of the analytical procedure. The values of $A$ and $B$ for van Laar equation curves were obtained as 0.38969 and 0.55954 by determining $A$ and $B$ as terminal values of $\log \gamma_1$ at $x_1 = 0$, and $\log \gamma_2$ at $x_2 = 0$, using the Carlson, Colburn (*4*) relationship:

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B} \cdot \frac{x_1}{x_2}\right)^2}$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A} \cdot \frac{x_2}{x_1}\right)^2}$$

Values of $y_1$ were calculated based on these values of $A$ and $B$, and are given as $y_{\text{calcd.}}$ in Table I. The maximum percentage deviation between $y_{\text{exptl.}}$ and $y_{\text{calcd.}} = (100\ \Delta y/y_1)$, is less than 2%. Plots of $\log (\gamma_1/\gamma_2)$ *vs.* $x_1$ in accordance with Redlich and Kister equation (*6*) showed variation in net area under the curve of less than 2%, which is quite reasonable considering the difference of over 37° C. in the boiling points of benzene and 1-butanol.

## NOMENCLATURE

$A$ and $B$ = constants in van Laar equation
$P°$ = vapor pressure, mm.
$x$ = mole fraction in liquid phase
$y$ = mole fraction in vapor phase
$\gamma$ = activity coefficient
$\pi$ = total pressure
$t$ = temperature, ° C.
$\Delta y$ = $y_{\text{exptl.}} - y_{\text{calcd.}}$

### Subscripts

1 = benzene
2 = 1-butanol

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# Relative Volatility Data for Isopentane: *n*-Pentane Mixtures

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**This paper discusses the experimental measurement and the thermodynamic prediction of the relative volatilities of isopentane: *n*-pentane at pressures of 25 to 150 p.s.i.a. A six-stage equilibrium unit was used because of the low relative volatility. The equilibrium samples were analyzed by gas chromatography. Literature values of physical property data were used in the thermodynamic calculations. The agreement of the predicted values with the experimentally measured values given in this paper illustrates that accurate relative volatilities can be predicted for close boiling mixtures, provided adequate physical property data are available.**

THE PRESENT INVESTIGATION to determine the relative volatility data for the isopentane: *n*-pentane system is a part of a continuing program to supply the needs of industry with fundamental design data for separational processes.

Accurate experimental vapor-liquid equilibrium data for many close boiling systems such as isopentane (2-methylbutane):*n*-pentane have not been previously determined, mainly because of the difficulties in analyzing accurately the small changes in concentration obtained in the conventional one-stage equilibrium devices.

The present data were determined in a six-stage equilibrium unit covering a pressure range of 34 to 114 p.s.i.a. and the full concentration range of this binary system. Gas chromatography was used to determine accurately the composition of the equilibrium samples.

Because of a lack of experimental data on vapor-liquid equilibrium relationships, many theoretical prediction methods have been proposed to calculate the relative volatility (alpha) of close boiling mixtures. The only experimental vapor-liquid data available in the literature for isopentane:*n*-pentane mixtures are those of Redlich and Kister (*9*) who have predicted that the ratios of the activity coefficients for this system are essentially unity. The method used by these authors is based on total pressure measurements for binary mixtures at constant temperature. The present experimental data, consisting of measured compositions of vapor and liquid phases at equilibrium, serve to check the results of Redlich and Kister as well as the theoretical prediction methods.

