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Experimental Vapor-Liquid Equilibrium Data for Propane-Isobutane

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Isothermal vapor-liquid equilibrium data for propane-isobutane, a system of industrial importance, have been obtained in two pieces of apparatus at temperatures from 20° to 250°F. Over this temperature range, propane-isobutane form ideal solutions. The paper discusses the sampling errors which occur in volatile systems.

There are several reasons for making an experimental investigation of the propane-isobutane system, besides the fact that it has not been reported previously. This system controls the separation in all depropanizers, columns that have caused more than their share of design and operating troubles. Many depropanizers operate at pressures above 250 lb./sq.in., where the relative volatility is less than 2.0, and where the magnitude of the relative volatility has a great effect on both number of trays and minimum reflux ratio. Both these factors materially affect the cost of the fractionator. This paper presents experimental data for five isotherms from 20° to 250°F., covering most of the two-phase region above atmospheric pressure.

APPARATUS

The data were taken in two different pieces of apparatus. The 20°F. isotherm was run in the low-temperature unit shown schematically in Figure 1. This type of equilibrium apparatus has been used by Dodge and Dunbar (*1*), Katz and co-workers (*2* to *6*), Price and Kobayashi (*7*), and by Cines et al. (*8*, *9*), among others. Ruhemann (*10*) has stated that this is the most accurate and reliable of all low-temperature methods.

The apparatus of Figure 1 is entirely of stainless steel, operates from ambient to — 300°F. at pressures to 3,000 lb./sq. in. abs., and embodies some interesting design features. The cell has a gauge-glass window to permit observation of solids or a second liquid phase. The bath temperature is automatically controlled to within 0.05°F. Pressures are read on a dead-weight gauge, isolated from the system by a sensitive diaphragm. Temperature in the cell is read with a laboratory platinum resistance thermometer and a Mueller bridge. Vapor is circulated around the loop with a diaphragm compressor to eliminate leakage and oil contamination. There are two liquid sample valves to permit sampling coexisting liquid phases.

The pressure still used for superambient temperatures is based on the design of Jones, Schoenborn, and Colburn (*11*). Similar stills for atmospheric pressure or vacuum have been used by Scatchard, Raymond, and Gilman (*12*), Amick et al. (*13*), Hipkin and Myers (*14*), and Weber et al. (*15* to *21*). In all these devices circulation of the vapor phase is accomplished thermally by condensing the vapor, draining the condensate to a point below the still, revaporizing it, and passing it up through the still liquid.

The apparatus of Figure 2 operates with a refrigerant circulating between the still condenser, where it picks up heat and is partly vaporized, and the head tank, where it surrenders heat to the primary coolant and is condensed. The pressure level in the still is set by the temperature of the refrigerant and by the heat input to the still vaporizer. The temperature of the refrigerant is set, in turn, by the choice of primary coolant (dry ice, water, air, or boiling water) and by the heat input to the head-tank heaters. To operate, a vapor-recirculating still must be kept adiabatic. As in the Hipkin and Myers still (14), this is accomplished by surrounding the body of the still with a vapor jacket, maintained at the same temperature as the still by a differential thermocouple which controls the heat input to the jacket heaters. The jacket condenser is

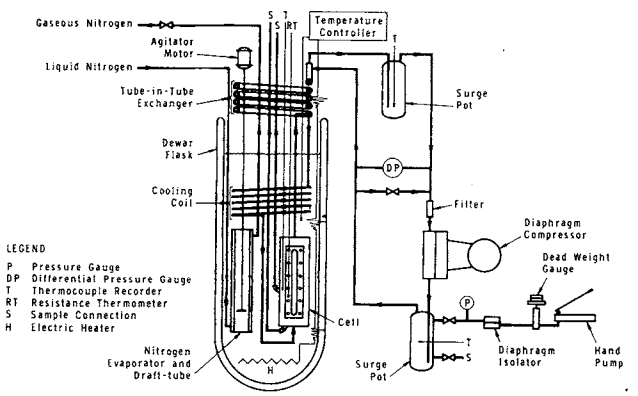

Fig. 1. Low-temperature vapor-liquid equilibrium apparatus.

