PHASE EQUILIBRIA

IN THE

PROPANE-BUTANE SYSTEM

Thesis by

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Introduction

A very important factor in the design of equipment used
in transforming, separating, or otherwise handling of hydro-
carbons is an exact knowledge of the physical properties of
the hydrocarbon mixtures themselves under various temperatures
and pressures. A large store of information concerning the
physical properties of pure hydrocarbons and mixtures of these
hydrocarbons has been amassed during the past few years but
even so, there remains much to be done before the volumetric
and phase behavior of uninvestigated mixtures can be quanti-
tatively predicted from the properties of their components.
Among the physical properties of interest are the P-V-T-N
relations. These relations are of much value not only in
themselves but also in the fact that many other physical
properties may be calculated from such data through the use
of thermodynamic principles.

At pressures in the neighborhood of 1-5 atmospheres,
Raoult's Law and Dalton's Law may be used with fair accuracy
to determine phase equilibrium data for hydrocarbon mixtures.
At higher pressures and at temperatures approaching the cri-
tical temperature, however, deviations become large and these
laws must be supplanted with experimentally determined facts.
Souders, Selheimer, and Brown (1), have used fugacity instead
of vapor pressure in an attempt to predict more accurately the
equilibrium conditions at the higher pressures where experi-

mental data were lacking.

There have been developed at least two distinctly different types of apparatus for the determination of the P-V-T relations of hydrocarbon mixtures. One of these, described in detail by Sage, Schaafsma, and Lacey (2), consists of a thermostated steel cell in which the sample to be investigated is placed. Suitable auxilliary apparatus is set up in conjunction with the steel cell, so that the volume of the sample and the pressure may be changed by the addition to or removal of mercury from the cell. The mercury level inside the cell, and thus the volume occupied by the sample, is accurately measured by a movable electric contact.

A different type of apparatus has been used by Young (3), Bahlke and Kay (4), and Cummings (5), similiar to the apparatus that was used to obtain the data presented in this thesis. It has a small diameter thick walled glass tube in place of the steel cell for holding the sample. The upper end of the glass tube is sealed, while the lower end is fitted into the steel block which has connections for evacuating the tube, adding the sample, and also for adding or removing mercury to change the volume and pressure on the sample. In this case the volume can be measured by visually noting the height of the mercury level in the glass tube. Other details of construction and procedure will be found in the section devoted to the apparatus and experimental procedure.

Each type of apparatus has its advantages and limitations. The variable volume steel cell may be used at pressures up to several thousand pounds, while with the glass tube about one

thousand pounds per square inch appears to be the upper limit.
The steel cell may be made large enough to hold a sample
weighing 20-50 grams whereas the total sample for the glass
tube used in these experiments was never over 0.1 gram. The
large sample may or may not be an advantage. The larger sam-
ple increases the accuracy with which the weights of the dif-
ferent components of the sample can be determined but, at the
same time, the larger sample requires a great deal more material.
It is usually necessary to study several different compositions
of a mixture. The amount of sample required may be quite im-
portant where the purification is a problem. All the results
presented in this thesis required less than 1 gram of the fi-
nally purified propane and butane.

A further advantage of the glass P-V-T apparatus is that
the phase boundaries may be determined quite accurately by di-
rect observation. The dew point and bubble points may be deter-
mined by observing the pressure, volume, and temperature when
a very small amount of the liquid or gas respectively is in
equilibrium with the remainder of the sample in the other
phase. With the steel cell, the dew points and bubble points
may be obtained only by taking a great many readings in the
vicinity of these points and determining the discontinuities
in the pressure-volume curve at constant temperature.

Another advantage of the glass apparatus is the rapidity
with which the temperature may be changed. The steel cell in
a liquid bath with a large heat capacity requires considerable
time for changing temperature. The glass tube is thermostated
by a condensing vapor from a liquid boiling under reduced pres-

sure. The temperature may be changed and the apparatus brought to equilibrium again in a few minutes merely by changing the pressure on the boiling liquid.

Apparatus

The apparatus used and the procedure followed will be described in detail with reference to Figure 1, which shows a schematic diagram of the assembly,and Figure 2, which shows the pressure tube and jacket in detail. The glass pressure tube, A, was made of pyrex glass capillary tubing with 1.88 mm. average inside diameter and a wall thickness of 3.1mm. The upper end was sealed carefully, keeping the thickness of glass over the end about the same as that of the walls. In the preliminary runs, the end was sealed in such a way that the inside of the tip was flat and a large amount of glass was accumulated at the top. This seal satisfactorily withstood the pressure, after annealing, until it was cooled to liquid air temperature. Apparently the cooling to liquid air temperature caused strains in the glass for it invariably fractured in a plane across the flat surface at a lower pressure than that at which it had been tested before cooling. By keeping the inner surface of the sealed end rounded and the wall thickness over the sealed end uniform, the pressure tube could be cooled repeatedly with liquid air, without fracturing, when pressure was again applied.

To the lower end of the pressure tube, A, Figure 2, was sealed a 1.5 inch length of 1.2 inch diameter pyrex tubing in the shape of a thistle tube. This glass assembly was then fitted into the upper removable part of the steel block, B, with a rubber gasket, C, held in place by the gland nut, D,

