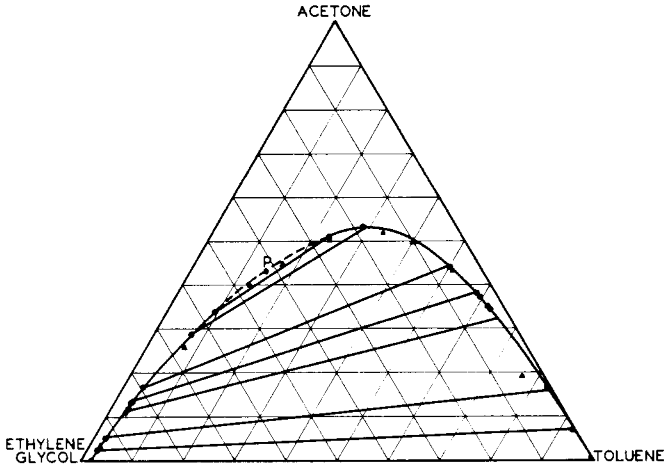

Figure 2. Liquid-liquid equilibrium at 0° C. for the system ethylene glycol–toluene–acetone
Points, raw data; lines, smoothed data; mole basis

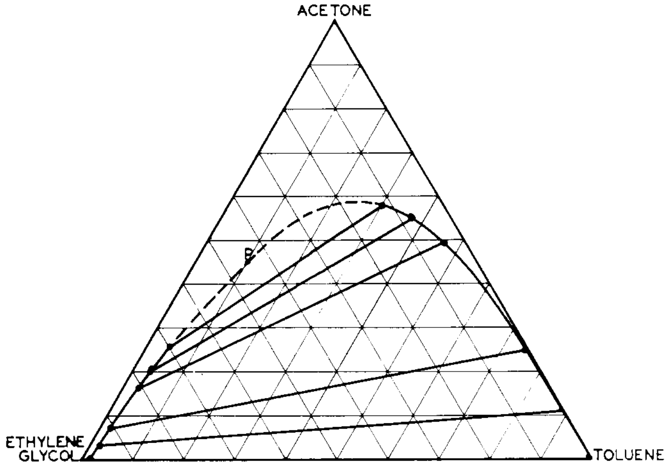

Figure 3. Liquid-liquid equilibrium at 24° C. for the system ethylene glycol–toluene–acetone
Circles, raw data; lines, smoothed data; triangles, Trimble and Frazer at 27° C.—all on mole basis

**Comparison with Previous Work.** The only previous work reported on this system is that of Trimble and Frazer (*3*) who present phase data and tie line data obtained at 27° C. Representative data from their work are shown as triangles in Figure 3. They made their determinations by turbidimetric procedures and reported their results in terms of volume per cent. Agreement between the two sets of data is good, except for ethylene glycol solubility in toluene at acetone concentrations below 40 mole %. Trimble and Frazer report only one datum point in this area, that of 4.3% ethylene glycol, 76.5% toluene, and 19.1% acetone. Since the phases appear to separate well in 5 to 10 minutes, (a faint blue-gray haze might be claimed) but require a much longer time for the toluene phase to reach a steady analysis, and since the data reported in this work were collected by a method designed to assure complete separation, it would appear that the data reported in this work are true equilibria. It is quite possible that the data of Trimble and Frazer accurately describe the separation which could be obtained in a continuous commercial process.

## LITERATURE CITED

(1) Kabel, R.L., Johanson, L.N., J. Chem. Eng. Data 6, 497 (1961).
(2) Treybal, R.E., "Liquid Extraction," 2nd ed., McGraw-Hill, New York, 1963.
(3) Trimble, H.M., Frazer, G.E., *Ind. Eng. Chem.* 21, 1063 (1929).

Received for review July 6, 1964. Accepted December 21, 1964.

# Virial Coefficients and Stockmayer Parameters for Propyne

JEROME BREWER
Midwest Research Institute, Kansas City, Mo.

EXPERIMENTAL *P-V-T* measurements on propyne at temperatures from 50° to 200° C. and at pressures to 315 atm. have been recently performed by Vohra and coworkers using a Beattie-type apparatus (*4*). The data were presented in a graph of compressibility factor *vs.* pressure for various isotherms. While this presentation is useful for many purposes, the data may be better analyzed in the low to moderate pressure regions by plotting $(Z\text{-}1)\,V$ *vs.* $1/V$. This analysis permits the determination of the second and third virial coefficients as well as a check upon the internal consistencies of the data. In this study, such an analysis was carried out for each isotherm.

