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A DIRECT METHOD FOR HEAT OF
VAPORIZATION BY GAS-LIQUID
CHROMATOGRAPHY

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ABSTRACT

A DIRECT METHOD FOR HEAT OF VAPORIZATION BY GAS-LIQUID CHROMATOGRAPHY

by Joseph E. Schiller

An equation was derived which predicts that the heat of vaporization of a compound may be calculated from the change in retention time as a function of temperature in a gas-liquid chromatographic column. The retention time-temperature behavior of the compounds studied were compared with that of a reference compound from the same homologous series for which the heat of vaporization was known. From the ratio of slopes of the $\log$ retention time-reciprocal temperature plots of a compound and the reference, the heat of vaporization of the first compound was calculated. A squalane column was used, and data was obtained for n-paraffins, acetate esters, ethers, and haloalkanes. The method was shown to give suitable results for these families of compounds.

A DIRECT METHOD FOR HEAT OF VAPORIZATION
BY GAS-LIQUID CHROMATOGRAPHY

By

Joseph E. Schiller

A THESIS

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Table of Contents

	<u>Page</u>
Title Page	1
Acknowledgments	ii
Table of Contents	iii
List of Tables	iv
List of Figures	v
History	1
Theory	7
Experimental	11
Results and Discussion	15
Conclusion	28
Bibliography	29

List of Tables

<u>Table</u>		<u>Page</u>
1	Results for Heat of Vaporization	21
2	Results for n-Alcohols	23
3	ΔH of Vaporization and ΔH of Mixing of n-Alcohols	24

List of Figures

<u>Table</u>	<u>Title</u>	<u>Page</u>
1	Retention Time-Temperature Data for n-Paraffins	16
2	Retention Time-Temperature Data for Acetate Esters	17
3	Retention Time-Temperature Data for Ethers	18
4	Retention Time-Temperature Data for Haloalkanes	19
5	Retention Time-Temperature Data for n-Alcohols	22
6	Variation of Retention Time With Sample Size	26

History:

Gas chromatography has developed into one of the most powerful analytical tools available, with the separation and determination of mixtures as its major application. Gas chromatography, however, has been used to determine thermodynamic constants and physical properties by two distinct approaches.^{10,11} In the first case, the phenomena under study takes place outside the chromatographic system, and the chromatograph is used as a convenient analytical tool. Secondly, with the development of the theory of gas chromatography, it became evident that the direct measurement of thermodynamic constants and physical properties was possible.

The composition of the vapor over a solution as a function of solute concentration and temperature has been determined by gas chromatography.²⁵ A sample of the vapor above the solution was introduced into a gas chromatograph where the components were separated and determined. The partition isotherms of the systems studied have been determined by repeating the experiment with varied parameters.

The solubility of hydrocarbons in water has been determined¹² by passing helium carrier gas through a known volume of a hydrocarbon saturated aqueous solution

directly into the chromatographic column. Water was removed from the gas stream by a drying tube, and the remaining hydrocarbon passed to the detector. The results obtained were in good agreement with spectrophotometric measurements.

The heat of vaporization of gasses and liquids has been measured in the following way.^{8,14} A bulb containing the sample was connected to a bypass sampling system of known volume. The bulb and sampling system were thermostatted, and the sample was allowed to equilibrate with the previously evacuated bypass system. The sample in the fixed vapor volume was then passed through the column and determined quantitatively at the detector. The heat of vaporization was calculated using the Clausius-Clapeyron equation. For this technique, samples must be pure, and the compound studied must obey the Clausius-Clapeyron equation.

The direct determination of thermodynamic and physical quantities by gas-liquid chromatography has been done by treating the interaction of the sample and stationary liquid in the column as the solution of a gas in a liquid. The equations which describe the distribution of a vapor between the gas phase and the solution are thus applicable. These are combined with the

equation which relates retention volume and the partition coefficient for a chromatographic system.⁹ The heat of solution, heat of mixing, activity coefficient, partition coefficient, and several other quantities may be calculated directly from gas-liquid chromatographic data.¹⁰

The partition coefficient was first determined by Porter, Deal, and Stross.²³ A number of columns were prepared, and the parameters such as the flow rate of carrier gas, weight of liquid phase in the column, dead volume, etc. were known accurately. The retention volumes were corrected for pressure drop across the column. No comparison between the results published in this paper and previous measurements were made, but values for the partition coefficient were of a reasonable value. Further investigation has shown the approach of Porter, Deal, and Stross to be valid.^{10,11}

The partition coefficient is directly proportional to the Henry's Law constant, so solubilities may be calculated from gas-liquid chromatographic data. The solubility of benzene and cyclohexane in di-n-nonyl phthalate was determined by gas-liquid chromatography and found to be in excellent agreement with conventional measurements.¹⁸ More recently, the solubilities of group III, IV, and V hydrides were measured by Devyatykh, et.al.²⁴ using water as the stationary liquid phase.

The parameters of the system were known accurately, and the results for the solubilities were in very good agreement with previously published values.

It can be seen from equation 15 that the molecular weight of the stationary liquid may be measured if all of the other values in the equation are known. Martire and Furnell¹⁶ determined the molecular weights of three liquids of molecular weight approximately 300, 400, and 1200 respectively with good results and demonstrated the possibility of using gas-liquid chromatography to make this measurement.

Rearrangement of equation 15 yields an expression for the activity coefficient in terms of measurable quantities. The measurement of very large or very small activity coefficients may be made conveniently by this technique. A very large activity coefficient would be difficult to measure by conventional techniques because the solubility would probably be extremely low. In cases where results from gas-liquid chromatography may be compared with previously published results, there is excellent agreement.¹⁹⁻²² The measurement of activity coefficients by gas-liquid chromatography is sufficiently reliable that it has been suggested as an undergraduate experiment.¹³

Muhs and Weiss determined the formation constants of silver-olefin complexes in ethylene glycol using gas chromatography.¹⁵ The partition coefficient of the olefin with pure ethylene glycol was first determined. A solution of silver nitrate in ethylene glycol was made and used as the stationary liquid in a chromatographic column to determine the partition coefficient between the solution and the vapor phase. Since the concentration of silver nitrate in the ethylene glycol was known, the formation constant for the complex could be calculated.

