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Vapor Pressures for the System Isobutane–Isobutylene–*n*-Butane

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New experimental vapor pressures for the ternary system composed of isobutane–isobutylene–*n*-butane from 40 to 160 °F and 20 to 160 psia are presented. The data have an estimated average accuracy of 0.04%. The pure component data are compared with existing data from the literature.

Introduction

The design of commercial distillation columns to separate the components of a system of close boiling chemicals requires extremely accurate vapor–liquid-phase equilibrium data. One method of acquiring these data is to measure the vapor pressures over liquid mixtures of the components to be separated and then to calculate the associated vapor compositions using the Gibbs–Duhem equation and some assumptions on the volumetric behavior of both phases.

We have used the apparatus described by Steele et al. (18) to measure 152 data points (76 duplicate values) at six temperatures over liquid mixtures of known compositions. Different conditions, ranging from 40 to 160 °F and 20 to 160 psia, for 15 different compositions are presented. The probable error is estimated to be no greater than $\pm 0.03\%$. These data are suitable for use in the design of distillation equipment for the separation of C_4 hydrocarbons and should also be useful in analyzing the molecular interactions between paraffin and olefin hydrocarbons. A significant amount of new vapor pressure data for pure isobutane, isobutylene, and *n*-butane are presented, and these data should prove to be valuable since very few data are available under the conditions reported in this paper [Zudkevitch (21)].

Experimental Section

The experimental apparatus used in this work has been described most recently by Steele et al. (18). It was designed and constructed by Walker (20).

The materials used in this work are Phillips research-grade chemicals and have the following stated purities: isobutane (Lot No. 1272), 99.99 mol freezing point purity, a trace impurity detected by gas chromatography was *n*-butane; isobutylene (Lot No. 1525), 99.93 wt % by vapor–liquid chromatograph determinations on a representative sample from this lot, the most probable impurity is 1-butene; *n*-butane (Lot No. 1466), 99.99 mol % freezing point purity, 99.9+ mol % by gas–liquid chromatography, most probable impurities are isobutane and 2-butene. Gas chromatography in our facilities confirmed the high purity of the materials.

The hydrocarbons were transferred as vapors from the original cylinder to a working cylinder in order to reduce the amount of heavy impurities. They were transferred as liquids from the working cylinder to the measuring cell in order to reduce the amount of light impurities and to avoid contamination. Prior to each transfer a thorough evacuation was performed in addition to flushes with the chemicals to be transferred.

Prior to use, the hydrocarbons were carefully degassed by a venting–cooling–evacuating–heating cycle. The cycle was repeated until the vapor-phase analysis by gas chromatography, for air, indicated that no air was present. The chromatograph was capable of measuring air mole fractions as low as 0.001 (vapor-phase sample of the hydrocarbons), equivalent to a partial

pressure of air in the final pressure measurement of at most 0.02 psi.

The temperature was maintained at worst to within ± 0.02 °F (equivalent to a $\pm 0.03\%$ error in the vapor pressure of the most volatile component, isobutane at 100 °F), by a Bayley Precision Temperature Controller Model 251 in a Neslab Instruments RTE 4 circulating temperature bath, and was measured with a Leeds and Northrup platinum resistance thermometer (calibrated by the NBS) in conjunction with a Rubicon Instruments Mueller Bridge. The bridge circuit was balanced using a Leeds and Northrup DC null detector. The accuracy with which the temperature was measured is believed to be ± 0.02 °F. The pressure measurements were made with a Ruska dead weight gauge which has been calibrated by Ruska, Corp., against the reference gauge which has been calibrated by the NBS. The accuracy with which the pressure was measured is believed to be ± 0.02 psi.

The barometric pressure was measured with a Princo Instruments, Inc., barometer, and the raw reading was corrected for temperature and gravity according to manufacturer's instructions. The accuracy of this barometer is estimated to be ± 0.2 mmHg (± 0.004 psi).

Liquid mixtures were made up with the aid of a Ruska metering pump, and were determined to an estimated accuracy of ± 0.0001 mole fraction units. The composition of samples was determined by weighing the components with a Mettler analytical balance.

The raw vapor pressures (11) were corrected to rounded temperatures, the largest temperature correction (excluding extrapolations) was equivalent to 0.05 psi. The rounded temperature data were corrected for the difference between the measured overall composition and the desired liquid composition. The largest z to x correction was equivalent to 0.02 psi. The P – x data were then corrected to rounded liquid composition values. The largest composition correction was equivalent to 0.02 psi.

Results and Discussion

The final vapor pressure data for the three pure components, for the nine binary systems, and for the three ternary systems are presented in Table I. To simplify the notation, isobutane, isobutylene, and *n*-butane are referred to as components 1, 2, and 3, respectively. The vapor pressures were measured twice for each data point to verify the reproducibility of the apparatus. The maximum pressure difference among the 76 pairs of pressure measurements reported was 0.12 psi, for isobutylene at 160 °F. The maximum pressure difference expressed as a percentage was 0.13% for the 50–50 mol % of isobutylene and *n*-butane at 40 °F. The probable error in pressure measurement was 0.013 psi, 0.021%.