TO VACUUM PUMP

6 ⊗

P

Q

5 ⊗

O

4

M

N

7 ⊗

R
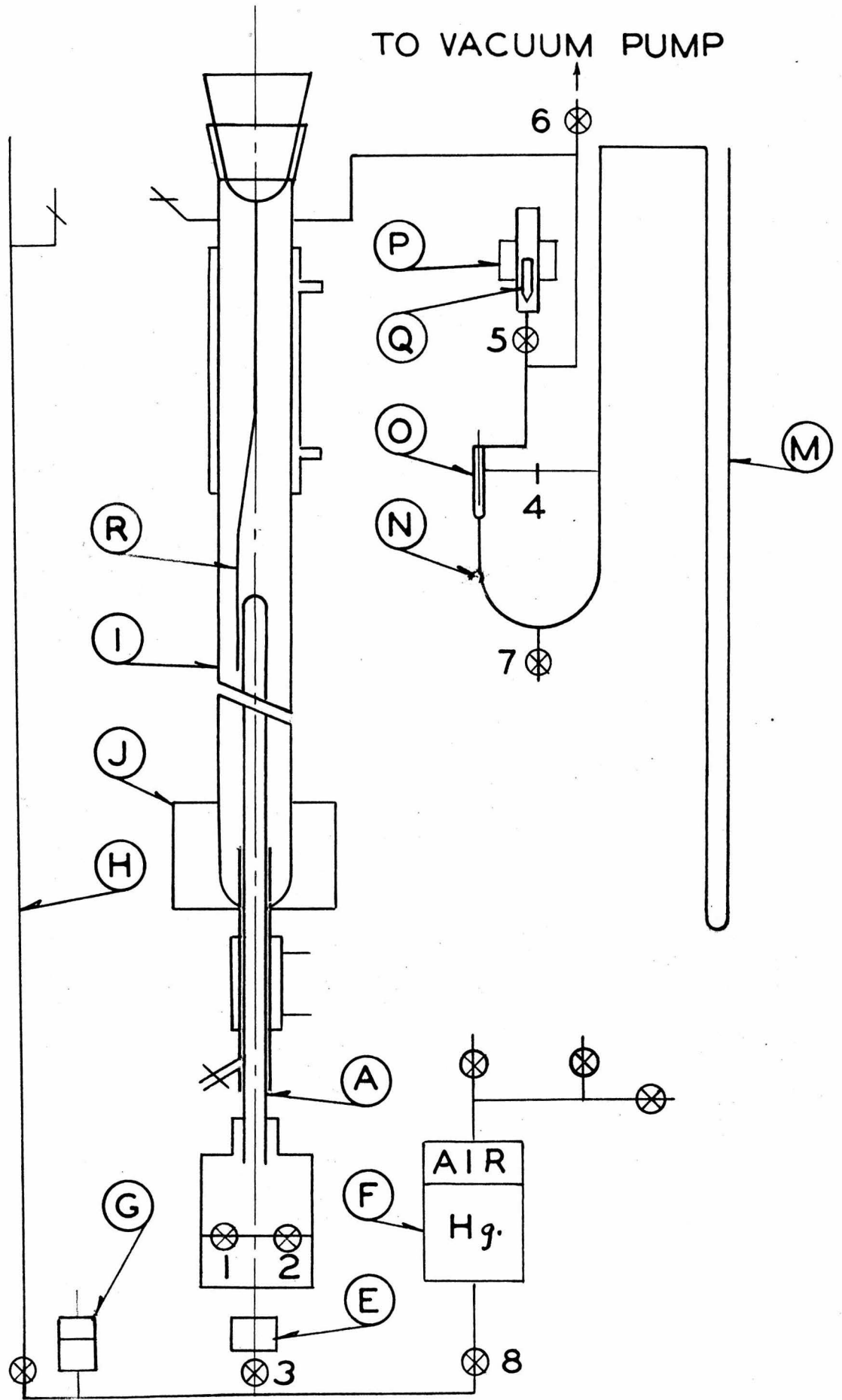
I

J

H

A

G

1   2

AIR
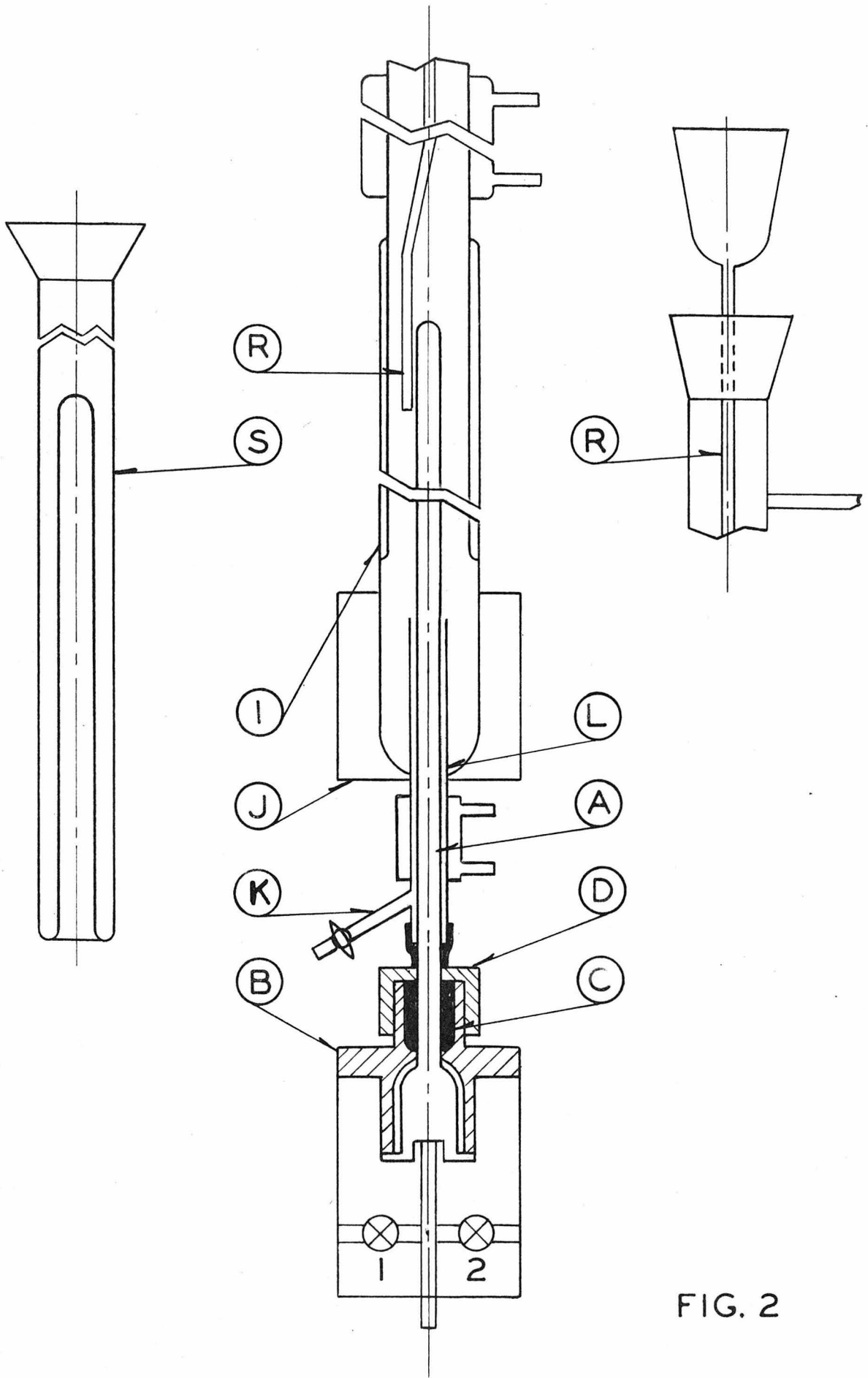
F

Hg.

E

3 ⊗

8 ⊗

FIG. I.

