PHASE RELATIONS OF BINARY
HYDROCARBON SERIES
n-BUTANE- n-OCTANE

A Thesis
Presented in Partial Fulfillment of the Requirements
for the Degree Master of Science

by
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SUMMARY

An investigation of the phase relations in the critical region of the binary system n-butane-n-octane was made in order to check the correlation of Kay and Etter.

A plot for each system of average molecular weight on the weight basis versus critical pressure, cricondentherm pressure, or cricondenbar pressure yields a horseshoe-shaped curve. Straight lines drawn through points of constant weight fraction for several systems tend to meet at a common point that is near the critical point of the low molecular weight component.

A plot of log of average molecular weight versus log of critical temperature, log of cricondentherm temperature, or log of cricondenbar temperature yields a crescent-shaped curve. Straight lines drawn through points of constant weight fraction for each system radiate from a common point.

Based on this investigation and investigations by Kay and Etter, the indications are that all binary mixtures composed of normal paraffin hydrocarbons will show this behavior.
STATEMENT OF THE PROBLEM

It was desired to determine the critical locus curve of the n-butane-n-octane system in order to check the correlation of Kay and Etter. The critical locus was to be found by determining the crown of the P-T border curves of a series of mixtures.
INTRODUCTION

The P-T phase diagram of a natural gas mixture is of great practical importance to chemical and petroleum engineers. It is useful to the petroleum engineer in recovery operations in high pressure gas fields. The chemical engineer uses it in certain refinery and chemical synthesis processes involving natural gas under pressure. The P-T diagram usually can be calculated with fair accuracy outside of the critical region, but to determine the location of the curve in the critical region, three unique points must be known. They are the critical point (the convergence point of the quality lines of a mixture), the cricondenbar point (point of maximum pressure), and the cricondentherm point (point of maximum temperature). The only reliable method of determining these points is by experiment.

In 1954, Kay and Etter undertook a project to find relations between the composition, temperature and pressure at these unique points. This project involved a study of the P-T-X data of systems reported in the literature, and an experimental determination of the critical constants for a series of multicomponent mixtures containing from two to six
hydrocarbons. The study has been limited to mixtures composed of normal paraffin hydrocarbons of low molecular weight. The relationship discovered by Kay and Etter (3) involves the pressure, temperature and average molecular weight calculated on a weight basis.

The project undertaken by this author was an attempt to extend this relationship to hydrocarbon mixtures of higher molecular weight. For this study, the n-butane-n-octane system was chosen.
EQUIPMENT

The P-V-T Apparatus

The apparatus used for the determination of the P-V-T properties of the n-butane-n-octane mixture was developed by Kay (5). Figure One is a schematic diagram of the apparatus assembled for operation. Figure Two shows a picture of the assembled apparatus.

The sample A was confined in a thick-walled capillary tube D over a mercury column C. A steel ball B was agitated by a permanent magnet to mix the sample in order to bring about rapid equilibrium. The permanent magnet was rapidly moved up and down by hand.

The temperature was regulated by varying the pressure over different boiling liquids. The boiling liquids used were chlorobenzene, aniline, naphthalene, 1-bromonaphthalene, and bromobenzene. The experimental tube was surrounded by a jacket E in which the vapors of the boiling liquid F condensed. The boiling liquid was vaporized by an electric heater G. The jacket was supported by a rubber stopper J. In order to keep the rubber from being dissolved by the boiling liquid, a mercury seal or layer H was used to prevent their contact. A water-cooled condenser K was provided to
Figure 2

General View of the P-V-T Apparatus
prevent any vapors from entering the vacuum pump. The condenser was connected by means of a rubber hose L to a mercury manometer M which could be used to read the pressure in the system. Extremely small changes in pressure could be made by using the bulbs N and P, each of which had a volume of about 5.3 cubic inches. Bulb N was open to the atmosphere; bulb P was connected to the vacuum pump Q. Three five-gallon bottles R were used to increase the volume of the system to minimize pressure fluctuations and to allow small changes in pressure.

The temperature was measured by means of a thermocouple V. The cold junction of the thermocouple T was immersed in a Dewar flask U filled with finely divided ice. A Leeds-Northrup model 734287 potentiometer S was used to read the potential of the thermocouple. The potentiometer is shown in Figure Three.

Pressure was applied to the sample by means of compressed nitrogen from a cylinder. The experimental tube D was held securely by one leg of the compressor block W. The other leg of the compressor block was connected to a manifold X. Six other lines also were connected to the manifold X. The Bourdon guage Y was used to measure the pressure on the sample. It was graduated in two psi intervals over a range of 0-2000 psi. Line Z was for the dead
Figure 3

Potentiometer Arrangement
weight gauge tester, which was used to calibrate the Bourdon gauge Y. The mercury manometer CC was used to get the "zero setting" for the Bourdon gauge. Pressure was transmitted to the manifold from the nitrogen cylinder GG. Bulb DD permitted extremely small increases in pressure to be made. Bulb AA was a similar bulb that could be opened to the atmosphere to reduce the pressure by a minute degree. The surge tank FF was used to increase the volume of the system so that pressure fluctuations could be minimized. The valve AA was open to the atmosphere and was used to reduce the pressure on the sample.

The Compressor Block and Experimental Tube Assembly

The compressor block assembly was used to firmly hold the experimental tube without strain. Figure Four shows a cross-sectional view of the compressor block, its construction and the method of holding the experimental tube.

The compressor block consisted of two steel cylinders L and S which were filled with mercury and connected through a check valve U. Pressure was applied to the mercury surface in leg R by nitrogen gas and was transmitted through the mercury to the experimental tube A which was held securely in a leg L.

