x_h = mole fraction of specified component in the hot channel, Equation (14), dimensionless
$\bar{x}_h$ = average mole fraction of the specified component in the hot channel, Equation (12), dimensionless
x_P = mole fraction of specified component in the product, Equation (20), dimensionless
Z = length of channel in the thermal diffusion column, Equation (27), L
z = coordinate of channel length of the thermal diffusion column, Equation (6), L

Greek Letters

δ = thickness of membrane, Equation (3), L
μ = coefficient of viscosity, Equation (6), $ML^{-1}t^{-1}$
ρ = molar density, Equation (1), ML^{-3}
σ = fraction of membrane surface open to diffusion, Equation (3), dimensionless
τ_c = transport of specified component in the $+z$ direction in the cold channel, Equation (18), Mt^{-1}
τ_h = transport of specified component in the $+z$ direction in the hot channel, Equation (12), Mt^{-1}
$1 + \psi$ = stage separation factor, Equation (26), dimensionless
ψ_0 = coefficient in representation of ψ, Equation (29), dimensionless

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The Phase and Volumetric Relations in the Helium—*n*-Butane System: Part I.

Phase and Volumetric Behavior of Mixtures of Low Helium Concentration

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The *P-V-T-x* phase relations of helium–*n*-butane system were measured in the region of low helium content (up to 10.4 mole % helium). The system exhibits the *gas-gas* equilibrium originally predicted by Kamerlingh-Onnes and Keesom. The term *gas-gas* equilibrium is applied because the critical temperatures of the mixtures are higher than the critical temperature of either component. This behavior is quite unlike that observed in most binary systems, in which the critical temperature of the mixtures lie between those of the pure compounds. As a consequence of the shape of the critical locus curve, the system exhibits isothermal retrograde condensation of the second kind.

Some recent investigators of phase equilibria in binary fluid mixtures have reported the existence of a so-called *gas-gas* equilibrium. Krichevskii and co-workers (*10, 12*) apparently were the first to observe this phenomenon and to study it extensively, although Kamerlingh-Onnes and Keesom (*6*) had predicted many years before that it was possible for a fluid mixture to separate into two phases at temperatures above the critical temperature of either component. Kamerlingh-Onnes and Keesom speculated that both phases should have the properties of gases at such temperatures, and hence gave the name gas-gas equilibrium to this phenomenon. This argument was accepted by Krichevskii and co-workers and they have applied the title gas-gas equilibrium to their experimental observations.

Although the accuracy of this nomenclature has been sharply attacked (*11, 15*), there is no doubt that there are binary fluid mixtures which exhibit two phases in equilibrium at temperatures above the critical temperatures of both pure components. There are two classes of mixtures which exhibit this behavior, both composed of compounds which differ greatly in their critical temperatures. The first class consists of mixtures having one polar and one nonpolar component such as ammonia-nitrogen (*10*). The second class is composed of mixtures containing helium and a heavier compound, either polar or nonpolar (*13*). The distinguishing feature of the latter type is that the critical locus curve (the locus of critical points in *P-T-X* space), when plotted in *P-T* coordinates, leaves the critical point of the less volatile component with a positive slope. Thus, as small amounts of helium are added to the initially pure second component, the critical temperatures and the critical pressures of the resulting mixtures increase monotonically.

The sharp contrast of the behavior of these binary systems containing helium to the more commonly observed phase behavior of binary systems (for example, binary systems of aliphatic hydrocarbons) created an interest in a detailed study of one such helium system in the region of small helium concentrations. The system helium–*n*-butane was chosen for this work, because of experimental convenience and because apparently it had not been studied previously.

MATERIALS

The helium used was furnished by the Helium Research Center of the U.S. Bureau of Mines, Amarillo, Texas. It was designated as research grade and contained less than 10 p.p.m. of impurities. The chief impurity was neon. The *n*-butane was Phillips research grade, supplied by the Phillips Petroleum Company. The butane as received was reported to be 99.78% pure, the chief impurity being isobutane. It was further purified before use by distillation and degassing in vacuo. The isothermal dew point and bubble point pressures of all samples of butane used differed by less than 2 lb./sq. in. at 86°C.

