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Prediction of Absolute Entropies From Gas Chromatographic Retention Data

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ABSTRACT

Absolute entropies of compounds in homologous series of hydrocarbons, ketones, and alcohols have been found to be directly related to the logarithm of the retention volumes obtained from gas-liquid chromatographic measurements. Different liquid substrates and column temperatures have been employed in the collection of retention data. The retention volume method can be employed as a fast and relatively inexpensive way of predicting absolute entropies of organic compounds.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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PREDICTION OF ABSOLUTE ENTROPIES FROM GAS CHROMATOGRAPHIC RETENTION DATA

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INTRODUCTION

Over the years several physical parameters have been related to gas chromatographic retention data for homologous series of organic compounds. Purnell (1) summarizes some of the physical measurements that can be made by gas chromatography. Retention volume is the most widely used. It is defined as the volume of gas, measured at column outlet pressure and temperature, required to sweep the compound under consideration from the sample injector to the detector. James and Martin (2) in the original publication on gas-liquid chromatography showed that there existed a steady increase in retention volumes for members of a homologous series. Straight chain and iso-acids exhibited a constant increase for each CH_2 group added above four carbon atoms. Several authors have shown a similar effect for other homologous series extending over wide ranges in molecular weights (3-6). Other studies (7-9) have related the boiling points of compounds in homologous series to the logarithm of retention time or volume. These empirical relationships for homologous series involve "retention volume increments" (10), or what is referred to by James and Martin (3) as a "CH_2 separation factor," which are constant at any one temperature in a given stationary phase. The purpose of the present work was to investigate the possibility of establishing a quantitative relationship between chromatographic retention data and the absolute entropies of organic compounds—entropy being a more fundamental property of a substance than its boiling point or carbon number.

The absolute entropy data for compounds at various temperatures are sparsely located throughout the literature. The most exhaustive listing of entropies of hydrocarbons is found in the American Petroleum Institute Tables (11). By the use of entropy data and heat content, a highly valuable means is available for the determination of free energy changes and, hence, equilibrium constants for numerous reactions. Therefore, additional entropy data would be highly desirable.

The uncertainty of heat capacity data at low temperatures coupled with the necessity of having extremely pure samples make the determination of absolute entropies difficult. In predicting the entropy of organic compounds by retention data, it is not necessary to have pure compounds, as the method of gas chromatography separates the impurities from the compounds being studied. For the higher members of homologous series, the entropies of the compounds vary by a constant amount which is termed the entropy increment. Entropy increments are not constant for the first few members of the series.

The plot of absolute entropy versus the logarithm of retention volume for homologous series follows the general relationship of

$$\log V_R = AS^0 + B$$

where A and B are constant for a given homologous series under isothermal conditions, constant flow rate, and for a particular liquid phase. The other term V_R is the true

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retention volume which is defined as the volume of gas, measured at column outlet pressure and temperature, required to sweep the compound under consideration through the column, correcting for the dead volume of the system. The term S^0 is the absolute entropy. Most of the absolute entropy values used in this work are at 25°C, since entropies in the literature are almost exclusively given as a gas at 25°C. This method is not limited to entropies at 25°C, as is shown in the experimental portion of this report.

EXPERIMENTAL PROCEDURE

The hydrocarbons used in this study were obtained from Phillips Chemical Co., pure grade (99 mol-%), Scott Research Chemicals Laboratories, Inc., and Aldrich Organic Chemicals. The alcohols and ketones were from U.S. Industrial Chemicals Co., J. T. Baker Chemical Co., and Eastman Chemicals (white label).

Three different gas chromatographs were used to obtain the retention volume measurements: a Perkin-Elmer Vapor Refractometer Model 154C, an F and M Scientific Corp. Model 810, and a Beckman GC-2A, all equipped with flame and thermal conductivity detectors. The columns used in this work are listed in Table 1.

Table 1
Columns Used to Obtain Retention Data

Column	Mixture Separated
F and M Scientific Corporation's 15% Se 30 column 1/8 inch O.D. and 6 feet long	hydrocarbons
Perkin Elmer's diisodecyl phthalate column 1/4-inch O.D. and 2 meters long	hydrocarbons
A squalane (May and Baker Ltd.) column, 3.5% by weight on Chromsorb RZ (60/80 mesh) in 1/4-inch O.D. stainless steel tubing 3 feet long	hydrocarbons ketones
A Dow Corning 550 silicone oil loaded 15% by weight on Chromsorb P (30/60 mesh)	hydrocarbons
Polyethylene glycol 400 column loaded 15% by weight on Gas-Chrom R (60-80 mesh) in 1/4-inch O.D. stainless steel tubing 8 feet long	alcohols

The following mixtures of each homologous series were made: the normal, 2-methyl, 2,2-dimethyl, 2,3-dimethyl, and 3-methyl alkanes. Other mixtures were normal alkylbenzenes, normal alkylcyclohexanes, methyl alkyl ketones, normal alcohols, and the 1-alkenes. Mixtures of homologous series were made in order to correlate retention data better.