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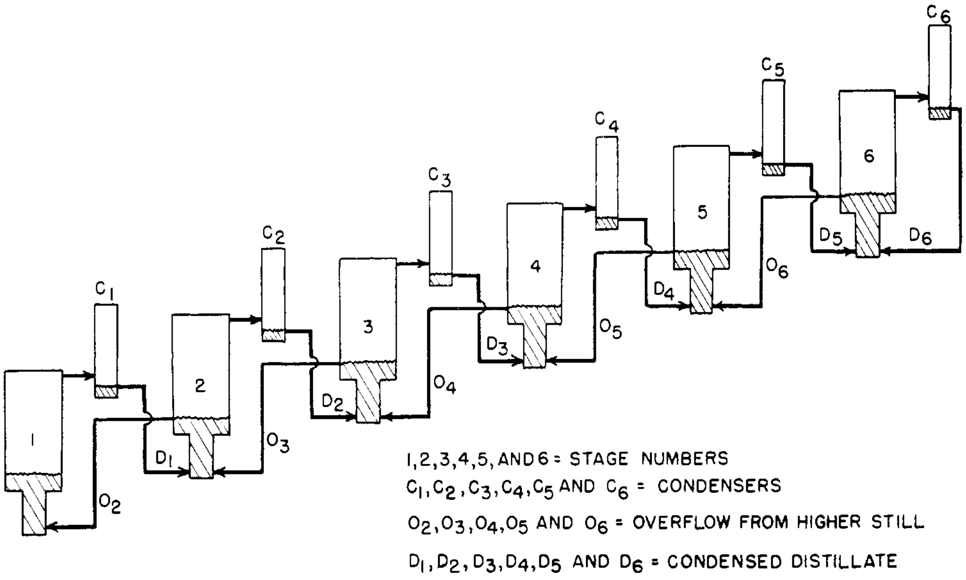

Figure 1. Flow diagram of six-stage vapor-liquid equilibrium unit

## EQUILIBRIUM UNIT

The details on the construction and operating features of the six-stage equilibrium unit employed for these studies have been published (*8*), and will be discussed only briefly.

The unit basically consists of six modified, Othmer-type equilibrium stills. Each still, or stage, is equipped with a cold finger condenser, a still heater, a magnetically operated vapor-liquid mixer, and auxiliary lines to interconnect the individual stages. The six stages are connected through the condensers to a common surge tank for pressure operation as high as 400 p.s.i.a. The complete six-stage unit is mounted in a well-insulated constant temperature box in which the temperature can be controlled from 25° to 400° F. A simplified flow diagram of the unit is shown in Figure 1.

Samples of the vapor and the liquid can be removed from each of the six stages, so equilibrium relationships can be determined over any number of the stages. The stages in this unit have proved to be essentially 100 per cent efficient when tested with hydrocarbon systems of known relative volatility. Therefore, by operating this unit at total reflux the terminal samples, or the liquid sample from stage 1 and the vapor sample from stage 6, represent a six-stage separation. This means that the enrichment factor (*4*) over these six stages will be the relative volatility to the sixth power ($\alpha^6$).

**Experimental Data.** The starting mixtures for the 13 equilibrium runs made on this system contained from 5 to 95% of each component and the concentration of the end samples ranged from 2 to 98%. Therefore, for all practical purposes the complete concentration range of the system was studied.

To determine the effect of pressure on the relative volatility, absolute pressures of 34, 74, and 114 p.s.i. were employed over the concentration range of the system. The boiling points of the mixtures for these pressures range from 131° to 233° F.

The starting isopentane had a purity of 99.73 wt. %, and contained 0.21 wt. % *n*-pentane and traces of *n*-butane and 2,2-dimethylpropane. The *n*-pentane had a purity of 99.27 wt. % and contained 0.29 wt. % isopentane and traces of $C_5$ olefins.

The equilibrium data, the conditions used, and the resulting relative volatility values are shown in Table I. These equilibrium data and the relative volatility values listed include only the terminal equilibrium samples from the unit. However, during the experimental runs, samples were removed from other stages in the unit. These data are in good agreement and confirm the results of the terminal samples over the six stages.

The experimental relative volatility values from Table I are plotted in Figure 2 as a function of temperature. These values were calculated from the analysis of the terminal samples, using the Fenske equation (*4*), and correspond to the average liquid composition and to the average temperature in the six stills.

