# Vapor-Liquid Equilibrium Constants: Ethane–*n*-Butane–*n*-Pentane System at 150° F.

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COMPOSITION of vapor and liquid equilibrium phases form the basis for the calculations of distillation, extraction, and absorption processes. In order to add to the number of systems investigated, the ethane-*n*-butane-*n*-pentane system has been studied at 150° F.

## APPARATUS AND PROCEDURE

The apparatus used (*6*) included an equilibrium cell into which the ternary mixture was charged. The cell was equipped with a movable piston to control the pressure of the system which was measured to within 2 p.s.i. with Heise gages. The cell was surrounded by an air bath to maintain its temperature constant to within 0.2° F. Agitation was provided with a stirrer magnetically coupled to an external mechanical drive.

Approximately 2 hours were required for the vapor and liquid phases to reach equilibrium; for conditions near the critical region, more time was required. After equilibrium was reached, microscopic quantities of the vapor and liquid phases were removed and analyzed. The samples were analyzed with a gas chromatography unit, and the results are believed to be accurate to within 0.5 mole %.

## MATERIALS

The hydrocarbon used were reagent grade and were supplied by the Phillips Petroleum Co. The ethane had a purity of 99.91 mole %; *n*-butane, 99.91 mole %; *n*-pentane, 99.80 mole %.

## EXPERIMENTAL

To test the apparatus and experimental procedure, the ethane-*n*-pentane system was investigated at 150° F. and compared with the data reported by Reamer, Sage, and Lacey (*5*). A comparison of the data from both sources is shown in Figure 1.

The phase behavior of the individual components of a ternary system can best be described by their vapor-liquid equilibrium constants,

$$K_i = \frac{y_i}{x_i} \tag{1}$$

Equilibrium constants are functions not only of temperature and pressure but also of composition. Therefore, a complete study of a ternary system requires data throughout the entire range of compositions.

In a two-phase region, ternary systems have three degrees of freedom. Therefore, if temperature and pressure are fixed one other intensive property must be specified in order to define the system. Such an intensive property which has found widespread use, "the composition parameter," is defined as follows (*1, 3*):

$$C = \frac{x_l}{x_l + x_h} \tag{2}$$

The composition parameter varies from zero to unity throughout the entire range of ternary compositions. The composition parameter is zero for the ethane-*n*-pentane system and unity for the ethane-*n*-butane system. The fact that the related binaries represent extreme values of the composition parameter lend a distinct advantage to the use of this parameter, since these binaries provide boundary conditions for the ternary system.

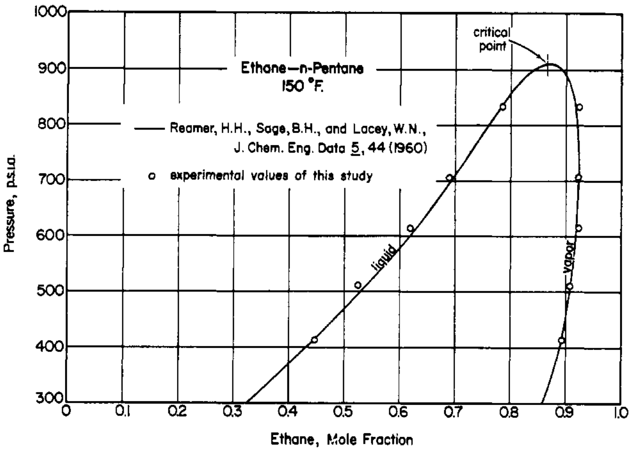


Figure 1. Comparison of experimental vapor-liquid equilibrium compositions of this study for the ethane–*n*-pentane system with reported results (*5*)