Small samples of the mixtures were used in order to get true retention data. The retention data for the components of the mixtures were corrected for dead volume but not for gas compressibility. The flow rates at the exhaust of the detectors were measured with a soap bubble flow meter in order to convert retention times to retention volumes. Chromatograms were run in duplicate and rechecked some weeks later to test the reproducibility of the method. The entropies determined by this method were completely reproducible.

RESULTS AND DISCUSSION

n-Alkanes

The normal hydrocarbons, propane through tetradecane, follow a straight line function when the logarithm of the true retention volume is plotted against the absolute entropy of the hydrocarbons as shown in Fig. 1. The absolute entropy values used are for the gaseous state at 25° C. The same type of straight line plot arises when using entropy values corresponding to the liquid state for a specific temperature. Figure 1 shows a plot of n-propane through n-octane eluted from a squalane column at 43.5°C, n-pentane through n-dodecane from a diisodecyl phthalate column at 140° C, and n-octane through n-tetradecane from a Se 30 column at 130° C. The retention times range from 10 seconds to an hour. As can be seen from the figure, the function is a straight line over the entire range. Numerous retention data values taken from the literature for various columns have been plotted against entropy and have also been found to give straight line plots for homologous series.

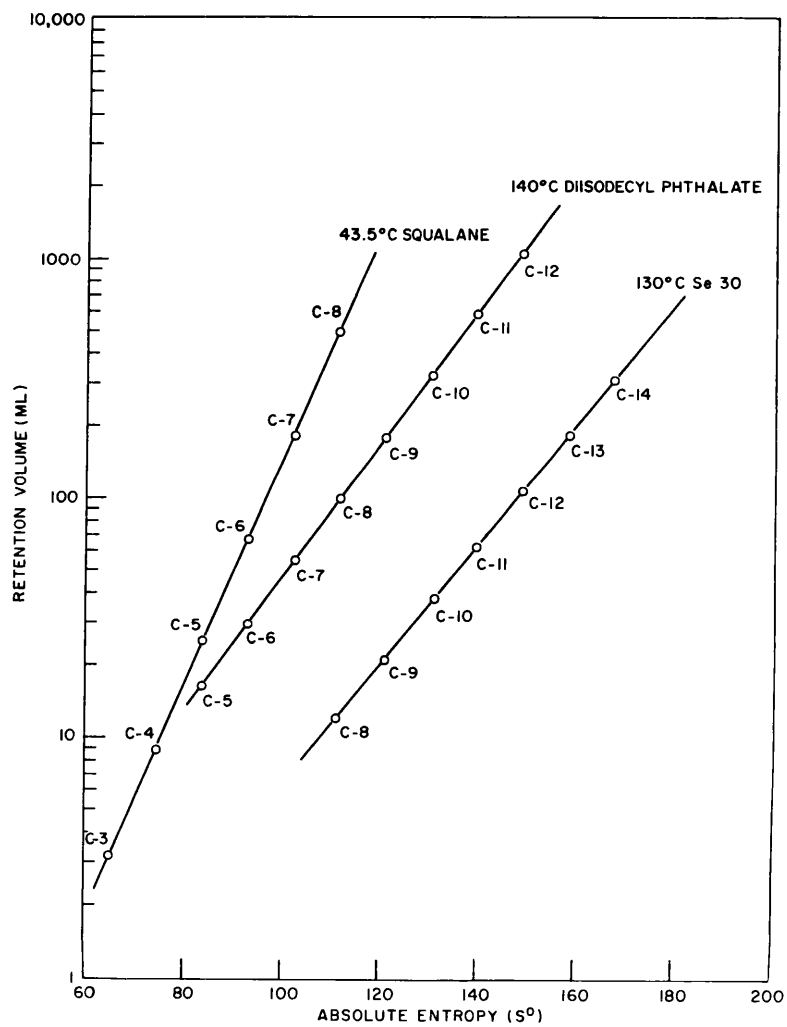

Fig. 1 - Relationship between absolute entropy and log retention volume for normal hydrocarbons with squalane, diisodecyl phthalate, and Se 30 columns

Over the extended ranges covered in this study, plots of the logarithms of retention volumes versus boiling points do not give straight lines, as is illustrated in Fig. 2.

