature somewhat greater than the saturation temperature of the component. This is required in order to supply the energy necessary to force the liquid away forming the bubble. Normally the bubble is disengaged from the nucleation site when its buoyancy is great enough to overcome physical property affects that hold the bubble in place. Much smaller bubbles are formed when the liquid's momentum is used to disengage the bubble from the surface. This requires a smaller temperature difference between the nucleation site and the saturation temperature. This indicates that as the agitation rate increases the momentum increases requiring a smaller temperature differential.

The phenomenon of pure component liquid superheating has apparently been recognized previously but was not general knowledge. The International Practical Temperature Scale of 1948 (8) suggests that the vapor phase be the phase in which the standard temperature is to be measured for all vapor-liquid equilibrium phase situations. The reference components are oxygen, water, and sulfur; secondary components are naphthalene, benzophenone, and mercury. If possible, a solid-liquid phase equilibrium should be used as a reference point. This is very acceptable for low and high temperatures; but in the normal range of application, water is about the only cheap high purity component available for reference. This, then, normally requires a vapor-liquid equilibrium phase system to be used. If a vapor-liquid system is to be used, the findings here indicate that extreme care must be taken to insure that the two phases are actually in equilibrium, which includes thermal equilibrium. This may be aided by agitation of the liquid phase, and all reference temperature measurements should be made in the vapor phase.

A SELECTED BIBLIOGRAPHY

- (1) Burns, M.D. Distillation Tray Efficiencies--An Experimental Study with a Ternary System. Ph.D. Thesis, Oklahoma State University, Stillwater, Oklahoma, 1969.
- (2) Hartman, M., K. Grigar, and G. Standart. Chemical and Process Engineering. Vol. 48, No. 7, (July, 1967).
- (3) Liang, S.T. and W. Smith. Chemical Engineering Science. Vol. 17, (Jan., 1962), 11.
- (4) Standart, G. Chemical Engineering Science. Vol. 20, (June, 1965), 611.
- (5) Leeds and Northrup Company. Conversion Tables for Thermocouples, 077989 Issue 4 (From National Bureau of Standards Circular 561).
- (6) Handbook of Chemistry 10th Ed. N. A. Lange, Editor, McGraw-Hill Book Co., Inc., New York, (1961).
- (7) Rossini, et al. American Petroleum Institute Research Project 44, Circular of National Bureau of Standards, C461 (1947).
- (8) Stimson, H. F. Journal of Research of National Bureau of Standards. Vol. 42, Research Paper No. 1962, (1949), 209-17.
- (9) Carlson, H. C. and A. P. Colburn. Ind. and Eng. Chem. Vol 34, No. 5 (1942), 581.
- (10) Langdon, W. M. and D. B. Keyes. Ind. and Eng. Chem. Vol. 34, No. 8 (1942), 938.
- (11) Othmer, D. F. Ind. and Eng. Chem. Vol. 20, No. 7 (1928), 743.
- (12) Othmer, D. F. Ind. and Eng. Chem. (Anyt. Ed.). Vol. 4, No. 2 (1932), 232.
- (13) Todd, W. G. and M. Van Winkle. Ind. Eng. Chem. Process Des. Devel. Vol. 11, No. 4 (1972), 579.

APPENDIX A

VAPOR PRESSURE CALCULATION

The Antoine vapor pressure equation was used to calculate the boiling temperature of toluene. The operating conditions from Table I were used.

Antoine vapor pressure equation:

$$\log P^* = A - [B/(C + t)] \quad (1)$$

Solving for t:

$$t = [-B/(\log P^* - A)] - C \quad (2)$$

$$P^* = 734.6 \text{ mm Hg} \quad [\text{from Table I}]$$

$$A = 6.95464$$

$$B = 1344.80$$

$$C = 219.482 \quad [\text{from Lange (6)}]$$

Calculations:

$$t = [-1344.80/(2.865 - 6.95464)] - 219.482$$

$$t = 328.831 - 219.482$$

$$t = 109.482^\circ\text{C}$$

$$T = 228.980^\circ\text{F}$$

APPENDIX B

EXPERIMENTAL AND CALCULATED DATA

TABLE VI

THERMOCOUPLE READINGS FOR n-HEPTANE AT VARIOUS AGITATION RATES

Rate (rpm)	Agitator Reynold's Number (x 10 ⁻³)	*Differential Thermocouple (mV)	Thermocouple (ΔT ^{°F})	Liquid Thermocouple (mV)	Thermocouple (°F)
0	0	0.0485	1.94	4.2050	209.23
45	1.429	0.0560	2.24	4.2075	209.33
60	1.909	0.0600	2.40	4.2120	209.50
97.5	3.235	0.0490	1.96	4.2020	209.12
180	5.727	0.0470	1.88	4.1955	208.86
284	9.031	0.0419	1.68	4.2050	209.23
430	12.736	0.0238	0.95	4.1885	208.58
630	20.049	0.0178	0.71	4.1823	208.33
840	26.732	0.0141	0.56	4.1789	208.20
1750	55.697	0.0026	0.10	4.1676	207.75
2480	78.916	0.0013	0.05	4.1661	207.01

$$* Re_a = [(rpm) (d_a^2) (\rho)] / \mu$$

TABLE VII

DIFFERENTIAL THERMOCOUPLE READINGS FOR n-PENTANE FOR VARIOUS
HEAT FLUXES WITH AGITATOR REYNOLD'S NUMBER OF 6820

Heat Input to Flask (watts)	Thermocouple Reading	
	(mV)	(°F)
13.84	0.0047	0.188
23.84	0.0064	0.256
53.64	0.0118	0.472

TABLE VIII

LIQUID THERMOCOUPLE READINGS FROM INITIATION OF HEAT
INPUT TO BOILING FOR n-HEPTANE

Time (min)	Thermocouple Reading		Heat Input (watts)
	(mV)	(°F)	
0	1.0040	77.64	13.84
10	1.0791	81.85	13.84
60	1.3895	94.50	13.84
70	1.4447	96.80	13.84
120	1.6584	106.06	13.84
130	1.6956	107.65	13.84
150	1.7766	111.10	13.84
160	1.8187	112.90	13.84
180	2.0089	120.91	23.84
190	2.1175	125.44	23.84
230	2.5036	142.50	23.84
240	2.5991	145.40	23.84
310	3.1398	167.31	23.84
320	3.1971	169.60	23.84
385	3.5657	184.27	23.84
395	3.6069	185.88	23.84

TABLE VIII (Continued)

Time (min)	Thermocouple Reading		Heat Input (watts)
	(mV)	(°F)	
435	3.9335	198.71	30.49
445	4.0104	201.74	30.49
465	4.1394	206.67	30.49
475	4.1785	208.18	30.49
485	4.1863	208.49	30.49
490	4.1877	208.55	30.49
495	4.1875	208.54	30.49
500	4.1953	208.85	37.96
503	4.1917	208.71	30.49
505	4.1939	208.80	30.49
510	4.1916	208.70	30.49

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