Four ternary charges (designated as III, IV, V, and VI) were prepared with composition parameters of approximately 0.2, 0.4, 0.6, and 0.8. For each charge, the compositions of vapor and liquid phases were determined at several pressures in the two-phase region above 500 p.s.i.a. The experimentally determined compositions for the four charges are presented in Table I, and the data for each charge were smoothed by plotting them against pressure, as shown in Figure 2 for Charge III. For this charge, vapor and liquid compositions were obtained for pressures up to 825.7 p.s.i.a., and the resulting curves were extrapolated to an apex, which at this stage will be designated as the "point of convergence." For Charge III at 150° F., the point of convergence was 846 p.s.i.a. for mole fraction compositions of 0.840 ethane, 0.102 *n*-butane, and 0.058 *n*-pentane. For Charges IV, V, and VI, plots similar to Figure 2 were extrapolated to their points of convergence;

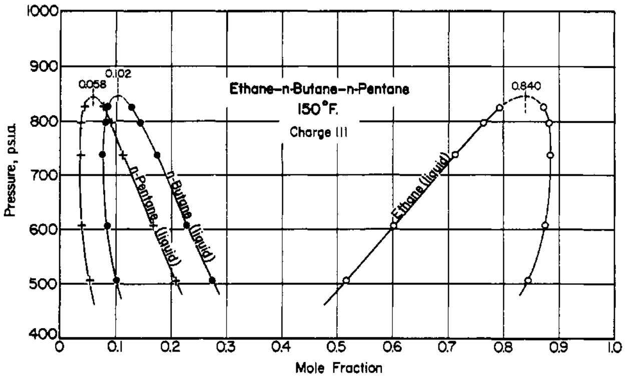
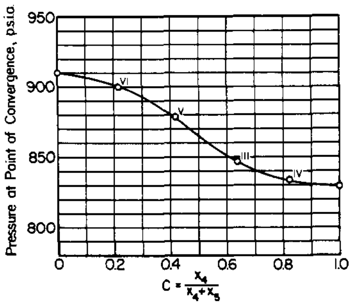


Figure 2. Vapor-liquid equilibrium composition-pressure relationships for a mixture of ethane, *n*-butane, and *n*-pentane (Charge III)



← Figure 3. Relationship between convergence pressure and composition parameter for the ethane–*n*-butane–*n*-pentane system at 150° F.

the pressures and compositions at these points are presented in Table II. These compositions should coincide with the compositions of the over-all charges; however, these latter compositions were not established precisely.

From the smoothed curves for each charge, equilibrium constants were determined and plotted against pressure to verify the point of convergence of each charge as the point where the curves of the charge coincided at $K = 1.0$. The pressure at the point of convergence for the four charges and the critical pressures of the two binaries (*4, 5*) were plotted against the composition parameter as shown in Figure 3 to obtain a single relationship for this ternary system at 150° F.

Vapor-liquid equilibrium constants obtained from the smoothed curves for each charge were plotted against the

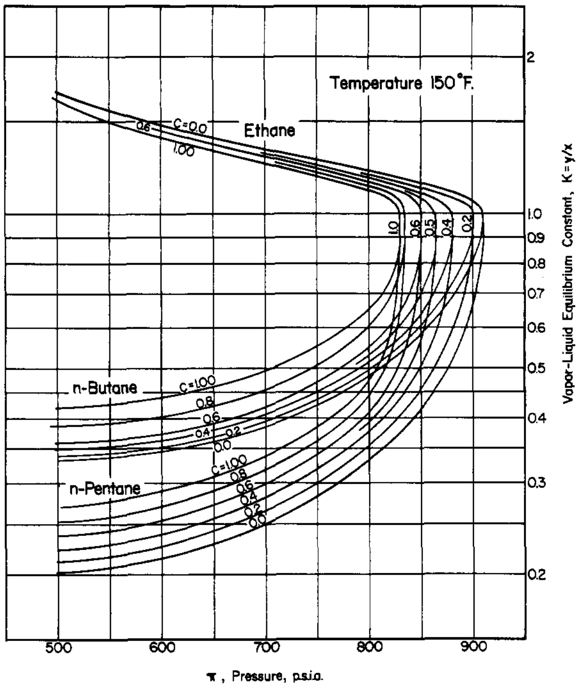


Figure 4. Relationships between *K* values and pressure for constant composition parameters