The check valve was used as a safety device. Under
normal conditions, the steel ball V floated on the mercury surface and did not interfere with the flow of mercury. If the experimental tube should burst while under pressure, however, the sudden surge of mercury would drive the steel ball into the valve seat W and stop the flow of mercury. The plug T was used to gain access to the internal parts of the check valve.

A "Bridgeman seal" was used to hold the experimental tube securely in leg L of the compressor block. This method of securing the tube permitted pressures of 1700 psi to be applied to the sample without mercury leakage and held the tube in such a manner that it touched no metal.

The primary vertical support assembly K rested on the shoulder in leg L. The detail of K shows the actual construction. A removable split-ring Q was used to support the rubber cylinder H and was held securely against the outer member P by the inner member N. Above the support assembly was another rubber cylinder J on which sat a steel washer F. The rubber washers M and H were the actual contacts so that no steel touched the glass. The steel washer F was indented to prevent lateral movement of the tube.

The rubber cylinder E was sandwiched between the steel washers D and F. The sleeve C and screw collar B were used to compress the rubber cylinder E against the side
of the leg L. The collar B was tightened by hand. As pressure was applied to the sample, the rubber cylinder E compressed against the leg L forming a mercury tight seal that prevented mercury leaks.

The experimental tube was constructed of pyrex tubing. The dimensions of the tube are shown in Figure Five. The closed end section was made from precision bore tubing and was used for making the volumetric measurements. The 1.5 cm bulge served as a seal in the compressor block assembly. The 1.8 cm diameter bulb was used as a reservoir for the butane gas during loading and had a volume of approximately 10 cc. The open end of the experimental tube was fitted with a standard 10/30 taper so that it could be attached to the vacuum train to be loaded with octane.

The Liquid Loading Apparatus

The liquid loading apparatus was used to purify the n-octane and to load a small amount into the experimental tube. Figure Six shows a schematic diagram of the apparatus. Figures Seven and Eight show a general view of the loading train.

The apparatus was made entirely of pyrex glass and was so constructed that the air could be evacuated. All the stopcocks had mercury seals and were lubricated with "A-piezon M" brand stopcock grease. Outlet A was joined to
FIGURE 5, EXPERIMENTAL TUBE

TAPER, 3.3 PER CM.
3.1 LONG

1.5 OD
0.9 ID

0.9 OD
0.3 ID

0.2 CM PRECISION BORE
0.75 OD

1.8 OD

19.1
2.0
31.0
19.0
72.6

ALL DIMENSIONS IN CM.
Figure 7

General View of Liquid Loading Apparatus Showing Mercury Diffusion Pump and Mc Cloud Guage
Figure 8

General View of Liquid Loading Apparatus
Showing Distilling Bulbs
a system composed of a mercury diffusion pump and mechanical force pump connected in series; this pumping system could reduce the pressure inside the apparatus to less than $10^{-6}$ mm of mercury. The pressure in the system was checked by means of a McCloud gauge or with the mercury manometer X. The cold trap B, which was cooled with liquid nitrogen, was used to keep condensible gases away from the vacuum pumps.

Bulb L was used to load n-octane into the loading train. This bulb was connected to the apparatus by means of a standard ground glass taper joint and was securely held by two springs. A mercury seal was used to make certain that air could not leak through the connection. Figure Nine shows this connection.

Bulbs M, N, P, Q and R were used for degassing and storing the octane. Each bulb had its own stopcock, which made it possible to isolate it from the other bulbs.

Tube J was used to measure the amount of pure n-octane loaded into the experimental tube G. Tube J was a 1 mm capillary which had been calibrated so that the volume was known as a function of its length.

Figures Ten and Eleven show how the experimental tube and apparatus were joined. The experimental tube G was attached to the adapter F by a standard ground glass taper lubricated with stopcock grease. The adapter F was connected
Figure 9

Connection Between Removable Bulb and Loading Train
Figure 10

Connection Between Experimental Tube and Apparatus Without Mercury Seal
Figure 11

Connection Between Experimental Tube and Apparatus Showing Mercury Seals
to the vacuum train by means of a ground-glass joint. Both connections had mercury seals. Bulb Y was a reservoir for the mercury that was used to fill the experimental tube after the sample had been loaded. The mercury was poured into the experimental tube through the fine capillary tube E which was connected to the main body of the apparatus by a ground-glass joint. Figure 12 shows a view of the mercury reservoir D and the apparatus.

The Gas Microburette

The gas microburette was used to accurately measure and load small samples of n-butane into the experimental tube. Figure 13 is a schematic diagram of the microburette and Figure 14 is a general photograph. This piece of equipment was designed by Kay (4).

The gas was measured in a 2.54 mm diameter precision bore capillary tube that was graduated in one millimeter divisions for a total length of 50 cm. The burette delivered 0.005069 cc of gas for every millimeter division. The delivery tip R of the microburette was reduced to a straight section of approximately 1.5 mm diameter so that it could be inserted into the end of the experimental tube (Figure 17). The U-shaped section between the delivery tip and the measuring section was flexible so that little strain would occur when the tip was inserted into the experimental tube.
Figure 12

View of Apparatus Showing Part of Mercury Reservoir at Left
FIGURE 13
DIAGRAM OF GAS MICROBURETTE
Figure 14

General View of Gas Microburette
The calibrated measuring section was surrounded by a water jacket $X$ to stabilize the temperature of the gas in the burette. Air was slowly bubbled through the water in order to remove temperature gradients; tube $S$ served as the air inlet and tube $U$ as the outlet. The water temperature was measured with thermometer $Z$. The water jacket $X$ was supported by rod $V$ and the clamps $W$ and $Y$.

