

VOLUMETRIC BEHAVIOR OF
LIQUID MIXTURES OF
PROPANE AND n-PENTANE

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INTRODUCTION

In the design of modern petroleum refining equipment, a knowledge of the volumetric and phase behavior of hydrocarbon systems is useful. It aids in the prediction of capacities and the pressures and temperatures of operation in situations for which no experience is available. At present there is no universally applicable method for the determination of these data from the behavior of the pure components which compose the system. Consequently investigations of individual systems is necessary in many cases and much work of this sort remains to be done.

However, the experimental investigation of the properties of a multicomponent hydrocarbon system, one of n components, is difficult, due to the large number of variables which must be fixed to determine the state of the system, the exact number being given by the phase rule. Then, too, the compositions of the phases must be determined and when the components are many and closely related the necessary analysis becomes complicated. It is fortunate that, in many cases, data obtained from studies of binary mixtures can be applied to more complex systems. Engineering accuracy can usually be obtained in the use of volumetric and phase data for one component from a binary mixture investigation to predict the behavior of that component in a more complex system, provided the average molecular weight of the other components present is similar in the two mixtures. Correlation of phase and volumetric properties for one component

against the average molecular weight of the other substances present is frequently used in the case of naturally occurring oils, for which an exact analysis would be very laborious to obtain.

Volumetric data are conveniently reported either as densities or as specific volumes, usually of the system as a whole, though in some cases these quantities are obtained for each phase. Throughout this thesis specific volumes are reported in cubic feet per pound. The specific volume of a substance is defined as its volume at the existing pressure and temperature, divided by its weight. The symbols used to represent this quantity and others of importance in this discussion are tabulated below.

P	Pressure, pounds per square inch absolute.
T	Absolute temperature, degrees Rankine.
t	Temperature, degrees F.
V	Specific volume, cubic feet per pound.
y_1	Mole fraction of component 1 in the gas phase.
x_1	Mole fraction of component 1 in the liquid phase.
K_1	The "equilibrium constant" for component 1 ($= y_1/x_1$). Component 1 is taken as the more volatile component.
n_1	Mole fraction of component 1 in the system.
\bar{V}_1	Specific volume of component 1 $= (\partial \underline{V} / \partial m_1)_{PTn_2}$ in cubic feet per pound.
\underline{V}	Total volume, cubic feet.
m_1	Weight of component 1 added.
b	Specific gas constant.

3.

U Internal energy of a system.

THEORY

According to the Phase rule ($F = C - P + 2$) a binary system in the single phase region has three degrees of freedom, and requires the determination of three variables to fix the intensive properties of the system. C , the number of components, is two; P , the number of phases, is one; and thus F , the number of degrees of freedom, equals $2 - 1 + 2$, or three. Those variables most commonly specified are pressure, temperature, and composition, usually of the system as a whole. A binary mixture of fixed composition is generally considered as a definite and independent system, because its properties usually cannot be predicted from those of its constituents. Thus relationships between pressure, volume and temperature for pure substances are of little use in determining these properties for binary systems.

Gas Laws: Many correlations have been attempted between temperature, pressure and volume of a substance or mixture in the gas phase. The most common of these is the classical gas law, which may be expressed in engineering units by the equation $PV = bt$, where b is the universal or molar gas constant divided by the molecular weight of the gas. This relation holds fairly well for hydrocarbon gases at conditions far removed from their critical states, but breaks down badly as

the critical region is approached. Refinements, such as those of the van der Waals equation, improve the accuracy but fail too in the critical region. A perfect gas is defined as one which obeys the gas laws and for which $(\partial U/\partial V)_T = 0$, where U is the internal energy. For any actual gas, the ideal law is modified to the expression, $PV = ZbT$ where Z , the compressibility factor, equals PV/bT , and is thus defined by the equation itself. $Z' = PV/P_a V_a$ and $Z'' = PVT_a/P_a A_a T$ are also used, but in each case these quantities are functions of P , T and the composition and nature of the gas. Before they can be determined, the volume of the system must be investigated as a function of these variables.

Liquids: An ideal liquid is defined as one for which $(\partial V/\partial P)_T = 0$ and $(\partial V/\partial T)_P = 0$. For actual liquids these relations do not hold, since as the temperature increases, the isothermal compressibility, $-(\partial V/\partial P)_T$, increases but decreases as P increases. For hydrocarbons in general, $(\frac{\partial(\frac{\partial V}{\partial T})_P}{\partial T})_P =$

$(\frac{\partial^2 V}{\partial T^2})_P$ is positive, and $(\frac{\partial(\frac{\partial V}{\partial P})_T}{\partial P})_T = (\frac{\partial^2 V}{\partial P^2})_T$ is negative.

At high pressures and low temperatures, actual liquids approach ideal behavior. Correction factors of various kinds have been applied to liquid volumes, but in each case the volume must be determined as a function of pressure, temperature and composition. At low pressures the additive volume relation, $V = n_1 V_1 + (1 - n_1) V_2$, applies fairly well for liquids, where n_1 is the weight fraction of component 1 in the mixture;

V_1 , is the specific volume of that component in the pure state; and V is the specific volume of the mixture. This rule fails in the critical region, and does not apply to associating substances. A similar relation which applies quantitatively results when partial volumes of each component are substituted for specific volumes, but to obtain these partials, the volume of the mixture must be determined as a function of P , T , and composition.

Two-phase Region: In the single-phase region, a binary system behaves like a pure substance, but in the two-phase region differences begin to appear. Since in the graphical portrayal of the relations of three variables, solid figures are necessary and these are difficult to construct, a set of curves is commonly used. To depict the volumetric behavior of a system of fixed composition, curves of pressure vs. volume, temperature vs. volume and pressure vs. temperature are sufficient. On V - P and V - T diagrams, $(\partial V/\partial T)_{Pn_1}$ and $(\partial V/\partial P)_{Tn_1}$, the slopes of the isobars and isotherms, change abruptly at two points, the dew point and the bubble point of the system. The state at which the system is entirely gaseous but in equilibrium with an infinitesimal amount of liquid is known as the dew point, and the state at which the system is entirely liquid but in equilibrium with an infinitesimal amount of gas is known as the bubble point. The properties of the system at these points are those of the gas or liquid at the dew or bubble point conditions. For such a mixture the isobars and iso-

therms are not straight and horizontal between the dew and bubble points, through the two phase region, and thus differ from those of a pure substance.

Equilibrium Constants: In any given mixture there are three compositions of importance: n , the composition of the system as a whole, and x and y , the compositions of the coexisting liquid and gas phases respectively. Knowledge of these two latter quantities is frequently of importance. The ratio of y to x for a given component in a system is a useful quantity, which is often called the "equilibrium constant", K . This quantity is a function of the pressure, temperature, and nature of the system considered, and is not in any sense a constant. $K_1 = y_1/x_1$ and $K_2 = y_2/x_2 = (1 - y_1)/(1 - x_1)$. At a constant temperature when the pressure equals the vapor pressure of the more volatile component 1, $K_1 = 1$. As P decreases, K_1 increases, but ceases to have any meaning when the pressure becomes less than the dew point pressure of the mixture under consideration. As P approaches the dew point pressure, K_1 becomes indeterminate. When the pressure equals the vapor pressure of the more volatile constituent, K_1 equals unity. Equilibrium constants for a substance are applicable only in systems similar to those in which they were determined, thus limiting their range of usefulness.

Critical Region: The critical point of a system is defined as that state at which all the intensive properties of the

coexisting phases become continuously identical. For binary and multicomponent systems it is not necessarily the point of highest pressure or temperature for the existence of two phases in a mixture of fixed composition. It will be noted on the P-V diagram (Fig. 4) that there is a point of tangency between the dew point curve and an isotherm for a temperature higher than the critical temperature. This temperature is the highest at which two phases can exist in a mixture of the particular composition considered, and is known as the cricondenthem. It is in no sense a critical point, for the properties of the two phases are not identical. It will be noted also, that if the pressure is continually decreased at a constant temperature above the critical temperature but below the cricondenthem, a liquid phase will appear and disappear again, and the isotherm in question crosses the dew point curve in two places. This phenomenon is called retrograde condensation, and occurs in the two-phase region of a binary system at temperatures above that of the critical state.