Table I. Vapor-Liquid Equilibrium Compositions at 150° F. for the Four Charges of the Ethane–*n*-Butane–*n*-Pentane System

| Pressure, | Vapor, Mole Fraction | | | Liquid, Mole Fraction | | | $K = y/x$ | | | C |
|---|---|---|---|---|---|---|---|---|---|---|
| P.s.i.a. | Ethane | *n*-Butane | *n*-Pentane | Ethane | *n*-Butane | *n*-Pentane | Ethane | *n*-Butane | *n*-Pentane | $x_4/(x_4+x_5)$ |
| | | | | | Charge III | | | | | |
| 506.0 | 0.846 | 0.102 | 0.052 | 0.517 | 0.274 | 0.209 | 1.636 | 0.372 | 0.249 | 0.567 |
| 606.2 | 0.875 | 0.086 | 0.039 | 0.602 | 0.229 | 0.169 | 1.453 | 0.376 | 0.231 | 0.575 |
| 737.9 | 0.886 | 0.077 | 0.037 | 0.713 | 0.175 | 0.112 | 1.243 | 0.440 | 0.330 | 0.610 |
| 797.7 | 0.882 | 0.081 | 0.037 | 0.765 | 0.144 | 0.091 | 1.153 | 0.563 | 0.407 | 0.613 |
| 825.7 | 0.872 | 0.085 | 0.043 | 0.794 | 0.128 | 0.078 | 1.098 | 0.664 | 0.551 | 0.621 |
| | | | | | Charge IV | | | | | |
| 514.9 | 0.828 | 0.149 | 0.023 | 0.510 | 0.378 | 0.112 | 1.608 | 0.394 | 0.205 | 0.771 |
| 611.5 | 0.858 | 0.122 | 0.020 | 0.599 | 0.312 | 0.089 | 1.432 | 0.391 | 0.225 | 0.778 |
| 708.0 | 0.871 | 0.111 | 0.018 | 0.690 | 0.245 | 0.065 | 1.262 | 0.453 | 0.277 | 0.790 |
| 767.2 | 0.871 | 0.110 | 0.019 | 0.740 | 0.208 | 0.052 | 1.177 | 0.529 | 0.365 | 0.800 |
| 816.7 | 0.865 | 0.115 | 0.020 | 0.788 | 0.170 | 0.042 | 1.098 | 0.676 | 0.476 | 0.802 |
| | | | | | Charge V | | | | | |
| 527.7 | 0.893 | 0.046 | 0.061 | 0.560 | 0.131 | 0.309 | 1.595 | 0.351 | 0.197 | 0.298 |
| 621.8 | 0.898 | 0.043 | 0.059 | 0.641 | 0.113 | 0.246 | 1.401 | 0.381 | 0.240 | 0.315 |
| 712.9 | 0.904 | 0.041 | 0.055 | 0.718 | 0.093 | 0.189 | 1.259 | 0.441 | 0.291 | 0.330 |
| 808.7 | 0.911 | 0.038 | 0.051 | 0.793 | 0.076 | 0.131 | 1.149 | 0.500 | 0.389 | 0.367 |
| 838.7 | 0.910 | 0.038 | 0.052 | 0.823 | 0.068 | 0.109 | 1.106 | 0.559 | 0.477 | 0.384 |
| 857.7 | 0.904 | 0.041 | 0.055 | 0.836 | 0.061 | 0.103 | 1.081 | 0.672 | 0.534 | 0.372 |
| | | | | | Charge VI | | | | | |
| 517.5 | 0.899 | 0.016 | 0.085 | 0.534 | 0.049 | 0.417 | 1.684 | 0.327 | 0.204 | 0.105 |
| 616.2 | 0.910 | 0.020 | 0.070 | 0.617 | 0.044 | 0.339 | 1.475 | 0.455 | 0.206 | 0.115 |
| 711.5 | 0.917 | 0.018 | 0.065 | 0.703 | 0.039 | 0.258 | 1.304 | 0.462 | 0.252 | 0.131 |
| 808.7 | 0.921 | 0.017 | 0.062 | 0.797 | 0.033 | 0.170 | 1.156 | 0.515 | 0.365 | 0.163 |
| 878.7 | 0.919 | 0.017 | 0.064 | 0.858 | 0.030 | 0.112 | 1.071 | 0.567 | 0.571 | 0.211 |