These values varied from 1.24 to 1.25 at 34 p.s.i.a., 1.185 to 1.195 at 74 p.s.i.a. and 1.145 to 1.17 at 114 p.s.i.a. as

Table I. Vapor-Liquid Equilibrium Data for the Isopentane:*n*-Pentane System

| Pressure, P.S.I.A. | Avg. Temp., ° F. | Avg. Liquid Composition, Wt. % Isopentane | Analysis, Wt. % Isopentane: Stage 1 Liquid | Analysis, Wt. % Isopentane: Stage 6 Vapor | Relative Volatility, $\alpha$ Isopentane/*n*-Pentane |
|---|---|---|---|---|---|
| 34 | 131 | 96 | 93.45 | 98.2 | 1.25 |
| 34 | 132 | 96 | 93.65 | 98.3 | 1.25 |
| 34 | 137 | 50.5 | 34.65 | 66.3 | 1.245 |
| 34 | 144 | 4.5 | 2.3 | 7.85 | 1.24 |
| 34 | 145 | 4 | 2.15 | 7.5 | 1.245 |
| 74 | 185 | 95.5 | 93.15 | 97.55 | 1.195 |
| 74 | 192 | 48 | 36.85 | 61.75 | 1.185 |
| 74 | 192 | 48 | 36.8 | 63.0 | 1.195 |
| 74 | 199 | 4.5 | 2.65 | 7.0 | 1.185 |
| 114 | 218 | 94 | 91.15 | 96.4 | 1.17 |
| 114 | 226 | 43.0 | 34.2 | 55.9 | 1.16 |
| 114 | 233 | 4.0 | 2.95 | 6.55 | 1.15 |
| 114 | 232 | 4.5 | 3.15 | 6.85 | 1.145 |

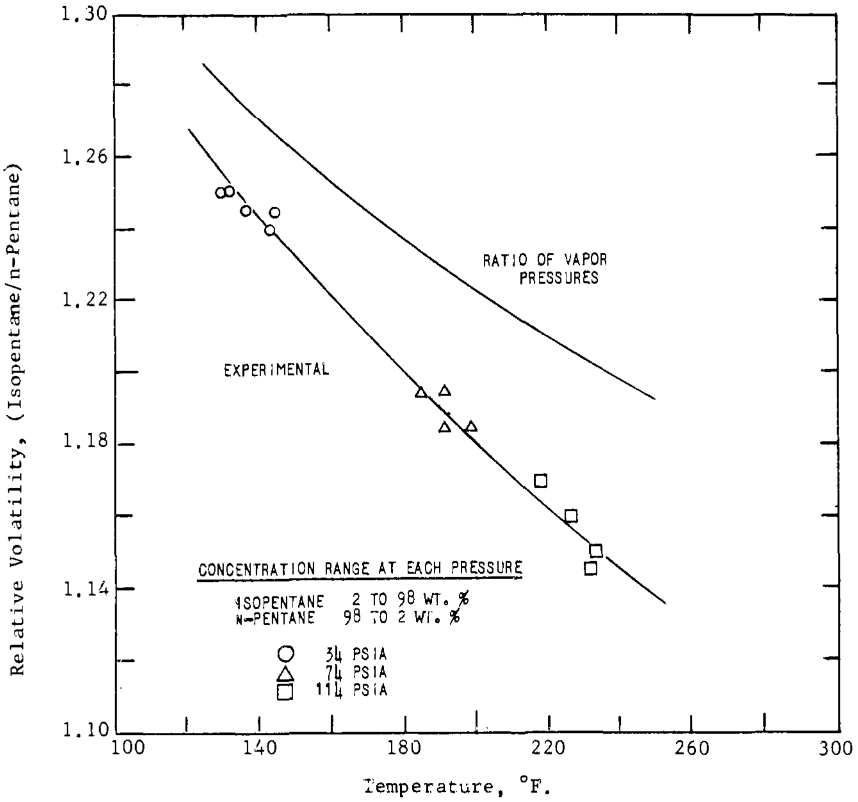

Figure 2. Effect of temperature on the relative volatility of the isopentane: *n*-pentane system

the average concentration of isopentane was increased from about 5 to 95 vol. %, respectively. The accuracy of these values is ±0.01 unit.