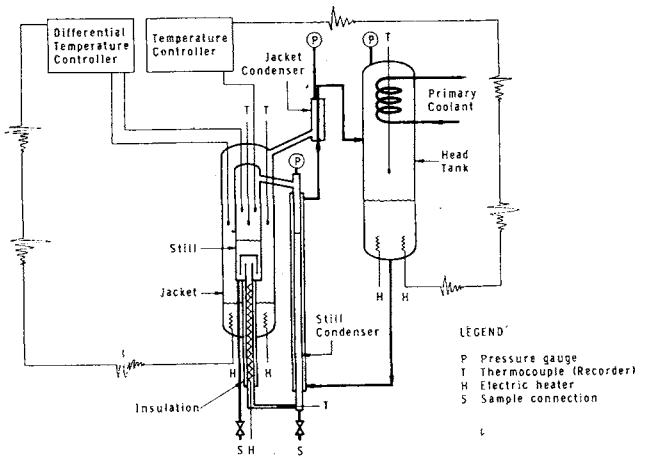

Fig. 2. Vapor-liquid equilibrium still.

cooled by the same refrigerant that circulates through the still condenser.

Experience has shown that the still is easier to operate at constant temperature, since operation at constant pressure requires the temperature of a large mass of metal to change periodically as composition is changed. The temperature controller uses two thermistors in the still as two arms of a Wheatstone bridge. The output from the bridge is amplified to control a pair of power thyratrons which vary the current to the head-tank heaters. With this type of control, there is no need to vary the electrical input to the still vaporizer, and the circulation rate in the still remains constant.

The apparatus is built entirely of stainless steel. Pressures are read on calibrated Bourdon tube gauges, and temperatures are measured with copper-constantan thermocouples and recorded on a variable-range recorder. The operating range for this unit is from — 50° to 500°F. and from atmospheric to 1,200 lb./sq.in. abs. All valves have Teflon seats, and all valves except the sample valves are outside the insulation, at ambient temperature, and accessible for maintenance.

MATERIALS

Both the propane and the isobutane were Phillips instrument grade hydrocarbons with stated purities of 99.5%. Chromatograph scans of the vapor from the cylinders showed small amounts of air in both cylinders, traces of ethane in the propane, and traces of propane in the isobutane. Some vapor was bled off both cylinders to eliminate the air, and the components were charged to the apparatus through molecular sieve drying tubes without further purification.

ANALYSIS

All samples were analyzed by gas-liquid chromatography, with 15 ft. of silicone on firebrick at 38°C. Peak areas were measured with a disc integrator on the instrument recorder. Calibrations with known mixtures showed that the peak area was linear with the molar content of the sample.

$$y_1 = \frac{1}{1 + c\,A_2/A_1} \qquad y_2 = \frac{c\,A_2/A_1}{1 + c\,A_2/A_1} \tag{1}$$

where A_1 and A_2 are the peak areas for propane and isobutane, respectively, and c is a constant unique for the instrument and operating conditions, established by calibration.

SAMPLING

A sampling problem exists with any apparatus whenever a sample undergoes a phase change between the apparatus and the analytical device; and the problem is accentuated, if, in addition, the apparatus is a below ambient temperature.

For superambient still temperatures, the material in the line between the still and the sample valve exists as subcooled liquid, since the valve is close to ambient temperature. This liquid may not be of representative composition and must be purged before taking the sample. If the still is under pressure when the sample valve is cracked, the liquid flashes to a two-phase mixture immediately downstream of the valve, cooling the valve and the line. Thus, the sample valve and line exhibit a temperature gradient which may be as much as 100°F. in the propane-isobutane system. Because the purge and sampling period is probably not long enough for this hardware to reach a thermal steady state, the ratio of liquid to vapor in the line varies during the sampling period. The variation in holdup is accentuated by the slugging caused by unsteady boiling which occurs as the two-phase mixture flows through the line. The net result of the variable line holdup is that the composition of the vapor or mixture leaving the line is different from the composition of the liquid entering the line. This can be seen by writing a material balance around the line. The error can be minimized by reducing the line holdup and making the sample size large relative to the line holdup.