FIG. 2

When the steel parts were fitted together the lower end of the thistle tube and the lower protective shield of steel slipped into the annular channel below the level of the outlet from this enclosed space. After these parts had been assembled, the procedure was to evacuate the tube through valve 1, down to about .001 mm. of mercury vacuum. Then by opening valve 3, shown in Figure 1, mercury flowed into the annular channel, effectively sealing the inside of the pressure tube and the thistle tube from the annular space between the thistle tube and the steel block.

Built into the lower part of the steel block were two needle valves, 1, in the vacuum line and 2, in the line to the sampling hook-up. Below this block was an electrical contact, E, with which the level of mercury could be kept in the approximate vicinity while adding the sample. Extra heavy steel pipe connected the contact assembly with the mercury reservoirs, F and G, and the manometer, H. Reservoir G, was simply a junction between the mercury in the system and the oil in the pipe to the fluid pressure balance. An electrical contact inside this reservoir made it possible to keep the mercury level at a fixed point while taking pressure readings. The reservoir, F, was connected by a manifold with a source of air pressure, a vacuum, and a vent. The air pressure was used to force mercury into the pressure tube and thus change the volume and pressure on the sample as desired. The vent allowed the release of pressure when desired. The vacuum was used to pull the mercury down out of the tube when the pressure in the tube was less than one atmosphere.

The manometer, H, was useful in checking the amount of sample added, in the calculation of the pressure correction, and in indicating directly the pressures on the samples when they were in the range of the manometer. The first two uses will be described in detail later.

Temperature Control

A vacuum jacket, I, surrounded the pressure tube in the section between the boiler, J, and the condenser at the top. This vacuum jacket was silvered except for narrow vertical apertures, in front and back, for observing the phenomena inside the tube. The length of the vacuum jacketed portion was 27.5 inches, the inside diameter, 1.1 inches, and the outside diameter 1.5 inches. The liquid providing the vapor was pulled by suction into the annular space around the pressure tube and up into the boiler space, below the vacuum jacket, through the projecting glass tube, K. A rubber tubing connection prevented liquid from escaping between the lower end of the jacket and pressure tube. To prevent deterioration of this rubber connection by the organic liquids used, a small amount of mercury was run into the lower end of the jacket up to the level of the projecting glass tube. Glass beads were placed in the boiler section to prevent bumping. To prevent the beads from wedging around the pressure tube, the glass tubing through the small water condenser was extended up several inches into the boiler section. A small hole, L, in the wall of this tube, just above the point where it was sealed into the outer jacket, permitted the liquid to be drained out when desired. Above the vacuum jacketed section a water condenser was placed to condense the

the tube. The liquids used and the temperature ranges for
which they were found satisfactory are as follows:

Acetone, C. P._____100-130° F.

Ethyl Alcohol, 96 %_____140-170° F.

Toluene, C. P._____180-220° F.

Chlorobenzene, E. K. Practical_____230-265° F.

Bromobenzene, K. K. Best Grade_____265-300° F.

The junction of the thermocouple was located slightly
above the middle of the length of the pressure tube, used in
the measurements, and just to one side. Error due to radiation
was considered negligible since the double walls of the jacket
were silvered except for the narrow apertures for observation.
The copper constantan thermocouple was calibrated throughout
the entire temperature range required in a thermostated oil-
bath or lead bath against a set of Bureau Standards thermometers
which could be read with an accuracy of 0.03° F.

Pressure Measurement

A fluid pressure balance with an accuracy of 0.1 pound per
square inch was used to measure the pressures below 300 pounds
per square inch and a pressure balance with accuracy of 1 pound
per square inch was used to measure the higher pressures. A
number of correction factors were considered in determining the
final pressure on the sample. These corrections included the
barometer corrections, changes in the height and density of the
mercury in the pressure tube, and the correction due to the
difference in level of the pressure balance and the apparatus.

Correction due to the capillary depression of the mercury was automatically made in the constant for the apparatus. This constant was obtained by reading several pressures both on the pressure balance and on the manometer, H. After correcting these pressures for the density of the mercury and the height in the pressure tube, the average difference between the pressure balance reading and the manometer reading was taken as the constant. In a series of three different pressure readings the constants found were: -20.03, -19.94, and -19.88, and the average value of -19.90, was used. The correction due to vapor pressure of mercury was so small as to be considered negligible in the temperature range of these experiments. The equation for correcting the pressures is as follows:

$$P(corrected) = SP + A + K (R_0 - R) + B$$

A is the constant for the apparatus when $R = R_0$ and the density of the mercury in the pressure tube is corrected to 32^0 F. K is a factor converting a column $(R_0 - R)$ of mercury at the temperature of the experiment to pounds per square inch. R_0 is the reference point at the uppermost point in the inside of the tube. R is the actual height of mercury in the pressure tube. B is the barometer reading in pounds per square inch.

Volume Measurement

The volume of the pressure tube as a function of the distance from the sealed end, was calibrated by measuring the length of a weighed amount of mercury as it was moved, in a single mass, up and down inside the tube. All the measurements

of length or height of mercury column or liquid level were made with a cathetometer whichwas accurate to .01 cm. Knowing the weight of the mercury and the temperature, its volume could be obtained. Then applying the meniscus corrections to both ends, an average volume per cm. of tube length was obtained. By making a series of such readings over the portion of the tube used in the experiments a value for the volume of each cm. of the tube was obtained. These values could have been integrated on a plot of volume versus distance, but to obtain greater accuracy a method of plotting residual volumes was used. A nominal or base volume equal to .02785 cc. per cm. of tube length was decided upon and this amount was subtracted from the actual volume of each cm. of tube length. Then these residuals were plotted against tube length both as actual residual for each cm. of length and also as total cc. of residual from the sealed tip (ref. point) to each cm. distance from the sealed tip. These curves are shown in Figure 3. Thus the actual volume at any distance (R_O-R) from the reference point, R_O, equaled .02785 (R_O-R) plus residual corresponding to that distance. The volumes were also corrected for the meniscuses of both the liquid and the mercury and also for the volume of the small steel agitator used. The specific volume of the material above the mercury level,

$$V = \left[.02785 \ (R_O-R) \ + \ \text{Residual} \ -.01331 \right] \frac{.01602}{\text{weight of sample}}$$