The driving mechanism $AA$ was essentially a stainless steel bellows $A$ that was extended or compressed by means of a threaded rod and sleeve arrangement. Figure 15 shows a diagram of the arrangement and Figure 16 shows a photograph.

The bellows $A$ had 18 corrugations, an inside diameter of about 1.5 inches and a normal length of approximately three inches. The maximum volume change between extended and compressed positions was 70 cc.

Tube $B$, which held the measuring section $T$ by means of a rubber stopper and the screw cap $Q$, was welded to the bellows and was also held rigidly to the top plate $D$ by the set screws in the yoke $C$. The bottom of the bellows was welded to plate $E$. A cup was attached by a machine screw to the boss on the underside of plate $E$. The threaded rod $F$ had 18 threads per inch and was constructed with a flanged end that was rigidly held in the recess in the bottom of the cup.
Figure 15

Diagram of Displacement Mechanism
Figure 16
General View of Displacement Mechanism
The driving sleeve G surrounded the rod F. This sleeve was mounted between ball bearings in the housing H, which was attached to the bottom fixed plate M. The rotating knob J was attached to the sleeve by a set screw and extended or compressed the billows.

A worm gear was provided for the fine adjustment of the mercury surface. The worm wheel L was connected to the sleeve G by means of a set screw. The worm K was mounted in a separate housing that was hinged to the housing H. The worm could be meshed with the worm wheel by depressing lever M. One revolution of the worm was equivalent to 1/100 revolution of knob J. The pointer O was used to indicate the amount of expansion or compression of the billows. The arm P was attached to the top plate D and supported rod V (Figure 11).

The whole assembly was mounted on a stand with rack BB and pinion CC shown in Figure 11 so that the height of the microburette could be easily and rapidly adjusted.
PROCEDURE

Degassing and Loading Procedure for n-Octane

The liquid loading apparatus was used to purify the n-octane and to load the proper amount into the experimental tube.

The experimental tube was cleaned by washing with chromic acid solution and rinsing with distilled water. The tube was then dried by rinsing with reagent grade ethyl ether and then blowing with filtered air. A 1/16 inch steel ball was cleaned by stirring with a pair of tweezers in a small beaker of acetone. The dry ball was dropped into the clean, dry experimental tube and the tube was then sealed on the loading apparatus.

After the tube was sealed in place, the system was evacuated and then was pumped out for several hours to remove any traces of air or moisture from the system. With the system still under a vacuum, stopcock K, referring to Figure Six, was closed and the detachable bulb L was removed from the train. About twenty milliliters of n-octane was put in the bulb L and it was then attached to the apparatus again. The purity of the octane charged into the apparatus was reported by the Phillips Petroleum Company to be 99.81 mole % n-octane.
The purification or degassing of the octane was done in the following manner. Stopcock K was opened and the vacuum in the apparatus swept out a large amount of the dissolved air in the octane, as well as some octane vapor. These vapors were caught and frozen in the nitrogen cold trap B. Stopcock C was closed and stopcocks L and S opened. The octane was distilled into bulb M by placing a dry ice-acetone bath around it. After all the material was transferred, stopcock C was opened and the frozen octane was exposed to the vacuum for about fifteen minutes. The material was then distilled again into bulb L, and the pumping repeated again. This procedure of distillation followed by pumping was repeated eight to ten times and removed essentially all the air and non-condensible gases from the n-octane.

The n-octane was then loaded in the sample tube G in the following manner. Stopcock C was closed and stopcock H to the measuring tube J was opened. A small quantity of octane was then distilled into the measuring tube. After the proper amount had distilled into the measuring tube, stopcock H was closed and an ice bath was placed around the measuring tube. Stopcock H was closed and stopcock C was opened to sweep the octane vapors from the apparatus.

The height of liquid in the tube J was measured with a cathetometer so that the volume of the octane could be
calculated. After this stopcock C was closed, stopcock H was opened and the octane was distilled into the experimental tube G and frozen with liquid nitrogen. The distillation was allowed to run for one hour to make sure all the octane had been transferred. After all the material had been transferred to the experimental tube, stopcock D was closed and the frozen octane was allowed to melt. After being mixed by means of a magnet, it was refrozen.

The experimental tube was then filled with mercury by tilting the mercury reservoir Y and allowing mercury to flow into the tube E until the mercury level had risen up into the bottom of the adapter F. The mercury reservoir Y was then carefully removed for a moment to allow the space above the mercury in the adapter to reach atmospheric pressure.

The experimental tube loaded with sample was then ready to be transferred to the compressor block of the P-V-T apparatus. The experimental tube was removed from the loading apparatus by sucking the mercury from the adapter mercury seal with a vacuum flask and then opening the joint. The experimental tube was then lowered and removed. With the tip of the experimental tube still immersed in the liquid nitrogen bath, the tube was taken to the P-V-T apparatus. The tube was then seated in the compressor block. About 50 psig pressure was applied to the sample and the mercury and
sample thawed. This loading procedure took about seven hours.

**Procedure for Loading n-Butane**

The gas microburette was used to introduce a known volume of n-butane into the experimental tube. The n-octane had been previously loaded into the experimental tube.

The sample tube was held in the compressor block when the gas was loaded. The liquid octane in the end of the tube was frozen with a dry ice cooler and then the pressure on the sample was released. Next, the screw collar B and sleeve C, Figure Four, were removed from the experimental tube. The mercury pot and gasket, Figure 17, were then screwed tightly on the front leg of the compressor block. The sample tube was partially raised out of the front leg as mercury was poured in the back leg to maintain the mercury seal. Next, a cork or solid plug was placed tightly in the back leg of the compressor block. The experimental tube was clamped so that it would not float in the mercury, and then the mercury pot was filled about 90% full of mercury. This was equivalent to about 20 pounds of mercury. The experimental tube, with the sample still frozen by the cooler, was raised until the open end rested on the bottom of the pot and then clamped in place.