For engineering purposes Raoult's and Dalton's Laws are frequently assumed to apply to close boiling mixtures, and the ratio of the vapor pressures of the pure components is used to estimate the relative volatility of the components in a mixture.

A comparison of the experimental relative volatilities and those calculated as the ratio of the vapor pressures is shown in Table III and plotted in Figure 2.

By using as coordinates the logarithm of the relative volatility and the reciprocal of the absolute temperature the curved lines of Figure 2 approach a straight line relationship.

The comparison of these two curves shows quite clearly that the alpha values calculated as the ratios of the vapor pressures of the pure components differ considerably from the experimental values, and that this difference increases as the temperature increases.

It should be pointed out that a consideration of the phase rule indicates that this system has two degrees of freedom and, therefore, one more parameter should be specified in addition to the temperature. Although relative volatilities were determined experimentally at concentrations ranging from 5 to 95 per cent of each component, these values follow a single smooth curve of alpha *vs.* temperature within the accuracy of the experimental data. Therefore, any effect of an additional parameter, such as pressure or concentration, superimposed on the alpha *vs.* temperature curve, can be assumed to be negligible for all practical engineering purposes.

The effect of the second parameter can be shown to exist if a rigorous theoretical prediction method is used to determine relative volatilities.

Accurate relative volatilities can be calculated theoretically if sufficient physical property data are available for the accurate calculation of the fugacity coefficients for each of the components at the conditions being considered. It is convenient to combine all of the fugacity coefficients pertaining to a given compound into one "volumetric imperfection coefficient." This procedure has been discussed previously (*5*).

The general method to predict relative volatilities of a binary mixture employs the following equation:

$$\alpha_{1,2} = \frac{y_1x_2}{y_2x_1} = \frac{\gamma_1P_1^\circ\theta_2}{\gamma_2P_2^\circ\theta_1} \qquad (1)$$

where $P_1^\circ/P_2^\circ$ is the ratio of vapor pressures of the components; $\gamma_1$ and $\gamma_2$ are the activity coefficients in the liquid phase of the two components and $\theta_1$ and $\theta_2$ are "volumetric imperfection coefficients." These coefficients correct for deviations of the vapor from perfect gas behavior and for the effect of pressure on liquid fugacity.

A critical review was made of the vapor pressure data to be used in the prediction, since the ratio of the vapor pressures is the major factor in the calculation. Experimental data on the vapor pressure of isopentane are available in the literature (*2, 11, 12, 13*). The review and smoothing of the data were concentrated on the range between the boiling and the critical points.

The review and treatment of data for *n*-pentane were similar. The selection of smoothed data for this compound was simplified since available data (*2, 3, 10, 12, 13*) are in better agreement than those for isopentane.

The vapor pressure values for isopentane and *n*-pentane, which were accepted and used in this study, are listed in Table II.

Table II. Physical Properties of Isopentane and *n*-Pentane

(Selected and smoothed values used in the present work)

| | Isopentane | *n*-Pentane |
|---|---|---|
| Boiling Point, ° F. | 82.13 | 96.93 |
| Critical Temperature, ° F. | 370.0 | 385.9 |
| Critical Pressure, atm. | 33.2[a] | 33.31 |

| | ←Vapor Pressure, atm.→ | |
|---|---|---|
| Temperature, ° F. | Isopentane | *n*-Pentane |
| 20 | 0.254 | 0.176 |
| 40 | 0.412 | 0.294 |
| 60 | 0.642 | 0.469 |
| 80 | 0.961 | 0.717 |
| 100 | 1.388 | 1.058 |
| 120 | 1.953 | 1.514 |
| 140 | 2.68 | 2.11 |
| 160 | 3.59 | 2.87 |
| 180 | 4.73 | 3.82 |
| 200 | 6.11 | 4.99 |
| 220 | 7.77 | 6.42 |
| 240 | 9.74 | 8.13 |
| 280 | 14.77 | 12.56 |
| 300 | 17.91 | 15.35 |

[a] This assumed value of critical pressure for isopentane is between the two reported values (*11* ,*12*), and served best in the vapor pressure smoothing operation.