Table II. Pressures at Points of Convergence and Corresponding Compositions at 150° F. for the Four Charges Used

| | $P_k$, | Mole Fraction | | | Compn. |
|---|---|---|---|---|---|
| | P.s.i.a. | Ethane | *n*-Butane | *n*-Pentane | Parameter |
| Charge III | 846 | 0.840 | 0.102 | 0.058 | 0.638 |
| Charge IV | 833 | 0.830 | 0.140 | 0.030 | 0.821 |
| Charge V | 878 | 0.880 | 0.050 | 0.070 | 0.417 |
| Charge VI | 900 | 0.898 | 0.022 | 0.080 | 0.216 |
| Ethane-*n*-Butane | 829[a] | 0.813 | 0.187 | | 1.000 |
| Ethane-*n*-Pentane | 910[a] | 0.865 | | 0.135 | 0.000 |

[a] For binary systems, convergence pressure is critical pressure.

composition parameter for convenient pressures and cross plotted as $K$ against pressure for constant composition parameters, as shown in Figure 4. In general, the equilibrium constants resulting from the experimental data are in close agreement with the smoothed values presented in Figure 4. Final $K$ values for the ternary system obtained from Figure 4 are presented in Table III.

The vapor-liquid equilibrium behavior for this system at 150° F. is presented in the form of a triangular plot in Figure 5. The points for the vapor and liquid phase compositions fell approximately on a separate straight line for each pressure, which terminated at the compositions of the related binaries. In addition, the tie lines, when extended, were found to meet near the apex of the triangle.

Recent studies by Grieves and Thodos (2) have introduced a method by which critical temperatures of ternary systems may be predicted from information for the related binaries. They have shown that, when plotted on a triangular plot, ternary compositions having the same critical temperature produce a straight line which terminates at the composition of the corresponding binary systems. For the ethane-rich portion of the ternary system, a plot of critical temperatures is presented on triangular coordinates in Figure 6. The compositions of the four charges at the point of convergence are also included in this figure. A temperature of 150° F. appears to be very close to the critical temperature of Charges III and IV; consequently, the pressures at the points of convergence for these two charges are also very close to the critical pressures of the charges. This fact is corroborated by the other triangular plot of Figure 6, which presents critical pressure isobars for the ethane-rich region of this ternary system. The critical pressure isobars for 750 and 800 p.s.i.a. are well defined because they terminate at the critical compositions of the binaries. The remaining three isobars are above the critical pressure of the ethane-$n$-butane system; consequently, they do not extend to the ethane-$n$-butane coordinate. Therefore, for the 850, 900, and 950 p.s.i.a. isobars, only portions of the curves are presented. These curves were drawn so that they were consistent with the 750 and 800 p.s.i.a. isobars. In this plot, the position of the points for Charges III and IV indicate that the pressures at the points of convergence of these charges are also very close to the critical pressures. Therefore, the critical point of Charge III is approximately 150° F. and 846 p.s.i.a., and the critical point of Charge IV is approximately 150° F. and 833 p.s.i.a.