EXPERIMENTAL APPARATUS AND PROCEDURES

The apparatus and experimental technique for the determination of the *P-V-T* relations of a fluid mixture of constant composition in the heterogeneous and homogeneous regions were, in general, the same as those employed in earlier studies (*8*, *9*) in this laboratory. The fluid mixture was confined over mercury in a heavy-walled glass capillary tube which was surrounded by a constant-temperature jacket. The tube was held rigidly in a mercury-filled compressor with means provided for controlling and measuring the pressure on the sample. The volume was determined by a measurement of the length of the tube occupied by the sample, the length having been related to the volume by a previous calibration with mercury. To bring about equilibrium quickly, the sample was stirred by a steel ball bearing which had been inserted in the tube prior to the loading of the sample. The bearing was moved through the liquid and vapor phases by a magnet around the outside of the constant-temperature jacket. The critical point was obtained by raising both the pressure and the temperature in small steps with intermittent stirring, following the 50% quality line. At a pressure nearly equal to the critical pressure and a temperature about 0.03°C. below the critical temperature, the meniscus between the phases becomes very faint, the phases separate slowly after stirring, and the characteristic critical opalesence is observed. The temperature is then raised in 0.01°C. intervals until no phase separation is observed and the sample appears homogeneous throughout. This point is taken as the critical point.

A problem peculiar to the system being studied was the prevention of the loss of helium from the sample by diffusion through the glass tube. Tubes of borosilicate glass could not be used due to the high rate of helium permeation through this glass (*1*). The permeability of helium through soda-lime glass is only about 1/100 of that through borosilicate glass (*1*). Thus experimental tubes of soda-lime glass were employed, although difficulties were encountered because of the susceptibility of the glass to fracture due to thermal stresses.

In the experimental measurements, the temperature of the vapor surrounding the experimental tube was measured to within 0.01°C. with a calibrated copper-constantan thermocouple whose output was balanced against a sensitive potentiometer. The thermocouple was calibrated by comparison at nine temperatures between 0° and 230°C. with a platinum resistance thermometer which had been calibrated by the National Bureau of Standards.

The sample pressure in the single-phase regions was measured by a dead weight gauge with a sensitivity of 0.05 lb./sq. in. Dew point and bubble point pressures were measured with a precision Bourdon gauge with a 16-in. dial. This gauge covered a range from 0 to 2,000 lb./sq. in. abs. and was graduated in 2 lb./sq. in. divisions. Both the dead weight and Bourbon gauges were calibrated against a standard dead weight gauge. The length of the sample tube occupied by the sample was determined with a cathetometer reading to 0.02 mm.

The sample was charged to the sample tube by admitting one component at a time from a calibrated gas burette (*9*). The tube was initially filled with mercury under high vacuum and inverted in a mercury reservoir. The gas was then admitted so as to displace the mercury from the closed end of the tube. From a knowledge of the compressibility factors of the pure gases, the mass of each gas was calculated.

Additional details regarding the experimental procedure are given in reference 5.

EXPERIMENTAL RESULTS

The phase behavior of the helium–*n*-butane system was investigated by studying three mixtures containing 1.89, 5.03, and 10.42 mole % helium, respectively. The *P-V-T* relations of the mixtures along the saturated vapor and liquid curves were determined. These data are listed in Table 1,* and the pressure-temperature relations shown graphically by the *P-T* border curves are shown in Figure 1. Isothermal compressibility measurements of the liquid and superheated vapor were made on 1.89 and 5.03% helium mixtures. These data are listed in Table 2.* The critical constants of the mixtures and the pure *n*-butane are given in Table 3.

PRECISION AND ACCURACY OF DATA

The results of an extended statistical analysis of the experimental error in the data are summarized in Table 4.

DISCUSSION OF RESULTS

The most significant result of the phase equilibrium measurements is the fact that the critical temperatures of the mixtures studied are all greater than the critical temperature of *n*-butane. In fact, the critical temperatures of the mixtures increase with increasing helium content (Table 3). This type of *P-T* phase diagram in which the critical locus curve leaves the critical point of the less volatile component with a positive slope has been reported

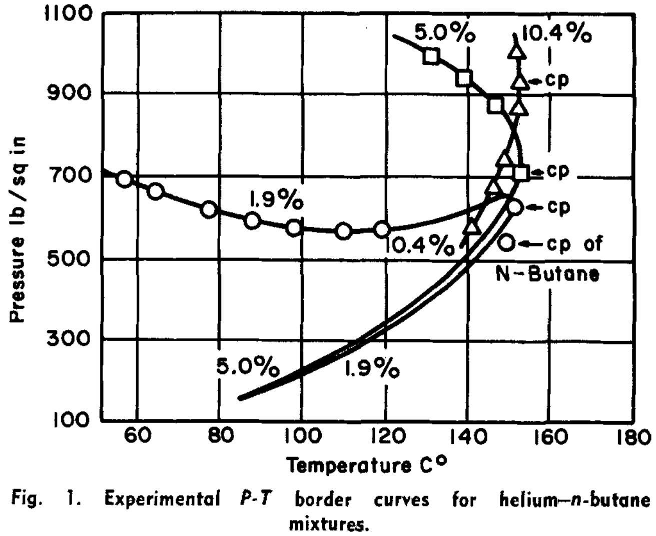

Fig. 1. Experimental *P-T* border curves for helium–*n*-butane mixtures.