For isothermal chromatograms of a given homologous series the slope of the entropy function plot depends on column temperature. Figure 3 shows the data for a mixture of hydrocrabons from n-pentane through n-nonane eluted from a squalane column at 40, 70, 100, and 130°C. The lines representing the data for these different temperatures converge at a common point, corresponding to C_0H_2. It is interesting to note that if entropy values corresponding to column temperatures are used, the convergence point corresponds to the absolute entropy range of hydrogen over these temperatures, as though hydrogen were the first member of this homologous series. The absolute entropy range for hydrogen from 40 to 130°C is 31.6 to 33.3 e.u.

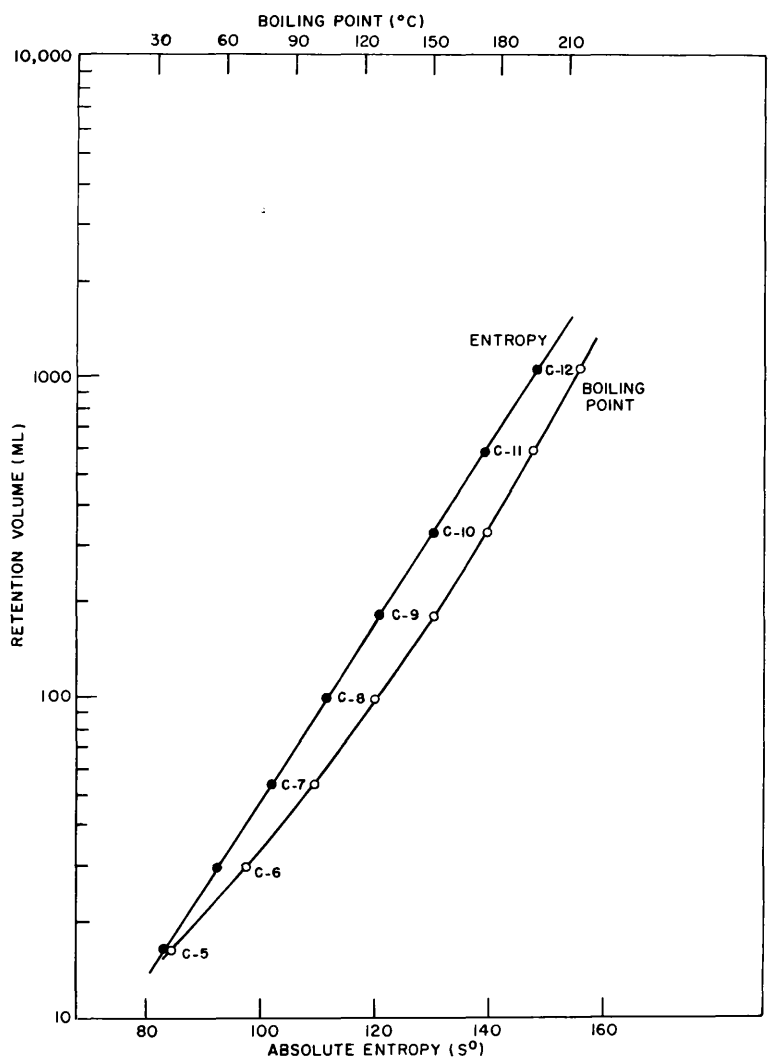

Fig. 2 - Comparison of entropy and boiling point versus log of retention volume for n-hydrocarbons on diisodecyl phthalate column at 140°C