The surface of the mercury was cleaned by means of a vacuum flask. The open bulb of the gas collecting tube was
Figure 17
Diagram of Gas Loading Apparatus
then placed slightly below the mercury surface in the pot and was clamped in place as shown in Figure 17. After the collecting tube stopcock was closed, a suction line was attached to the upper end. The stopcock was opened, which allowed the mercury to slowly rise inside the gas collecting tube until it was above the stopcock. The suction line was then removed and the collecting tube was lowered further into the mercury. The tube was clamped in place.

The n-butane was stored in a gas sample bulb. The purity was 99.78±0.08 mole % n-butane. The capillary tip of the bulb was scratched with a file and inserted under the mercury surface into the collecting tube. The scratched tip was then broken, releasing the gas into the collecting tube.

The U-tube of the microburette was now filled with mercury and placed into the mercury pot with the microburette tip above the surface. All the residual air was displaced from the tip R (Figure 13) by forcing mercury from it. The microburette was now purged using the following procedure. The tip was placed under the gas collecting tube and the tube was lowered until the burette tip protruded into the butane gas. Gas was then drawn into the microburette to flush it and expelled into the atmosphere. The burette was flushed three times to remove all the air.

The butane sample for injection into the experimental tube was now obtained. A sample large enough to almost
fill the calibrated section of the microburette was drawn into the burette. Mercury from the pot was drawn in behind the sample to keep air from the n-butane.

A cathetometer or traveling telescope was then used to adjust the mercury level in the pot to the height of the microburette zero mark. The mercury level in the pot could be adjusted by raising or lowering the gas collecting tube. The levels were adjusted to insure that the gas in the microburette was at atmospheric pressure. Air was slowly bubbled through the water in the burette to eliminate temperature gradients within the butane. The mercury at the top of the section containing the butane gas was brought to the microburette zero mark by rotating the fine adjustment knob on the burette. The length of the gas column in the measuring tube T (Figure 13) was now read.

The delivery tip R of the microburette was placed inside the experimental tube and the butane gas was then forced into the large bulb of the experimental tube. Since a maximum of about 2.5 cc of butane could be injected in one pass, this procedure was repeated until the desired amount of gas was in the experimental tube. After all the gas had been loaded, the microburette and the gas collecting bulb were removed from the mercury pot.

The butane gas in the large bulb of the experimental tube was transferred into the capillary portion of the tube
by vigorous tapping. Care was taken to prevent air from entering the tube. After the gas had risen into the upper part of the tube, it was frozen by lowering the nitrogen cooler.

The bulb of the experimental tube was pushed back into the compressor block and the mercury was removed from the pot. The pot itself was then removed, along with the cork or plug in the back leg of the compressor block. The sleeve and screw collar were again placed on the experimental tube and the tube was sealed in the front leg. The depth of mercury below the top of the back leg was measured before the back leg of the compressor block was closed. About 100 psig pressure was applied to the system to hold the octane-butane mixture inside the experimental tube. The dry ice cooler was now removed and the mercury, butane and sample thawed. The apparatus was then ready for experimental observations.

The P-V-T Experimental Procedure

Before the P-V-T apparatus was started up, the pressure gauge was checked. The valve connecting the compressor block and the manifold was closed so that the pressure could be maintained on the sample. Then the valve connecting the manifold and the mercury manometer CC was opened. Exactly 30 psig pressure, as measured by the manometer, was applied
to the pressure guage. The scale of the guage was then adjusted to read 30 psig. After the guage had been corrected and the system pressurized to 100 psig, the manometer valve was closed and the compressor block valve again opened.

The system was next set at the correct temperature by turning on the vacuum pump and adjusting the pressure in the jacket to correspond to the desired temperature. Next the pressure on the sample was applied. This sample pressure was greater than the expected cricondenbar pressure in order to keep the sample from vaporizing and escaping from the experimental tube. The electric heater was now turned on. When the ring of condensing vapors rose to the top of the insulated portion of the jacket, the powerstat was adjusted so that the condensate could go no higher. When the temperature in the jacket became steady, the bubble and dew points were determined for that temperature. The temperature was considered to be constant when the potentiometer reading became constant. The bubble, dev, and critical points were observed visually. The bubble point was taken when a bubble about the size of a pin point was visible at the top of the experimental tube after vigorous agitation. The dew point was the point where a minute amount of liquid was last observed between the mercury meniscus and the tube wall after vigorous agitation. The critical point was the condition at
which the meniscus between the liquid and vapor phase could no longer be observed. At the critical point, the butane-octane sample appeared smoky to reflected light and brown to transmitted light.
RESULTS

The pressure, temperature and volume were experimentally measured at the bubble and dew points for five different compositions of n-butane and n-octane. The P-V-T data for the pure components were obtained from the International Critical Tables. These data were then used to obtain the pressure-temperature-composition-density relationships for the butane-octane system. These relationships are shown in Figures 18 through 22 and in Figure 24.

The temperature-composition relationship at constant pressure was derived from Figures 18, 20 and 21. The log K vs. log pressure plot (Figure 23) was then derived from the temperature-composition relationship. Figures 25 through 28 were derived from various pressure-temperature-composition data and from Figures 20 and 21.