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* Deposited as document 9436 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

TABLE 3. CRITICAL CONSTANTS OF *n*-BUTANE AND HELIUM–*n*-BUTANE MIXTURES

Comp., mole % helium	Critical data T, °C.	P, lb./sq. in.	V, cc./g.-mole
1.89	152.03	617.3	249.8
5.03	152.22	730.6	242.5
10.42	152.55	951.6	225.7
0	151.90	550.1	258.3

only for systems containing helium or for systems which form a negative azeotrope. According to Tsiklis (*14*), any phase equilibrium observed in a system containing helium at temperatures higher than the critical temperature of the less volatile component is a gas-gas equilibrium. Although his interpretation of the observed behavior has been disputed (*11, 15*), the present results show that the helium–*n*-butane system must be classed with the other helium systems for which this behavior was reported.

The three mixtures studied exhibit isothermal retrograde condensation of the second kind. Figure 2 shows the shape of the *P-T* border curve and the critical locus curve (not to scale). The two curves meet at the critical point of the mixture. Since this point is on the underside of the border curve, there exists a region of temperatures between T_c and T_m for which an isotherm will intersect the bubble point curve at two points. This temperature region was only 0.01°C. wide for the 1.9% helium mixture, 0.02° wide for the 5.03% mixture, and 0.03° wide for the 10.4% mixture. In each case, however, it was quite unmistakable and the bubble points in this region were experimentally reproducible.

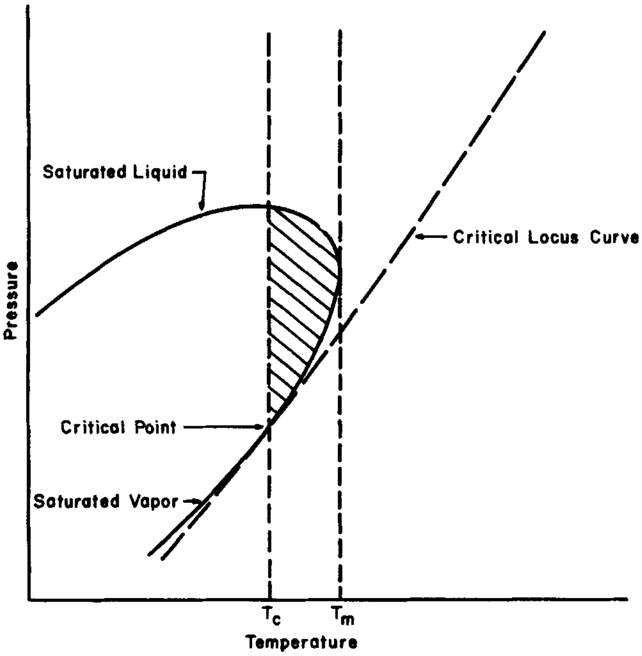

Fig. 2. The region of isothermal retrograde condensation of the second kind.

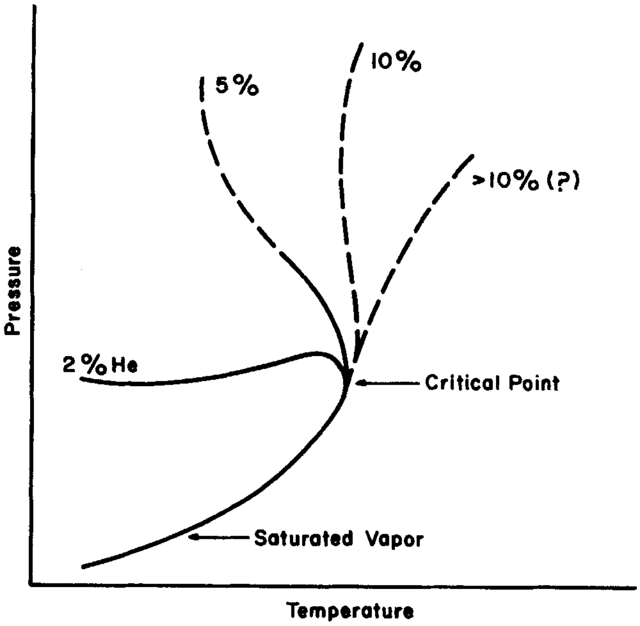

Fig. 3. The anticipated change in the shape of the bubble point curve with composition.