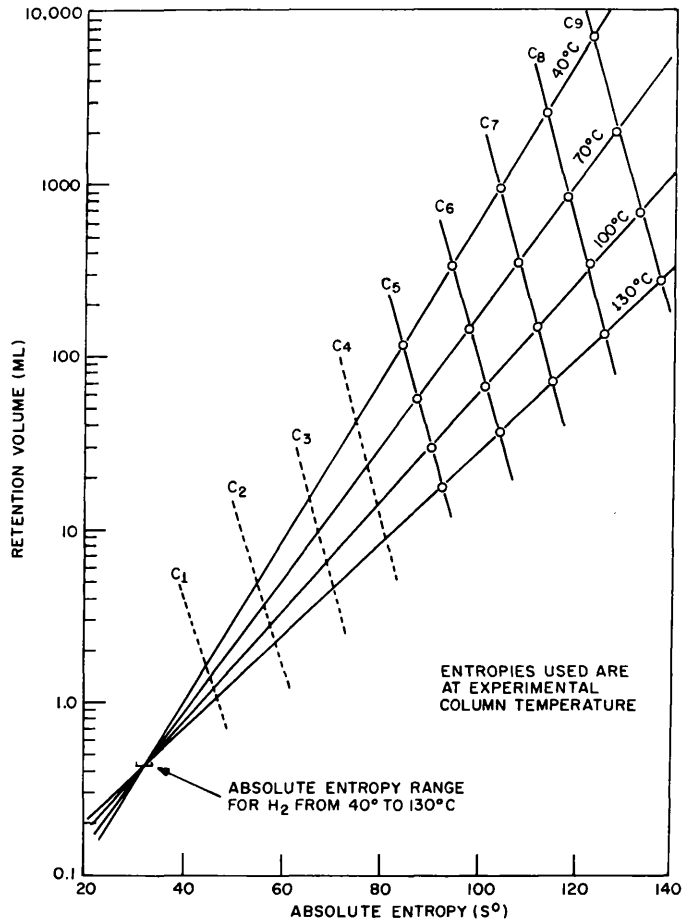

Fig. 3 - Effect of column temperature on log of retention volume versus absolute entropy

Other Hydrocarbons

In the case of branched hydrocarbons, including 2-methyl, 2,2-dimethyl, 2,3-dimethyl, and 3-methyl derivatives eluted under isothermal conditions from the same column, a series of parallel lines results from the plots of logarithm of retention volume versus the absolute entropy. Figure 4 shows this relationship with the 2-methyl series line to the right of the normal paraffin line, the other homologous series being to the left. The 3-methyl line is not shown, as it is very close to the 2,2-dimethyl line. A squalane column at 40° C was used for these separations.

By replotting Fig. 4 to encompass the longer retention volumes, it is possible to extrapolate the lines to estimate the entropies of compounds of higher molecular weight in the series, as is shown in Fig. 5. For example, predicted entropies for 2-methyldodecane and 2,3-dimethylheptane are given in Table 2.

The homologous series of α-olefins from propene through 1-hexene also follows a straight line when the logarithm of retention volume versus entropy is plotted as shown in Fig. 5.

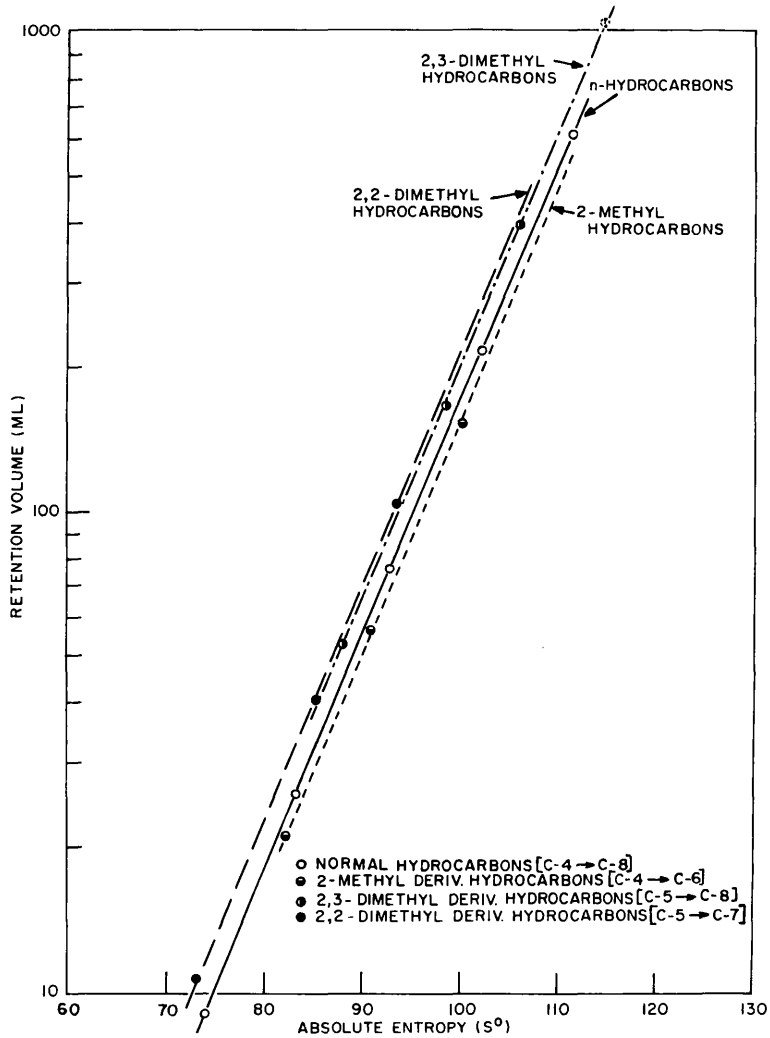

Fig. 4 - Parallel relationship of branched hydrocarbons to normal hydrocarbon series