The volumetric imperfection coefficient, $\theta$, for each component in the mixture can be calculated from known physical properties of the pure components by the following expression:

$$\ln \theta_i = \frac{1}{RT} \int_{P_i^\circ}^{\pi} (\beta_i - V_{Li}) dP \qquad (2)$$

where $V_{Li}$ is the liquid molal volume of pure component $i$ expressed as a function of pressure, $P$, and $\beta_i$ is the vapor phase residual volume of this pure component where $\beta_i = V_i - RT/P$.

A more rigorous form of Equation 2 should contain the partial molal properties $\bar{V}_L$ and $\bar{\beta}_i$ instead of the properties of the pure compound $i$. It should also include more terms to account for changes in fugacity resulting from expansion or contraction due to mixing. However, it is believed that volume changes, in either phase, due to the mixing of these two close-boiling isomers, are negligible under the conditions of the present study and that the vapors may be considered ideally mixed.

The term $\beta$ may be related to pressure either by an equation of state or by compressibility data, thus making it possible to integrate Equation 2. For the present work, values of $\beta$ were calculated for isopentane and *n*-pentane from compressibility factors using the equation:

$$\beta = RT \frac{(Z-1)}{P} \qquad (3)$$

where $Z$ is the compressibility factor.

The values for $\theta_1$ and $\theta_2$ were calculated for selected temperatures and total pressures, $\pi$, by means of Equations 2 and 3. The temperatures and total pressures were selected to correspond to the experimental data so that the calculated relative volatility values could in turn be correlated with liquid composition and temperatures, and compared with the experimental relative volatility values.

The results from sample calculations of the ratio $\theta_2/\theta_1$ from generalized values of $Z$ (*7*), using Equation 2 and 3, agreed with those calculated using values of $Z$ picked from the literature (*1, 10, 11*). This finding justified the use of the smoothed values from the generalized chart, which simplified the calculations. Values of $\beta$ thus obtained were used in Equation 2 with literature data on $V_L$ (*1, 10, 12*) to calculate $\theta_1$ and $\theta_2$.

Table III. Comparison of Experimental and Calculated Relative Volatility Values for the Isopentane:*n*-Pentane System

| Temp., ° F. | Total Pressure, P.S.I.A. | Ratio of of Vapor Pressures[a] | Relative Volatility Isopentane/*n*-Pentane Calculated[b] | Experimental[c] |
|---|---|---|---|---|
| 125 | 26 | 1.29 | 1.26 | 1.26 |
| 150 | 41 | 1.26 | 1.23 | 1.23 |
| 175 | 60 | 1.24 | 1.205 | 1.21 |
| 200 | 81 | 1.22 | 1.18 | 1.18 |
| 225 | 110 | 1.21 | 1.155 | 1.16 |
| 250 | 147 | 1.19 | 1.135 | 1.14 |

[a] Using vapor pressures from Table II. [b] Predicted using $\alpha = [(Y_1/Y_2)\ (X_2/X_1)] = [(\gamma_1/\gamma_2)\ (P_1^\circ/P_2^\circ)\ (\theta_2/\theta_1)]$, where $(\gamma_1/\gamma_2)$ is assumed equal to unity. [c] From smoothed experimental curve of figure 2.

By substituting the calculated values of $\theta_1$ and $\theta_2$ in Equation 1, and assuming the ratio of the activity coefficients, for the liquid phase, $\gamma_1/\gamma_2$, to be unity, the corrected relative volatility values were calculated for the various conditions.

These values are compared with the experimental relative volatilities in Table III.

## CONCLUSIONS

The agreement between the experimental and theoretical values in Table III is considered to be excellent and illustrates that the ratio of activity coefficients for isopentane and *n*-pentane can be taken equal to unity, in accord with the conclusions of Redlich and Kister (*9*).

The availability of these accurate experimental values for the relative volatility of isopentane and *n*-pentane provides a check for the many theoretical methods for the prediction of vapor-liquid equilibria of close boiling mixtures. The agreement of the predicted values with the experimentally measured values given in this paper illustrates that accurate relative volatilities can be predicted provided adequate physical property data are available.