APPARATUS FOR P-V-T MEASUREMENT

Two general types of apparatus have been used for the measurement of the pressure-volume-temperature relations of hydrocarbon systems. These utilize the same principle, differing only in material of construction. In effect, both consist of a chamber which can be maintained at a constant temperature, while the volume is changed, the pressure and volume being measured. In one of these devices the chamber is of steel, (1)*, while in the other it consists of a glass capillary tube, sealed at the upper end (2,3,4). The steel apparatus is capable of carrying on investigations at pressures far in excess of those which are possible in a glass tube. The greater volume of this type of chamber makes possible the use of a larger sample. However dew and bubble points can be determined only by locating breaks in the isotherms and isobars, a procedure which becomes so difficult as to be nearly impossible in the critical region. Since the sample may be seen in the glass tube, dew and bubble points can be located visually, and the number of phases present is known at all times. This is not always the case with the steel equipment. The apparatus used in the work here reported utilizes a glass capillary tube.

This apparatus consists in essence of a thick-walled glass

* Literature references are listed at the end of this thesis.

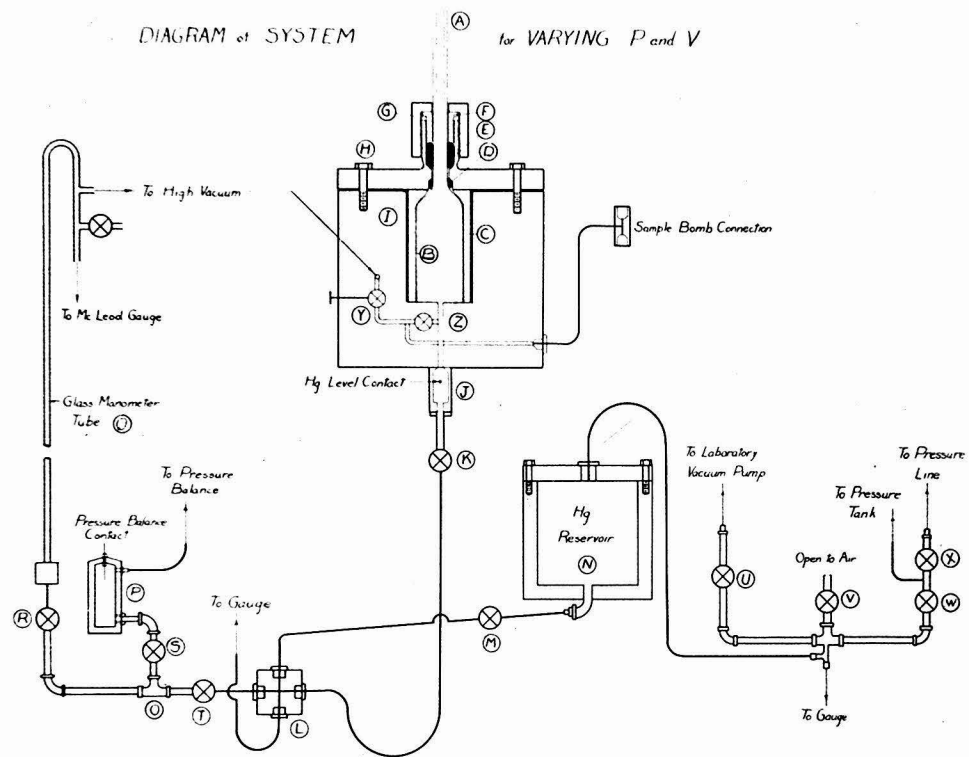


Figure 1. Diagram of system for varying pressure and volume of sample.

capillary tube, sealed off at the upper end, and connected to a steel chamber at the lower end. This chamber connects to a mercury reservoir upon which pressure can be applied, and also to a device for measuring the pressure. Around the outside of the glass tube is a glass jacket, within which a pure substance is boiled. By means of automatic valves, the pressure above the boiling liquid is maintained constant and thus the temperature within this vapor bath is fixed.

The pressure tube, as the glass capillary tube will be called, is thick walled, the outside diameter being $1/2$ inch and the inside diameter, $3/16$ inch. The upper end is sealed off in such a manner that the thickness of glass at the end is the same as the wall thickness, in order to avoid unnecessary stresses with change in pressure and temperature. The open end of the tube is expanded to a thinner walled cylinder $1\ 1/4$ inches in outside diameter, and $1\ 7/8$ inches long. Referring to the diagram of the system shown in Figure 1 these portions of the tube are labeled A and B, respectively.

It will be noted in the same diagram, that the large end B of the pressure tube fits snugly into a steel shell C, which is a part of the cover of the steel chamber. A rubber washer D, protects the top of the enlarged glass section from actual contact with the steel. The tube is sealed into this cover by an arrangement similar to the packing of a valve. A rubber gasket E replaces the packing and is held tightly

against the tube by a packing gland F, forced down by a gland nut G. As in the case of a valve stem, the packing gland and the seat of the gasket in the cover are beveled so that pressure on the gland presses the gasket tighter against the tube and effects a tight closure. In tightening the gland nut, care is required in order to avoid developing stresses in the glass tube which might cause fracture at this point when temperature conditions change. The cover into which the tube is connected is held tightly to the steel chamber by steel bolts H, and a monel metal gasket I, between cover and chamber, makes the connection pressure tight.

The volume of the sample in the apparatus is varied by forcing in or withdrawing mercury from the steel chamber. A small passage connects this chamber with a smaller contact chamber J, in an extension on the bottom of the steel block. Within this space is an insulated contact point, so connected that when mercury rises to this level, a circuit is closed and a signal light comes on. From the bottom of this contact chamber steel tubing leads thru a needle valve K into a four-way connection L. This line is brought down below the connection and back up to it, forming a trap, and thus preventing the leakage of air from the mercury system into the pressure tube with resultant contamination of the sample. From the connection L, one line leads to a pressure gauge, so that the pressure on the mercury at this point (which normally is nearly

the same as that within the pressure tube) can be approximately measured. Another line leads thru a needle valve M, slightly upward into the bottom of the mercury reservoir N. This reservoir is located above the connection and most of the rest of this part of the system, so that any air that leaks in will rise into the reservoir, from which it can be removed without difficulty. The fourth line from the connection leads to a tee O, from which branch pipes to the pressure balance contact chamber P and the manometer Q. Valves R, S, and T, make it possible to shut off either or both of these parts of the system.

The mercury reservoir N is a heavy-walled steel cylinder, with a gasketed top bolted to it. Steel tubing leads from the top of this chamber to the valve system U, V, W, and X. This system makes possible the application of either pressure or vacuum to the reservoir. Pressure is supplied from compressed air in a pressure tank, direct connection with the laboratory pressure lines being avoided, because of the very high pressure carried in them which would make regulation difficult, and might damage the apparatus in event of the failure of a valve. Connection to the pressure tank is made between valves W and X. Valve X was originally used for inflating the pressure tank from the pressure lines, but this connection has been discontinued and it is no longer necessary. Valve W controls the pressure. Valve V, opening to the air, is used

to bleed down the system to atmospheric pressure and valve U serves to regulate the removal of air from the reservoir by the laboratory vacuum pump in case pressures below atmospheric are desired.

The pressure existing within the system is measured on a pressure balance, reading to 0.01 pound per square inch. A copper tubing line containing oil connects this balance with the contact chamber P.