The n-alkylbenzenes follow the same relationship as the other hydrocarbons as can be seen in Fig. 6. Benzene is the first compound in this series and is in line with the other members of the series. A useful tool for preliminary identification of unknowns in chromatographic work is the correlation of logarithm of retention volume with carbon number. In the majority of cases this yields a straight line, but in the case of the n-alkylbenzene series, benzene is out of line, as can be seen in Figure 6.

The retention data for the first two members of the n-alkylcyclohexane series do not lie on the line for the entropy correlation, as shown in Fig. 6. The carbon number plot for the n-alkylcyclohexane series is not shown, but the first two members of its series are also out of line with the others. No explanation is available for this apparent anomaly.

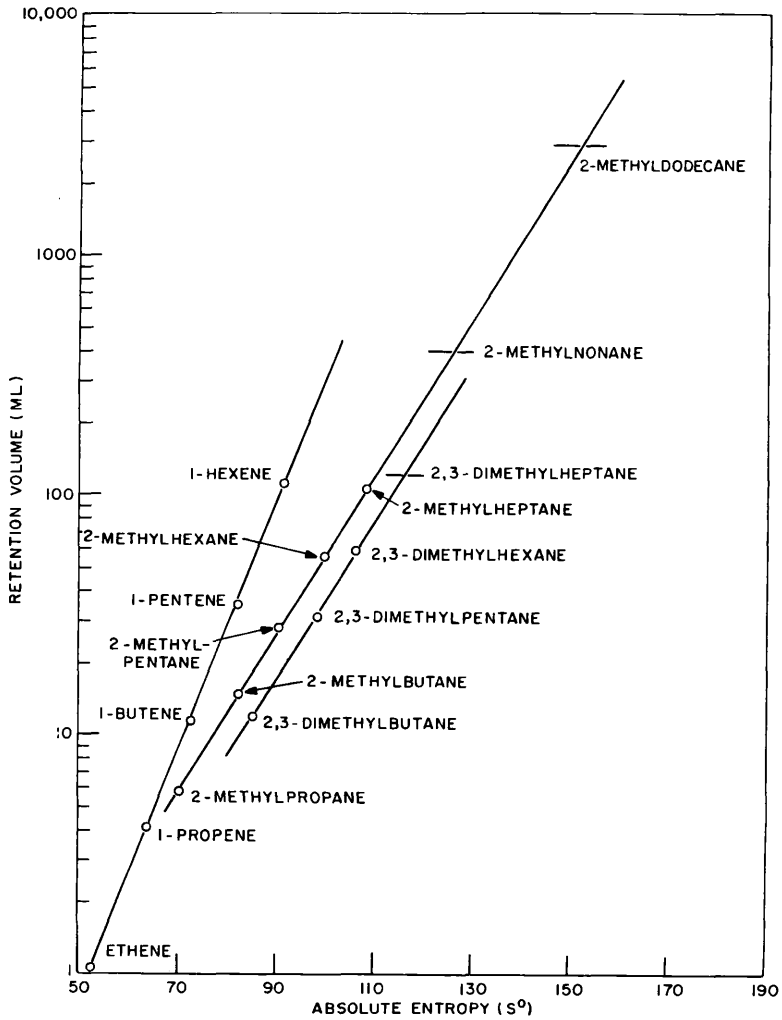

Fig. 5 - Prediction of entropies in homologous series from retention data

Table 2
Absolute Entropies (at 25°C) Predicted from Retention Volume Measurements

Compound	Entropy (e.u.)	State
2, 3-dimethylheptane	116	gas
2-methylnonane	126.3	gas
2-methyldodecane	152	gas
1-pentanol	62.7	liquid
1-hexanol	70.2	liquid
1-octanol	85.3	liquid

