for six alkyltellurium compounds. These averages exclude three single occurrences: one tertiary mercaptan, one double branched alkyl selenide and one double branched alkyl diselenide. In eleven of 108 compounds errors in calculated b.p.s exceed $5.0^{\circ}$, namely: $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{SH}, 5.3^{\circ} ; \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}-$ $\left(\mathrm{CH}_{3}\right) \mathrm{SH}, 5.6^{\circ}, \mathrm{HS}\left(\mathrm{CH}_{2}\right)_{10} \mathrm{SH}, 5.1^{\circ} ;\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~S}, 6.1^{\circ} ;\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~S}_{2}$, $8.5^{\circ} ;\left(n-\mathrm{C}_{4} \mathrm{H}_{9}\right)_{2} \mathrm{~S}, \quad 7.7^{\circ} ; \mathrm{CH}_{3} \mathrm{SeH}, 6.1^{\circ} ;\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{Se}_{2}, 5.9^{\circ}$ $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{Se}_{2}, 5.9^{\circ} ; \mathrm{CH}_{3} \mathrm{TeH}, 5.9^{\circ} ; n-\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{TeH}, 6.6^{\circ}$.
Slight association through hydrogen bonding is the probable cause of a higher b.p.n. for sulfur in mercaptans and dithiols than in sulfides and disulfides.

With one exception, in single branched selenols, the greater the branching of the alkyl group or groups, the less the value of b.p.n. for sulfur, selenium, or tellurium. Selenium shows a relative constancy of b.p.n.; upon omission of the two lone occurrences, the b.p.n. $9.84-0.33 \mathrm{fits}$ the 14 alkylselenium compounds fairly well. In selenium there is less displacement of valence electrons than in tellurium, and also less association through hydrogen bonding than in sulfur. The tellurols, RTeH, have no association through hydrogen bonding, but have some slight displacement of valence electrons.

In the two comparable series of compounds RMH and RMR-in which M is sulfur, selenium or tellurium-the b.p.n. increases from sulfur to selenium to tellurium. Oxygen (2) varies too much for comparison.

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Received for review August 9, 1963. Accepted December 4, 1963

# Specific Volumes of $n$-Alkanes 

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#### Abstract

A table of the specific volumes of eight pure $n$-alkanes from seven to forty carbons in chain length is presented. The values are listed at seven even temperatures from ambient to $300^{\circ} \mathrm{C}$., and at eleven even pressures from ambient to 5000 bars. These values are believed to be accurate to within $0.2 \%$ for $97 \%$ of the specific volumes listed.


IN 1954-58, Simon and Cornish of Arthur D. Little, Inc., under contract to Union Carbide Corporation, made some very accurate measurements on eight pure $n$-alkanes over broad ranges of temperature and pressure. A sampling of these data was published in 1960 (1-3). The experimental method chosen by Simon and Cornish did not provide means for the direct calculation of the specific volumes from the measurements taken. Computer time was required in order to convert these measurements into specific vol-umes-thus, the delay in presenting these data for publication.

With the cooperation of S.S. Kurtz, Jr., of the Sun Oil Company, these calculations have now been completed and a table has been compiled (Table I) giving the specific volumes of eight pure $n$-alkanes from seven to forty carbons in chain length at seven even temperatures from ambient to $300^{\circ} \mathrm{C}$., and at eleven even pressures from ambient to 5000 bars. Although the precision of the measurements is at least $0.02 \%$, the overall accuracy for $97 \%$ of the specific volumes reported is believed to be of the order of $0.2 \%$.

The method of measurement chosen by Simon and Cornish was selected because it provided a very accurate
direct measurement of the length of the column in the piezometer. With this method, however, the mass of the sample contained in the piezometer could be measured with only one-tenth of this accuracy. It is not necessary to know the weight of the sample in order to compute the specific volumes-hence the limitation of the experimental method chosen lies only in the amount of machine time required to make these calculations.
Essentially, it is not necessary to know the weight of the sample in the piezometer because the computations described below deal with compressions which are dimensionless ratios entirely independent of the quantity of sample involved. Compressions are the ratios of the measured volumes to the hypothetical volume of the sample at the same temperature but at zero pressure. These ratios would be the same for any sample weight.
It has been explained in a prior publication (2) that the Hudleston equation:

