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R. E. Pauls[ab]; N. H. Mahle[acd]; A. T. Shepard[ae]; Jenny Chow Gaw[ad]; L. B. Rogers[a]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA, ATHENS, GEORGIA [b] Amoco Research Center, Naperville, Illinois [c] Dow Chemical Company, Midland, Michigan [d] Purdue University, [e] Department of Chemistry, Purdue University, West Lafayette, Indiana

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Chromatographic Determination of the Relative Retention of Isotopic Species of Oxygen in Methanol and Methan-d^3-ol

R. E. PAULS,* N. H. MAHLE,†,‡ A. T. SHEPARD,§
JENNY CHOW GAW,‡ and L. B. ROGERS

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF GEORGIA
ATHENS, GEORGIA 30602

Abstract

A high-precision gas chromatograph was used in conjunction with a quadrupole mass filter and an on-line computer to study the fractionation of oxygen isotopes by Porapak T and glycerol in CH_3OH and CD_3OH as a function of temperature. Values of relative retention on the order of 1.002 compared favorably with results for the vapor pressure ratio obtained by classical means. Differences from unity were much smaller for the activity-coefficient ratio than for the vapor-pressure ratio. Differential thermodynamic data were also reported.

INTRODUCTION

The first theoretical treatment on the effect of isotopic substitution on the vapor pressure of a condensed phase was developed about 60 years ago (*1*), and since then numerous papers (*2–7*) have been published on this

* Present address: Amoco Research Center, P.O. Box 400, Naperville, Illinois 60540.
† Present address: Dow Chemical Company, Midland, Michigan 48640.
‡ Work done at Purdue University.
§ Present address: Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.

subject. Most of these treatments are inadequate because they attempt to relate the thermodynamic properties of the isotopic species to their molecular weight. More recently, Bigeleisen (*8*) has developed a statistical theory of isotope effects in condensed systems. In that work, Bigeleisen pointed out that the lighter isotope did not always have the higher vapor pressure, that the vapor-pressure ratio of isotopically substituted molecules was temperature dependent, and that crossover temperatures occurred where the vapor-pressure ratios were reversed. Bigeleisen stressed that any theory of isotopic substitution had to take into account the molecular structure since isotopic substitution affected the mass assymmetry of the molecule.

Van Hook (*9–12*) has simplified the expressions for the vapor-pressure ratio of isotopically substituted molecules developed by Bigeleisen and has gone on to show how this equation could be applied to gas chromatographic separations. The vapor-pressure ratio is given by the general expression

$$\ln \frac{P'}{P} = \ln \frac{P_0'\gamma'}{P_0\gamma} = \ln \alpha = A/T^2 - B/T \tag{1}$$

where the primes designate the lighter isotope, P_0 is the vapor pressure of the pure liquid, γ is the activity coefficient, α is the ratio of the corrected chromatographic retention times of the two isotopic species, T is the absolute temperature, A is a generalized term which depends upon the lattice frequencies of the condensed phase, and B is a term which arises from differences in the zero-point energies of the isotopic species. The A term is given by (*13*)

$$A = \frac{h}{24k^2}[F_1^2/M_1 - F_2^2/M_2] \tag{2}$$

where h is the Planck constant, k is the Boltzmann constant, F^2 is the mean square force on the molecule and is assumed not to change with ^{18}O substitution, M is the molecular weight, and the subscripts 1 and 2 refer to the light and heavy isotopes, respectively.

The normal technique for determining the vapor-pressure ratio of isotopically substituted molecules is a distillation technique developed by Bigeleisen and Ribnikav (*14*) in which the vapor-pressure ratio was determined from the initial rate of change of the isotopic abundance and from the final steady-state enrichment. This technique was used by Borowitz and Klein (*13*) to determine the relative vapor pressure of ^{13}C- and ^{18}O-substituted CH_3OH, CD_3OH, CH_3OD, and CD_3OD. Van Hook and

Philips (*10*) have previously calculated the activity-coefficient ratio for C_6H_6/C_6D_6 on squalane and on silicone 702 using published data. They showed that the activity coefficient ratios were of the same magnitude as the vapor-pressure ratios and that the ratio was greater than unity on a nonpolar squalane column and less than unity on a more polar silicone column.

Borowitz and Klein also evaluated the A and B terms in Eq. (1) and correlated those values with spectroscopic data. They noted that the vapor pressures of the deuterated methanols increased as the strength of the hydrogen bonding decreased and that effects of ^{13}C and ^{18}O on the vapor pressure decreased with increasing molecular weight.