(R_O-R) is the distance between the reference point and the mercury level. Then .02785 (R_O-R) is the base volume above R. Residual is the correction between the base volume and the actual volume and is taken from Figure 3. The figure, .01331, in-
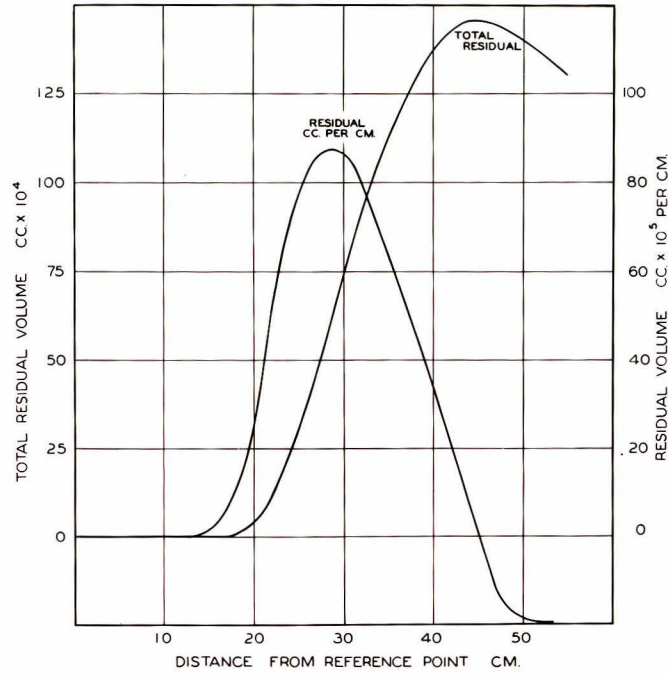
Fig. 3. Residual Volume Corrections for the Pressure Tube.

cludes the volume of the steel agitator and the mercury meniscus correction. These volumes are in cubic centimeters. To convert the total volume in cubic centimeters into cubic feet per pound, the conversion factor, (.01602 ÷ weight of sample), is applied.

Purification of Materials

The propane and butane were obtained from the Philgas Company. According to the specifications, the original propane contained less than 0.1% impurities. It was further purified by fractional distillation in a glass-ring packed column (6), four feet long and 0.5 inches inside diameter, equipped with vacuum jacket and with adequate facilities for maintaining very constant reflux. The middle fraction, amounting to about three-fourths of the charge, was collected in a liquid air cooled receiver connected with a high vacuum degassing apparatus. The material was then distilled under vacuum back into the boiler of the fractionating tower and refractionated. This time about 90% of the charge was collected in the liquid air cooled trap as before and later transferred to a steel storage bomb. An isotherm on this material through the two phase region indicated that its purity was satisfactory.

The original butane contained 0.3% isobutane. This material was purified by the same general procedure as described above for the propane.

Method of Adding Sample

Samples were added to the apparatus in the following manner: samples of purified propane and n-butane were kept in small steel weighing bombs. Before attaching one of these bombs to the line leading to valve 2, the bomb was washed in acetone, dried in a vacuum desicator, and carefully weighed. The mercury was pulled out of the pressure tube, lower chamber, and manometer, H, down to the level of the electrical contact, E, and valve 8, closed. With the bomb valve closed, valve 2, was opened and the pressure tube and connecting lines evacuated through valve, 1. The top of manometer, H, was connected to the same vacuum system. The vacuum was produced by a mercury vapor pump backed up by a Hi-Vac pump. When a vacuum of .001 mm. was produced as measured by a McLeod gage, valve, 1, was closed and the bomb valve carefully opened, allowing the hydrocarbon sample to enter the pressure tube. This gas caused the manometer to raise and the mercury at the electrical contact to fall, but by adding mercury through valve 8, the mercury level was kept at the contact. When the desired amount of gas had been added as indicated by the height of the manometer level, valve, 2, was closed. Then the bomb was cooled in liquid air to reduce the amount of gas in the connecting lines to the vapor pressure of the hydrocarbon at liquid air temperature. The bomb valve was closed, the bomb warmed to room temperature, washed in acetone, dried, and reweighed. The sample of the other hydrocarbon was added in the same manner.

It is admitted that the accuracy of this gravimetric method

of determining the amount of sample may not appear to be as accurate as some volumetric methods which have been used. When the straight forwardness of the method and the absence of any assumptions as to gas volumes, etc., are considered, the overall accuracy was felt to be as good. In only one run, No. 9, was the composition questionable, and this run was made with a very small sample to obtain additional dew points at lower temperatures.

However in this run, several bubble points and dew points were taken at the higher temperatures where the phase boundaries as functions of pressure and composition, and temperature and composition had been definitely determined by previous runs on larger samples. Thus it was considered justifiable, in this case, to change the composition from that determined gravimetrically, to one which would permit the dew points and bubble points at the higher temperatures to fall upon the definitely established curves. This involved a shift of the mol percent of propane from 68.2% to 65.0%.

Although the simplified diagram shows the valves, 1 and 2, some distance to either side of the vertical center hole, the valves were actually placed so that no gas could be trapped when the mercury level was raised above that point. When the mercury level was raised, compressing the sample into the portion of the tube where the measurements were made, frequently at room temperature, the sample would begin to liquify below the boiler. It was found that an appreciable amount of the liquid adhered to the glass walls. To prevent this, the sample

was condensed with liquid air into the upper tip of the tube
while the mercury level was raised up above the boiler. The
liquid air trap, S, was slipped inside the vacuum jacket down
around the tip of the pressure tube. After the mercury level
was gotten above the boiler, it was kept there until the measure-
ments on the sample were completed.

Experimental

The single phase measurements of the isotherms were simple
to make, consisting merely of taking readings of the pressure and
the corresponding volumes over the range desired. Since the in-
vestigation was largely concerned only with the phase boundaries,
the single phase measurements were limited to those in the
neighborhood of the dew and bubble points.

The measurements in the two phase region were more difficult
due to the difficulty with which equilibrium was attained between
the phases. The sample was thoroughly agitated by means of a
small iron stirrer which was moved up and down the inside of the
tube with a magnet around the outside of the jacket. All
measurements were taken with valves, 3 and 8, open. This allowed
the equilibrium to be reached before each reading by an iso-
baric process. The pressure having been set at the desired
point by adding to or removing air from the chamber, F, the
sample would be agitated, at the constant pressure, until the
total volume, occupied by both phases ceased to change with
further agitation. This gave a simple way of determining when
equilibrium had been reached.

The bubble points were determined in the following manner:
with the sample in the liquid phase at a pressure slightly above
the bubble point, the pressure was reduced very slowly by vent-
ing air while the liquid was continually and vigorously agitated.
At the first sign of a bubble forming, the air release valve was
closed. If on further agitation the bubble did not become
larger than being barely visible, this was considered to be the
bubble point and the pressure and volume were recorded as such.
If the bubble did become appreciably larger on further agitation
the pressure was raised a few pounds and the process repeated.
These points could be checked by approaching from the two phase
region but this method was much more difficult since it involved
equilibrium in two phases instead of one just before the bubble
point was reached.