$$
\begin{equation*}
\ln \frac{P v^{2 / 3}}{\left(v^{0}\right)^{1 / 3}-(v)^{1 / 3}}=A+B\left[\left(v^{0}\right)^{1 / 3}-(v)^{1 / 3}\right] \tag{1}
\end{equation*}
$$

may be used as a tool to extrapolate highly accurate
measurements of volume $v$ made under high pressures $P$ to the corresponding (hypothetical) volume $v^{\circ}$ at zero pressure. (If the measurements are not precise to at least $0.04 \%$, however, the value of the zero-pressure volume obtained by means of this extrapolation is uncertain and the method fails.) Since the piezometer tube is of uniform cross section, the volume of the contained sample is proportional to the length of the column of sample, which is measured as the distance $d$ between a steel float resting on the mercury column and a steel plug at the top of the piezometer. Therefore, the extrapolation to zero pressure may be made with the Hudleston equation using the $d$ 's as the variable just as well as with the $v$ 's. This is the principle of the first set of calculations. In carrying out the experimental procedure, it was simple to vary the pressure, but a considerable period of time was required to reach equilibrium after each change in temperature. Consequently, many "runs" were made consisting of a large number of pairs of measurements of pressure $P$ and distance $d$ at constant temperature $T$.

In prior publications (2-4), most of the results reported were based on calculations involving "duplicate points". That is, measurements of $P$ and $d$ on different samples of the compound, each taken at the same pressure and temperature. Since not very many of the measurements were taken at identical pressures and temperatures, the duplicate points represented only about $10 \%$ of the total number of measurements taken. In the prior publications, the results of duplicate point measurements were averaged, but in the present study no averaging or smoothing was introduced at this stage. Instead, each one of the 101 runs was analyzed as if it were a separate experiment, and $d^{\circ}$, the zero-pressure distance, was computed in each case. This was done by finding the best line through the points for each of a number of assigned values of $d^{\circ}$, then selecting the value of $d^{\circ}$ that gave the least Standard Percentage Error (SPE) in $d$. Once $d^{\circ}$ was known, the compressions ( $d / d^{0}$ ) were computed for each value of $d$ for each run. Conversion of compressions to specific volumes is straightforward at temperatures well below the normal boiling point, because the specific volume of a liquid at a given temperature at atmospheric pressure is substantially the zero-pressure volume of one gram of the substance at that temperature. This is so because liquids are so incompressible that an increase of pressure of from zero to one bar, at temperatures well below the normal boiling point, will not affect the specific volume by more than two units in the fourth decimal place. Thus $\beta=-\left[(1 / v) /(\partial v / \partial P)_{T}\right]$ has the following values for $n$-heptane (4) at $P=0$.

IBM listings giving the experimental values of $d$ and $P$ at each temperature of measurement for the 68 valid experimental runs have been deposited with the American Documentation Institute.

| $T,{ }^{\circ} \mathrm{C}$. | $\beta$ |
| :---: | :---: |
| 0 | 0.00011 |
| 30 | 0.00015 |
| 50 | 0.00018 |

Whence a change of one bar for $n$-heptane at zero pressure (specific volume approximately unity) could not exceed 0.0002 up to $50^{\circ} \mathrm{C}$. For higher molecular weight $n$-alkanes, the error is less. At temperatures well below the normal boiling point of each compound, therefore, the specific volumes were taken to be $1 / \rho$, in which the density $\rho$ was obtained from API 44 tables (5).

Volumes under pressure are merely the product of the zero-pressure volumes and the compressions. The zeropressure volumes are in the same ratio as the zero-pressure distances. Hence, at temperatures above the normal boiling points, the zero pressure volumes could be calculated from the known values at lower temperatures, provided only that the same sample weight was involved in all cases.

In some instances, different sample weights were used at the high and the low temperatures, and in these cases the equivalent zero-pressure distances were obtained from simulated sample weights calculated from other considerations.

In this manner, specific volumes were claculated corresponding to the $d$ 's for about two-thirds of the total number of runs made. These were put through the Hudleston equation routine to establish the degree of conformance to the smooth curve through all of the points for each run (SPE), and likewise in order to generate values of $v$ at even temperatures and pressures for use in subsequent calculations.

At this point, plots of $\ln v$ vs. $P$ were made for each of the 68 valid experimental runs that survived the first screening.