Maintainance of Temperature: The temperature of the pressure tube and sample, which is kept constant by jacketing the tube with a vapor bath containing a pure liquid boiling at a constant pressure, is adjusted by varying the pressure. The jacket consists of a doubled-walled glass cylinder A shown in the diagram of the temperature control system presented in Figure 2. The space between the walls is evacuated to minimize conduction losses and the inside and outside walls of this space are silvered to reduce radiation losses. An unsilvered strip makes possible the viewing of the pressure tube. Low temperatures of boiling are attained by reducing the pressure in the space above the liquid with a Cenco pump. Reference to Figure 2 will aid in understanding the operation of the pressure control system. A U-tube B, containing mercury, is connected at one end to the line leading from the vacuum pump to the jacket, while the other end leads to a chamber C, which

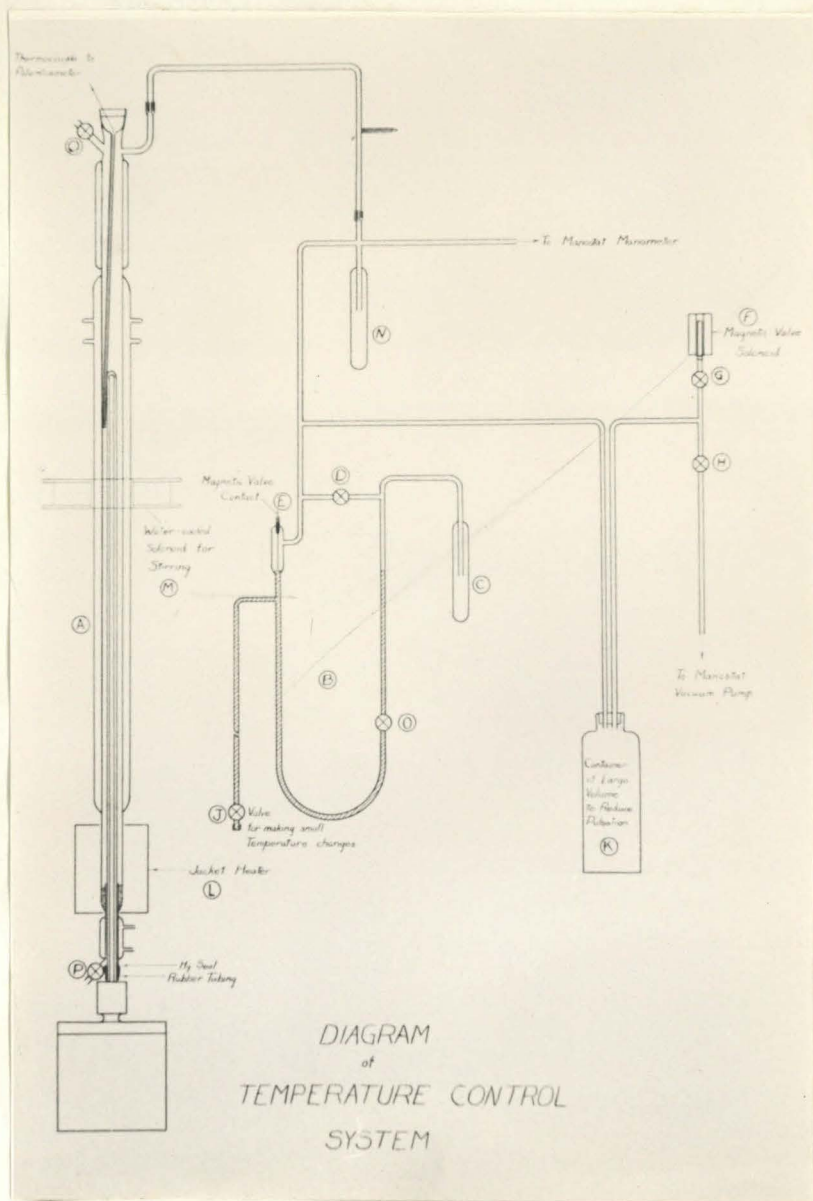


Figure 2. Diagram of temperature control system.

is a large sealed glass tube. The two arms are connected thru the stopcock D. When the pressure in the jacket, as indicated by the manostat manometer, has been reduced to the desired value, the stopcock D is closed and the chamber sealed off. Further operation of the pump causes the mercury in the jacket arm of the U tube to be forced up by the greater pressure in the chamber and to make contact with a wire E, sealed into the tube. This completes an electrical circuit, operating a relay which controls a mercury switch. The closing of this switch allows current to flow thru the coils of a solenoid F, which activates a magnetic valve. The magnetic field produced lifts a valve stem and permits air to bleed into the system, increasing the pressure and forcing the mercury down, away from the contact, thus breaking the circuit. The stem then drops back into place, stopping the admittance of air, and the vacuum pump evacuates the jacket until the process is repeated. By controlling the rate of pressure increase and reduction thru valves G and H, movement of the mercury can be reduced to a very small amount.

A condenser is attached to the top of the jacket, to condense the vapors and return them to the bath. This is done not only to conserve the liquid being boiled, but also to prevent their carrying over into vacuum pump, where, by dissolving in the oil, they would cause difficulties. The trap N, serves as a further precaution against the boiling over of liquid from the bath. A container K of large volume is included

in the vacuum system to reduce the pulsations produced by strokes of the pump. The stopcock O may be used to prevent movement of the mercury in the U tube B.

The energy necessary for boiling the liquids in the vapor bath is supplied by an electrical heater L, which fits around the bottom of the jacket below the double walls. Resistances in series with the heater allow the rate of heating to be controlled. "Bumping" of the boiling liquids is avoided by small glass rings placed in the heater section. To prevent contact of these sharp rings with the pressure tube, it is surrounded by a short section of glass tube which is attached to the bottom of the boiler. A small water cooler below the boiler lowers the temperature of the liquid around the connection of the jacket to the pressure tube. This connection is accomplished by means of a section of rubber tubing, slipped over the outside of the bottom of the jacket and over the pressure tube. The introduction of sufficient mercury to cover this seal protects the rubber from the organic liquids which are boiled in the vapor bath. The stopcock P enables the liquid to be drawn off, while stopcock Q serves to relieve the vacuum in the jacket.

Small temperature changes are made while the control system is in operation by raising or lowering the pressure slightly. This is accomplished by varying the amount of mercury in the manostat by means of an auxiliary valve J,

connected to a line full of mercury and located more than 75 centimeters below the level of the mercury in the U tube. Running the stem into this valve displaces some of the mercury and thus increases the pressure in the jacket; turning it outward has the opposite effect. The valve was placed below the system to eliminate danger of leaks and the admittance of air.

The temperature existing in the vapor bath is measured with a copper-constantan multi-lead thermo-couple, connected with a White potentiometer. This thermo-couple was calibrated against a Bureau of Standards platinum resistance thermometer and it is believed that the temperature within the vapor bath was determined to within a tenth of a degree relative to the International platinum scale. The ground glass stopper forming the top of the jacket was elongated into a thin tube, sealed at the lower end, and the thermocouple was placed within this tube. The level of the junction was about three inches below the top of the pressure tube.

Only very pure liquids can be used successfully in the jacket, since the presence of impurities causes the boiling temperature to change even at constant pressure, as distillation changes the composition of the original mixture. Although a condenser is built into the jacket between the boiling liquid and the vacuum pump, some vapor is not condensed, and is drawn off into the pump. The liquids used, (2) and the temperature ranges for which they are found suitable are:

Ethyl Alcohol, 95%	100-170°F
Toluene, C.P.	170-220°
Chlorobenzene	220-265°
Bromobenzene	265-300°
Aniline	300-350°

Agitation: Proper agitation of the sample within the pressure tube is essential to assure the attainment of equilibrium between the phases. Since the sample is entirely enclosed, no direct mechanical stirrer can be conveniently employed. Consequently stirring is done by means of a magnetic agitator which consists of a small piece of soft iron wire located within the tube. This is moved up and down by means of a water-cooled solenoid M, which fits around the exterior of the vapor bath jacket. Current flowing through these coils produces a magnetic field of sufficient strength to lift the stirrer within the tube, and moving the solenoid up and down, either by hand or with the motor provided, agitates the mixture, and insures equilibrium. Considerable agitation was found necessary before a reading was taken. Manual movement of the solenoid was usually employed, as it seemed most convenient.