The most difficult measurements of all were those of the
dew points. The technique finally developed was similar to
that for bubble points. With all the sample in the gas phase,
the pressure was very slowly raised while the gas was being
thoroughly agitated. At the first sign of liquid forming, the
pressure valve was closed. If on further agitating no more
liquid was formed this was considered dew point. Although
these points could be checked from the opposite side, that is,
from the two phase side, it was an almost endless task. It
meant setting the pressure and agitating thoroughly; if liquid
remained, the pressure was reset, lower, and the process re-
peated. If one was fortunate, after a few trials the exact
pressure was found at which, after thorough agitation, only

a very small amount of liquid remained.

Since pressure and volume measurements were taken on both sides of each of the phase boundaries for each isotherm, the exact positions of the boundaries were checked by locating the discontinuities in the curves of pressure versus volume at constant temperature. In nearly all the determinations, the dew point and bubble point pressures as determined by observation checked within .5% of these pressures as indicated by the breaks in the isotherms.

Figure 4, shows the isotherms obtained from run No. 5, on the system containing 69.8 mol percent of propane and 30.2 mol per cent butane. It was impossible to obtain dew points over the entire temperature range unless very small samples were used, due to the small volume of the pressure tube. It was found advisable to make runs with large samples primarily for bubble points over the entire temperature range and dew points at the higher temperatures and then subsequently to fill in the dew point data with runs on smaller samples.
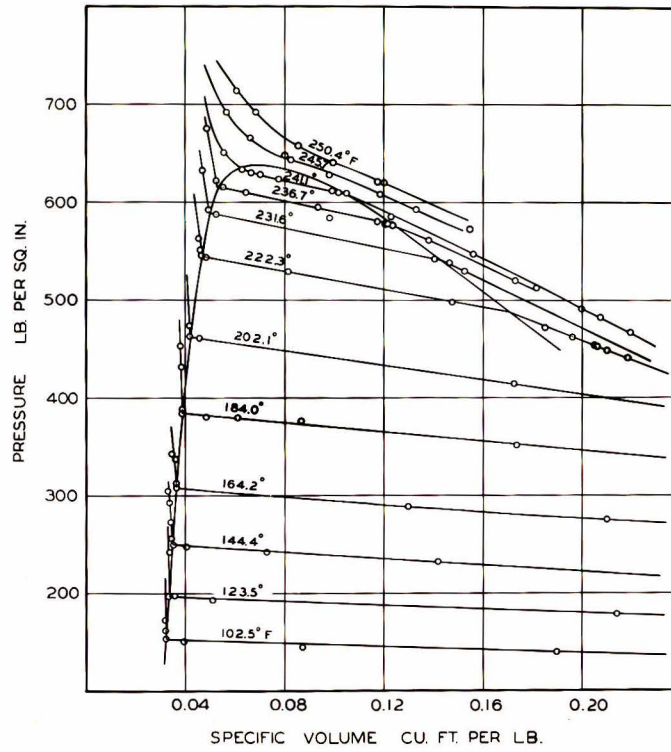
Fig. 4. Isotherms of System Containing 69.8 Mol Percent Propane and 30.2 Mol Percent Butane

Results

The experimental determinations included the measurements of the volumes of the phases under the different conditions of temperature and pressure, but these volumetric data have not been used in the preparation of this thesis other than to check, or in some cases to establish, the dew points and bubble points by the discontinuities in the relation, $\left(\frac{\partial V}{\partial P}\right)_T$. A number of these isotherms for the system of composition, 69.8 mol percent propane and 30.2 mol percent butane are shown in Figure 4. Measurements were made upon nine different compositions in all, but the results of only the last five have been used. The measurements on the first two compositions were of a preliminary nature during which time a technique was being developed and certain improvements were being made in the apparatus. The results of the next two compositions studied were so fragmentary, due to the breaking of the pressure tube, that they were of no value. The compositions of the five remaining runs are given in Table I, along with the pressures and temperatures at the critical point, the point of maximum pressure, and the point of maximum temperature for each composition.

Figure 5, shows the phase boundaries of the five mixtures on a pressure-temperature diagram, each loop representing a different mixture. From left to right, these mixtures are No. 7, No. 5, No. 8, and No. 6, as numbered in Table I. The sample of mixture, No. 9, was too small to be studied satisfactorily in the critical region. The broken line, tangent to
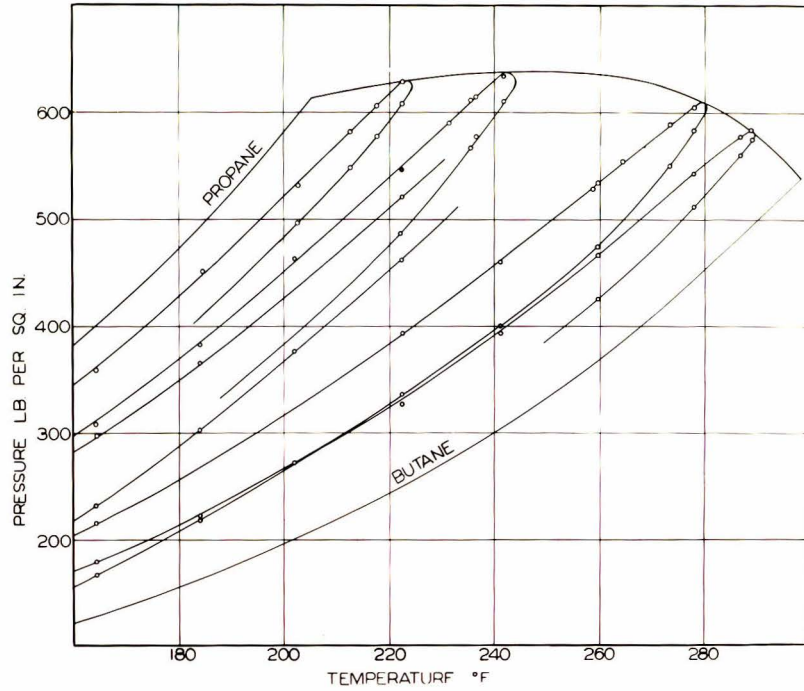
Fig. 5. Pressure-Temperature Diagrams at Constant Compositions

TABLE I. Some Characteristics of the Mixtures Studied.

Mixt. No.	Composition Mol %		Point of Max.Pressure	
	C_3	C_4	Press. #/sq. in.	Temp. °F.
5	69.8	30.2	638	242.6
6	20.8	79.2	584	288.6
7	85.5	14.5	630	223.2
8	33.8	66.2	610	279.2
9	65.0*	35.0	---	-----

*Corrected value.