The vapor pressure data were fit to the Antoine equation:

$$P_{\text{calcd}} = \exp\left(A + \frac{B}{C + T}\right) \quad (1)$$

with T in °F and P in psia. Values of the constants A , B , and C for the three pure components are given in Table II. Figures 1, 2, and 3 show the percentage deviation from pressures calculated by the Antoine equation for the data from this study, as well as for original data from the literature. These figures bear out the fact that for the compounds and temperature ranges

Table I. Experimental Data Corrected to Rounded Temperatures and Mole Fractions

T, °F	Vapor pressure, psia						
	Isobutane (1)	Isobutylene (2)	n-Butane (3)	x ₁ = 0.25 x ₂ = 0.75	x ₁ = 0.50 x ₂ = 0.50	x ₁ = 0.75 x ₂ = 0.25	x ₂ = 0.75 x ₃ = 0.25
40	26.57	22.48	17.68 ^a	23.87	25.01	25.88	21.50
70	45.30	39.18	31.23	41.27	42.99	44.26	37.48
100	72.60	63.93	51.58	66.88	69.18	71.09	61.24
130	110.62	98.89	80.64	102.87	106.11	108.57	94.88
160	161.48	146.18	120.32	151.43	155.61	158.97	140.56
160	161.45	146.30	120.31	151.44	155.62	158.99	140.59
130	110.62	98.92	80.62	102.90	106.15	108.64	94.89
100	72.61	63.90	51.57	66.87	69.22	71.12	61.26
70	45.34	39.16	31.24	41.27	42.97	44.27	37.49
40	26.59	22.47	17.69 ^a	23.87	25.03	25.88	21.48
150			105.83				
150			105.84				

T, °F	Vapor pressure, psia							
	x ₂ = 0.50 x ₃ = 0.50	x ₂ = 0.25 x ₃ = 0.75	x ₁ = 0.25 x ₃ = 0.75	x ₁ = 0.50 x ₃ = 0.50	x ₁ = 0.75 x ₃ = 0.25	x ₁ = 0.25 x ₂ = 0.25 x ₃ = 0.50	x ₁ = 0.25 x ₂ = 0.50 x ₃ = 0.25	x ₁ = 0.50 x ₂ = 0.25 x ₃ = 0.25
40	20.40	19.14 ^b	19.95 ^c	22.13	24.37	21.41	22.67	23.60
70	35.67	33.58	34.79	38.22	41.80	37.16	39.21	40.64
100	58.39	55.17	56.84	61.99	67.28	60.47	63.67	65.71
130	90.62	85.92	88.05	95.45	102.96	93.37	98.14	100.85
160	134.47	127.79	130.50	140.51	150.89	138.00	144.80	148.31
160	134.45	127.78	130.44	140.52	150.91	138.01	144.78	148.33
130	90.64	85.92	88.02	95.44	102.98	93.42	98.17	100.92
100	58.39	55.23	56.84	62.00	67.32	60.43	63.68	65.75
70	35.68	33.59	34.79	38.26	41.81	37.18	39.21	40.65
40	20.42	19.14 ^b	19.95 ^c	22.15	24.36	21.42	22.64	23.59

^a Extrapolated from 46.6 °F. ^b Extrapolated from 42.5 °F. ^c Extrapolated from 40.6 °F.

Table II. Antoine Equation Constants:^a $P_{\text{calcd}} = \exp(A + B/(C + T))$; T, °F; P, psia

	A	-B	C	σ_p , psi
Isobutane (1)	12.0979	4114.62	426.654	0.02
Isobutylene (2)	12.1112	4109.62	416.711	0.03
n-Butane (3)	12.0571	4176.93	414.792	0.02

^a Constants determined with ten points (five duplicates) at five different temperatures for isobutane (1) and isobutylene (2); 12 points (six duplicates) at six different temperatures for n-butane (3).

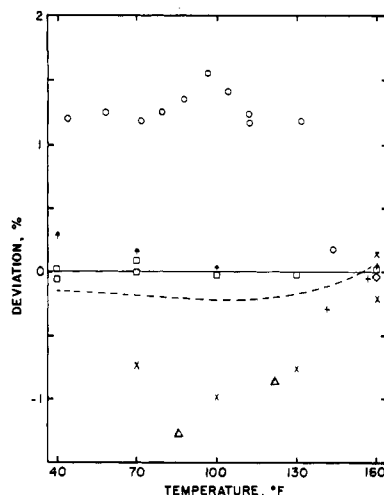


Figure 1. Literature study of isobutane: □, raw experimental data of this study; O, Dana et al., 1926 (6); Δ, Beattie et al., 1949 (3); X, Sage and Lacey, 1938 (14); ◇, Morris et al., 1940 (12); ↑, Steele et al., 1975 (18); X, Connolly, 1962 (6); +, Hirata et al., 1969 (8); --, A.P.I. 44, 1974 (2).