OPERATION

Addition of Sample: To make possible the addition of samples of hydrocarbons to the pressure tube, there is a set of passages within the steel walls of the base chamber. Reference to Figure 1 will make these connections clear. Well above the mercury level contact, the vacuum line within the block connects to the tube leading into the sample chamber. A built-in needle valve Z enables this connection to be snut off. On the vacuum side of this valve there is a passage leading to the sample bomb connection on the right of the block. The vacuum line leads thru another built-in needle valve Y to the high-vacuum pump.

The high vacuum necessary for removing air from the pressure tube is maintained by means of a mercury diffusion pump, backed up by a Cenco Hyvac pump, and the system is capable of producing vacua of the magnitude of 10^{-4} mm. of mercury. As indicated in Figure 1, this vacuum system also connects with the top of the manometer on the side of the apparatus, and the McLeod gauge attached at this point makes measurements of the vacuum possible.

To introduce a sample of gas into the pressure tube, a steel bomb containing a purified sample of the hydrocarbon to be used is carefully weighed and attached to one end of the sample bomb connection. A similar bomb containing the other

component of the system is attached to the other end of the connection. The high-vacuum pump is then started, and the entire line is evacuated. When a fairly high vacuum has been attained, the pressure on the mercury reservoir is reduced, ^{mercury} allowed to flow and out of the pressure tube and down to a point below the contact J. Valve Z, connecting the vacuum line to the inside of the sample chamber, is then opened and the pressure tube itself is evacuated. The mercury level in the pressure system must be close to the contact level before this connecting valve is opened or mercury will flow over into the vacuum system. After the system has been evacuated to a large extent, it is purged with the hydrocarbon component other than the one being added, and re-evacuated. When a high vacuum has been attained and all air purged out of the system, the chamber is shut off from the vacuum pump by closing valve Y, the mercury level is adjusted until it is just at the level of the contact, the bomb valve is opened slightly, and sample is admitted slowly to the system. The entering gas increases the pressure within the capillary tube, and forces the mercury below the contact. More mercury is then admitted until the level returns. A rough estimate of the amount of sample introduced may be obtained by noting the pressure on the manometer, Q. With the reservoir N shut off, this manometer and the pressure tube itself form a U tube, the pressure on each arm of which at the beginning of admission is the same. However the gas in the

pressure tube builds up the pressure there, causing the mercury to rise in the other arm. By admitting mercury and thus keeping the level in the closed side always at the same height an estimate of the amount of sample added can be made from the pressure existing in the working section. When sufficient gas has been added, the bomb valve is closed, and the top of the pressure tube cooled with liquid air, in order to condense and freeze the sample at this point. This procedure avoids wetting the tube walls and mercury with the hydrocarbon. Before cooling however, valve Z is closed. Mercury is then brought up slowly into the pressure tube, confining the sample above it. The rate of rise must be slow, to prevent the occlusion below the mercury surface of any of the sample which might be adhering to the walls of the tube. The liquid air is removed, and the sample allowed to melt. The sample bomb is then cooled in liquid air, and the valve reopened to the connecting line, so that the hydrocarbon remaining in the line will be condensed back into the bomb. The amount lost will be that corresponding to the vapor pressure of the hydrocarbon at liquid air temperature, this pressure ordinarily being very low. The bomb valve is then closed, and the bomb removed and weighed. The weight of sample added is the difference between the weights of the bomb, before and after addition. The other constituent is added in the same manner, except that the pressure tube is not evacuated again, but the sample in

it is frozen at the top while the other is being added. All additions of samples are carried out with the vapor jacket removed.

Volume Measurement: The volume occupied by the sample was determined by measuring the distance of the mercury surface in the pressure tube from the sealed end of the tube. The volume of the tube was calibrated as a function of this distance. However instead of plotting these quantities, one as a function of the other, it is more accurate to determine an average diameter of the tube, and plot residual volumes, the difference between the actual volume, and the volume calculated from the average diameter, as a function of the distance. This gave a smooth curve. The actual measurement of these lengths was done by the use of a cathetometer with a precision of 0.1 millimeter.

It was found impractical to calibrate the volume of the tube by moving a weighed slug of mercury back and forth along its length, for the diameter of the tube was too large. Calibration was accomplished by suspending the tube vertically, open end up, weighing in samples of purified mercury, and measuring with the cathetometer the total height of the mercury column after each addition. Knowing the temperature, and the density of the mercury, the volume of the tube as a function of the length of the column was calculated, and from this, residual volumes determined.

Readings: No particular technique was found essential for taking readings in the single phase region of this system. The sample was brought up to temperature and the control valves set. Mercury was then forced into the tube, the sample thoroughly agitated, and the position of the top of the mercury read with the catheter^{to}. This reading was then recorded as N. It was also found convenient to record for each position of the mercury, N_T , the zero reading of the top of the pressure tube, as this value varied with the pressure within the tube. The scale reading of the pressure balance was then obtained, together with the potentiometer reading for checking temperature.

When two phases were present, the technique was essentially the same, except that another quantity, the level of the liquid within the tube, was recorded, and considerably more agitation and time for the attainment of equilibrium were necessary. The whole sample was stirred, especially in the neighborhood of the phase boundary.

However in determining bubble or dew points, greater care was required. These points were approached from the single phase region, to avoid the greater difficulty of attaining two phase equilibrium. In the case of a bubble point, a rough approximation was first obtained by reducing the pressure until the two phases appeared. The volume was then decreased until the tube was again all filled with liquid. By venting compressed air from the reservoir, mercury was allowed to slowly flow out of the pressure tube, until a small bubble formed. At this point the pressure was fixed by closing the

air outlet valve, and the sample vigorously agitated. If the bubble did not become larger, this condition of pressure and volume was recorded as the visual bubble point. If it continued to grow, the pressure was increased until it disappeared, and the process repeated. In every case many readings were taken in this range. Dew point was approached from the gas phase, the appearance of dew which did not change in amount at constant pressure being taken as the criterion of their establishment. It was found that the states thus visually determined coincided with the points at which the isotherms and isobars changed slope on pressure-volume, and temperature-volume diagrams, (Figures 3 and 4) and conveniently located the bubble point and dew point of the mixture. In the critical range, where breaks in the isotherms are scarcely perceptible, these visual points were almost essential in fixing the boundaries of the two phase region.

CALCULATIONS

Pressure Calculations: The pressure balance used in these measurements was first calibrated against the mercury manometer on the side of the apparatus so that its zero correction, due to differences in elevation of the pressure tube and balance, might be obtained. The scale correction factor for the balance used was known from a previous calibration. Further correction for the height of the mercury in the pressure tube itself was applied and thus the pressure on the sample above atmospheric calculated. To this was added the corrected barometric pressure, giving the absolute pressure on the sample in the tube. The formula used was: .

Absolute Pressure = $A(\text{Scale} + B + \text{Barometer}(\text{Corr}) - K(N - N_0))$
 where A is the scale correction factor of the pressure balance, B, is the zero correction due to differences in elevation; Barometer(corr.) is the atmospheric pressure, as measured on a mercury barometer corrected for brass scale expansion, in pounds per square inch; and $K(N - N_0)$ is the correction for the column of mercury within the pressure tube. K is a conversion factor for converting centimeters of mercury to pounds per square inch, and varies with the temperature as the density of the mercury changes. N is the level of the mercury within the tube, and N_0 is the reference level at which this correction is zero. N_0 was taken as 70.00 cm. below N_T , the level of

the top of the tube, and B was evaluated with the mercury at this level.