Figure 28 shows the general behavior for a plot of log average molecular weight versus log critical temperature. Similar plots for the cricondenbar temperature and criconden therm temperature show the same behavior. Tables 1 through 3 compare the experimental values and the correlated values obtained from the constant weight fraction lines.
FIGURE 18
P-T DIAGRAM FOR
BUTANE-OCTANE SYSTEM
COMPOSITIONS ARE IN MOLE
PER CENT BUTANE
FIGURE 19
CRITICAL LOCI OF BINARY BUTANE-HYDROCARBON SYSTEMS
FIGURE 20
PLOT OF COMPOSITION VS. CRITICAL TEMPERATURE, CRICONDENTHERM TEMPERATURE, AND CRICONDENBAR TEMPERATURE.
FIGURE 22
TEMPERATURE-COMPOSITION
DIAGRAM AT CONSTANT PRESSURES
FIGURE 21
PLOT OF COMPOSITION VS. CRITICAL PRESSURE, CRICONDENTHERM PRESSURE, AND CRICONDENBAR PRESSURE.
Figure 24
Temperature - Density Diagram at Constant Compositions
Compositions are in Mole Per Cent Butane
FIGURE 25
PLOT OF CRICONDENTHERM
PRESSURE VS. AVERAGE
MOLECULAR WEIGHT
FIGURE 27
PLOT OF CRITICAL PRESSURE VS. AVERAGE MOLECULAR WEIGHT
FIGURE 28:
GENERALIZED PLOT OF LOG CRITICAL TEMPERATURE VS. LOG AVERAGE MOLECULAR WEIGHT
### TABLE 1

**LOG CRICONDENDBAR TEMPERATURE - LOG MOLECULAR WEIGHT DATA**

#### BUTANE-OCTANE BINARY

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<tr>
<th>WEIGHT % BUTANE</th>
<th>EXPERIMENTAL TEMPERATURE</th>
<th>CORRELATION TEMPERATURE</th>
<th>ACTUAL MW</th>
<th>CORRELATION MW</th>
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<td>152.3 °C</td>
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#### BUTANE-HEPTANE BINARY

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<th>CORRELATION TEMPERATURE</th>
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<th>CORRELATION MW</th>
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The constant composition lines converge at 164.8 °C and 58.1 molecular weight.
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<table>
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</table>

The constant composition lines converge at 162.3 °C and 58.1 molecular weight.
## Table 3

**Log Critical Temperature - Log Molecular Weight Data**

### Butane-Octane Binary

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<tr>
<th>Weight % Butane</th>
<th>Experimental Temperature</th>
<th>Correlation Temperature</th>
<th>Actual MW</th>
<th>Correlation MW</th>
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</thead>
<tbody>
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<td>152.3 °C</td>
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### Butane-Heptane Binary

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<th>Actual MW</th>
<th>Correlation MW</th>
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The constant composition lines converge at 157.0 °C and 58.1 molecular weight.
The sources of error in determining the composition of the mixtures were measurement of the volume of components added, measurement of the temperature of the butane and octane, inaccurate values of density for butane and octane, and measurement of the barometric pressure and mercury depression for the butane. The largest source of error was in measuring the volume of butane added. The reported compositions are accurate to about ±0.452 mole per cent or ±0.518 weight per cent.

The major sources of error in the pressure determinations were from reading the Bourdon guage and from hysteresis of the pressure guage. Negligible errors were caused by measurement of the barometric pressure, by obtaining the hot and cold zone lengths, and in determining the mercury depression. The accuracy of the pressure measurements is estimated to be ±0.433 psia.

Possible sources of error in the temperature determinations were from jacket heat losses, temperature gradients in the condensing vapors, calibration of the thermocouple and sensitivity of the millivolt meter. The temperature data are accurate to about 0.0173°C.

Errors in volume measurement were caused by reading the cathetometer, calibration of the experimental tube, thermal expansion of the tube, obtaining the mercury meniscus
volume, measuring the volume of the steel ball and the volume of the dew or bubble. The largest source of error was reading the cathetometer. The reported values for volume are accurate to 0.000757 cc.

The main source of error in the density measurements was the determination of the weight of octane in the sample. The expected variation of the density is ±0.00262 g/cc.
DISCUSSION OF RESULTS

The critical locus of the n-butane-n-octane system is shown in Figure 19, along with the critical locus of the n-butane-n-heptane system. Figures 19 and 29 show that the critical locus of the n-butane-n-octane system is following the general pattern of other paraffin binaries. These figures show that the maximum pressure of the critical locus curve is related to the difference between the critical temperatures of the two components of the binary mixture. The maximum pressure becomes greater as the difference between critical points becomes greater.

The plots of average molecular weight vs. critical pressure, cricondentherm pressure, and cricondenbar pressure show that the lines of constant weight fraction converge to a common point. This behavior is consistent with that observed by Kay and Etter (3). The latter investigations, however, found that the common point was the critical point of the low molecular weight component. In this investigation, it was found that the common point was near the critical point of the low molecular weight paraffin, but that the two points did not have to coincide.
FIGURE 29
GENERAL PATTERN OF CRITICAL LOCI FOR PARAFFIN HYDROCARBON BINARIES.
The curves for average molecular weight vs. log of critical temperature, log of cricondentherm temperature, and log of cricondenbar temperature also show that lines of constant weight fraction of butane converge to a common point. This general pattern was also observed by Kay and Etter (3). For weight fractions above 0.5 approximately, however, the accuracy of the correlation diminishes. Since the probable variation in composition is 0.518 weight percent, and the average molecular weight is dependent on the composition, the deviations in the correlation of Kay and Etter can probably be attributed to the variation in composition. It is also possible that the lines of constant weight fraction are slightly curved instead of being linear.
CONCLUSIONS

The results of this investigation show that the n-butane-n-octane system follows the general pattern of the correlation of Kay and Etter (3).