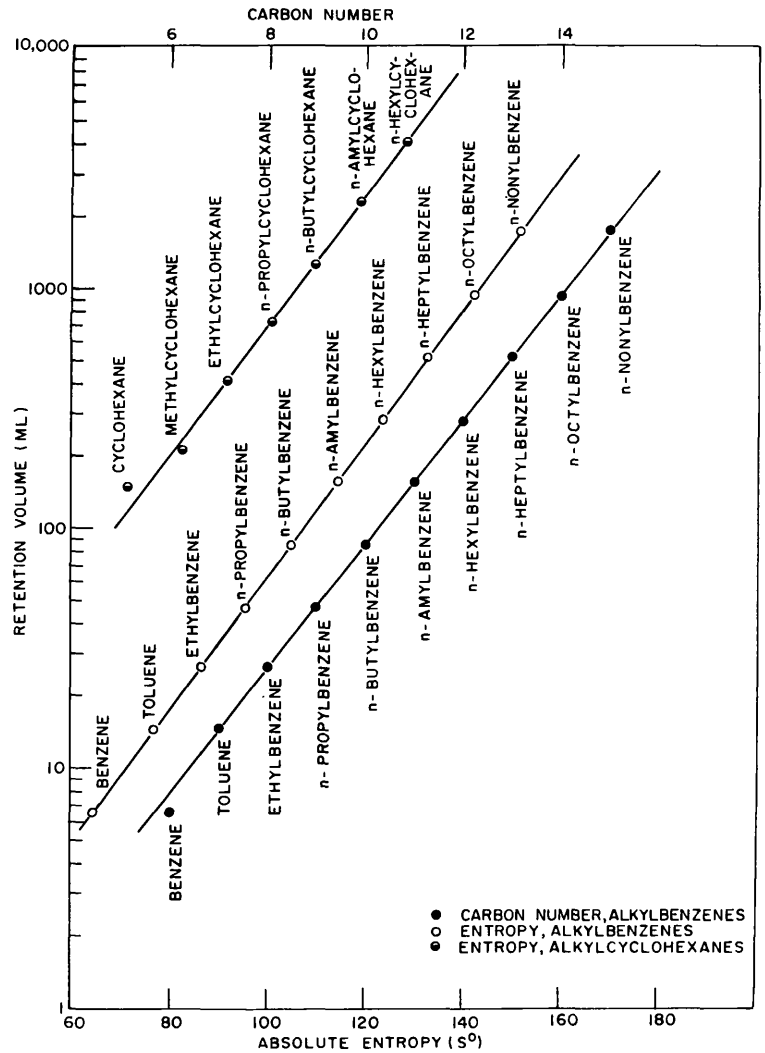

Fig. 6 - Correlation between log of retention volume versus absolute entropy and carbon number for n-alkylbenzenes with squalane column at 130° C and n-alkylcyclohexanes with DC 550 column at 130° C

Alcohols

In the alcohol series methanol shows a deviation from the rest of the series for the entropy plot, as can be seen in Fig. 7. This anomaly appears also in the work of Ray (6) for the boiling point plots. Methanol in the gaseous state exists as a tetramer (12). Since the retention data are for the gaseous state and the entropies are for liquid at 25°C, it is not surprising that methanol deviates from the series. The entropies used for plotting the alcohol series were: methanol 31.0 e.u., ethanol 38.4 e.u., 1-propanol 46.1 e.u., and 1-butanol 54.5 e.u. from data of Parks, Kelley, and Huffman (13); and 1-heptanol 77.9 e.u. from data of Parks, et al. (14). Chromatographically the alcohols are among the most difficult compounds to obtain Gaussian curves from, yet logarithm of retention volume versus entropy gives a straight line plot. By the extrapolation of the alcohol curve, the absolute entropies of other alcohols can be determined. Table 2 gives the