Volume Calculation: As has been previously mentioned, the position of the mercury level in the tube was used as a measure of the volume occupied by the sample within the tube. The length of tube filled with sample was obtained by subtracting N from N_T . This quantity was either obtained for each value of N , or was calculated from the experimentally determined variation of N_T with pressure. The former method was more reliable, and was used in the computation for most of the data reported. This difference was then multiplied by a constant, π times the square of the average radius of the tube, giving the total apparent volume in cubic centimeters of the space above the mercury level. However since the steel stirrer, floating on the mercury was also in this space, its volume had to be subtracted from the total to give the apparent volume of the sample, V_R . The volume of the stirrer wire was calculated from its weight and known density. To obtain the actual volume occupied by the sample, from V_R was subtracted the residual volume, \bar{V} corresponding to the length of tube $N_T - N$. This quantity was obtained from a plot of \bar{V} vs. $N_T - N$. The total apparent volume of the sample, minus the proper residual volume, gave the volume in cubic centimeters occupied by the sample, \underline{V} . \underline{V} multiplied by a constant and divided by the weight in grams of sample within the tube gave V , the specific volume of the mixture in cubic feet per pound. The formulae

used were:

$$\underline{V}_R = .20742 (N_T - N) - .0203 \quad .20742 = \pi X (\text{Ave. Radius of Tube})^2$$

:0203 = volume of stirrer wire.

$$\frac{V}{\bar{v}} = f(N_T - N) \quad (\text{Determined from plot of } \underline{V} \text{ vs } N_T - N)$$

$$\underline{V} = \underline{V}_R - \frac{V}{\bar{v}}$$

$$V = .01602 \underline{V} / \text{Wt. of Sample (gr.)} \quad .01602 = \text{constant for converting}$$

CC/gr. to Cubic
feet/pound.

Calculation of Composition: Although theoretically the weighing of the hydrocarbons as gases into the apparatus should have determined both the composition and the total weight of the sample, it was found actually that the results of this method were of insufficient accuracy, especially for the very small quantities necessary to obtain dew points at the lower temperatures in this apparatus. Consequently although four mixtures were investigated for dew points, their compositions were so imperfectly known that results of only the bubble point work will be reported here. With the larger amounts used for bubble point measurements the results were correct to within one or two percent. It was found desirable even with the larger samples to check the accuracy of the weight and composition of the sample. Fortunately this could be done without great difficulty, by running an isotherm on the pure pentane introduced at a standard low temperature, 130° F, before the addition of any propane. From the known specific volume of pentane

(5) the weight of this substance present could be calculated. It has been determined (6) that liquid mixtures of propane and n-pentane follow closely the laws of ideal solutions at low temperatures, and thus the additive volume law can be applied, using the specific volumes of the pure components (7). Application of this law will give the weight percent of propane present, and from the known weight of pentane, the total weight of the sample can be determined. A sample calculation follows:

Additive volume law

$$V_t = V_1 W_1 + V_2 W_2$$

V = specific volume

W = Weight percent

w = Actual weight (Grams)

From the volume calculations of the apparatus:

$$V_t = .01602 \frac{V}{w_t}$$

Now:

$$W_1 = w_1/w_t \quad \text{and}$$

$$W_2 = w_2/w_t$$

Thus:

$$V_t = V_1 w_1/w_t + V_2 w_2/w_t = .01602 \frac{V}{w_t}$$

$$V_1 w_1 + V_2 w_2 = .01602 V$$

In a particular case for mixture 3:

$$t = 130^\circ, \quad P = 310.10 \text{ lb./in}^2 \quad \underline{V} = 1.6449 \quad w_2 = .4854 \text{ gr.}$$

$$V_1 = 0.03581 \text{ cubic ft./lb.} \quad (7)$$

$$V_2 = 0.02692 \text{ cubic ft./lb.} \quad (5)$$

$$.03581 w_1 + .02692 \times .4854 = 1.6449 \times .01602$$

$w_1 = .3710$ gr.

A similar method might have been used for determining the composition of the gaseous mixtures, had isotherms been run on the pentane added. In this case it would have been necessary to assume that the substances behaved as an ideal solution at infinite attenuation, and thus that the value of the compressibility factor, Z , was unity at zero pressure. Volume measurements of these small samples in the liquid region are not accurate enough to afford a particularly good correlation, as the length of tube occupied by the sample is small. The calculation of weight and composition on the basis of the corrected compressibility factor would seem to be the best solution to this problem, although compositions might be established by a carefully determined curve of dew point pressure vs. composition at a fixed temperature. Such a curve would make possible the determination of the composition of the mixtures already investigated for dew point but not reported here.

RESULTS

The data presented in this thesis are the results of measurements on three mixtures of propane and n-pentane. The amount of sample used in each case precluded investigation of anything but the liquid phase and bubble point region, save at temperatures near the critical. Volumetric data for these liquids are presented in Table I reported as pressures for even volumes at various temperatures, and volumes for even pressures and temperatures. Table II gives the pressure, temperature and volume of the mixtures at bubble point conditions and bubble point pressures at even temperatures and compositions. Table III gives critical and cricondentherm data for mixtures 1 and 3, and for even compositions thruout the system.

The data in Table I are limited as to accuracy by uncertainties in the composition of the mixtures. These compositions are probably good to within one tenth of one percent. For each particular system the error is considerably less than this, it is believed. The necessity of composition correlations in obtaining part of the data of Table II increased the probability of error, so that the bubble point pressures at even compositions are probably accurate only to the nearest pound per square inch. The critical and cricondentherm data are probably good to within 0.2 - 0.4 percent.

Vapor pressures and the critical constants of pure pentane

were obtained from the publications of Young (2). Specific volumes of this substance were taken from the work of Sage Lacey and Schaafsma (5). Pressure-volume-temperature relations of propane as determined by Nellis (7) were utilized.

Figure 3 is a plot of the volumetric data on the first mixture in Table I on the pressure-volume plane. Isotherms at thirty degree intervals from 220° to 330° are shown, extending from the liquid into the two-phase region. It will be noted that the slopes of these isotherms change abruptly at the bubble point in each case. The change in slope becomes less pronounced as the critical region is approached where the properties of liquid and gas become more nearly the same. It will be noted too that the slope of these isotherms in the liquid region becomes increasingly negative as the temperature of the system is raised. Thus $-(\partial V/\partial P)_T$, the isothermal compressibility of the liquid mixture, increases as the temperature is raised. Also it can be seen that the volume of the saturated liquid increases as the temperature is raised, the volume increase due to thermal expansion being greater than the decrease caused by the higher vapor pressure of the substance. The volume of the saturated gas, (not shown on this diagram) decreases as the temperature increases, until at the critical point the volumes of saturated liquid and gas become equal.