Table III. Final *K* Values for the Ethane–*n*-Butane–*n*-Pentane System at 150° F.

| Pressure, P.s.i.a. | Vapor-Liquid Equilibrium Constant, $K = y/x$ Ethane | $n$-Butane | $n$-Pentane |
|---|---|---|---|
| | $C = 0.00$ | | |
| 500 | 1.711 | | 0.202 |
| 600 | 1.485 | | 0.215 |
| 700 | 1.332 | | 0.251 |
| 800 | 1.209 | | 0.335 |
| 820 | 1.186 | | 0.360 |
| 830 | 1.175 | | 0.372 |
| 840 | 1.161 | | 0.395 |
| 860 | 1.136 | | 0.447 |
| 880 | 1.105 | | 0.522 |
| 900 | 1.063 | | 0.667 |
| 910 | 1.000 | | 1.000 |
| | $C = 0.20$ | | |
| 500 | 1.695 | 0.340 | 0.22 |
| 600 | 1.47 | 0.355 | 0.23 |
| 700 | 1.32 | 0.395 | 0.27 |
| 800 | 1.18 | 0.495 | 0.36 |
| 820 | 1.14 | 0.540 | 0.39 |
| 840 | 1.12 | 0.575 | 0.43 |
| 860 | 1.10 | 0.64 | 0.49 |
| 880 | 1.07 | 0.73 | 0.57 |
| 900 | 1.02 | 0.90 | 0.87 |
| | $C = 0.40$ | | |
| 500 | 1.68 | 0.345 | 0.224 |
| 600 | 1.455 | 0.368 | 0.24 |
| 700 | 1.30 | 0.413 | 0.285 |
| 800 | 1.165 | 0.515 | 0.38 |
| 820 | 1.12 | 0.57 | 0.420 |
| 840 | 1.11 | 0.61 | 0.480 |
| 860 | 1.075 | 0.69 | 0.560 |
| 880 | 1.00 | 1.00 | 1.000 |
| | $C = 0.50$ | | |
| 700 | 1.295 | 0.420 | 0.275 |
| 800 | 1.16 | 0.530 | 0.400 |
| 820 | 1.12 | 0.590 | 0.440 |
| 840 | 1.10 | 0.655 | 0.545 |
| 860 | 1.05 | 0.79 | 0.700 |
| | $C = 0.60$ | | |
| 500 | 1.665 | 0.360 | 0.24 |
| 600 | 1.44 | 0.375 | 0.25 |
| 700 | 1.285 | 0.425 | 0.30 |
| 800 | 1.14 | 0.55 | 0.41 |
| 820 | 1.12 | 0.61 | 0.466 |
| 840 | 1.08 | 0.72 | 0.645 |
| | $C = 0.80$ | | |
| 500 | 1.65 | 0.380 | 0.255 |
| 600 | 1.42 | 0.398 | 0.275 |
| 700 | 1.29 | 0.450 | 0.320 |
| 800 | 1.125 | 0.590 | 0.450 |
| 820 | 1.09 | 0.660 | 0.535 |
| 830 | 1.06 | 0.825 | 0.670 |
| | $C = 1.00$ | | |
| 500 | 1.64 | 0.420 | |
| 600 | 1.405 | 0.441 | |
| 700 | 1.247 | 0.494 | |
| 800 | 1.109 | 0.651 | |
| 820 | 1.073 | 0.735 | |

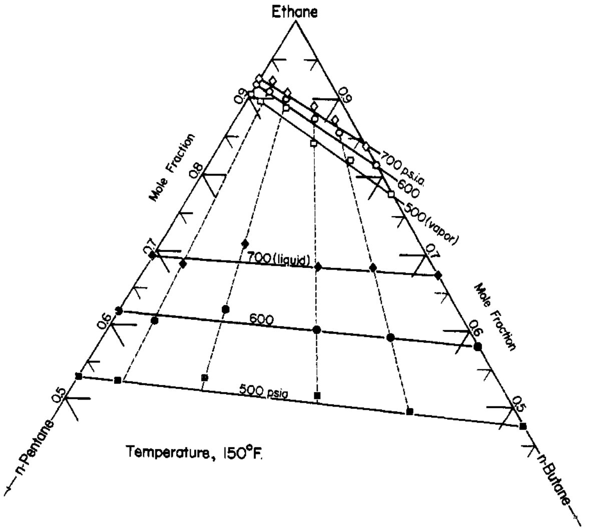


Figure 5. Vapor-liquid equilibrium relations for pressures of 500, 600, and 700 p.s.i.a.