The bubble point curves for the three mixtures (Figure 1) show an interesting pattern. The curve for 1.9% helium mixture begins at the critical point and passes through a maximum pressure point. The bubble point pressure then decreases as the temperature is reduced until 105°C. is reached. It passes through a minimum at that point and begins to increase again as the temperature is lowered still further. No such minimum was observed in the bubble point pressures for the 5.0 and 10.4% mixtures. In fact, the bubble point pressure rises very steeply for the 5.0% mixture and more steeply yet for the 10.4% mixture as the temperature is reduced. Similar behavior has been observed in binary mixtures whose components differ greatly in their critical temperatures. In particular, the minimum in the bubble point curve which was first reported by Kay (*7*) for solutions of hydrogen in petroleum naptha has been observed for dilute solutions of helium in nitrogen (*4*) and hydrogen in hydrocarbons (*3*).

The spreading apart of the dew point and bubble point curves with increasing helium concentrations appears to be the results of the limited solubility of helium in liquid *n*-butane. At a given temperature a very small amount of helium can be dissolved. To force additional helium into the liquid phase the pressure must be greatly increased. It may be that at higher concentrations it is impossible to dissolve all the helium in the liquid phase no matter how high the pressure. In this case the bubble point curve would have opened out until the bubble point temperatures were increasing with increasing pressure. Figure 3 shows how this progressive opening out of the bubble point curve with increasing helium concentration might appear.

Measurements of the phase and volumetric behavior of the system helium-xenon were recently reported by

TABLE 4. PRECISION AND ACCURACY OF DATA

	Accuracy T, °C.	P, lb./sq. in.	V, cc.	Precision T, °C.	P, lb./sq. in.	V, cc.
Phase equil. data and high pressure isotherms	±0.015	±0.75	0.00030 to 0.00082	±0.12	±3.06	0.0006 to 0.0016

Arons and Diepen (*2*). This system exhibits gas-gas equilibria of the same type as observed in the helium–*n*-butane system. The bubble point curves in this system indeed open out in the manner postulated in Figure 3 as the helium concentration increases (see Figure 6 of reference *2*). Isothermal retrograde condensation of the second kind was also observed in this system for several mixtures rich in xenon. It must be concluded that the type of phase behavior observed in the helium–*n*-butane system is typical of binary systems containing helium and a much heavier fluid. This type of gas-gas equilibrium, then, must result from the large disparity in size and intermolecular energy of the component molecules. This question is examined further in Part II.

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Part II. Second Virial Coefficients for Helium—*n*-Butane Mixtures

The second virial coefficients of pure *n*-butane and of two mixtures of helium and *n*-butane were determined in the range 100° to 225°C. from isothermal compressibility measurements. Values of B_{11} (pure *n*-butane) agree closely with those of McGlashan and Potter (*11*) at low temperatures and of Hirschfelder et al. (*7*) at higher temperatures. Values of the mixed second virial coefficient B_{12} were computed from the mixture data. B_{12} shows little variation with temperature over this interval. The interpretation of the data as the behavior of a mixture composed of hard sphere (helium) in a real gas (*n*-butane) is discussed.

The occurrence of the gas-gas equilibrium, observed in the helium–*n*-butane system (see Part I), can be qualitatively ascribed to the large differences in the molecular sizes and energies of the two components. However, a more quantitative description of the intermolecular forces in this system is desirable when examining its phase behavior. It was decided therefore to include in our experimental program the determination of B_{12}, the mixed second virial coefficient representing the interaction of a helium atom with a molecule of *n*-butane.

The second virial coefficients of pure *n*-butane, B_{11}, and of the two helium–*n*-butane mixtures containing 35.3 and 38.3 mole % helium, respectively, were determined at six temperatures in the range 100° to 225°C. from isothermal compressibility measurements of the superheated vapor. Measurements were made in a range of densities from 0.1 to 0.5 mole/liter. Values of the second virial coefficient of helium B_{22} were obtained from the work of Schneider and Duffie (*17*).

EXPERIMENTAL PROCEDURE

As in the phase and volumetric measurements reported in Part I, the fluid sample was confined over mercury in a glass tube surrounded by a constant-temperature jacket. A sample