Figure 4 is a plot of the critical region of mixture 1 on

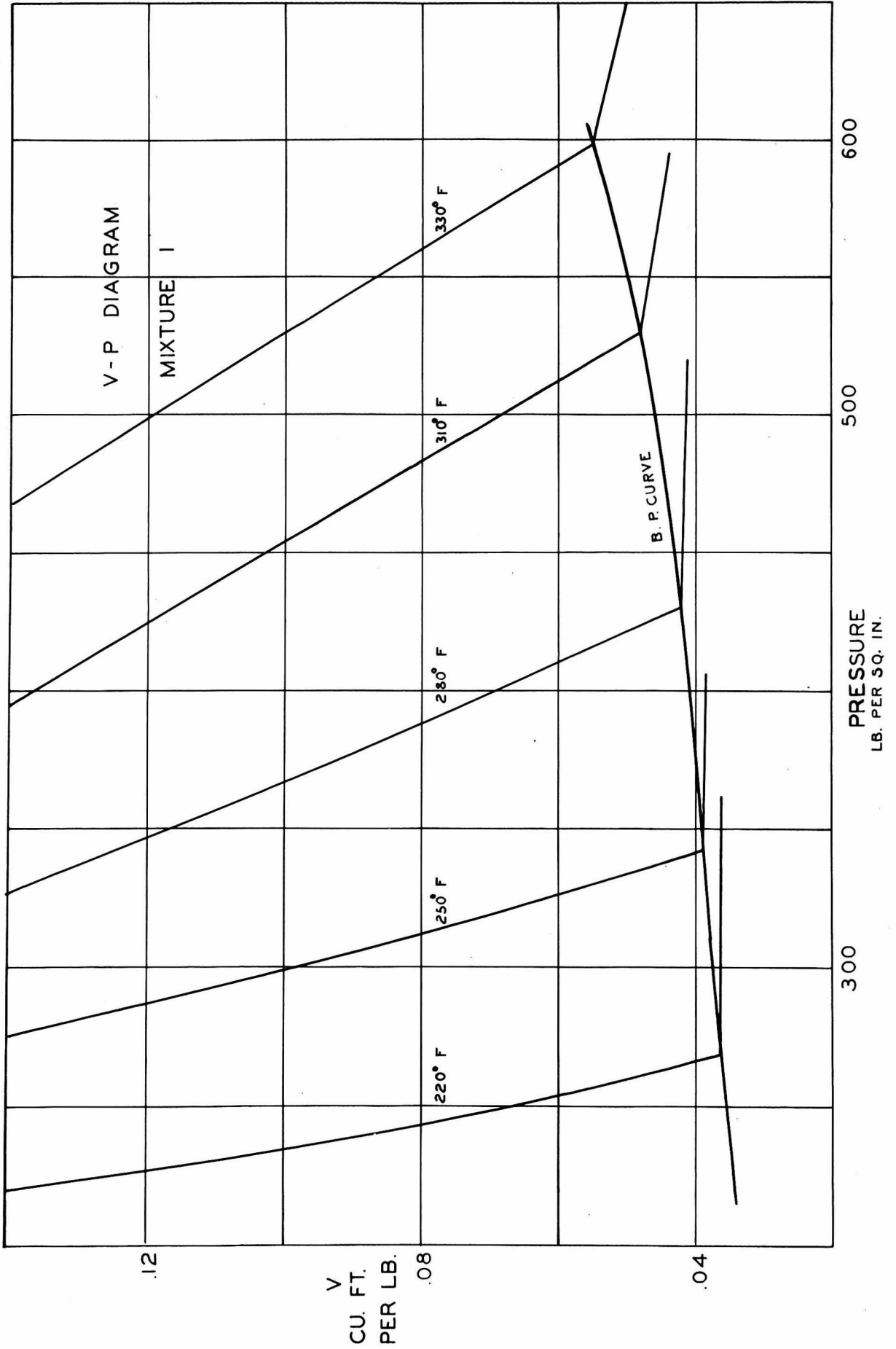


Figure 3. Volume-Pressure diagram for Mixture 1 at temperatures below the critical.

an enlarged pressure-volume scale. It is really a continuation of Figure 3. Isotherms here are spaced at much closer intervals. The straightness of these curves thru the two-phase region at temperatures well below the critical is illustrated by the curve for 330° F. As the critical temperature is approached and exceeded, the lines thru this area show more curvature. At these temperatures the slopes of the isotherms change but little at the dew and bubble points. It can be seen that an isotherm for 344.2° would be tangent to the two-phase dome at the point T. This is the highest temperature at which two phases can exist for a mixture of this particular composition, and is several degrees above the critical point, C. This point T, is known as the cricondentherm. The phenomenon of retrograde condensation is well illustrated by considering the isotherm for 343°, which is above the critical temperature but below the cricondentherm. Starting at a pressure of 525 pounds per square inch, increase in the pressure causes a decrease in volume of the gas phase until a pressure of about 570 pounds per square inch is reached. At this pressure a liquid phase begins to separate as dew, and a dew point is recorded. However, upon further increase in pressure, the liquid first increases in amount, and then rapidly decreases, the mixture reaching another dew point at about 607 pounds per square inch. Further increase in pressure decreases the volume of the single-phase material present. Whether this material

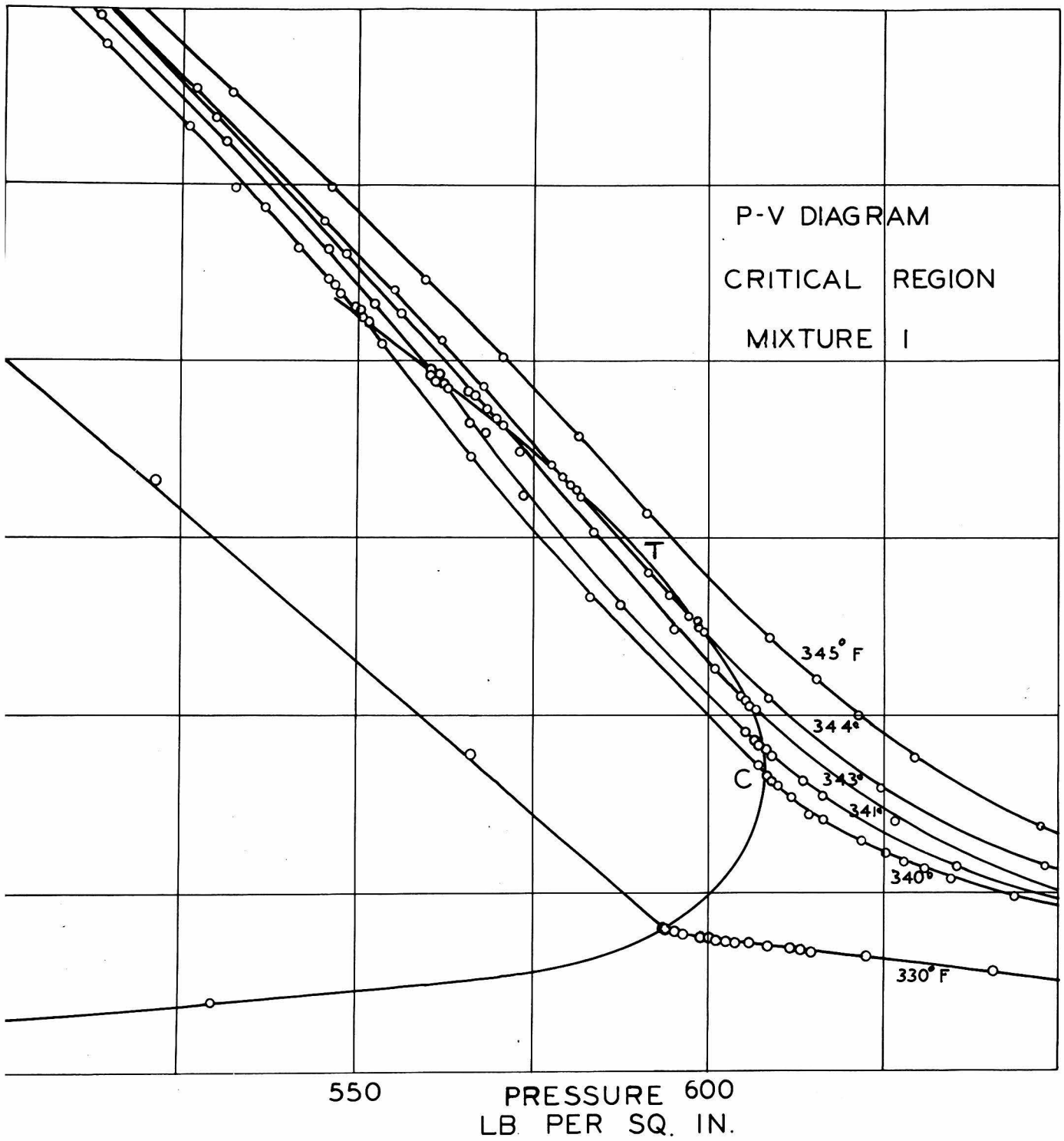


Figure 4. Specific volume-Pressure diagram for Mixture 1 in the critical region.

is liquid or gas is difficult to say. The isotherm for 345° F. is above the cricondenthem and thus shows no discontinuity of phase as the pressure is increased. A few experimentally determined points were shown on this figure to illustrate the care with which bubble and dew points were located. Many points actually taken were not shown to avoid crowding. Visually determined bubble points were used to locate the dome. The difficulty of attempting to fix this curve by breaks in the isotherms in the critical region is obvious.