The change in partition coefficient or retention volume with temperature for a given system allows the calculation of additional constants. It has been predicted and found experimentally that when the log of retention volume for a solute is plotted against reciprocal temperature that a straight line is obtained.⁹ The slope of this line is the heat of solution divided by $2.303R$. By determining experimentally the retention volume as a function of temperature for a given solute-solvent system, the heat of solution of the solute may be calculated. The heat of solution is composed of two terms, the heat of condensation and heat of mixing. If the heat of vaporization of the solute is known, the heat of mixing may be obtained by difference. However, if the solute and solvent form an ideal solution, the

heat of mixing is zero, whereupon the heat of solution equals the heat of vaporization.¹ This possibility for measuring heat of vaporization, however, is essentially restricted to hydrocarbons.

Vapor pressure as a function of temperature and the boiling point of the solute may be determined by an extension of the above. Hoare and Purnell¹ found that under the proper conditions, some families of compounds have a common log retention volume-log vapor pressure plot. The retention volume as a function of vapor pressure was measured for one member of such a series, and the retention volume as a function of temperature was measured for another compound in the series. The vapor pressure as a function of temperature and the boiling point were calculated for the second compound. Data were obtained for n-paraffins and n-olefins, and results were in good agreement with previously published results.

Theory:

When a vapor is dissolved in a liquid, the partial pressure of the vapor over the solution, P_A , is given by Roults Law:

$$(1) \quad P_A = P_A^{\circ} \beta X_A$$

P_A° is the vapor pressure of the pure solute, β the activity coefficient, and X_A the mole fraction of the solute in the solution. The mole fraction of the solute may be expressed by the equation.

$$(2) \quad X_A = \frac{N_A}{N_A + N_B}$$

If the solution is very dilute in component A, then

$$(3) \quad X_A \approx \frac{N_A}{N_B}$$

If V_B^m is the molar volume of the solvent, equation 3 may then be written:

$$(4) \quad X_A = \frac{N_A}{V_B} \cdot V_B^m = C_A^1 V_B^m$$

The partial pressure of A in the vapor phase may be expressed by the ideal gas equation:

$$(5) \quad P_A = \frac{N_A^V RT}{V_A^V} = C_A^V RT$$

Substituting equations 4 and 5 into 1,

$$(5) \quad C_A^V RT = P_A^{\circ} \beta C_A^1 V_B^m$$

Rearranging:

$$(7) \quad \frac{RT}{P_A^{\circ} V_B^m} = \frac{C_A^1}{C_A^V} = K_A$$

K_A is the distribution coefficient of component A between the solution and the vapor space over the solution. A Clausius-Clapeyron type equation for the vaporization of component A from solution is:

$$(8) \quad \beta P_A^O = e^{-\frac{\Delta H_s}{RT}} e^C$$

ΔH_s is the heat of vaporization of component A from solution. A constant (a) is defined as:

$$(9) \quad a = \frac{\Delta H_s}{\Delta H_V}$$

ΔH_V is the heat of vaporization of pure A. For component A the Clausius-Clapeyron equation is:

$$(10) \quad P_A^O = e^{-\frac{\Delta H_V}{RT}} e^{C'}$$

Combining equations 9 and 10:

$$(11) \quad P_A^O = (P_A^O)^a$$

Equation 7 may then be written:

$$(12) \quad K = \frac{RT}{(P_A^O)^{a_{VB}}}$$

For a gas-liquid chromatographic system, the interaction of the sample vapor with the stationary liquid is simply the solution of a gas in a liquid. The equation

$$(13) \quad V_R = KV_1 + V_d$$

gives a relationship between the retention volume and the distribution coefficient.²³ V_1 is the volume of the

liquid phase, and V_d is the dead volume in the chromatographic system. Combining equations 12 and 13:

$$(14) \quad V_R = \frac{RT V_1}{(P_A^0)^a V_1^m} + V_d = \frac{RT N^1}{(P_A^0)^a} + V_d$$

N^1 is the number of moles of the stationary liquid in the column. If the retention volume is corrected for dead space,

$$(15) \quad \hat{V}_R = \frac{RT N^1}{(P^0)^a}$$

T is the temperature when the solute passes through the column, and P^0 is the vapor pressure of the pure solute at temperature T . If F is the flow rate of the carrier gas and t_R the retention time, then

$$(16) \quad Ft_R = \frac{RT N^1}{(P^0)^a}$$

The flow rate measured at ambient temperature must be corrected to give the flow rate at the column temperature.³ Then:

$$(17) \quad t_R F_a \frac{T}{T_a} = \frac{RT N^1}{(P^0)^a}$$

T_a is the ambient temperature and F_a is the flow rate measured at this temperature. Cancelling like terms and rearranging:

$$(18) \quad t_R = \frac{RT_a N^1}{(P^0)^a F_a}$$

The usual correction of retention volume for pressure drop across the column⁴ need not be made. The reason

for this will be discussed shortly. Taking the logarithm of both sides of equation 18:

$$(19) \quad \log t_R = -a \log P^0 + \log \frac{RT_a N^1}{F_a}$$

Substituting equation 10 into 19:

$$(20) \quad \log t_R = \frac{a \Delta H_V}{2.3RT} + C + \log \frac{RT_a N^1}{F_a}$$

The term $C + \log \frac{RT_a N^1}{F_a}$ may be easily held constant.