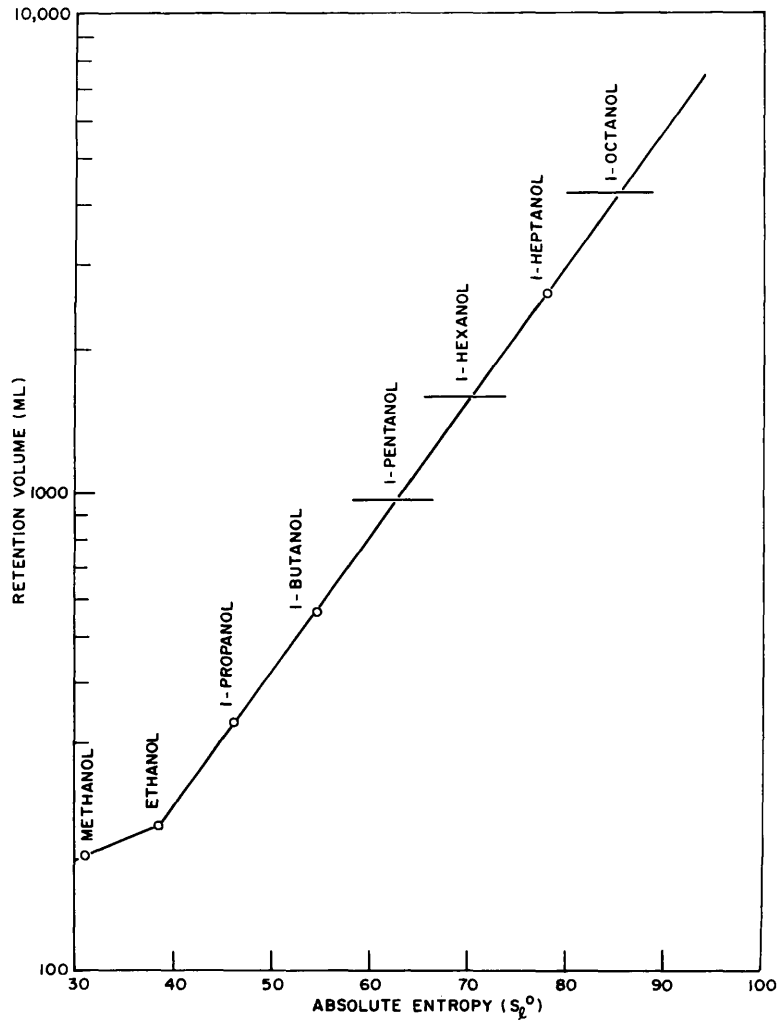

Fig. 7 - Relationship between absolute entropy and log retention volume for n-alcohols with polyethylene glycol column at 130°C

absolute entropies of the alcohols that were determined by this method and for which values could not be found in the literature.

Ketones

Using the entropy values of Oetting (15) for the methyl alkyl ketone series and their respective retention volumes from a squalane column, the same characteristic linear relationship results, as is seen in Fig. 8. This allows a further prediction of entropies in the series by extrapolation.

CONCLUSION

It has been shown that a plot of the logarithm of retention data versus absolute entropy gives a straight line for normal alkanes, 2-methylalkanes, 2,2-dimethylalkanes,

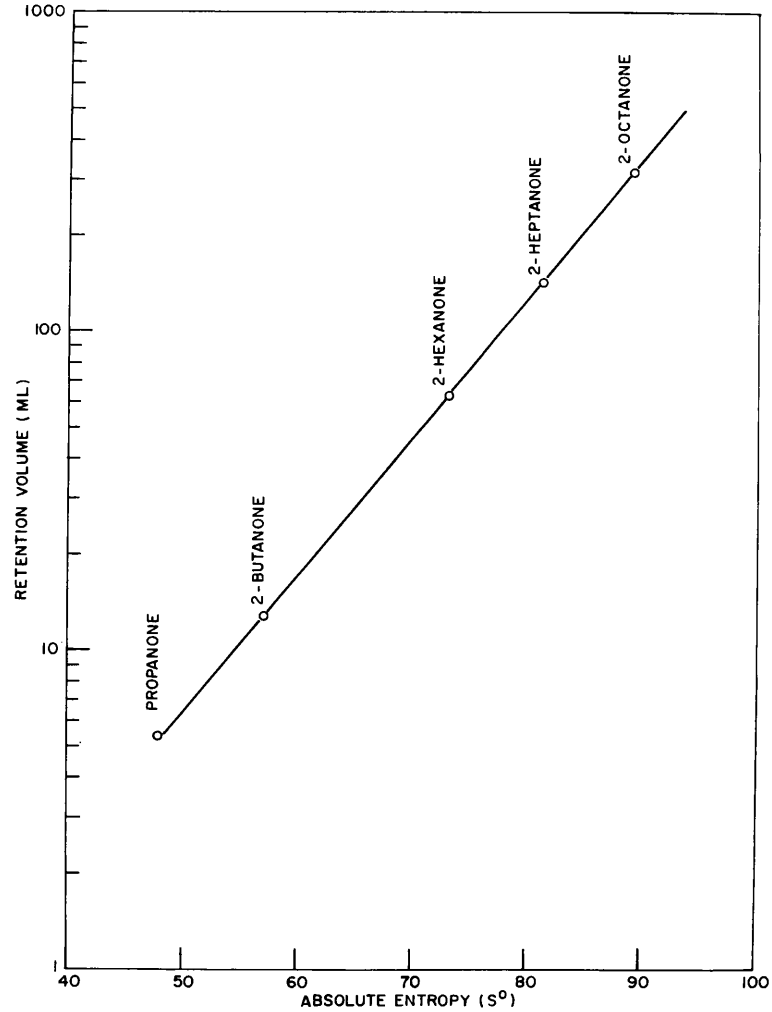

Fig. 8 - Relationship between absolute entropy and log retention volume for methyl alkyl ketone series with squalane column at 77°C