Figure 5 is a plot of bubble point pressure versus composition at a series of temperatures. These curves are nearly straight, bending slightly downward. The critical temperature of propane, 206.3° F. falls between the isotherms for 190 and 220°. Consequently the former curve is continuous across the diagram, while the latter merges with a dew point curve (not established) at a critical composition lower than 100% propane. These curves cannot cross the critical pressure-composition locus but become tangent to it, merging with the dew point curves at this point. The critical pressure-composition curve, shown across the top of this diagram forms the upper limit for the bubble point curves. These curves reverse curvature as the critical region is approached becoming concave downward and tangent to the critical locus at the critical pressure. At higher temperatures the bubble point curves are more limited in extent, meeting the critical locus at

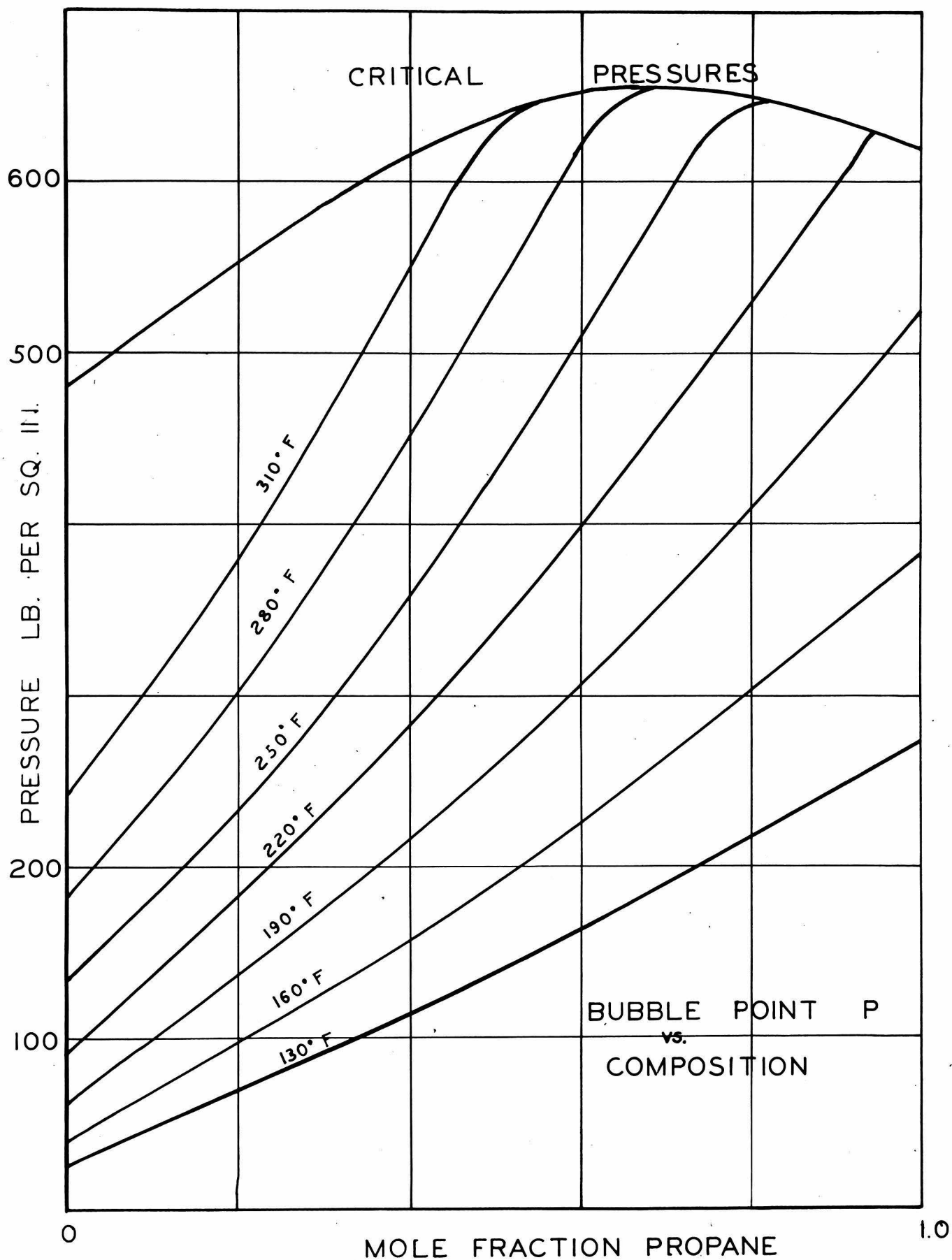


Figure 5. Bubble point pressure-Composition diagram.

compositions less rich in propane.

Figure 6 depicts the pressure-temperature relations for the three mixtures studied, together with the vapor pressure curves of the pure components and the pressure-temperature locus of critical points of all mixtures of propane and n-pentane. The maximum critical pressure is somewhat in excess of that for either component. For hydrocarbons it has been shown that the greater the difference in molecular weight between the components, the higher will be the maximum critical pressure of the system produced by mixing them. The maximum critical pressure of this system is not as great as might have been expected. A curve thru the critical points of both propane and pentane, and thru the point of maximum temperature for the existence of two phases in mixtures 1 and 3 would have defined the locus of the cricondenthern conditions for all compositions. This curve could have been shown on Figure 5. In either case it falls below the critical curve, for at a given composition the cricondenthern pressure is less than the critical pressure, while the temperature, by definition, is higher than that at the critical state.

The cricondenthern data of Table III indicate that at composition close to either pure component, the difference between the critical state and the cricondenthern is small, but that at compositions in the neighborhood of 30 mole percent propane, the difference becomes considerable, the maximum two-phase temperature being about 7° higher than the critical temperature at this point.