From the data of this investigation and from that of other systems, (2), (3), (9), (10), a general pattern for the shape of the curves for the temperature and pressure correlations is indicated. The pressure pattern is indicated by Figures 25, 26 and 27. The horseshoe-shaped curve for each system represents the relationship between average molecular weight on a weight basis and the critical pressure, cricondentherm pressure, and cricondenbar pressure. The lines of constant weight fraction connecting each system converge at a common point near the critical point of the lower molecular weight component of the binary systems.

The temperature pattern is indicated by Figures 28 and Tables 1 through 3. The solid curve in Figure 28 represents the relationship between the average molecular weight and the critical temperature. The dotted lines are lines of constant weight fraction which converge at a common point.
RECOMMENDATIONS

It is recommended that the correlation for the n-butane-n-pentane and n-butane-n-hexane systems be found to determine if they also will follow the general correlation of Kay and Etter (3).

To the present time, this study has been limited to normal paraffins. It would be interesting to determine if the correlation is valid for isomeric paraffins.

Methods for predicting from theory the correlation curves should be investigated. The most logical place to start this investigation would be the field of statistical mechanics.
BIBLIOGRAPHY


4. Kay, Webster B., Personal communication.


APPENDIX I

CALIBRATIONS

Thermocouple Calibrations

The copper-constantan thermocouple was calibrated by Michael Skaates (10). Appendix Figure 1 shows the calibration curve. A model 734287 Leeds and Northrup potentiometer was used to read the thermocouple voltage.

Experimental Tube Calibration

The experimental tube was calibrated by Soon Ng (9). By means of a regression analysis, he found that the relationship between volume and tube length was given approximately by the equation \( V = 0.0315198L - 0.0113814 \). \( V \) is the volume in cc and \( L \) is the length from the outside tip. Appendix Figure 2 shows the correction that must be added to the calculated volume to obtain the actual volume.

Pressure Guage Calibration

A Bourdon guage, OSU No. 202282, was used to measure the sample pressure. This guage was calibrated by Michael Skaates (10). Appendix Figure 3 is the calibration curve for the pressure guage.
APPENDIX FIGURE 1
THERMOCOUPLE CORRECTION CURVE

TEMPERATURE CORRECTION, °C.

+4.0
+3.0
+2.0
+1.0
+0.0

THERMOCOUPLE READING, MV.

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
APPENDIX FIGURE 2
VOLUME CORRECTION CURVE FOR EXPERIMENTAL TUBE

VOLUME CORRECTION IN CC x 10^5

TUBE LENGTH FROM OUTSIDE TIP IN CM.
APPENDIX FIGURE 3
CORRECTION CURVE FOR PRESSURE GUAGE
DOTTED CURVE IS HYSTERESIS

GAUGE CORRECTION, PSI

GAUGE READING, PSIG

+1.0
0
-1.0
-2.0
-3.0
-4.0
0 100 200 300 400 500 600 700 800 900 1000
Liquid Loading Apparatus Calibration

The measuring capillary tube on the liquid loading apparatus was calibrated by Robert Cherry. By a regression analysis, he found that the volume of the tube was related to the length by the equation $V = 0.0078114Z - 0.002380$. $V$ is the volume in cc and $Z$ is the length from the outside tip of the tube to the top of the meniscus.
APPENDIX II
SAMPLE CALCULATIONS

Calculations for Octane Loading

A sample calculation sheet for loading n-octane is shown in Appendix Table 1. Items 2 through 6 are determined experimentally. Item 2 is the temperature of the bath surrounding the measuring capillary tube. Item 4, the base of the octane meniscus, Item 5, the top of the meniscus, and Item 6, the end of the tube, are read with a cathetometer. Item 7, the length of the octane column, is the difference between Items 5 and 6. Item 8 is the calculated volume of liquid octane not including the meniscus volume. It is calculated from the tube calibration equation. The meniscus volume, Item 10, is calculated by assuming that the octane meniscus forms a segment of a sphere and by finding the difference between this and the volume of a cylinder the length of the meniscus height. Item 11 is the sum of Items 8 and 10. Item 12 is obtained from the International Critical Tables. Item 13 is the product of Items 11 and 12. Item 14 is the quotient obtained by dividing 114.23, the molecular weight of octane, into Item 13. Item 16 is the volume of the vapor above the liquid octane and is obtained
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<td>18</td>
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<td>Total moles octane</td>
<td>mole</td>
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by subtracting the liquid volume (Item 10) from the total volume of the measuring tube. Item 13 is calculated using the perfect gas law; it is the product of Items 15 and 16 divided by the product of 62363 and Item 17. Item 19 is the sum of Items 14 and 18.

Calculations for Loading Butane

A sample calculation sheet for loading gaseous butane and for the calculation of the sample composition is shown in Appendix Table 2. Items 4 through 6 are determined experimentally. Item 7 is the difference between Items 5 and 6. Item 8 is a correction to reduce the barometer reading to standard temperature and gravity. Item 9 is the difference between Items 7 and 3. Item 10 is Item 9 corrected for the capillary effect. Item 11 was data previously obtained by this laboratory (4).

Item 12 is experimental data. Item 13 is the product of Item 12 and 0.005069, since each mm of length is equivalent to 0.005069 cc of gas. Item 14 is the product of Items 11 and 13. Item 16 is the sum of Items 14 and 15. Item 17 is Item 16, plus the weight of octane in the sample.