A plot of log retention time versus reciprocal temperature should yield a straight line of slope $\frac{a \Delta H_V}{2.3RT}$ if data are obtained for retention time as a function of column temperature. The constant (a) has been found experimentally to be the same for each member of a homologous series.¹ If the heat of vaporization is known for one member of the series, the heat of vaporization of other members may be calculated from retention time-temperature data.

As indicated previously, the retention time was not corrected for pressure drop across the column. Since the change in retention time with temperature is of interest, multiplying the right side of equation 18 by a constant will not change the result.

Experimental:

To verify the equations derived above, retention time-temperature data were found for a number of homologous series of organic liquids. To obtain reliable data, the flow rate of carrier gas through the column and the column temperature had to be controlled precisely. The F&M Model 810 gas chromatograph (Hewlett-Packard, F & M Div., Avondale, Pa.) was found to be a suitable instrument for the study. The temperature in the column compartment was measured with a mercury thermometer accurate to $.1^{\circ}\text{C}$. After temperature equilibrium had been established in the column compartment, the temperature was found to vary less than $.1^{\circ}\text{C}$. A flow rate of approximately 40 ml/minute of Helium carrier gas was used, and the change in flow rate with temperature was found to be less than .1% for a 20°C change in column temperature. At constant temperature, no measurable change in the flow rate was observed. The flow rate was measured with a soap bubble flowmeter.

The column packing was prepared in the following way. Gas Chrom Q (Applied Science Labs, State College, Pa.), an acid washed, silanized, diatomaceous earth solid support was weighed accurately. The desired quantity of liquid phase was weighed and dissolved in a

suitable solvent. The solid support and the solution were put into a ribbed round bottom flask, and the flask was rotated as the solvent was removed under vacuum. The sides of the flask were washed down with the solvent, and the additional solvent was removed in the same way. The solid was then assumed to be coated uniformly with the liquid.

The Gas Chrom Q was 100-120 mesh, and 1/4 inch copper tubing was used for the column. A 4-foot column packed with 25% squalane (Eastman Organic Chemicals) on the solid support and a 5-foot column with 15% diisodecyl phthalate (Eastman Organic Chemicals) packing were made. The dead space in the instrument and column had to be determined since the column dead volume is not constant with temperature, and erroneous results would be obtained if these terms were neglected. The usual procedure for dead time correction is to measure the time between the emergence from the column of a compound not retained in the column and the emergence of the compound of interest. Methane was introduced with each sample since a flame ionization detector was used. This is the lowest boiling compound which will give a response with the detector used, and was found to be suitable, based on the following. From the retention time-temperature behavior of pentane, it was calculated that methane would be retained only 2.5 seconds at 40°C. More importantly, the change in retention time of methane with temperature

in the range of interest would be of the order of one second for a 100°C temperature change. No significant error was introduced into the results by assuming the retention time of methane to be essentially zero.

Retention time as a function of temperature was measured for n-paraffins, haloalkanes, ethers, and acetate esters using the column containing squalane. The n-alcohols were studied with the diisodecyl phthalate column because the retention time of the alcohols on the squalane column was too short for accurate data to be obtained. It also was of interest to see if the equations derived above could be applied when the stationary liquid was somewhat polar.

For each compound, the retention time was measured at at least four temperatures from approximately 10 degrees below the boiling point to approximately 10 degrees above the boiling point. The heat of vaporization at the boiling point was then calculated, and could be compared with previously published values.

The liquids to be measured were put in small vials and stoppered with a rubber septum. After standing for several hours, five microliters of the vapor above the liquid were withdrawn into a Hamilton ten microliter syringe. Approximately one microliter of natural gas was withdrawn from another container, and the contents

of the syringe were injected into the chromatographic column. A stopwatch was used to measure the time between the peak recorder response for methane and the sample. All measurements were made in duplicate.

Results and Discussion:

Data obtained for retention time as a function of temperature for the n-paraffins, acetate esters, ethers, and haloalkanes are plotted in Figures 1, 2, 3, and 4 respectively. The plots show very little scatter of the experimental points, and the slope of each line was determined by the method of least-squares.

The calculation of the heat of vaporization of each compound was done in the following way. One compound from each series was taken as a reference, and the slope of the retention time-temperature plot was calculated for each member of the series. Since the slope is proportional to heat of vaporization within a series, the ratio of the slopes for the unknown and reference compound was multiplied by the heat of vaporization of the reference compound. The result is the heat of vaporization of the unknown.

An alternate method of treating the data is to first determine the constant (a) for each series. This would be done by choosing a reference compound from each series and determining the retention time as a function of vapor pressure. Based on equation 19, a plot of the data would yield a straight line of slope $-(a)$. For other members of the series, a plot of the logarithm of