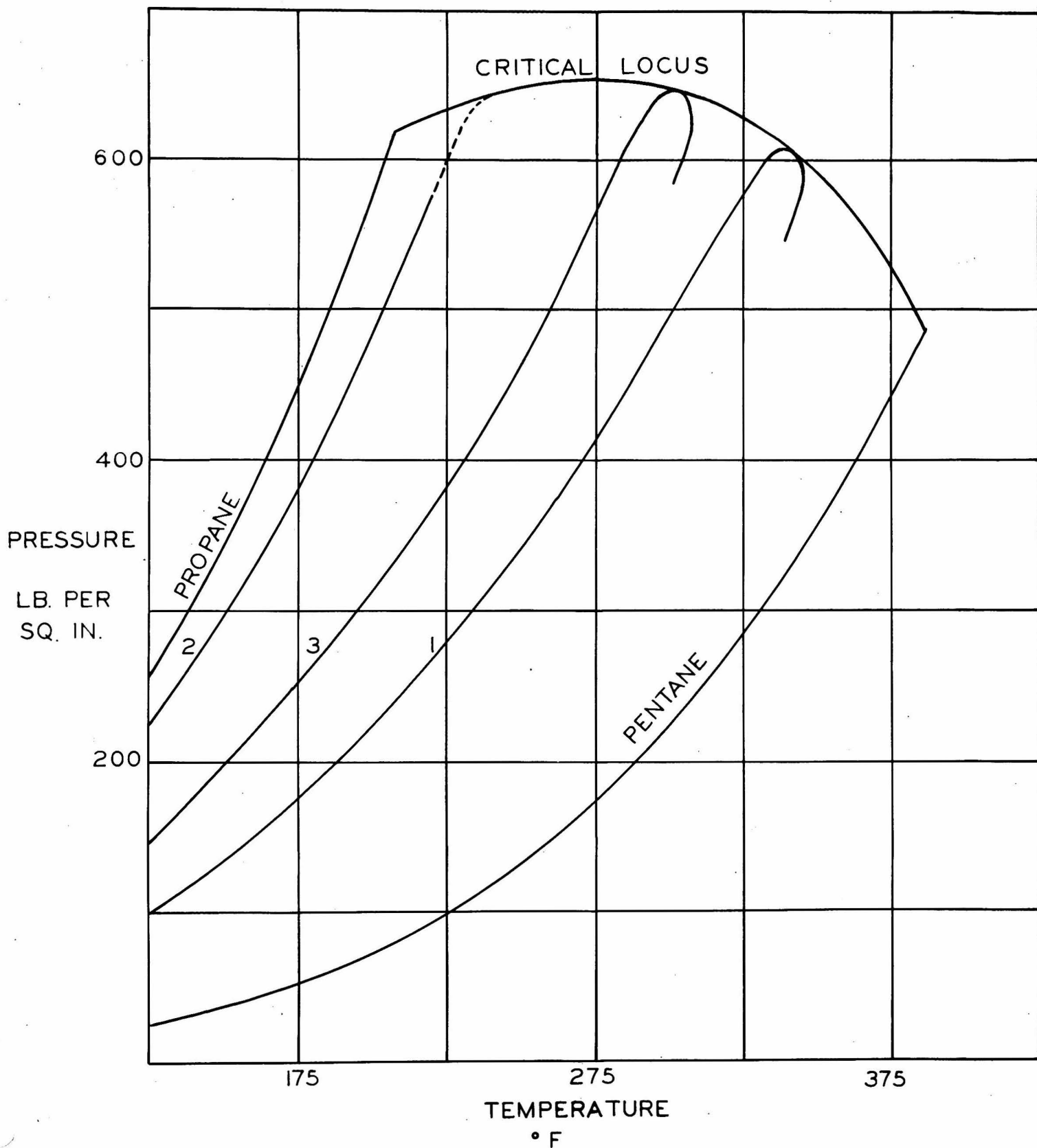


Figure 6. Bubble point pressure-Temperature curves for Mixtures 1, 2, and 3, showing vapor-pressure curves of propane and n-pentane.

DATA

TABLE I

Composition of Mixtures:

	Mole percent propane	Mole percent n-pentane
Mixture 1:	37.80	62.20
Mixture 2:	86.55	13.45
Mixture 3:	55.57	44.43

Pressures in pounds per square inch absolute at even specific volumes.

Mixture 1:

Volume, cu. ft. per pound	0.04	0.048	0.06	0.08	0.10
Temperature, °F					
130°	104.8	103.3	101.4	98.7	95.3
160°	146.7	144.9	142.3	138.1	134.3
190°	202.2	199.5	195.4	189.2	183.9
220°	266.3	261.1	254.0	243.1	234.5
250°	341.4	335.0	325.9	311.7	298.6
280°		423.6	410.0	388.0	366.7
310°		529.5	512.4	483.1	453.8
330°				560.0	529.0

Mixture 2:

Volume, cu. ft. per pound	0.04	0.05	0.06
Temperature, °F			
130°	237.0	236.0	235.2
160°	322.0	319.7	317.8
180°	400.7	397.5	394.9
210°		526.0	521.9
220°		571.5	565.0

Mixture 3:

Volume, cu.ft. per pound	0.04	0.05	0.06	0.08	0.10
Temperature, °F					
130°	154.3	152.9	151.3	148.2	145.9
160°	212.0	209.1	206.8	201.6	197.2
190°	286.0	281.4	277.7	269.3	262.0
220°	371.1	364.5	358.0	345.8	334.7
250°	507.3	483.2	454.1	437.0	419.6
280°		583.7	569.1	541.8	518.1

Specific volumes in cubic feet per pound at even pressures.

Mixture 1:

Temperature, °F	130°	160°	190°	220°	250°	280°	310°	330°
Pressure, lb. per sq. in.								
100	.0696							
150	.0316	.0330						
200	.0316	.0328	.0463					
250	.0316	.0327	.0344	.0666				
300			.0342	.0363	.0977	.1687		
350				.0362	.0388	.1165	.1734	
400					.0384	.0688	.1371	.1839
450						.0418	.1025	.1514
500						.0413	.0685	.1189
550							.0467	.0865

Mixture 2:

Temperature, °F	150°	160°	180°	210°	220°	230°
Pressure, lb. per sq. in.						
250	.03293					
300	.03280					
350	.03268	.03528				
400	.03260	.03510				
450	.03251	.03496	.03752			
500	.03245	.03480	.03723			
550	.03239	.03465	.03698	.04265		
600	.03229	.03450	.03679	.04168	.04492	
650	.03220	.03438	.03657	.04098	.04349	.04621
700	.03214	.03427	.03643	.04057	.04265	.04588

Mixture 3:

Temperature, °F 130° 160° 190° 220° 250° 280°

Pressure, lb. per sq. in.

200	.03093					
250	.03087	.03248				
300	.03080	.03238	.03453			
350	.03072	.03227	.03436			
400	.03066	.03220	.03421	.03710		
450		.03218	.03410	.03685		
500			.03400	.03660	.04010	
550			.03397	.03650	.03960	
600				.03640	.03924	.04668
650					.04880	.04504

TABLE II

Bubble Point Conditions

Mixture 1:				Mixture 2:			
Temperature	Pressure	Volume	Temperature	Pressure	Volume	Temperature	Pressure
°F	lb. per sq. in.	cu. ft. per lb.	°F	lb. per sq. in.	cu. ft. per lb.	°F	lb. per sq. in.
130°	106.2	.0317	130°	237.3	.03294		
160°	148.3	.0330	160°	323.3	.03539		
190°	204.2	.0346	180°	401.4	.03792		
220°	268.7	.0364	210°	529.8	.04323		
250°	342.2	.0388	220°	574.1	.04610		
280°	430.3	.0420					
310°	529.6	.0480					
330°	593.9	.0560					
340°	608.0	.0732					

Mixture 3:

Temperature °F	Pressure lb. per sq. in.	Volume cu. ft. per lb.
150°	156.3	.03097
160°	215.7	.03254
190°	289.1	.03456
220°	373.2	.03728
250°	474.0	.04055
280°	587.6	.04732

Bubble point pressure in pounds per square inch at even compositions.

Temperature, °F	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
130°	26.3	47.8	69.0	90.9	114.3	139.4	164.8	191.1	218.6	246.2	273.5
160°	41.8	69.1	97.0	126.4	158.6	192.2	226.9	262.3	299.0	339.1	383.2
190°	64.1	100.1	136.9	175.3	215.9	259.9	306.3	354.8	406.6	463.9	525.5
220°	94.0	138.7	183.5	229.9	281.0	337.9	399.2	463.1	530.3	599.8	
250°	133.2	180.3	231.7	290.5	357.7	431.4	508.7	593.6			
280°	182.7	241.1	302.0	370.9	448.1	536.2					
310°	246.6	309.7	378.9	458.7	551.0						

TABLE III

Critical and Cricondentherm Data

Mixture 1.		Mixture 3									
Pressure lb. per sq. in.	Temperature °F	Pressure lb. per sq. in.	Temperature °F								
Critical:	508.3	648.7	302.3°								
Cricondentherm:	590.	627.8	307.2°								
Critical and Cricondentherm conditions at even compositions											
Composition, n1	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Pressure *	485.4	516.1	552.0	584.9	613.3	637.8	651.4	655.0	650.8	637.0	617.4
Temperature, °F	387.0	377.7	366.0	353.3	338.0	317.2	296.5	275.7	255.1	231.3	206.3
Cricondentherm:											
Pressure *	485.4	510.6	540.7	559.4	595.2	618.8	632.0	635.9	633.5	627.5	617.4
Temperature:	387.0	378.5	368.0	360.0	341.0	320.0	298.0	278.0	257.0	232.0	206.3

* Pressures in pounds per square inch absolute.

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