Vapor-Liquid Equilibrium in the *n*-Butane-Nitrogen System

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During an investigation conducted in this laboratory on the methane-*n*-butane-nitrogen ternary system it was discovered that the data obtained in the ternary system as the methane concentration approached zero did not approach the published data of the *n*-butane-nitrogen system.

This paper describes the results of the subsequent investigation of the vapor-liquid equilibria in the *n*-butane-nitrogen binary system. The pressure range was from 236 to 3,402 lb./sq. in. abs. and the temperature range was from 100° to 280°F.

EXPERIMENTAL

The equilibrium cell used in this investigation was a Penberthy cell equipped with sight glass so that the contents of the cell could be observed. The equilibrium was attained at a desired pressure and temperature by means of circulating the vapor from the top of the equilibrium cell, through a magnetic piston pump, and into the bottom of the cell.

The entire apparatus, including the recirculating pump, was mounted inside a constant temperature air bath. The temperature variation throughout the air bath was appreciable only at higher temperatures and was held to a maximum of 1.5°F. Thermocouples, inserted in several places within the cell, were used to determine the temperature of the fluid within the cell. The cell pressure was determined with a calibrated Bourdon type of gauge.

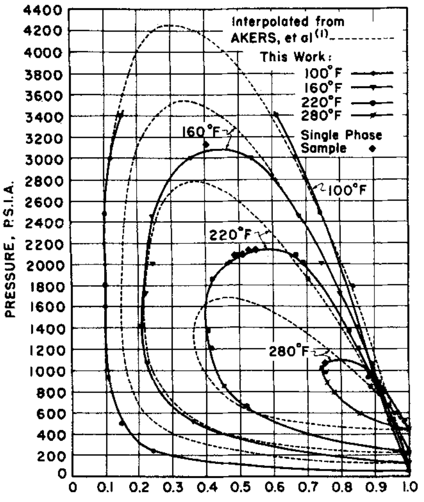

Fig. 1. Vapor-liquid equilibria for the nitrogen-*n*-butane system.

It was determined from earlier investigations that at least 1 hr. of recirculation of the vapor was required before equilibrium was attained. In this work the circulation of the vapor was maintained for at least 4 hr. Near the critical region the vapor recirculation was maintained for at least 12 hr. The pumping rate of the vapor was 20 to 25 strokes/min. at 10 to 15 cc./stroke. At the end of the recirculation period a minimum of 1 hr. was allowed for the phases to separate. During this time the temperature and pressure were maintained constant.

Many runs were made in order to define more clearly the critical region for each isotherm. With the over-all composition near that of the critical mixture the cell pressure was adjusted until the fluid was in the single-phase region just above the critical pressure. After the fluid had been recirculated at least 12 hr., it was sampled; then the pressure was decreased in increments of less than 5 lb./sq. in. by removal of mercury from the bottom of the cell. In this manner the transition from the single-phase to two-phase conditions was easily detected.

TABLE 1. EXPERIMENTAL DATA

Temperature, °F.	Pressure, lb./sq. in. abs.	Mole fraction *n*-butane Liquid phase	Vapor phase
100	236	97.5	24.1
	2,481	74.2	10.3
	3,008	66.8	12.1
	3,402	61.2	15.1
	1,800	83.6	10.0
	931	87.9	11.0
160	1,407	85.1	20.9
	1,724	79.8	22.1
	2,002	74.4	24.2
	2,451	67.9	24.3
	3,127 (single phase)	40.5	
	2,998	53.5	36.0
	1,065	89.5	22.4
	517	94.2	36.1
220	1,372	82.3	40.6
	1,858	70.3	42.0
	1,550 (single phase)		34.0
	1,204	85.2	41.5
	847	88.8	45.2
	661	93.4	52.1
	2,014	68.9	47.4
	2,081 (single phase)	48.6	
	2,004	68.9	46.6
	2,081	66.9	49.9
	2,136 (single phase)	55.1	53.1
	2,092 (single phase)	51.0	51.1
280	596	96.6	85.6
	793	92.7	77.8
	535	98.4	----
	837	92.2	76.9
	887	91.5	76.0
	981	88.7	75.7
	1,069 (single phase)	75.6	75.2
	1,026		74.3

ANALYTICAL

Each equilibrium phase was sampled for analysis. The samples were trapped between two needle valves in high pressure stainless steel tubing connected to the cell proper. The sampling procedure consisted of complete evacuation of the sample lines, filling these lines with mercury, and then displacing the mercury with the phase from the cell. At the same time mercury was added to the cell through another port in order to maintain constant pressure within the cell. When sufficient sample was withdrawn from the cell, the sample was expanded into 500-cc. glass flasks connected to the sample lines. The volume of the sampling and connecting tubing was not more than 20 cc. During the investigations many checks were made to insure that the sample was representative.

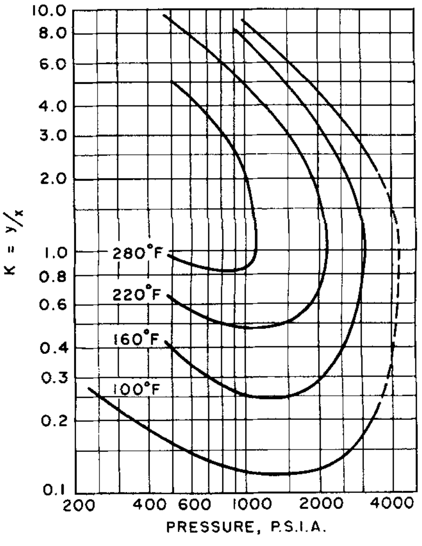

Fig. 2. Equilibrium distribution ratios.