examined the degree of disagreement among the original investigators is significant. The data of Seibert and Burrell (17) for isobutane and n-butane were considerably higher than the rest of the literature data and were omitted from Figures 1 and

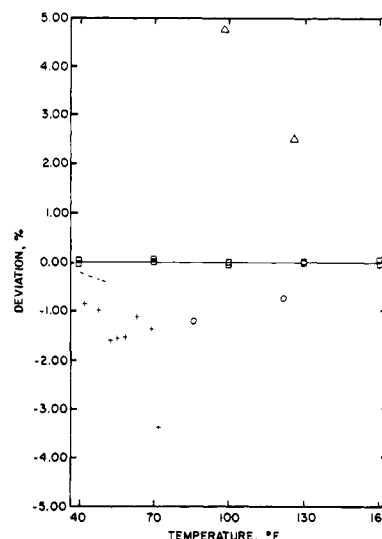


Figure 2. Literature study of isobutene: □, raw experimental data of this study; O, Beattie et al., 1942 (4); Δ, Scheeline and Gilliland, 1939 (16); +, Coffin and Maass, 1927 (5); --, A.P.I. 44, 1952 (7).

3. The data of Steele et al. (18) are slightly higher at 40 and 70 °F than those reported here. This difference is accounted for by the refined degassing technique and by the improvement in temperature control.

A literature search showed that there are no data available for the binary and the ternary systems under the conditions reported in this paper except for the system isobutane-n-butane at 160 °F. As shown in Figure 4 the data reported in the literature (6) for isobutane-n-butane at 160 °F agree closely with the data presented in this work.

Conclusions

Experimental vapor pressure data for the isobutane-isobutylene-n-butane system have been measured over the

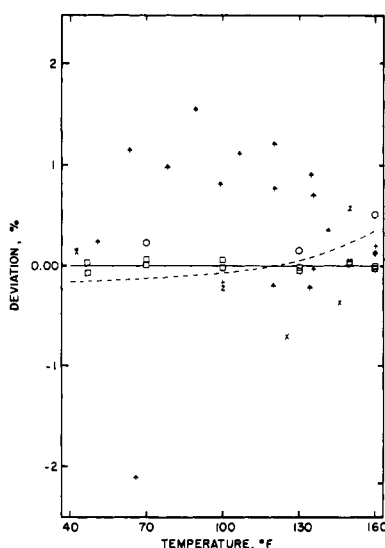


Figure 3. Literature study of *n*-butane: □, raw experimental data of this study; ○, Sage et al., 1937 (15); +, Olds et al., 1944 (13); ×, Kay, 1940 (9); ↑, Data et al., 1926 (7); ×, Wackher et al., 1945, (19); Z, Laurance and Swift, 1974 (10); ◇, Connolly, 1962 (6); Δ, Hirata et al., 1969 (8); --, A.P.I. 44, 1974 (2).

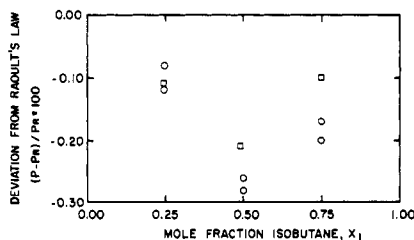


Figure 4. Comparison of deviation from Raoult's law for isobutane (1)-*n*-butane (3) at 160 °F: ○, this study; □, Connolly, 1962 (6).

temperature range of 40 to 160 °F with an estimated average accuracy of 0.04%. These data are suitable for use in the design of distillation equipment for the separation of C₄ hydrocarbons and should also be useful in analyzing the molecular interactions between paraffin and olefin hydrocarbons.

Glossary

A, B, C constants (Antoine constants) for eq 1

P pressure, psia
T temperature, °F
x liquid-phase composition
z overall composition
 σ_p standard deviation for pressure, psi

Subscripts

calcd calculated with eq 1
 1 component identification: 1 = isobutane, 2 = isobutylene, 3 = *n*-butane
P with respect to pressure
R pressure calculated by Raoult's law, psia

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Gas-Liquid Equilibrium of the Hydrogen/Bicyclohexyl System at Elevated Temperatures and Pressures

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Vapor-liquid equilibrium data are determined for the system hydrogen/bicyclohexyl at four temperatures from 190 to 430 °C and seven pressures up to 250 atm in a flow type apparatus. Attainment of equilibrium was checked by varying input flow rates and checking the thermodynamic consistency of the data by integration of the Gibbs-Duhem equation. The new data are compared with general correlations in the literature.

Introduction

Recently there has been an increased interest in vapor-liquid equilibrium data involving H₂/hydrocarbon systems at elevated temperatures and pressures in response to the development of coal liquefaction and hydrotreating processes. Such information is useful not only for the engineering design of gas-liquid contacting and separation equipment but also for the study of reaction kinetics in coal liquefaction mixtures.

Work in this laboratory has been concerned with gas-liquid