At subambient still temperatures, the variable holdup problem is the same. In addition, the material in the line between the still and the sample valve is either vapor or a two-phase mixture. Depending on the size of the line and its configuration, there may be either a bubble of vapor trapped next to the valve, or there may be a continuous circulation of material being vaporized at the valve and rising back into the still to be replaced by more liquid. This crude distillation leaves the material at the valve high in heavy ends. When the sample valve is cracked, this nonrepresentative material may be purged out. But, if the sampling flow rate is low and if the line upstream of the valve is large enough to permit countercurrent flow, there is a chance that the vapor produced in the upstream line will rise back to the still, leaving the heavy end to pass through the valve and be sampled.

Again, the cure is in the use of small lines and relatively large samples. Sampling at a rate high enough to maintain a reasonable velocity in the line upstream of the valve helps. The design used in our low-temperature unit eliminates most of the problem by having the valves built into the cell body and the whole valve kept at the cell temperature. In this unit the vapor sample is taken from a superheated vapor region of the circulating loop and no phase-change problems occur. In the pressure still, both samples exist as liquid upstream of the sampling valves.

The sample lines used in the pressure still and the low-temperature unit have an internal volume of 0.1 ml./ft. of length. Samples were taken into 400 ml. glass sample bulbs over mercury. Purging the sample line is simplified by the use of three-way cocks on the bulbs. Sampling is stopped when a few milliliters of mercury remain in the bulb, both cocks are closed, and the bulb is shaken to insure uniform composition. Then the bulb is connected to the chromatograph valve, and the mercury leveling bulb is raised to displace the vapor into the instrument.

RESULTS

The experimental data are listed in Table 1* and plotted as pressure vs. composition in Figure 3. The ordinate of Figure 3 is logarithmic for better separation of the low-temperature isotherms. The terminal points for each isotherm are experimental vapor pressures, measured in the same apparatus. These vapor pressures are in good agreement with literature data (22, 23).

Figure 4 is a plot of relative volatility against liquid composition for each temperature. This method of plotting amplifies the scatter of the data, because each composition appears twice in the expression for relative volatility. Even so, almost all of the one hundred and fifty

* The complete Table 1 has been deposited as document 8829 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

TABLE 1. PROPANE-ISOBUTANE EQUILIBRIUM DATA

Temp., °F.	Pressure, lb./sq. in. abs.	Mole % C_3 Liquid	Vapor
20.1	17.90	0.0	0.0
20.1	19.20	3.88	10.30
20.1	20.65	8.00	20.3
20.1	24.4	18.6	39.8
20.1	29.1	32.4	57.6
20.1	33.8	45.6	70.2
20.1	36.2	51.9	75.5
20.1	38.6	57.8	79.7
20.1	42.2	66.0	84.4
20.1	55.9	99.99	100.00
20.1	55.1	98.39	99.47
20.1	47.4	80.6	91.82
20.2	51.4	90.25	96.01
80	55	0.0	0.0
80	60	6.32	13.65
79	62	8.98	18.1
80	68	15.6	31.0
80	72	20.7	37.6
79	78	28.7	47.8
79	86	38.0	58.4
80	94	45.6	65.7
81	104	55.7	74.0
80	148	100.0	100.0
80	146	99.19	99.66
80	138	90.72	95.72
80	132	85.1	93.02
80	122	75.3	87.4
80	111	62.9	79.1
80	106	58.2	75.0
150	144	0.12	0.23
150	146	0.82	1.50
150	153	4.74	8.49
150	235	50.9	65.1
149	339	100.0	100.0
149	338	99.86	99.92
150	325	93.68	96.10
150	308	85.9	90.64
150	287	75.8	84.3
150	263	65.4	76.8
150	252	60.5	72.1
150	243	56.3	68.1
150	225	46.4	60.3
150	144	0.047	0.071
150	167	14.1	23.2
150	181	21.7	33.1
150	191	26.4	38.6
200	568	100.0	100.0
200	554	97.14	97.75
200	542	93.69	95.20
200	489	80.4	85.3
200	450	69.9	76.3
199	422	61.8	70.3
200	253	0.0	0.0
200	253	0.39	0.65
200	268	4.85	7.76
200	291	14.7	21.0
200	328	29.4	38.9
200	348	36.6	46.7
200	377	46.5	56.9
200	392	51.5	61.1
249	454	12.0	15.2
250	468	15.5	19.5
250	503	24.6	29.0
250	515	27.8	32.7
250	530	31.1	38.0
250	578	50.2	50.3
250	420	0.095	0.12
250	427	3.22	4.25
250	433	24.9	25.1
250	605	66.1	66.3
250	426	0.0	0.0
250	432	2.15	2.89
250	449	7.06	9.16
250	479	15.6	19.0
250	525	28.2	32.3
250	570	39.4	41.4
250	575	40.8	42.9
250	569	38.0	41.0
250	563	36.9	39.4
250	552	34.0	37.0
250	538	30.0	34.0
250	518	26.3	29.7
250	507	22.3	26.7
250	560	35.7	39.0
250	575	38.9	42.2
250	580	40.6	45.0