From these graphs, the one run for each compound at each temperature that appeareed to be most consistent with data at other temperatures was chosen. Thus, to this point in the research there had been no averaging or smoothing of the original measurements. Instead, the view was adopted that any of the 68 runs was just as likely to be accurate as any other. At this point, however, judgment was applied, based on the consistency of the $\ln v$ vs. $P$ plots, to decide which run to accept as "most accurate" at each level of temperature. The grand average SPE for the 46 "best" runs for the eight compounds at even temperatures between ambient and $300^{\circ} \mathrm{C}$. was $0.0234^{\sigma}$. This established the fact that the experimental measurements must be precise to at least this figure.

## MOLECULAR WEIGHT CORRELATION

The next step was to correlate these "observed" specific volumes with molecular weight using the equation:

$$
\begin{equation*}
\ln v=f(1 / m) \tag{2}
\end{equation*}
$$

A linear equation in $1 / m$ was generally satisfactory, although a second or third degree expansion was preferable for pressures below 200 bars, with $n$-heptane and $n$-nonane. There were a few points in the low pressure region where the agreement was not excellent, but for $97 \%$ of the cases, the average SPE of this correlation was $0.17 \%$.

Although the values that have been correlated with molecular weight are undoubtedly more accurate than the corresponding experimental values, the fact that there is this slight disparity between the "observed" and the "molecular-weight correlated" values indicates that the absolute certainty of the tabulated values could be in doubt by as much as $0.2 \%$ over $97 \%$ of the range of the variables.

## TEMPERATURE CORRELATION

The values of the specific volumes that were obtained from the molecular-weight correlation were chosen to represent the "true" values and are used in all subsequent claculations. These values were then correlated with temperature, using the following equation:

$$
\begin{equation*}
\ln [1+\ln (1+\ln v)]=f(T) \tag{3}
\end{equation*}
$$

A third degree expansion in $T$ gave a satisfactory fit in all cases except for $n$-heptane and $n$-nonane in the $0-100$ bar region, and $n$-undecane through $n$-heptadecane at zero pressure. The average SPE over the rest of the range ( $90 \%$ of the points) is $0.04 \%$.

## PRESSURE CORRELATION

A number of pressure correlation equations was tried, but none was found that would represent the variation
satisfactorily with a power series in $P$. Therefore, the pressure correlation was made with the Hudleston equation. Rejecting only one run ( $n$-heptane at $300^{\circ} \mathrm{C}$.) the pressure correlation gave an SPE of $0.10 \%$.

## RESULTS

Table I presents a set of specific volumes for eight pure $n$-alkanes from seven to forty carbons in chain length
at seven levels of temperature from ambient to $300^{\circ} \mathrm{C}$., and eleven levels of pressure from ambient to 5000 bars, that is believed to be accurate over $97 \%$ of the range to approximately $0.2 \%$.
The values listed are the experimental values (precise to $0.02 \%$ ) correlated against molecular weight. These molecular-weight correlated values were themselves correlated against temperature with agreement to $0.04 \%$ for $90 \%$ of the points, and against pressure with agreement to $0.10 \%$ over substantially the entire range.

Table I. Table of Specific Volumes
Correlated by Calculation from $\ln v v s .1 / m$ Lines
Temperature in ${ }^{\circ} \mathrm{C}$., pressure in bars, volumes in ml./gram


Table I. Table of Specific Volumes (Continued)
Correlated by Calculation from $\ln v$ vs. $1 / m$ Lines
Temperature in ${ }^{\circ} \mathrm{C}$., pressure in bars, volumes in ml./gram


Table I. Table of Specific Volumes (Continued)
Correlated by Calculation from $\ln v$ vs. $1 / m$ Lines
Temperature in ${ }^{\circ} \mathrm{C}$., pressure in bars, volumes in $\mathrm{ml} . / \mathrm{gram}$


## ACKNOWLEDGMENT

The assistance of the Sun Oil Company is gratefully acknowledged. The Sun Oil Company, Engineering Division computer staff, headed by J. R. Aicher, was most cooperative. C. S. Schrodel and Anne P. Castellan who programmed the calculations deserve particular credit. Without such assistance, this work could not have been completed.

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Received for review November 11, 1963. Accepted January 27, 1963. Material supplementary to this article has been deposited as Document No. 7816 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the number and by remitting $\$ 11.25$ for photoprints or $\$ 3.75$ for $35-\mathrm{mm}$. microfilm. Advance payment is required. Make Checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