2,3-dimethylalkanes, 3-methylalkanes, α-olefins, normal alcohols (except for methanol), normal alkylbenzenes, normal alkylcyclohexanes (except for cyclohexane and methylcyclohexane), and methyl alkyl ketones. By the extrapolation of the above curves, one can obtain absolute entropy values for other members of these homologous series. The technique of extrapolating to obtain absolute entropies should hold for almost any series with the exception in some cases of the first two members of the series.

The carbon numbers and the boiling point curves are related to retention data by the empirical relation of retention increment for each CH_2 group added. The lower members of a series more often deviate from other members of homologous series in the carbon numbers and the boiling point curves than in the entropy relationships.

Entropy increments for homologous series have been realized for some time. Although the entropy increment is not constant for lower members of a series, as can be seen in Table 3, the retention-entropy relation is in most cases a straight line function even with lower members of homologous series.

Table 3
Absolute Entropy Increments

Compound	Absolute Entropy*	Entropy Increment
n-Alkanes		
Methane	44.50	
		10.35
Ethane	54.85	
		9.66
Propane	64.51	
		9.61
n-Butane	74.12	
		9.28
n-Pentane	83.40	
		9.43
n-Hexane	92.83	
		9.41
n-Heptane	102.24	
		9.31
n-Octane	111.55	
		9.31
n-Nonane	120.86	
2-Methyl Alkanes		
2-Methylpropane	70.42	
		11.70
2-Methylbutane	82.12	
		8.83
2-Methylpentane	90.95	
		9.40
2-Methylhexane	100.35	
		8.46
2-Methylheptane	108.81	

*From Ref. 11.

It is suggested that the branched chain derivatives of normal alcohols, ketones, cyclics, and aromatics should exhibit the same parallel characteristics as the branched derivatives of normal alkanes; thus, entropies could be predicted from retention data of the various series with the previous knowledge of only one entropy value for a particular series.

The facts that the entropy-retention volume relationship holds for such extended ranges of molecular weights for a series and that hydrogen appears to be the first member of the n-hydrocarbon series, imply that there may be a theoretical basis for the entropy-retention volume correlation. This is now under further study.

REFERENCES

1. Purnell, H., "Gas Chromatography," New York:John Wiley and Sons, p. 425, 1962
2. James, A.T., and Martin, A.J.P., Biochem. J., 50:679 (1952)
3. James, A.T., and Martin, A.J.P., J. Appl. Chem., 6:105 (1956)
4. Ogilvie, J.L., Simmons, M.C., and Hinds, G.P., Jr., Anal. Chem., 30:25 (1958)
5. Patton, H.W., Lewis, J.S., and Kaye, W.I., Anal. Chem., 27:170 (1955)
6. Ray, N.H., J. Appl. Chem., 4:21 (1954)
7. Porter, R.S., and Johnson, J.F., Anal. Chem., 33:1152 (1961)
8. Desty, D.H., and Whyman, B.H.F., Anal. Chem., 29:320 (1957)
9. Baumann, F., Straus, A.E., and Johnson, J.F., J. Chromatography, 20:1 (1965)
10. Beaven, G.H., James, A.T., and Johnson, E.A., Nature, 179:490 (1957)
11. American Petroleum Institute Research Project 44 Carnegie Institute of Technology, Pittsburgh, Pa.
12. Weltner, W., Jr., and Pitzer, K.S., J. Am. Chem. Soc., 73:2606 (1951)
13. Parks, G.S., Kelley, K.K., and Huffman, H.M., J. Am. Chem. Soc., 51:1969 (1929)
14. Parks, G.S., Kennedy, W.D. Gates, R.R., Mosley, J.R., Moore, G.E., and Renquist, M.L., J. Am. Chem. Soc., 78:56 (1956)
15. Oetting, F.L., J. of Chem. and Eng. Data, 10:122 (1965)

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13. ABSTRACT

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Alcohols						
Ketones						
Organic compounds						
Prediction						

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