The resulting values of the second virial coefficients were compared with the Lennard-Jones and the Stockmayer potentials using graphical methods. These graphical procedures allow one to determine whether a given potential fits the data in a single graph. Furthermore, if a fit is found, the parameters of the potential are easily determined from the same graph.

The Lennard-Jones intermolecular potential energy function is as follows:

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] \qquad (1)$$

in which $r$ is the distance between interacting chemical

**The second and third virial coefficients for propyne from 75° to 200° C. were determined graphically by means of isothermal plots of $(Z\text{-}1)V$ *vs.* $1/V$ from the experimental data of Vohra and coworkers. The second virial coefficients could not be correlated by the Lennard-Jones potential; however, they were correlated unusually well with the Stockmayer potential. The Stockmayer parameters were determined by a novel procedure which consisted of plotting $\epsilon/k$ *vs.* $t^*$ for several isotherms. All curves intersected at a common point yielding a unique set of Stockmayer parameters: $\epsilon/k = 954°$ K. and $\sigma = 2.28$ A. With these parameters, the calculated second virial coefficients were within 2 cc./mole or 1% of the experimental values. This deviation is probably within the accuracy of the *P-V-T* data. The deviation in the third virial coefficients appeared to be about 6%.**

species, and $\epsilon$ and $\sigma$ are the Lennard-Jones parameters. These parameters are constants characteristic of the interacting molecules. The parameter $\epsilon$ is the depth of the potential well, and $\sigma$ is the closest distance between molecules for a potential energy of zero. The parameter $\epsilon$ is frequently reported as $\epsilon/k$, where $k$ is the Boltzmann constant.

The Stockmayer potential, used for polar molecules, is the sum of the Lennard-Jones function and a term to account for the interaction of the two dipoles:

$$\phi(r, \theta_1, \theta_2, \phi_2 - \phi_1) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] - (\mu^2/r^3)\,[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos(\phi_2 - \phi_1)] \quad (2)$$

where $\mu$ is the dipole moment, and $\theta_1$, $\theta_2$, $\phi_1$, and $\phi_2$ describe the orientation of the two dipoles in space. The Stockmayer parameters are $\mu$, $\sigma$, and $\epsilon$ (or $\epsilon/k$).

## ANALYSIS OF *P-V-T* DATA OF PROPYNE

The isotherms of the *P-V-T* data can be conveniently analyzed by means of the virial equation of state expanded in the reciprocal volume series as follows:

$$Z = PV/RT = 1 + B/V + C/V^2 + D/V^3 \ldots \quad (3)$$

When the density of the gas is not very high, up to nearly the critical density, the virial equation of state may be truncated at the third virial coefficient and rearranged to give the following:

$$(Z\text{-}1)\,V = B + C/V \quad (4)$$

The data may then be analyzed by plotting $(Z\text{-}1)\,V$ *vs.* $1/V$. If the data are consistent, the plot should yield a straight line of slope $C$.

The analysis of the experimental data of propyne for a typical isotherm of 125° C. shown in Figure 1 illustrates the consistency between two runs with different mass samples. In general, reasonable consistency was shown by all of the isotherms except 100° C. The greater deviation in the data for the isotherms of 175° and 200° C. could be due either to errors in measurement or a slight polymerization of propyne.

The best visual fit was made for straight lines drawn through the data points. It is believed that the error resulting from such a procedure is negligible compared with the errors in the original data. For these plots, only the low pressure data were used. Care was taken not to use the higher pressure data for which those virial coefficients higher than the third would be necessary in the equation of state. When the higher pressure data were used, the departure of the data points from a straight line was easily observed and such data were ignored.

The second and third virial coefficients as determined from the aforementioned plots are given in Table I. The errors were estimated to be 1 cc./mole and 700 (cc./mole)$^2$, respectively. With the second virial coefficients available, an effort was made to determine whether these could be correlated with the Lennard-Jones and the Stockmayer potential functions.