Calculations for P-V-T Data

A sample calculation sheet for a typical run is shown in Appendix Table 3. Item 2 is the type of point being
## APPENDIX TABLE 2

SAMPLE CALCULATION SHEET FOR LOADING BUTANE

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<table>
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</tr>
<tr>
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<td>Sample numbers</td>
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</tr>
<tr>
<td>3</td>
<td>Time of day</td>
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<tr>
<td>4</td>
<td>Room temperature</td>
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<tr>
<td>5</td>
<td>Barometer top</td>
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<td>6</td>
<td>Barometer bottom</td>
<td>cm 12.250</td>
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<td>7</td>
<td>Barometer reading</td>
<td>mm 748.55</td>
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<tr>
<td>8</td>
<td>Barometer correction</td>
<td>mm 2.9</td>
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<td>9</td>
<td>Barometric pressure</td>
<td>mm 745.7</td>
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<td>10</td>
<td>Sample pressure</td>
<td>psia 14.33</td>
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<tr>
<td>11</td>
<td>Specific volume of butane</td>
<td>cc/g 418.09</td>
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<tr>
<td>12</td>
<td>Length of butane added</td>
<td>mm 1344.6</td>
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<tr>
<td>13</td>
<td>Volume of sample added</td>
<td>cc 6.8158</td>
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<tr>
<td>14</td>
<td>Weight of sample added</td>
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<td>15</td>
<td>Weight butane previously added</td>
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<td>Total weight of sample</td>
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<td>18</td>
<td>Weight per cent butane</td>
<td>% 50.91</td>
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<tr>
<td>19</td>
<td>Mole per cent butane</td>
<td>% 67.09</td>
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# APPENDIX TABLE 3

## DATA AND CALCULATION SHEET

**DATE:** Jan. 15, 1962  
**COMPOSITION:** 67 Mole % butane

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<td>Fraction added</td>
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<td>7</td>
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<td>Actual sample temperature</td>
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<td>Barometer bottom</td>
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<td>Uncorrected barometric pressure</td>
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<td>16</td>
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<td>17</td>
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<td>20</td>
<td>Depth of mercury in back leg</td>
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<td>21</td>
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<tr>
<td>22</td>
<td>Top of meniscus</td>
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<tr>
<td>23</td>
<td>Length of tube occupied by sample</td>
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<tr>
<td>24</td>
<td>Hot zone bottom</td>
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<tr>
<td>25</td>
<td>Uncorrected length of hot zone</td>
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<td>26</td>
<td>Correction for depression of mercury</td>
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<td>27</td>
<td>Corrected length of hot zone</td>
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<tr>
<td>28</td>
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<td>29</td>
<td>Top of back leg</td>
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### APPENDIX TABLE 3 CONTINUED

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<th>Value</th>
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<td>Room zone length</td>
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<td>psi</td>
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<td>Mercury vapor pressure</td>
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<td>35</td>
<td>Actual sample pressure</td>
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<td>Volume correction</td>
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<td>Uncorrected volume of sample</td>
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<td>Temperature difference of hot tube</td>
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<td>40</td>
<td>Volume correction for thermal expansion</td>
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<td>Volume corrected for thermal expansion</td>
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<td>42</td>
<td>Volume correction for meniscus complement</td>
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<tr>
<td>43</td>
<td>Volume of steel ball</td>
<td>cc</td>
<td>0.21036</td>
</tr>
<tr>
<td>44</td>
<td>Actual sample volume</td>
<td>cc</td>
<td>0.00203</td>
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<tr>
<td>45</td>
<td>Sample density</td>
<td>g/cc</td>
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</table>
determined. Item 3, the potentiometer reading, is experimental data. Item 4 is taken from the reference chart for copper-constantan thermocouples. Item 5 is calculated using this chart. Item 6 is the sum of Items 4 and 5. Item 7 is the thermocouple correction taken from the calibration curve (Appendix Figure 1). Item 8 is the sum of Items 6 and 7.

Item 9 is experimental data. Item 10 is the gauge correction read from the pressure gauge calibration curve (Appendix Figure 3). Item 11 is the sum of Items 9 and 10. Items 12-14 are experimental data. Item 15 is the difference between Items 13 and 14. Item 16 is a correction for temperature and gravity applied to the Item 15. Item 17 is the sum of Items 15 and 16. Item 18 is the barometric pressure converted to psi; it is calculated by multiplying Item 17 by 0.019338. Item 19 is the sum of Items 11 and 18. Items 20 through 22 are measured experimentally. Item 23 is Item 22 subtracted from Item 21. Item 24 is measured experimentally and is subtracted from Item 22 to obtain Item 25. Item 26 is the capillarity effect correction which must be added to Item 25 to obtain Item 27. Item 28 is Item 27 multiplied by the density of mercury at the sample temperature and then converted to psi. Item 29 is measured experimentally with the cathetometer. Item 30 is Item 24 minus Item 29. Item 31 is the sum of Items 20 and 30. Item 32 is the product of Item 31
and the density of mercury at room temperature and then converted to psi. Item 33 is the sum of Items 28 and 32. Item 33 is then subtracted from Item 19 to obtain Item 34. The mercury vapor pressure, Item 35, is read from a handbook. The actual sample pressure, Item 36, is then obtained by subtracting Item 35 from Item 34.

Item 36 is the approximate sample volume calculated from the calibration equation. Item 37 is the volume correction that is read from the calibration curve (Appendix Figure 2). Item 39 is the sum of Items 37 and 38. Item 40 is the difference between the sample temperature (Item 8) and 25°C. The volume correction for thermal expansion, Item 41, is the product of $6.6 \times 10^{-6}$ and Items 39 and 40. The volume coefficient of expansion for Pyrex is $6.6 \times 10^{-6}$.