Mixt. No.	Point of Max.Temp.		Critical Point	
	Press. #/sq. in.	Temp. °F.	Press. #/sq. in.	Temp. °F.
5	630	244.0	638	242.6
6	580	289.2	583	289.0
7	626	224.2	630	223.2
8	605	280.3	609	279.6

TABLE II. Equilibrium Ratios for Propane and Butane

Propane

Pressures #/sq. in.	Temperatures °F.						
	100°	130°	160°	190°	220°	250°	280°
100	1.70	2.30					
200		1.31	1.76	2.20			
300			1.24	1.56	1.87		
400				1.25	1.46	1.69	
500				1.04	1.22	1.36	1.50

Butane

	100°	130°	160°	190°	220°	250°	280°
100	0.57	0.84					
200		0.47	0.64	0.89			
300			0.47	0.65	0.85		
400				0.53	0.71	0.88	
500				0.46	0.66	0.80	0.95

these curves and which ends at the critical points of propane
and butane, is the loci of the critical points of all possible
mixtures of propane and butane. It is evident from the flat-
ness of this curve, especially as it approaches the critical
point of propane, that there is not much difference between
the maximum pressures and the pressures at the critical points
of the different mixtures. As shown in Table I, for mixtures,
No. 5, and No. 7, the differences in these pressures are
negligible, while for mixtures, No. 6, and No. 8, the dif-
ferences are barely more than limits of the experimental error
of the pressure measurements. That it was found very difficult
to study experimentally the region of retrograde condensation
may be partially explained by the facts that the differences
between the maximum pressures and the critical pressures were
so small and that the differences between the maximum temper-
atures and the critical temperatures were also quite small,
the maximum being 1.6^{o} F., with mixture No. 5, Table I. It is
within these narrow limits that the phenomena of retrograde
condensation occurs.

Figure 6 includes a number of pressure-composition dia-
grams at constant temperatures ranging from 100° F. to 280° F.
This set of diagrams was made up by following constant temper-
ature lines on Figure No. 5, and reading the pressures at
the phase boundaries of the different compositions. These
pressures were then plotted upon the pressure-composition
coordinates and smooth curves drawn through the points for
each phase boundary at each temperature. Each pair of con-
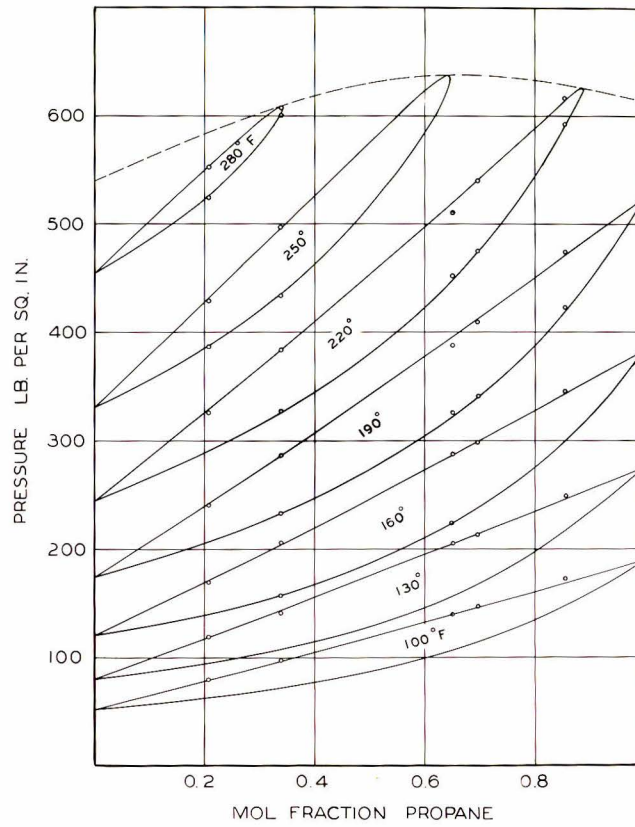stant temperature phase boundary curves terminates in common

Fig. 6. Pressure-Composition Diagrams at Constant Temperature.

points at the vapor pressures of pure butane and propane at
that temperature. Consider, for example, the curves at the
constant temperature of 190° F. These curves terminate at
the right hand ordinate (100% propane) at the vapor pressure
of pure propane at 190° F. and terminate at the left hand
ordinate (100% butane) at the vapor pressure of pure butane.
The region enclosed by this pair of curves is the only re-
gion in which two phases may exist in equilibrium at 190° F.
At all pressures above the upper curve, the loci of bubble
points at 190° F. for all mixtures of propane and butane,
only the liquid phase may exist. At all pressures below the
lower curve, the loci of dew points at 190°F. for all mix-
tures, only the gas phase may exist. If now a constant pres-
sure is taken, for example 300 pounds per square inch, it is
possible to determine the composition of the coexisting
phases at 190° F. by merely reading the composition of the
liquid phase on the bubble point curve and the composition
of the gas phase on the dew point curve, both at 190°F.
and 300 pounds per square inch pressure.

The curvature of the bubble point curves on this dia-
gram is a measure of the degree with which mixtures of butane
and propane agree with Raoult's Law and Dalton's Law. Straight
lines would indicate that the total vapor pressure of the
liquid of any mixture at any definite temperature is equal
to the sum of the mol fraction of butane times its vapor pres-
sure in the pure state, at the temperature in question, and
the mol fraction of propane times its vapor pressure at the

same temperature. Since the bubble point curves are not entirely straight, it is evident that mixtures of these hydrocarbons do not follow these laws, although the deviations are not as large as is found with some pairs of other hydrocarbons with more widely varying physical properties.