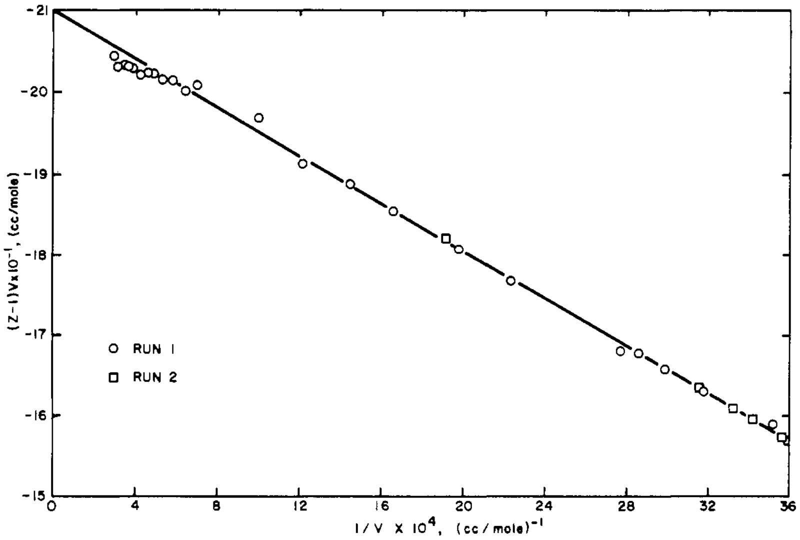

Figure 1. Compressibility isotherm of propyne for 125° C.

Table I. Experimental Second and Third Virial Coefficients of Propyne

| $t$, ° C. | $T$, ° K. | $(1/T) \times 10^{-4}$ | $B$, Cc./Mole | $C$, (Cc./Mole)$^2$ |
|---|---|---|---|---|
| 75 | 348.16 | 2.87 | −287.8 | 15120 |
| 100 | 373.16 | 2.68 | −244.0 | 15700 |
| 125 | 398.16 | 2.51 | −210.0 | 14750 |
| 129.25 | 402.41 | 2.48 | −203.6 | 14230 |
| 135 | 408.16 | 2.45 | −196.0 | 13500 |
| 140 | 413 | 2.42 | −191.1 | 13420 |
| 145 | 418 | 2.39 | −186.0 | 13150 |
| 150 | 423 | 2.36 | −182.8 | 13900 |
| 175 | 448 | 2.23 | −161.3 | 13350 |
| 200 | 473 | 2.113 | −144.0 | 13040 |

Table III. Comparison of Experimental vs. Calculated Values of Second Virial Coefficient Using Stockmayer Potential

| $T$ | $T^*$ | $B^*$ | $B_{\text{calcd.}}$, Cc./Mole | $B_{\text{exp}}$, Cc./Mole | $\left(\frac{B_{\text{calcd.}} - B_{\text{exp.}}}{B_{\text{exp.}}}\right) \times 100$ |
|---|---|---|---|---|---|
| 348.2 | 0.3655 | 19.3 | −289.5 | −287.5 | −0.6 |
| 373.2 | 0.3915 | 16.30 | −244.5 | −244 | −0.2 |
| 398.2 | 0.418 | 13.95 | −209.2 | −210 | +0.4 |
| 402.41 | 0.422 | 13.62 | −204.4 | −203.6 | −0.4 |
| 408.2 | 0.428 | 13.20 | −198 | −196 | −1.0 |
| 413.2 | 0.433 | 12.85 | −192.8 | −191.1 | −0.9 |
| 418.2 | 0.4385 | 12.47 | −187.0 | −186 | −0.5 |
| 423.2 | 0.4435 | 12.18 | −182.7 | −182.8 | +0.1 |
| 448.2 | 0.470 | 10.74 | −160 | −161.3 | +0.8 |
| 473.2 | 0.4955 | 9.60 | −144 | −144.0 | 0.0 |

## CORRELATION OF SECOND VIRIAL COEFFICIENTS

First, the data were tested to determine whether the Lennard-Jones potential could be fitted. The graphical procedure adopted permits a judgment on the quality of fit in a single graph. This was done using tabulated values of the Lennard-Jones potential (*2*). These tables contained reduced functions of the second virial coefficient, $B^*$, as a function of the reduced temperature, $T^*$, where $T^* = kT/\epsilon$, $b_0 = 2\pi N\sigma^3/3$, $B = b_0 B^*$ where $T$ is in degrees Kelvin and $B$ and $b_0$ are in cubic centimeters per mole.

For a given isotherm, $T$, the second virial coefficient, $B$, is obtained from the experimental data. A value of $T^*$ is arbitrarily chosen (entries in the table are chosen to avoid interpolation) from which $\epsilon/k$ is calculated. The corresponding value of $B^*$ taken from the table enables $b_0$ to be determined. This step is repeated for several other selected values of $T^*$. The resulting values of $\epsilon/k$ and $b_0$ are then plotted against each other for this isotherm. This process is repeated for other isotherms, and the resulting family of curves showed that there was no common point of intersection. Therefore, the Lennard-Jones potential does not fit the *P-V-T* data of propyne. One might have expected such a result since the propyne molecule is quite polar.