MATERIALS USED

The n-butane was research grade with a purity of over 99.9%. The nitrogen used was research grade and had a purity of over 99.9%.

RESULTS

The analyses of the equilibrium mixtures are shown in Table 1 and Figure 1. In Figure 2 is shown the equilibrium distribution ratios, $K = y/x$, which were calculated from the smoothed data from Figure 1.

In Figure 1 there are also shown the interpolated data of Akers, et al. (*1*) on the same system. The considerable disagreement which results between this work and that of Akers, et al., at temperatures above 100°F., may be attributed in large part to the fact that their cell did not have a glass window for observation of the phases and also to the unusual sensitivity required in the use of an Edwards gas density balance (their method of analysis) for precision data in the binary system such as nitrogen and n-butane. Since the limiting working pressure of our equilibrium cell is 3,500 lb./sq. in., this investigation did not cover the critical region of the system at 100°F.

ACCURACY

The accuracy of the indicated pressure is ± 4 lb./sq. in. abs. Other sources of error are temperature variations during the recirculation, sampling procedures, pressure gauge readings, and analytical errors. Consideration of the analytical procedure shows that the analyses were reliable to ± 0.002 mole fraction. The maximum temperature variation within the cell during the recirculation was ± 0.5°F. and was ± 0.1°F. during settling and sampling time.

ACKNOWLEDGMENT

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Use of the Mechanical Energy Balance for Two-Phase Flow

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Attention is called to the improper use of the mechanical-energy balance for describing the distribution of the static pressure drop for two-phase flow systems into components of frictional, head, and momentum terms. Consider an upward gas-liquid flow system for an annular flow regime in a vertical pipe. The proper momentum balance with transfer between phases is given in references *1* and *2*:

$$dP + \frac{1}{g_c A} d[W_G V_G + W_L V_L] + \frac{g}{g_c}\left[\rho_L \frac{A_L}{A} + \rho_G \frac{A_G}{A}\right]dz = \frac{A_L}{A}\left(\frac{dP}{dz}\right)_{LTP} dz + \frac{A_G}{A}\left(\frac{dP}{dz}\right)_{GTP} dz \qquad (1)$$

For a single-phase (turbulent) flow system the mechanical energy balance is written as

$$\frac{dP}{\rho dz} + \frac{VdV}{g_c dz} + \frac{g}{g_c} + \frac{dF}{dz} = 0 \qquad (2)$$

Some investigators have tried to apply Equation (2) or a similar form to a two-phase system by weighting each phase by the mass flow (W_L or W_G) and then adding the equations together. This procedure is wrong. First Equation (2) does not apply for the case of mass transfer between phases. Even if the momentum and friction terms are considered negligible, the procedure is still wrong and yields an improper evaluation of the head term.

Equation (2) may be used for a two-phase flow system with no transfer between phases by recognizing that the energy balance per pound mass of each phase is weighted by the mass of the phase in the differential volume contained in the section dz ($\rho_G A_G dz$ for the gas phase, $\rho_L A_L dz$ for liquid phase). With this weighting, and summing the equations, one obtains Equation (3):

$$dP + \frac{1}{g_c A}\cdot[W_G dV_G + W_L dV_L] + \frac{g}{g_c}\left[\rho_L \frac{A_L}{A} + \rho_G \frac{A_G}{A}\right]dz + \left[\frac{A_L \rho_L}{A} dF_L + \frac{A_G \rho_G}{A} dF_G\right] = 0 \qquad (3)$$

Note that

$$\rho_L \frac{dF_L}{dz} = -\left(\frac{dP}{dz}\right)_{LTP}$$

$$\rho_G \frac{dF_G}{dz} = -\left(\frac{dP}{dz}\right)_{GTP}$$

For constant W_G and W_L Equation (1) reduces to Equation (3).

Perhaps the easiest way to demonstrate that W_L and W_G are the wrong weighting factors is to show that in dt time the gas phase moves a distance $W_G dt/\rho_G A_G = V_G dt$, whereas the liquid moves $W_L dt/\rho_L A_L = V_L dt$. The only way for the incremental distance dz to be the same for the gas and liquid phase is for $V_G = V_L$, which is a very special case.

NOTATION

A = cross-sectional area of flow (sq.ft.), $A = A_G + A_L$
F = frictional energy loss per unit mass (ft.-lb. force/lb. mass)
g = gravitational constant, (4.17 x 10^8 ft./hr.^{2})
g_c = conversion factor (4.17 x 10^8 lb. mass-ft./lb. force-hr.^{2})
P = pressure (lb. force/sq.ft.)
t = time (hr.)
V = velocity (ft./hr.)
W = mass flow rate, (lb. mass/hr.)
z = vertical height, (ft.)
ρ = density (lb. mass/cu.ft.)

Subscripts

G = gas phase
GTP = frictional loss in gas in two-phase flow
L = liquid phase
LTP = frictional loss in liquid in two-phase flow

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