points in this figure fall within a ± 10% band around the solid lines. These lines are calculated as discussed in a later paragraph.

Activity coefficients were calculated from the relation

$$\frac{\gamma_L}{\gamma_v} = \frac{\pi y}{Px}\left[\frac{f_\pi/\pi}{f_P/P}\, e^{\frac{v(P-\pi)}{RT}}\right] \tag{2}$$

or

$$\frac{\gamma_L}{\gamma_v} = \frac{\pi y}{Px}\,\phi \tag{3}$$

in which the left side is the ratio of liquid phase activity coefficient to vapor phase activity coefficient, both for the

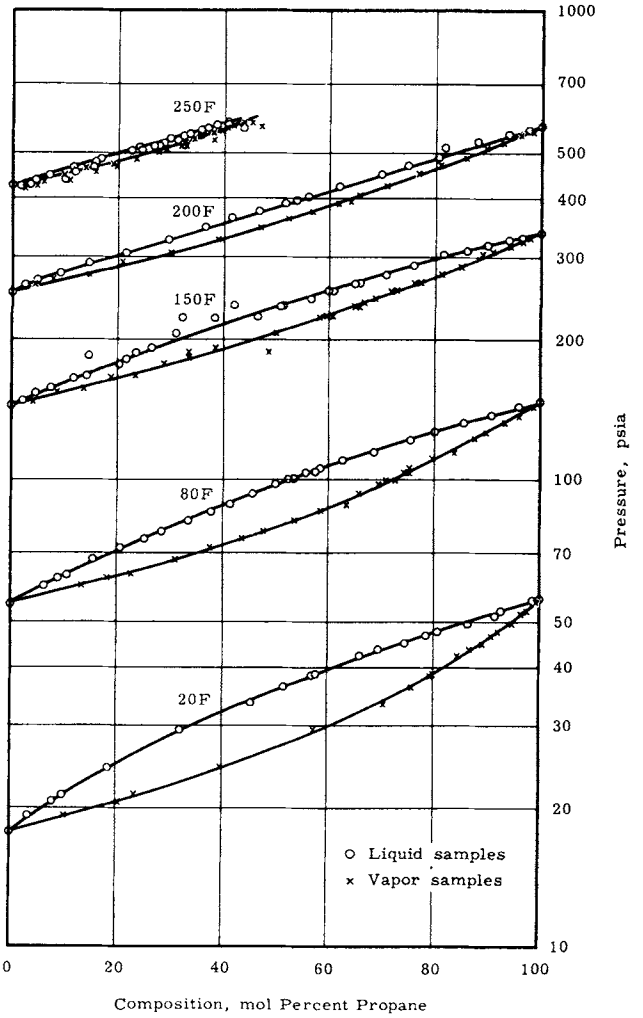

Fig. 3. Pressure-composition diagrams for propane-isobutane.