The next attempt to correlate the experimental data was to employ the Stockmayer potential (*3*). The value of the dipole moment was taken from the literature as 0.75 debye (*1*). In the Stockmayer potential, a new parameter, $t^*$, is used which is defined by

$$t^* = 8^{-1/2}\mu^2/\epsilon\sigma^3 \tag{5}$$

Preliminary trials indicated that the $t^*$ should be between 0.1 and 0.3, and that $T^*$ should be between 0.30 and 0.55 for propyne. To avoid errors arising from a linear interpolation of the tables for the Stockmayer potential (*2*), a graphical interpolation procedure was used. From these tabulated values two preliminary graphs were prepared, $B^*$ *vs.* $t^*$ with $T^*$ as a parameter and $B^*T^*/t^*$ *vs.* $T^*$ with $t^*$ as a parameter. The quantity $B^*T^*/t^*$ can be calculated from $B$, $T$, and $\mu$. This is shown by simply substituting the mathematical definition of each variable as follows:

$$\frac{B^*T^*}{t^*} = \frac{3T\epsilon\sigma^3 B}{(\epsilon/k)\,(8^{-1/2})\mu^2 2\pi N\sigma^3}$$

$$= \frac{BTk8^{1/2}\,(3)}{\mu^2 2\pi N}$$

$$= \frac{BT}{3231\mu^2} \tag{6}$$

In this last equation, the value of $\mu$ is to be expressed in debyes ($1 \times 10^{-18}$ e.s.u.). When one uses values of the second virial coefficient, $B$, and its corresponding temperature and the known value $\mu = 0.75$ debye, the function is readily evaluated. Values of $T^*$ are then obtainable for given values of $t^*$ from the preliminary graphs, and for each value of $T^*$ the corresponding value of $\epsilon/k$ is found. These calculations were repeated for four values of $B$ covering the entire range of the *P-V-T* data. The selected data points were taken at 200°, 150°, 100°, and 75° C. The results of these calculations are given in Table II. It is recognized that the second virial coefficient for 200° C. is not as reliable as those for the other temperatures, but its inclusion was necessary to represent the full range of the data.

A plot of $\epsilon/k$ *vs.* $t^*$ was made to determine whether a unique set of parameters exists for the given *P-V-T* data of propyne. As shown in Figure 2, such a set was found by the common point of intersection of the four selected isotherms, thus indicating a fit with the Stockmayer potential. The intersection of the four isotherms appears to be at a value of 954° K. for $\epsilon/k$ and a value of 0.1275 for $t^*$. These yield $\sigma$ = 2.28 A. and $b_0$ = 15.00 cc./mole.

Table II. Data of Stockmayer Parameters

(Using graphical interpolation)

|  | $t^*$ |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | 0.1 | 0.12 | 0.14 | 0.16 | 0.18 | 0.20 |
| $(T^*/t^*)B^*$ | $T^{*a}$ and $\epsilon/k^b$ |  |  |  |  |  |
| −37.5<br>($T$ = 473.2) | 0.6175<br>766 | 0.52<br>910 | 0.4625<br>1022 | 0.426<br>1110 | 0.403<br>1174 | 0.386<br>1225 |
| −42.55<br>($T$ = 423.2) | 0.5375<br>787 | 0.4625<br>915 | 0.419<br>1010 | 0.390<br>1085 | 0.373<br>1134 | 0.361<br>1172 |
| −50.1<br>($T$ = 373.2) | 0.457<br>816 | 0.404<br>924 | 0.374<br>997 | 0.353<br>1056 | 0.340<br>1097 | 0.334<br>1117 |
| −55.2<br>($T$ = 348.2) | 0.420<br>830 | 0.376<br>926 | 0.350<br>995 | 0.335<br>1040 | 0.324<br>1074 | 0.320<br>1088 |

[a] First value in column = $T^*$. [b] Second value in column = $\epsilon/k$.