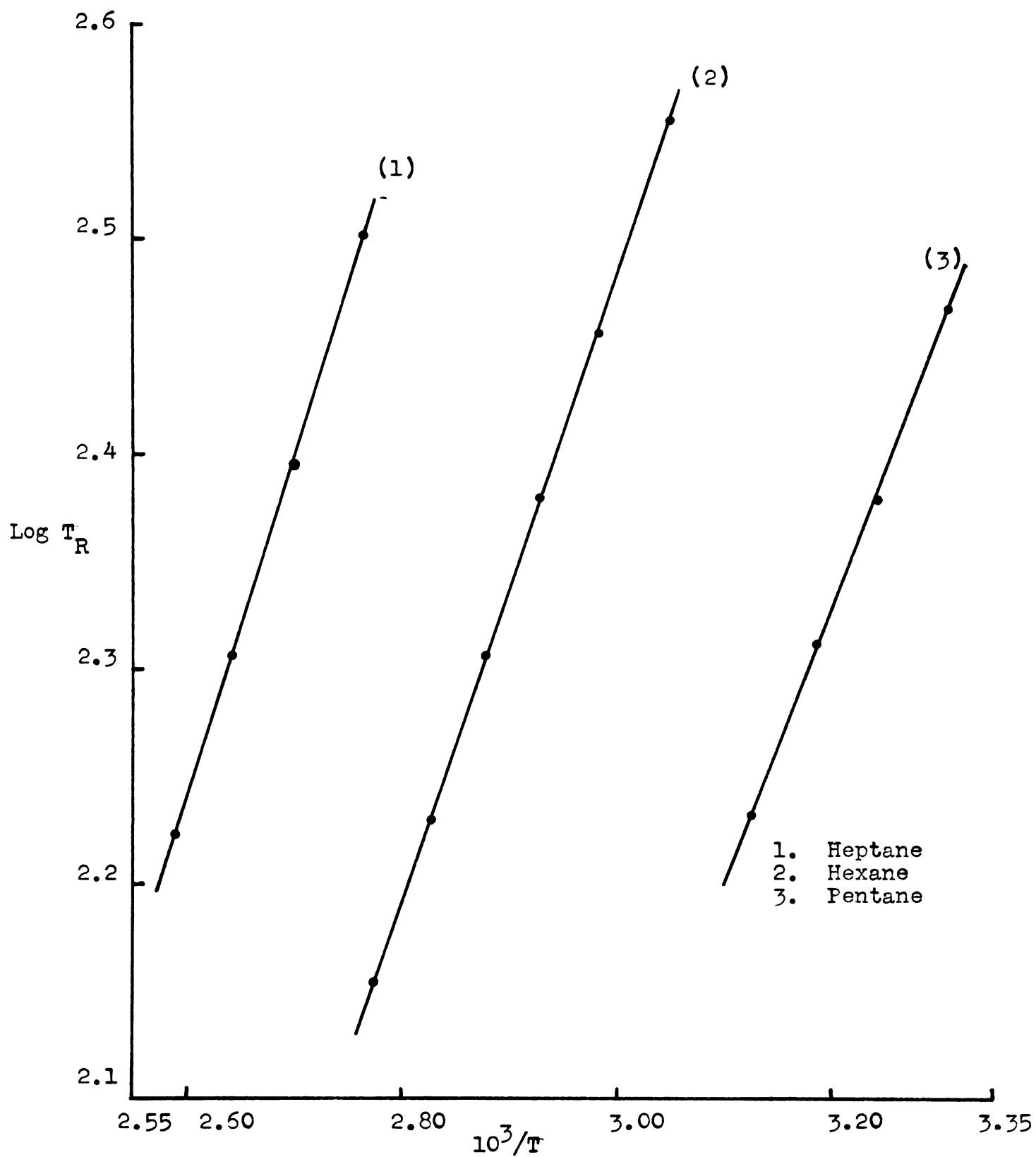


Figure 1. Retention Time-Temperature Data for n-Paraffins

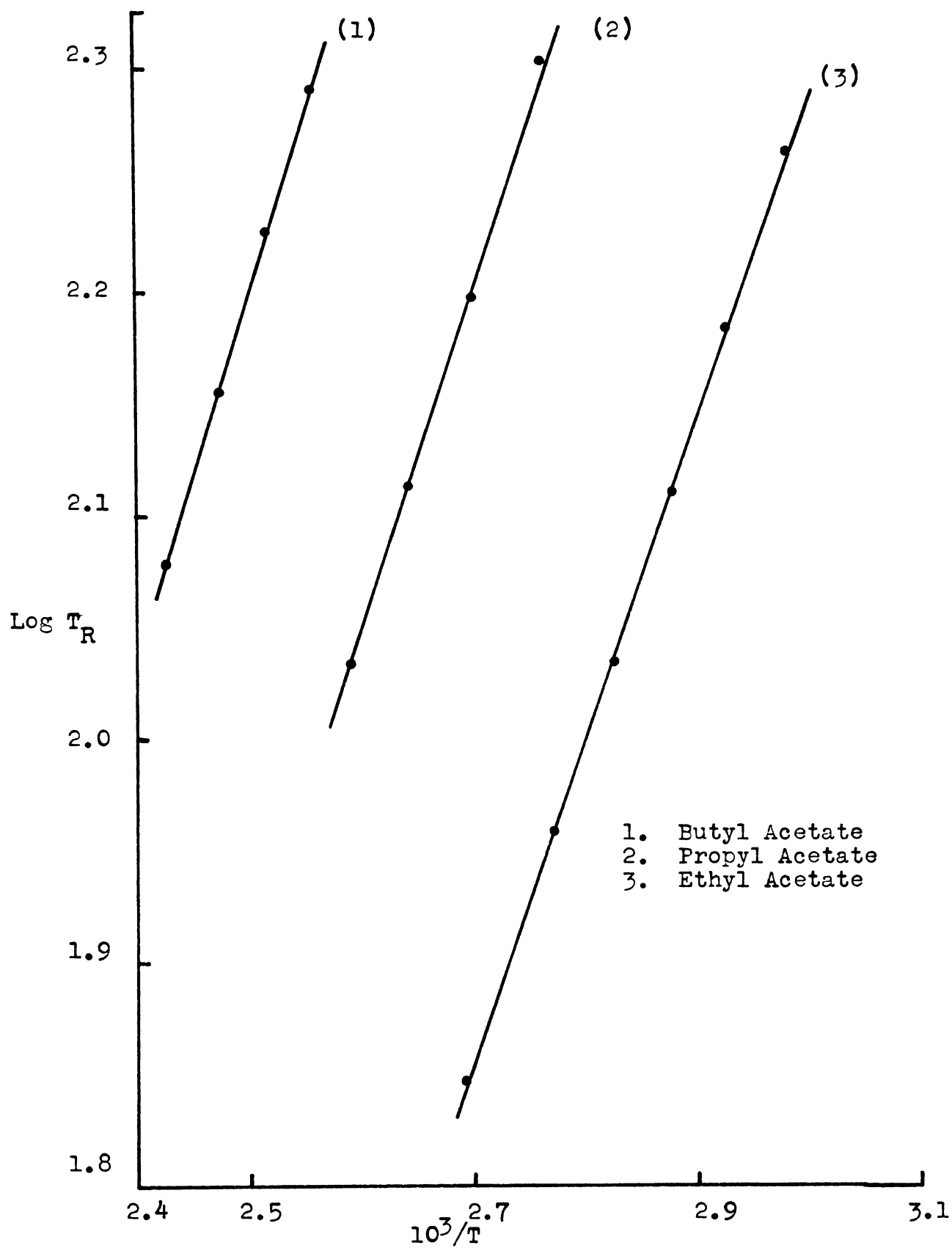


Figure 2. Retention Time-Temperature Data for Acetate Esters

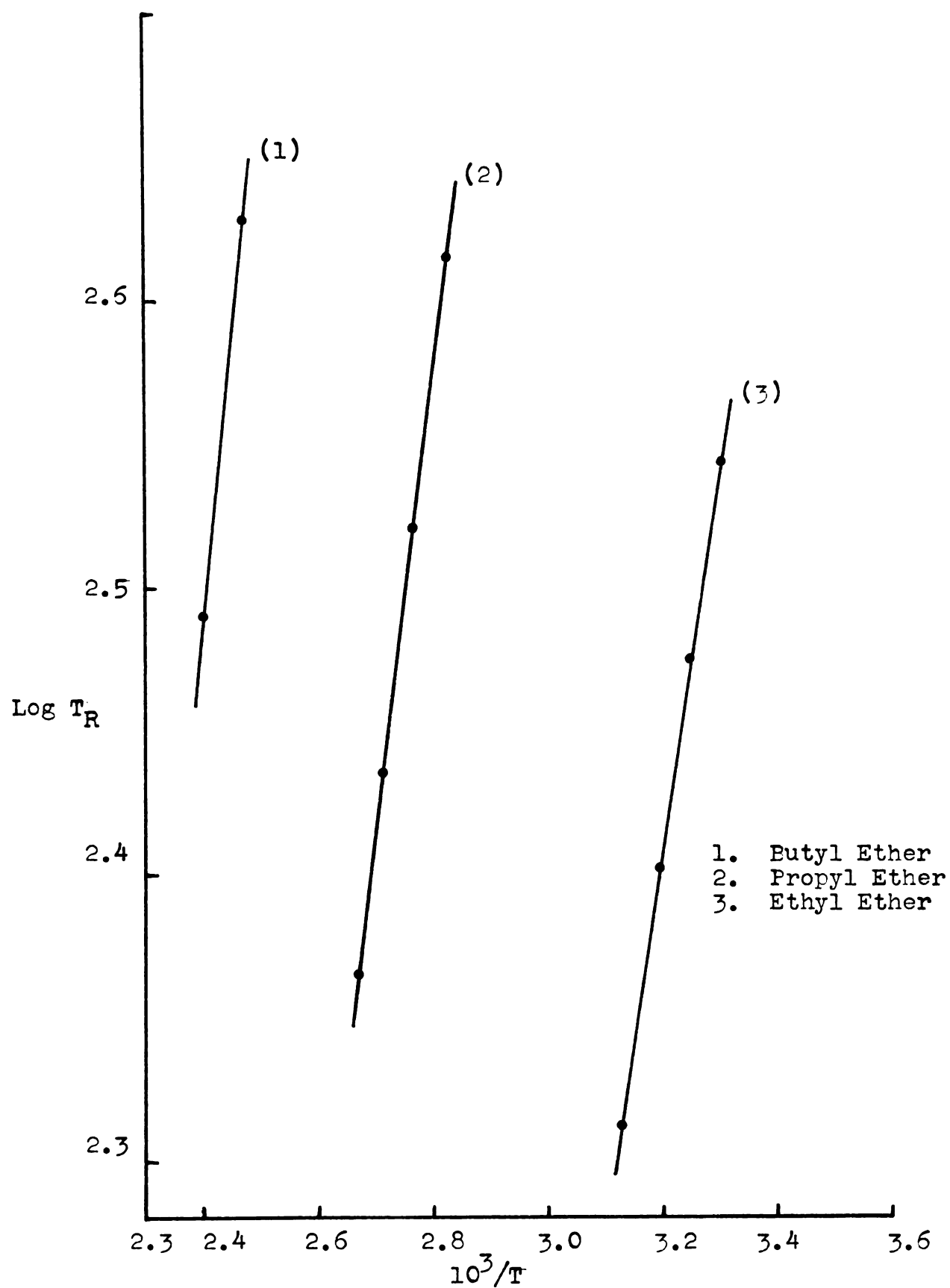


Figure 3. Retention Time-Temperature Data for Ethers

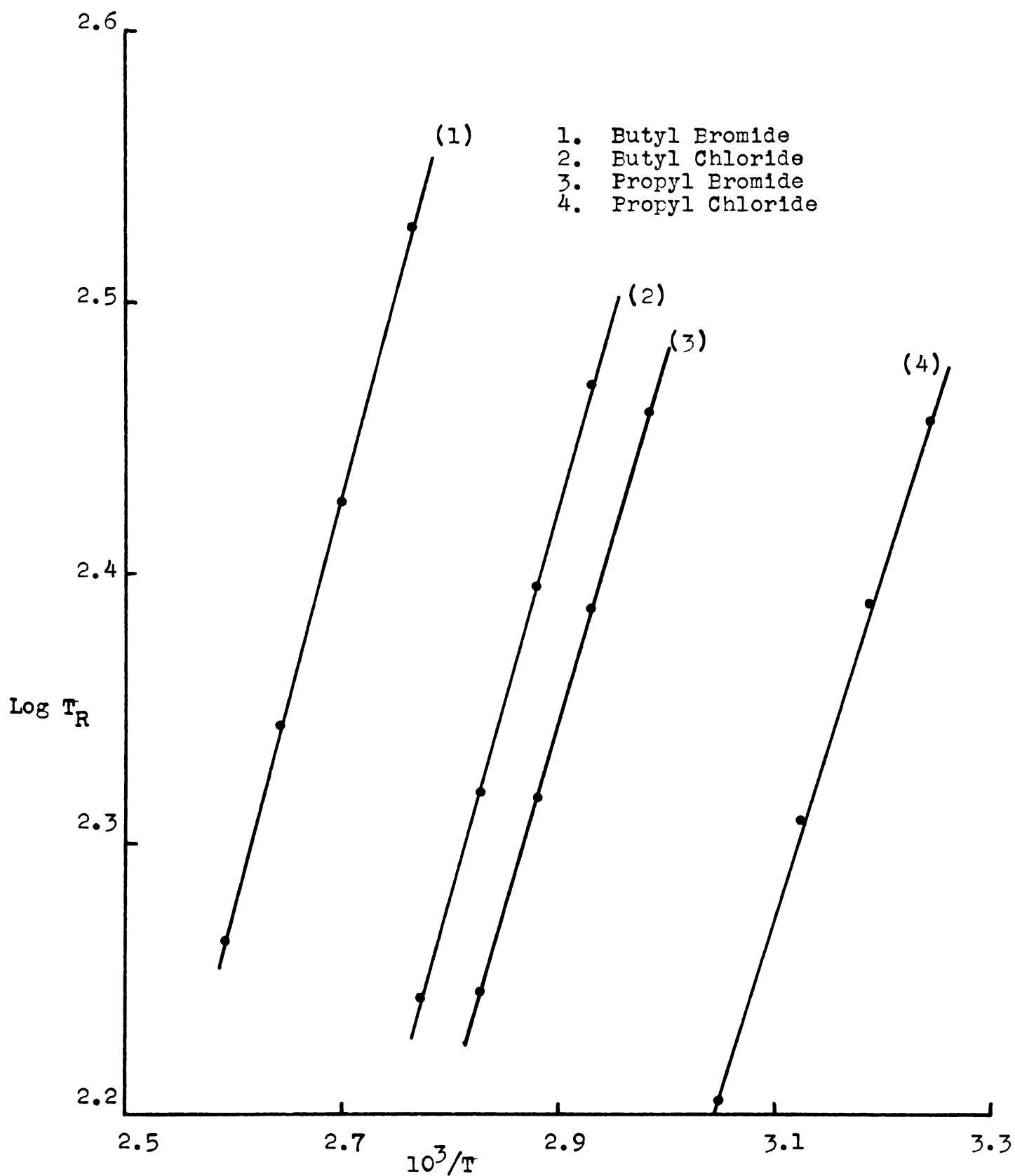


Figure 4. Retention Time-Temperature Data for Haloalkanes

the retention time versus reciprocal temperature has a slope of the value $a \Delta H_V / 2.3RT$. The heat of vaporization of the other members of the series could then be calculated, once (a) had been determined.

The first method is preferred for two reasons. First, very accurate vapor pressure data over the range desired are unavailable except for a few compounds which have been studied extensively. An