## NOMENCLATURE

$P$ = pressure
$P^\circ$ = vapor pressure of pure component
$R$ = gas constant
$T$ = temperature
$V_L$ = liquid molal volume
$V$ = vapor molal volume
$x$ = mole fraction of component in liquid phase
$y$ = mole fraction of component in vapor phase
$\alpha$ = relative volatility
$\beta$ = residual volume of pure component in vapor phase
$\gamma$ = activity coefficient of component in liquid phase
$\pi$ = total pressure of mixture
$\theta$ = coefficient correcting for liquid compressibility and for deviation of the vapor from a perfect gas

### Subscripts

1 = refers to low boiling component
2 = refers to high boiling component

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# Phase Equilibria in Hydrocarbon Systems.

# Volumetric and Phase Behavior of the *n*-Decane-$CO_2$ System

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**Experimental measurements of the volumetric and phase behavior of this binary system are reported at pressures up to 10,000 pounds per square inch in the temperature interval between 40° and 460° F.**

THE CONTINUED INTEREST of the production division of the petroleum industry in the use of $CO_2$ as at least one component of miscible displacement of hydrocarbon fluids within underground reservoirs makes a specific understanding of the volumetric and phase behavior of binary systems involving $CO_2$ and aliphatic hydrocarbons of importance. The volumetric behavior of the methane-$CO_2$ system has been studied at pressures up to 10,000 p.s.i.a. in the temperature interval between 100° and 460° F. (*16*). The partial volumetric behavior of the components of this system has also been established (*12*). Likewise the volumetric behavior of the ethane-$CO_2$ system has been investigated at pressures up to 10,000 p.s.i.a. at temperatures between 100° and 460° F. (*17*). The two foregoing studies did not involve any phase behavior investigations. More intensive studies of the propane-$CO_2$ (*20*) and *n*-butane-$CO_2$ (*11*) systems have been made. These investigations were carried out in both the homogeneous and heterogeneous regions at pressures up to 10,000 p.s.i.a. in the temperature interval between 40° and 460° F. in the case of the propane-$CO_2$ system and from 100° to 460° F. for the *n*-butane-$CO_2$ system. Throughout the above ranges of pressure and temperature only two phases have made their appearance. The volumetric behavior and the vapor pressure of $CO_2$ have been established by Michels and Michels (*10*) and Meyer and Van Dusen (*8*), respectively. Likewise, the volumetric behavior of $CO_2$ near the critical point has been studied in some detail by Michels, Blaisse, and Michels (*9*). The volumetric behavior at the higher pressures and temperatures has also been investigated (*4*). Earlier studies of binary systems of paraffin hydrocarbons and $CO_2$ were carried out by Kuenen (*5, 6, 7*), while the work of Poettman and Katz (*13*) confirmed the general behavior found by Kuenen. Poettmann and Katz (*13*) also reviewed to some extent the literature relating to binary mixtures of $CO_2$ and hydrocarbons.

There has been only limited work on systems involving $CO_2$ and pure hydrocarbons of higher molecular weight. For this reason, a study has been completed upon the volumetric and phase behavior of the *n*-decane-$CO_2$ system at temperatures from 40° to 460° F. and at pressures up to 10,000 p.s.i.a. throughout the entire range of composition.

## APPARATUS AND PROCEDURE

The apparatus and techniques employed in this investigation are similar to those used in an earlier study (*21*). Procedure consisted of introducing known weights of *n*-decane and $CO_2$ into a stainless steel container, the effective volume of which was varied by the introduction or withdrawal of mercury. The temperature of the stainless steel container was controlled by immersion in an agitated oil bath.

The temperature of measurement was related to the international platinum scale by use of a strain-free, platinum resistance thermometer. The latter instrument has been compared with the indications of a similar device calibrated by the National Bureau of Standards. Appropriate corrections for the influence of changes in room temperature upon the resistance of the coils of the Mueller bridge used in these measurements were made. Experience