Figure 7, a temperature-composition diagram at constant pressures, was prepared similarly to Figure 6, except that, in this case, constant pressure lines were followed on Figure 5, and the temperatures of the phase boundaries of the different mixtures plotted on the temperature-composition coordinates. On Figure 7, at the constant pressure of 300 pounds per square inch, as an example, the phase boundary curves terminate at common points, the point on the right being the temperature at which pure propane has a vapor pressure of 300 pounds per square inch, and the point on the left being the temperature at which pure butane has a vapor pressure of 300 pounds per square inch. These two curves inclose the two phase region at 300 pounds per square inch for all mixtures of propane and butane. The upper curve is the loci of dew point temperatures for all mixtures at this pressure and the lower curve is the loci of all bubble point temperatures at the same pressure. For any mixture at 300 pounds per square inch pressure, only the gas phase will exist above the dew point curve and only liquid phase will exist below the bubble point curve. If on this diagram, a constant temperature line, for example 190° F., is followed, it is possible to determine the composition of the coexisting phases at 300 pounds per
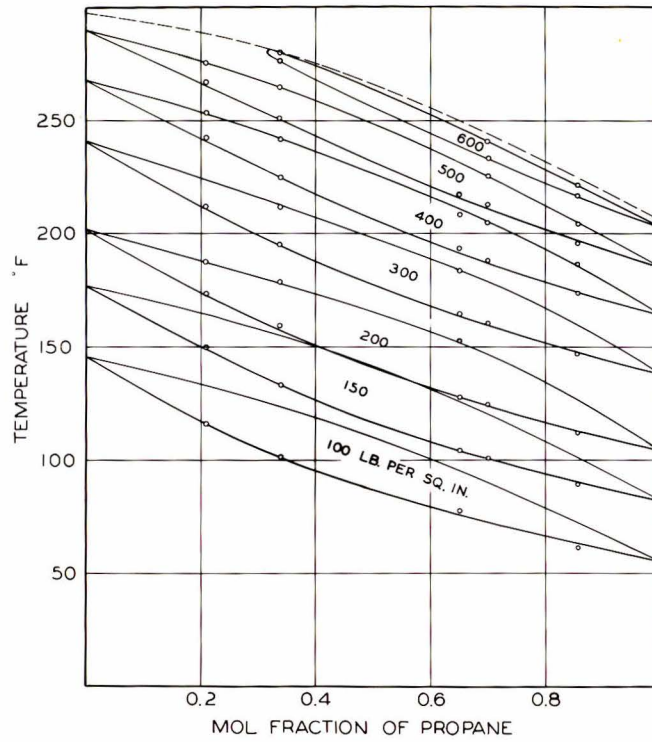
Fig. 7. Temperature-Composition Diagrams at Constant Pressure

square inch pressure by reading, as before, the composition
of the gas phase on the dew point curve and composition of
the liquid phase on the bubble point curve. Since, on both
diagrams, the same pressure and temperature have been used,
namely, 190° F. and 300 pounds per square inch, the composition
of the coexisting phases as determined in both cases will be
the same.

The ratio of the mol fraction of propane in the gas phase
to the mol fraction of propane in the liquid phase is called the
equilibrium ratio for propane. This quantity, K, is frequently
called the equilibrium constant although it varies with temper-
ature and pressure as well as the character and amounts of the
other components present in the mixture. If at equilibrium, X_p
is the mol fraction of propane in the liquid phase, and Y_p is
the mol fraction in the coexisting gas phase, then $K_P = Y_P/X_P$
In a like manner, the equilibrium ratio for butane, $K_B = Y_B/X_B$
or in this binary system, $K_B = 1-Y_P/1-X_P$.   These values
of K may be determined from the temperature-composition of the
pressure composition diagram as explained previously.

Equilibrium ratios taken at different pressures from
Figure 6, at each of the constant temperatures indicated there,
were multiplied by the pressures at which they were taken and
then plotted against these pressures in Figure 8. The curves
below the diagonal line represent constant temperature equi-
librium ratios for butane as functions of pressure. The curves
above the diagonal line represent constant temperature equilibri-
um ratios for propane as functions of pressure. If the equi-
librium ratio for propane is desired, for example, at 190° F.

and 400 pounds per square inch pressure, it may be determined
by dividing PK by P or, in this case, K = 500/400 = 1.25. Of
course, for the sole purpose of obtaining equilibrium ratios,
a plot of equilibrium ratios as functions of temperature or
pressure would be more convenient. This diagram, Figure 8,
was prepared to show more satisfactorily the behavior of these
ratios in the critical region. A number of equilibrium ratios
taken from this diagram are tabulated in Table II for both
propane and butane.

The diagonal line, Figure 8, is the loci of points where
the equilibrium ratios are equal to unity, that is, where PK = P.
The equilibrium ratios for either component approaches unity as
the total pressure on the system approaches the vapor pressure
of that component at the temperature of the system. Where the
temperature is above the critical point of one of the components,
both equilibrium ratios approach unity as the pressure approaches
the critical pressure corresponding to the temperature of the
system, which temperature becomes the critical temperature of
the system. These critical values, of course, correspond to
definite compositions. This is illustrated by the constant
temperature curves at 220° F., 250°F., and 280° F., and the
corresponding mixtures are 88.8 mol percent propane, 64.6 mol
percent propane, and 34.2 mol percent propane, respectively,
as may be ascertained by noting the points, on Figure 6, where
the phase boundary curves at these temperatures touch the loci
of critical pressures. Thus at temperatures above the critical
point of propane but below the critical point for butane, the
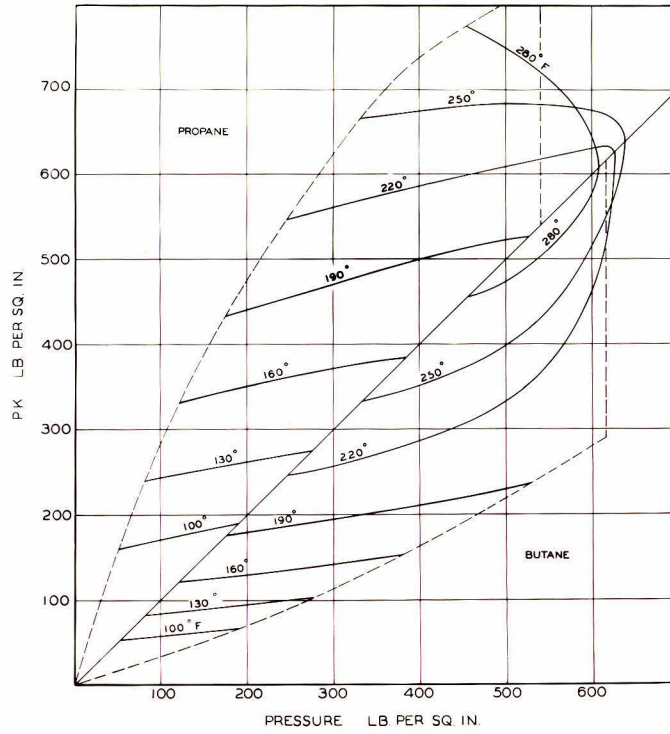butane equilibrium ratios start at unity at the vapor pressure

Fig. 8. Pressure Times Equilibrium Ratios at Constant
Temperature versus Pressure.

of butane and then return to unity at the critical pressure corresponding to the temperature on the system, which becomes the critical temperature.

At temperatures below the critical points of either component, the equilibrium ratios of either component become indeterminate as the pressure on the system becomes equal to the vapor pressure of the other component at the temperature of the system. The broken envelope curves, starting at the origin, are the loci of points at which the pressure on the system becomes equal to the vapor pressure of the other component at the temperature of the system. For example, the upper broken envelope line is the loci of points at which the equilibrium ratios for propane becomes indeterminate, that is, the points at which at the constant temperatures shown, the pressures become equal to the vapor pressure of butane. The vertical broken lines indicate the critical pressures of the pure components, the upper one for butane and the lower one for propane.