additional error is also introduced by plotting vapor pressure at a given temperature rather than temperature directly.

The results for heat of vaporization are shown in Table I. There is excellent agreement between values obtained by the method described above and those obtained by conventional techniques. In fact, because assumptions were made in the derivation, (that the sample obeys the ideal gas law and the Clausius-Clapeyron equation) the results indeed are much better than would be expected. However, one would expect deviation from the ideal gas law and the Clausius-Clapeyron equation to occur approximately to the same degree within a series. The effect of these deviations is essentially eliminated, since a compound from the series is used as a reference.

Table I

<u>Compound</u>	<u>Slope</u>	ΔH <u>Experimental</u> <u>kcal/mole</u>	ΔH <u>Literature</u> <u>kcal/mole</u>	<u>Reference</u>
Pentane	1.28	6.05	6.16	5
*Hexane	1.46	—	6.90	5
Heptane	1.62	7.66	7.66	5
*Propyl Chloride	1.30	—	6.51	6
Propyl Bromide	1.39	6.96	6.98	6
Butyl Chloride	1.45	7.26	7.17	6
Butyl Bromide	1.55	7.76	7.61	6
Ethyl Acetate	1.47	7.74	7.76	2
*Propyl Acetate	1.56	—	8.21	5
Butyl Acetate	1.64	8.63	8.59	5
*Ethyl Ether	1.32	—	6.22	2
Propyl Ether	1.61	7.58	7.77	2
Butyl Ether	1.94	9.14	9.01	2

* Reference compounds

Retention time as a function of temperature was also determined for n-alcohols eluted from diisodecyl phthalate. A plot of the data is shown in Figure 5. Using ethyl alcohol as the reference compound, the heat of vaporization of the other alcohols was calculated. The results are shown in Table 2. In this case