Item 42 is the sum of Items 39 and 41. Item 43 is the volume correction for meniscus complement, and this is added to Item 42 to obtain Item 44. The volume of the steel ball, Item 45, remains constant at 0.00203 cc, and is subtracted from Item 44 to obtain Item 45, the actual sample volume. The sample density, Item 46, is calculated by dividing Item 45 into the total weight of the sample.
APPENDIX III

EXPERIMENTAL DATA

N-BUTANE-N-Octane System

APPENDIX TABLE 4

DENSITY-P-T-X EXPERIMENTAL DATA

18.23 MOLE % BUTANE

<table>
<thead>
<tr>
<th>PRESSURE, PSIA</th>
<th>TEMPERATURE, °C</th>
<th>POINT</th>
<th>DENSITY, g/CC</th>
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<td>160.63</td>
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<tr>
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<td>217.24</td>
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<td>209.9</td>
<td>208.80</td>
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### 46.31 MOLE % BUTANE

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<td>DENSITY (g/cc)</td>
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<td>------------------</td>
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81.83 Mole % Butane
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84.61 MOLE % BUTANE
### APPENDIX TABLE 5

**CRICONDENBAR DENSITY-P-T-X DATA**

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### APPENDIX TABLE 6

**CRITICAL POINT DENSITY-P-T-X DATA**

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### APPENDIX TABLE 7

**CRICONDENTHERM DENSITY-P-T-X DATA**

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APPENDIX IV

DERIVED DATA

N-BUTANE-N-OCTANE SYSTEM

APPENDIX TABLE 8

K OCTANE-P-T DATA

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THE TABLE GIVES VALUES OF K.
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K_BUTANE-P-T DATA

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THE TABLE GIVES VALUES OF K.
## APPENDIX TABLE 10

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</tr>
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<td>568.8</td>
<td>574.5</td>
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</tr>
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<td>529.8</td>
<td>537.2</td>
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</tr>
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<td>494.2</td>
<td>463.4</td>
</tr>
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<td>450.0</td>
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</tr>
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<td>403.5</td>
<td>405.6</td>
<td>398.7</td>
</tr>
<tr>
<td>0</td>
<td>114.2</td>
<td>360.6</td>
<td>360.6</td>
<td>360.6</td>
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</tbody>
</table>
### APPENDIX TABLE 11

**AVERAGE MOLECULAR WEIGHT-CRITICAL TEMPERATURE-CRICOENDBAR TEMPERATURE-CRICOENDBERM TEMPERATURE DATA**

<table>
<thead>
<tr>
<th>WEIGHT % BUTANE</th>
<th>AVERAGE M W</th>
<th>CRICOENDBAR TEMPERATURE, °C</th>
<th>CRITICAL TEMPERATURE, °C</th>
<th>CRICOENDBERM TEMPERATURE, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>58.1</td>
<td>152.3</td>
<td>152.3</td>
<td>152.3</td>
</tr>
<tr>
<td>90</td>
<td>68.1</td>
<td>180.3</td>
<td>177.3</td>
<td>184.6</td>
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<tr>
<td>70</td>
<td>83.7</td>
<td>215.5</td>
<td>215.8</td>
<td>222.9</td>
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<tr>
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<td>242.8</td>
<td>247.2</td>
<td>252.5</td>
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<td>269.9</td>
<td>272.4</td>
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<td>286.9</td>
<td>287.6</td>
<td>288.2</td>
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<tr>
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<td>114.2</td>
<td>295.8</td>
<td>295.8</td>
<td>295.8</td>
</tr>
</tbody>
</table>
**APPENDIX TABLE 12**

**T-P-X DATA, BUBBLE POINT LINE**

<table>
<thead>
<tr>
<th>MOLE % BUTANE</th>
<th>PRESSURE, PSIA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td>0</td>
<td>282.3</td>
</tr>
<tr>
<td>8.6</td>
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</tr>
<tr>
<td>18.2</td>
<td>239.0</td>
</tr>
<tr>
<td>20.0</td>
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<tr>
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<tr>
<td>43.2</td>
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<tr>
<td>67.1</td>
<td>147.8</td>
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<tr>
<td>81.8</td>
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<td>92.8</td>
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<tr>
<td>94.6</td>
<td>121.1</td>
</tr>
<tr>
<td>100.0</td>
<td>116.2</td>
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</tbody>
</table>

The table gives values of temperature in °C.
The conditions for the maximum pressure point are 75.4 mole % butane, 208.6 °C, and 628.6 psia.
# APPENDIX TABLE 13

T-P-X DATA, DEW POINT LINE

<table>
<thead>
<tr>
<th>MOLE % BUTANE</th>
<th>PRESSURE, PSIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
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<tr>
<td>0</td>
<td>282.3</td>
</tr>
<tr>
<td>8.6</td>
<td>---</td>
</tr>
<tr>
<td>9.1</td>
<td>---</td>
</tr>
<tr>
<td>10.4</td>
<td>---</td>
</tr>
<tr>
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<td>264.6</td>
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<tr>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>43.2</td>
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<tr>
<td>44.8</td>
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</tr>
<tr>
<td>46.3</td>
<td>242.0</td>
</tr>
<tr>
<td>58.7</td>
<td>---</td>
</tr>
<tr>
<td>59.8</td>
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<tr>
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<tr>
<td>81.8</td>
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<td>92.8</td>
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<tr>
<td>94.6</td>
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</tr>
<tr>
<td>100.0</td>
<td>116.2</td>
</tr>
</tbody>
</table>

The table gives values of temperature in °C.

The conditions for the maximum pressure point are 75.4 mole % butane, 208.6 °C, and 628.6 PSIA.