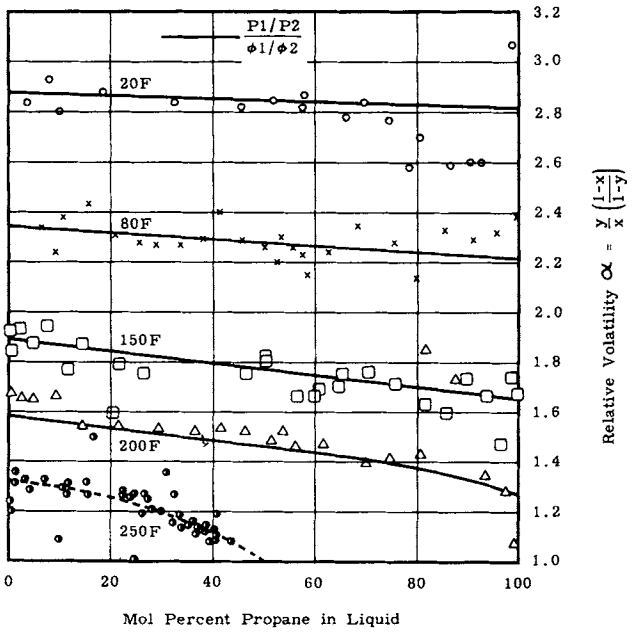

Fig. 4. Relative volatility for propane-isobutane.

same component. Equation (2) is usually applied with the assumption that $\gamma_v = 1.0$.

To evaluate this expression, π, P, y, and x were the experimental data. The fugacity coefficients were taken from the generalized corresponding states correlations in Perry (*24*). The generalized correlations permit extrapolation of $f\pi/\pi$ into the liquid region, which is necessary for the heavy component. The liquid molar volumes of the pure components were taken from Ritter, Lenoir, and Schweppe (*25*). No attempt was made to calculate activity coefficients for the 250°F. data, since this temperature is above the critical temperature of propane.

Calculation of the f_L/f_v ratio for the four lower temperatures showed that the ratio was 1.0 ± 0.10 for one hundred out of one hundred and seven data points. Moreover, the points showed no trend, but scattered about $\gamma_L/\gamma_v = 1.0$ in a random fashion. From this evidence it appears either that $\gamma_L = \gamma_v$ for all compositions and temperatures, or that the system forms ideal solutions over this range of temperatures. At 20° and 80°F., where the pressures are less than 150 lb./sq.in.abs., it is reasonable to assume ideal vapor phase solutions, and thus ideal liquid phase solutions also. At 150° and 200°F. the pressures are as high as 600 lb./sq.in.abs., and some vapor phase nonideality might be expected. But, in view of the considerable difference between liquid and vapor density, even at these pressures it is not reasonable for the vapor phase nonideality to equal the liquid phase nonideality. The data seem to indicate that this system forms ideal solutions, even at 600 lb./sq.in.abs.

If $\gamma_L/\gamma_v = 1.0$, Equation (2) can be rewritten in terms of relative volatility, as

$$\alpha = \frac{y(1-x)}{x(1-y)} = \frac{P_1\,\phi_2}{P_2\,\phi_1} \qquad (4)$$

The solid lines in Figure 4 were calculated from this relation. These lines follow the data points very well, and are visual evidence of the ideality of this system. The dashed line through the 250°F. points is the visually best line and has no thermodynamic significance.

NOTATION

A = area under a chromatogram peak, corrected to maximum instrument sensitivity, arbitrary units
c = calibration constant for chromatograph, defined by Equation (1)
f = fugacity of a component
f_π = fugacity of a pure component at system temperature and pressure
f_p = fugacity of a pure component at the system temperature and corresponding vapor pressure
f_L = fugacity of a component in the liquid solution
f_v = fugacity of the same component in the vapor solution
$f°$ = fugacity of the pure component at the system temperature and pressure
P = vapor pressure at temperature T
R = gas constant
T = absolute temperature
v = molar liquid volume of pure component
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Letters

α = relative volatility, $\alpha = (y_1x_2/x_1y_2)$
γ = activity coefficient, $\gamma = f/(f°y)$
π = system pressure
ϕ = grouped correction factor, $\phi = \dfrac{f_\pi/\pi}{f_p/P}\, e^{\frac{v(P-\pi)}{RT}}$

Subscripts

1 = more volatile component, propane
2 = less volatile component, isobutane

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