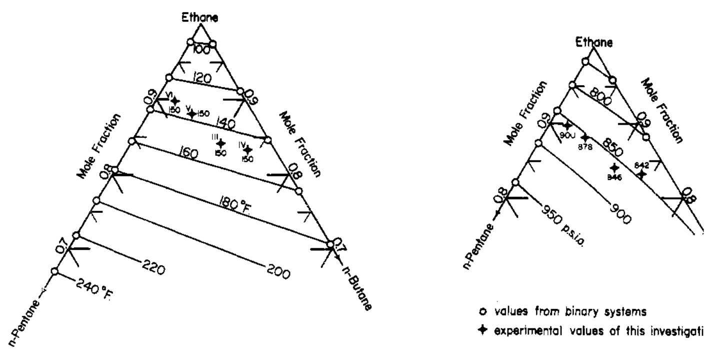


Figure 6. Critical temperatures and pressures of the ethane-$n$-butane-$n$-pentane system

## ACKNOWLEDGMENT

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## NOMENCLATURE

$C$ = composition parameter, $x_i/(x_i + x_h)$
$K_j$ = vapor-liquid equilibrium constant for $j$ component, $y_j/x_j$
$P_k$ = pressure at point of convergence, p.s.i.a.
$P_c$ = critical pressure, p.s.i.a.
$t_c$ = critical temperature, ° F.
$x_h$ = mole fraction in liquid phase of component of lowest volatility
$x_i$ = mole fraction in liquid phase of component of intermediate volatility
$x_j$ = mole fraction in liquid phase of $j$ component
$y_j$ = mole fraction in vapor phase of $j$ component
$\pi$ = pressure, p.s.i.a.

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# Vapor Pressures of Silicon Tetrachloride–Carbon Tetrachloride Mixtures

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VAPOR PRESSURE of silicon tetrachloride–carbon tetrachloride systems at 30°, 40°, and 50° C. are presented. The constant of the symmetrical van Laar equation which satisfies the total vapor pressure data is given as a linear regression against reciprocal temperature. Wood (*2*) obtained data on this system using chemical analysis but his results do not show thermodynamic consistency. The procedure and apparatus have been described previously by Ryder, Kamal, and Canjar (*1*).

## EXPERIMENTAL COMPOUNDS

Baker Analytical Reagent grade carbon tetrachloride and Fisher Scientific Technical grade silicon tetrachloride were used in the experimental work. No attempt was made to determine purity of the reagents.

## VAPOR-LIQUID EQUILIBRIUM THEORY

At low pressures, the total pressure exerted by a binary mixture may be written as

$$P_t = x_1\gamma_1 P_1^\circ + x_2\gamma_2 P_2^\circ \tag{1}$$

If log $\gamma$ does not vary much with pressure as in the present work, the Gibbs-Duhem equation can be assumed valid

$$x_1\left(\frac{\partial \log \gamma_1}{\partial x_1}\right)_T = x_2\left(\frac{\partial \log \gamma_2}{\partial x_2}\right)_T \tag{2}$$

and equations which satisfy the Gibbs-Duhem criteria such as the van Laar equations

$$\log \gamma_1 = \frac{Ax_2^2}{[(A/B)\ x_1 + x_2]^2} \tag{3}$$

$$\log \gamma_2 = \frac{Bx_1^2}{[x_1 + (B/A)\ x_2]^2} \tag{4}$$

can be used to describe the variation of log $\gamma$ with composition.

If $A = B$, the van Laar equations reduce to

$$\log \gamma_i = B(1 - x_i)^2 \tag{5}$$

By expressing $\gamma_i$ as a sum of an infinite series

$$\gamma_i = 1 + B(1 - x_i)^2 + (B/2)\ (1 - x_i)^4_T \tag{6}$$

and ignoring all but the first two terms, Equation 1 may be written as

$$P_t = x_1(1 + Bx_2^2)\ P_1^\circ + x_2(1 + Bx_1^2)\ P_2^\circ \tag{7}$$

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