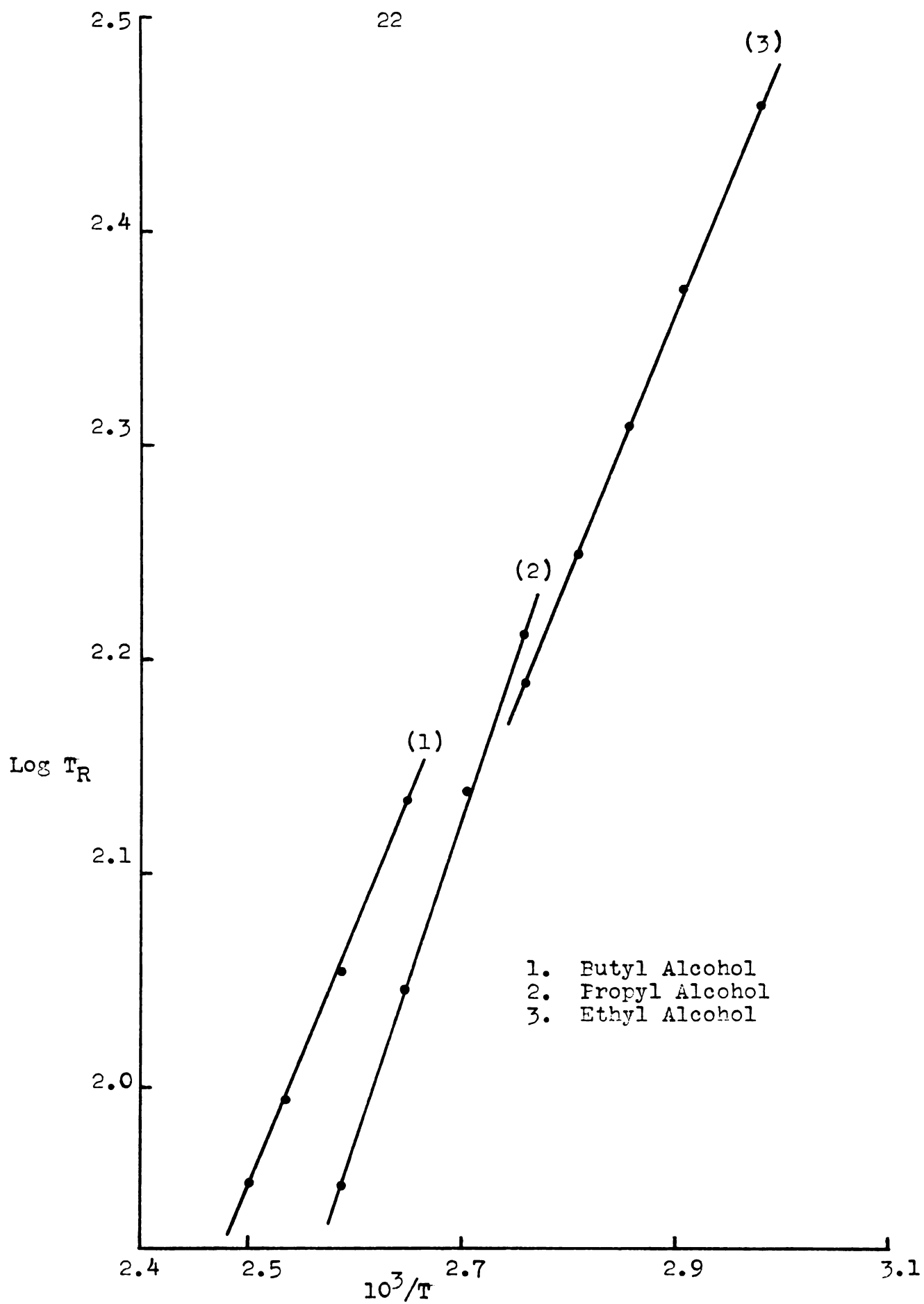


Figure 5. Retention Time-Temperature Data for Alcohols

there seems to be no correlation between experimental and accepted values for the heat of vaporization.

Table II

<u>Compound</u>	<u>Slope</u>	ΔH <u>Experimental</u> <u>kcal/mole</u>	ΔH <u>Literature</u> <u>kcal/mole</u>	<u>Reference</u>
Ethyl Alcohol	1.25	—	9.41	5
Propyl Alcohol	1.47	11.1	9.88	5
Butyl Alcohol	1.25	9.41	10.5	5

This, however, may be explained in the following way. Consider the solution of a rather polar gas in a nonpolar liquid. The heat of solution is composed of two parts, the heat of condensation and the heat of mixing. The constant (a) previously defined is of the form:

$$a = \frac{\Delta H_S}{\Delta H_V} = - \frac{\Delta H_V \quad \Delta H_m}{\Delta H_V}$$

Since the solvent can at most interact only slightly with the solute, the term ΔH_m arises mainly from removing the attractive forces between the solute molecules of a liquid which must be broken for vaporization to occur. Therefore, the term ΔH_m should be approximately a linear function of the heat of vaporization of the solute. Then (a) will be very nearly a constant over a wide temperature range.

In the case where both the solute and solvent are somewhat polar, the heat of mixing then is affected by considerable solute-solvent interaction. The heat of mixing is then not a simple function of ΔH_V of the solute, and therefore the constant (a) would vary with temperature. Reliable results then could not be expected for heat of vaporization by the method described above when a polar solvent is used.

To support the conclusions stated above, no accurate data from the literature could be found for the heat of mixing of polar compounds in hydrocarbons. For the heat of mixing of n-alcohols in diisodecyl phthalate at 100°C, Forter, Deal, and Stross obtained the results shown in Table III.²³

Table III

<u>Compound</u>	<u>ΔH Vaporization</u>	<u>ΔH Mixing</u>
Ethyl Alcohol	9.41	4.61
Propyl Alcohol	9.88	1.41
Butyl Alcohol	10.5	1.80

Again, there is no correlation between heat of mixing and heat of vaporization. This is probably due to solute-solvent interactions.

There is an additional point worthy of note which became evident during the course of this work. As indicated in the derivation, the sample size taken to determine retention time must be small so that a very dilute solution will result. The method used in this work was to introduce a very small amount of the sample into the chromatographic column. The alternate, and more widely used procedure, is to determine the retention time for a number of rather large sample sizes. The retention time as a function of sample size is found and a plot of the data is extrapolated to zero sample size. The retention time at zero sample size is assumed to be that for an infinitely dilute solution.