Figure 9, shows a comparison of the experimentally determined equilibrium ratios for butane and those calculated by Raoult's Law. It is evident that the deviation from Raoult's Law is not large at 150 pounds per square inch pressure and increases only slightly up to 300 pounds pressure. However, at 400 pounds per square inch pressure the deviation becomes relatively large as would be expected when the pressure approaches the critical pressure.

Where the necessary data have been lacking, values for equilibrium ratios have been calculated for engineering design, not only through the use of Raoult's Law and Dalton's Law, but also through the use of certain concepts of ideal solutions.
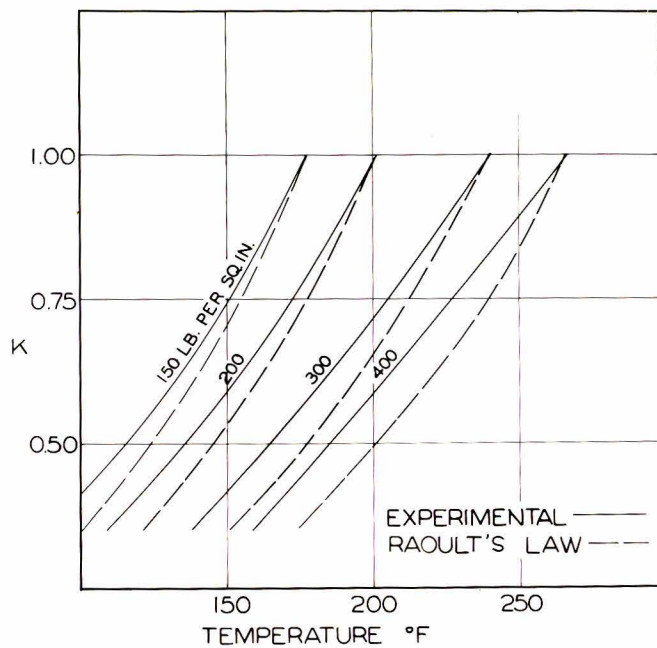
Fig. 9. Equilibrium Ratios for Butane, Experimental and
Calculated.

As defined by Lewis and Randall (8), "The ideal solution is one in which the fugacity of each component is proportional to the mol fraction of that component at every temperature and pressure." In ideal solutions, the fugacity of each component in a phase is equal to the fugacity of each component in the same phase in the pure state, at the same temperature, times its mol fraction in the ideal solution. If the propane-butane system was an ideal solution, the following equations would be true: $f'_{PL} = f_{PL} X_P$; $f'_{PG} = f_{PG} Y_P$; $f'_{BL} = f_{BL} X_B$; $f'_{BG} = f_{BG} Y_B$ (f' refers to the fugacity of the component in the system and f to the fugacity of the pure component. The subscript L, refers to the liquid; G, to the gas; P, to propane; and B, to butane. As used formerly, X is the mol fraction of the component in the liquid phase and Y, the mol fraction in the gas phase). From these equations it is possible to determine the compositions of the phases in terms of fugacities. Then, since the fugacity of each pure component is a function only of the temperature and pressure of the system, the compositions of the coexisting phases at any temperature and pressure may be determined with only the knowledge of the fugacities of the pure components at the desired temperature and pressure. Considering the above equations for propane, the following relation is obtained, $\dfrac{Y_P f_{PG}}{X_P f_{PL}} = \dfrac{f'_{PG}}{f'_{PL}}$. Since at equilibrium, the fugacity of the component in the liquid is equal to the fugacity of the component in the gas $\dfrac{Y_P f_{PG}}{X_P f_{PL}} = 1$, or $\dfrac{Y_P}{X_P} = K_P = \dfrac{f_{PL}}{f_{PG}}$. It was through the use of this relation that the curve, No. 4, of Figure 10, was obtained for propane at 190° F.
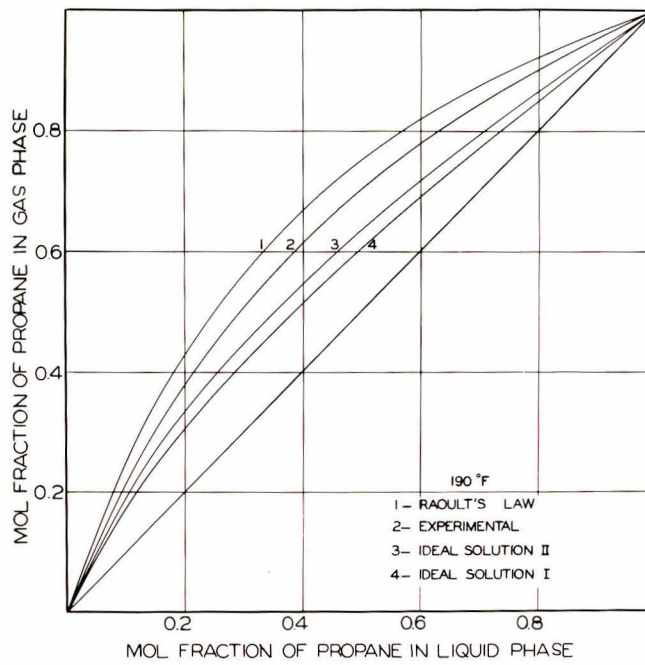
Fig. 10. Experimental and Calculated Equilibrium Curves for Propane at 190° F.

Frequently there are insufficient P-V-T data to permit the use of the laws of ideal solutions since these laws take into account the volume of the liquid phase and also the deviation of the gas phase from perfect gas behavior. Where no P-V-T data is available, other than the vapor pressure data of the pure components, Raoult's and Dalton's Laws may be used. Curve No. 1, of Figure 10, was obtained by use of these laws. If only the fugacities of the pure components are known, the volumes of the liquid phase may be neglected. Following this method, the curve, No. 3, of Figure 10, was obtained. For mixtures of propane and butane at 190°F., this adaption of the laws of ideal solutions appears to give phase equilibrium data nearer the experimental results, Curve 2, Figure 10. The experimental curve is nearer the Raoult's Law curve at higher concentrations of propane, while for the higher con-centrations of butane, it is about equidistant between the Raoult's Law curve and the curve prepared by the laws of ideal solutions, neglecting the volume of the liquid phase. It is probable that at higher pressures the laws of ideal solutions would more nearly fit the experimental results since the curves on Figure 9, indicate that, at the higher pressures, the deviation from Raoult's Law becomes greater.

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