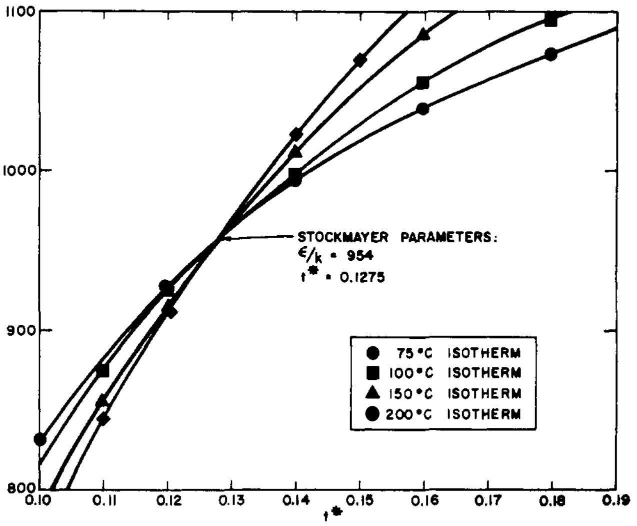

Figure 2. Determination of the Stockmayer parameters of propyne

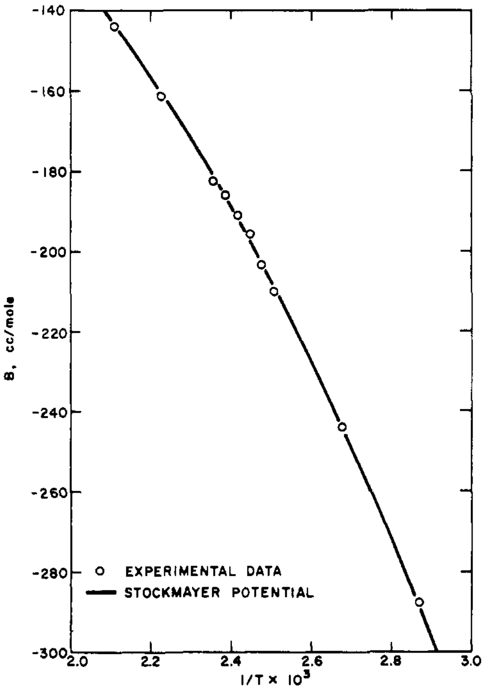

Figure 3. Second virial coefficients of propyne

With these Stockmayer parameters, a direct comparison of the original second virial coefficient data of propyne can be made with the Stockmayer potential. The results of these calculations are presented in Table III, showing that all calculated values of the second virial coefficient are within 1% of the values derived from the original $P$-$V$-$T$ data. The degree of fit is also shown graphically in Figure 3. The Stockmayer potential with the determined parameters of $\epsilon/k$ and $\sigma$ fit the derived second virial coefficients to a degree that is virtually equivalent to the accuracy of the original data.

The third virial coefficients were taken as the slope of $(Z\text{-}1)\,V$ *vs.* $1/V$ curves similar to that shown in Figure 1. The data points appear to be internally consistent within about 6%. The theoretical function of the third virial coefficient has not been evaluated for the low reduced temperatures involved in these data so, unfortunately, no comparisons could be made.

## ACKNOWLEDGMENT

The author is grateful to Midwest Research Institute for financial support of this work.

## NOMENCLATURE

$B$ = second virial coefficient, cc./mole
$B^*$ = reduced second virial coefficient = $B/b_0$
$b_0$ = co-volume, cc./mole = $2\pi N\sigma^3/3$
$C$ = third virial coefficient, (cc./mole)$^2$
$D$ = fourth virial coefficient, (cc./mole)$^3$
$k$ = Boltzmann constant
$N$ = Avogadro's number
$P$ = pressure, atm.
$r$ = distance between molecular species
$R$ = gas constant
$T$ = temperature, ° K.
$T^*$ = reduced temperature = $kT/\epsilon$
$t^*$ = Stockmayer parameter
$V$ = molar volume, cc./mole
$Z$ = compressibility factor = $PV/RT$

### Greek Letters

$\epsilon$ = parameter in Lennard-Jones and Stockmayer potentials
$\theta_1$ = orientation angle in Stockmayer potential
$\theta_2$ = orientation angle in Stockmayer potential
$\phi_1$ = orientation angle in Stockmayer potential
$\phi_2$ = orientation angle in Stockmayer potential
$\mu$ = dipole moment, debyes
$\sigma$ = parameter in Lennard-Jones and Stockmayer potentials

## LITERATURE CITED

(1) "Handbook of Chemistry and Physics," 39th ed., p. 2354, Chemical Rubber Publ., Cleveland, Ohio, 1957-1958.
(2) Hirschfelder, J.D., Curtiss, L.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(3) Stockmayer, W.H., *J. Chem. Phys.* **9**, 398 (1941).
(4) Vohra, S.P., Kang, T.L., Kobe, K.A., McKetta, J.J., J. Chem. Eng. Data **7**, 150 (1962).

Received for review July 13, 1964. Accepted January 25, 1965.