It was found, however, that there is no simple relationship between sample size and retention time when extremely small samples are used. This was observed also by Urone and Parcher.¹⁷ Data are shown in figure 6 for retention time as a function of sample size for propyl alcohol and chloroform eluted from squalane on Gas Chrom Q. As indicated by the plot, the extrapolation does not give the retention time for an infinitely small sample.

A solute in a chromatographic column is retained by both the solid support and the stationary liquid.

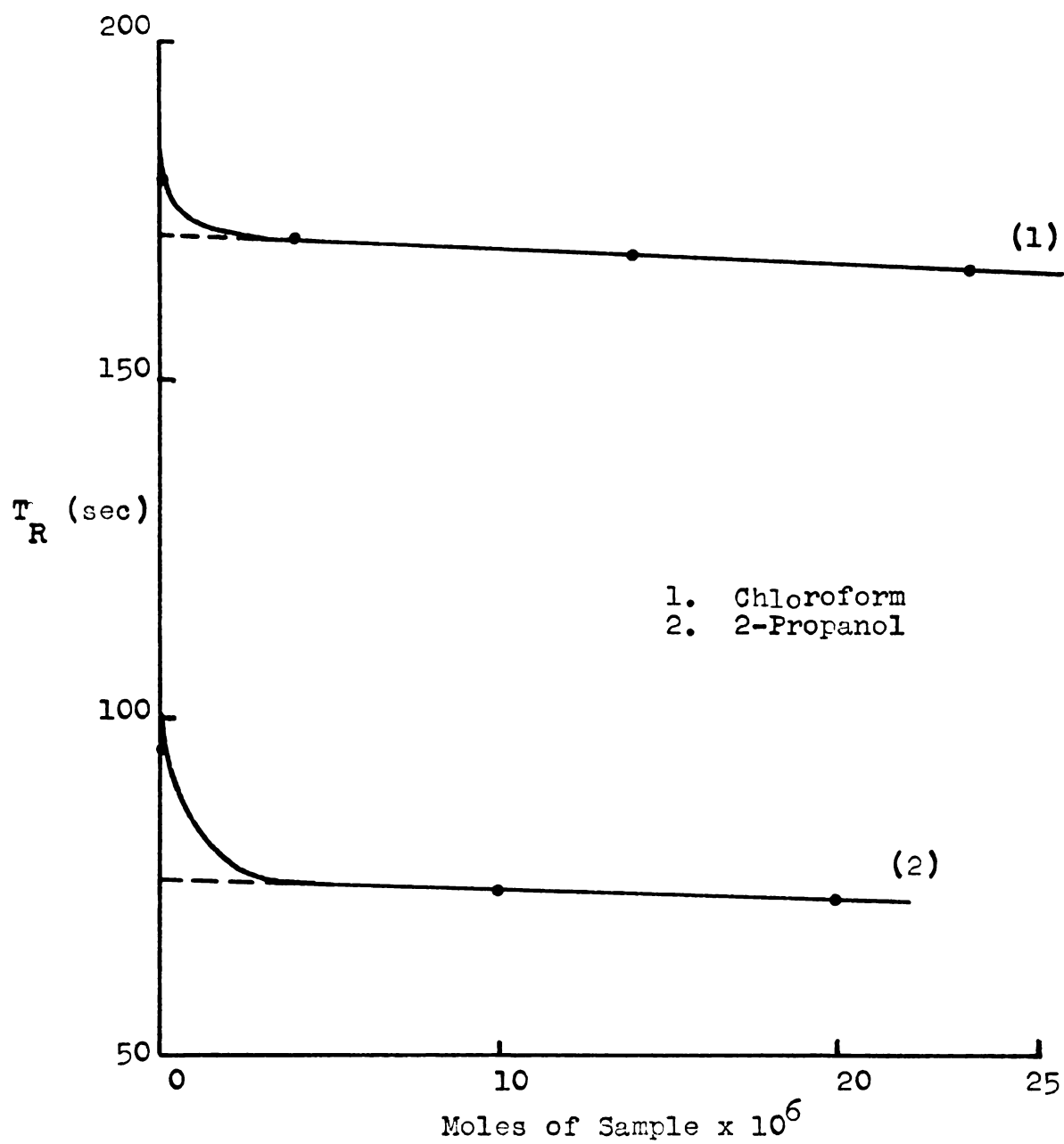


Figure 6. Variation of Retention Time With Sample Size

Even a very inert solid support has some active sites which may adsorb sample molecules. When a rather large sample is eluted from a column in which the solid support is quite inert, the solid support appears to have no effect on the retention time. This occurs because the number of molecules of sample is large with respect to the number of active adsorption sites. As the sample size is decreased, retention by the solid support becomes more significant since the relative abundance of active adsorption sites is increased. The extrapolation technique would, however, give accurate data if one were interested in absolute retention volumes for the liquid phase, since the effect of the solid support has been removed. In this work, satisfactory results were obtained using a constant small sample size. Retention by the solid support was either constant with temperature, or varied in such a way that the results were not affected.

Conclusion:

The method of gas liquid chromatography has been shown to be a general technique for determining the heat of vaporization of volatile liquids, and for many cases may be the only practical technique. Samples which are impure may be used since data for the compound of interest in the mixture may be determined. Since the sample size may be extremely small, toxic compounds and those not available in large quantities may be measured easily.

In addition to the work previously described, some additional related experiments should yield useful information. First, it was concluded from the data presented above that the heat of mixing of a polar solute in a non-polar solvent is a linear function of the heat of vaporization of the solute. This should be investigated either by conventional means or by gas chromatography.

The concept of a "homologous series" should also be defined more clearly. Experiments should be conducted which determine whether certain compounds are homologs. For example, 2 heptanol and 3 heptanol are both secondary alcohols, but one may not be a suitable reference for the other in determining heat of vaporization.

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