It is possible to calculate differential thermodynamic data for isotopically substituted molecules from relative retention times as was first suggested by Karger (*15*). Recently Shepard et al. (*16*) reported the values of $\Delta(\Delta G°)$, $\Delta(\Delta H°)$, and $\Delta(\Delta S°)$ for the ^{13}C and ^{18}O species of CO_2. In that work a Porapak Q column was used in the temperature range -13 to $-24°C$ and a silica gel column in the temperature range 38 to 50°C. The two adsorbents had noticeably different effects on the thermodynamic variables. For the $^{12}C/^{13}C$ pair the values of $\Delta(\Delta G°)$ were approximately equivalent for the two columns while $\Delta(\Delta H°)$ and $\Delta(\Delta S°)$ were a factor of 2 larger on the silica gel column. For the $^{16}O/^{18}O$ pair the values of $\Delta(\Delta G°)$, $\Delta(\Delta H°)$, and $\Delta(\Delta S°)$ were all a factor of 4 to 6 times larger on the silica gel than on the Porapak column. The large increase in $\Delta(\Delta G°)$ for the oxygen ratio on going from Porapak Q to silica actually made the $\Delta(\Delta G°)$ for oxygen larger than that for the carbon ratio. That increase may reflect the greater hydrogen-bonding ability of silica.

The purpose of the present study was to compare the results for the vapor-pressure ratio of $^{16}O/^{18}O$ species in CH_3OH and CD_3OH with those obtained from the ratios of the relative retention times on a glycerol and a Porapak T column. Instead of CD_3OH, CD_3OD was used as the sample, but exchange on the column rapidly produced CD_3OH.

In the case of a pure species the intermolecular forces are solely solute–solute and the ratio P'/P in Eq. (1) reduces to P_0'/P_0. However, in the case of gas–liquid chromatography there is an infinitely dilute solution, and the intermolecular forces are now solute–solvent. Since glycerol is structurally similar to methanol, we hoped that the interactions would closely approximate those in pure methanol. In this study, natural abundances of ^{18}O were used, and the chromatographic separations were carried out on relatively short packed columns using an on-line mass spectrometer to record the changes with time in the abundances of characteristic ions.

EXPERIMENTAL

Reagents

Porapak T, 100/120 mesh (Waters Associates, Inc., Framingham, Massachusetts); Chromosorb W, 100/120 mesh AW/DMCS (Alltech Associates, Arlington Heights, Illinois); glycerol (Mallinckrodt Chemical Works, St. Louis); methanol (spectrophotometric grade, Mallinckrodt); and d^4-methanol (99%D, Stohler Isotope Chemicals, Rutherford, New Jersey) were used as received. Helium (Selox, Inc.) was used as a carrier gas and nitrogen as the nonretained species. Hexamethyldisilazane (Pierce Chemical Co., Rockford, Illinois) and dichlorodimethylsilane (Aldrich Chemical Co., Milwaukee, Wisconsin) were used to silanize the Watson-Biemann separator.

Apparatus

The column oven was either a Becker Model 1452SH (Becker Delft, N.V., Delft, Holland) or a custom-made oven described previously (*16*). Temperature control of the oven was provided by a Melabs proportional temperature controller, Model CTC-IA equipped with a Model 1102 low-mass platinum sensor (Melabs Inc., Palo Alto, California). The temperature was measured using a platinum resistance thermometer (Omega Engineering, Stamford, Connecticut) in conjunction with a $5\frac{1}{2}$ digit multimeter (Data Precision, Wakefield, Massachusetts).

The carrier gas flow rate was controlled by a Chromatrol dual-column electronic flow controller (Applied Materials Inc., Santa Clara, California). The flow controller and all other electronics, as well as a temperature conditioning column for the carrier gas, were thermostated at 35°C to increase stability. An 8-port switching valve (Carle Instruments Inc., Fullerton, California) with dual 1 μl sampling loops was used to inject samples.

The column outlet was connected to the ion source of a UTI 100C quadrupole residual gas analyzer (Uthe Technology International, Sunnyvale, California) having a mass range of 0 to 300 amu. The ion current was measured with a Channeltron electron multiplier (Bendix Corp.). The vacuum in the mass spectrometer was measured using a Varian NRC Model 386 ionization gauge (Varian Vacuum Div., Palo Alto, California). A Watson-Biemann type separator (*17*), 4 cm in length and a 1-μ average pore size, was used to connect the column to the mass filter. A Hoke Model 1314 G4Y micrometering valve connected the separator to the ion source.

On-line data acquisition and analysis were performed using a PDP 11/20 minicomputer system described previously (*18*, *19*).

Procedures

Glycerol, 14% by weight, was pan-coated onto Chromosorb W and then packed into a 2.2 mm i.d. × 4 m SS column which had been previously rinsed successively with water, methanol, and methylene chloride. The Chromosorb W had been sieved to 100/120 mesh prior to use. A second column, 2.2 mm i.d. × 2.7 m, was packed with Porapak T.

Sampling was carried out by bubbling nitrogen into a saturator containing the methanol and then through one of the loops of the sampling valve for 40 sec. Then the sample was injected onto the column. The nitrogen flow rate was controlled by a manual flow controller (Porter Instrument Co., Hatfield, Pennsylvania).

The carrier gas flow rate was set at 0.3 ml/sec. The pressure in the mass spectrometer was controlled by the metering valve between the separator and the ion source. It was found that the width of the eluting peak was a function of the pressure in the mass spectrometer because of mixing in the separator. At lower pressures the peak was wider. As a result, a source pressure of 5×10^{-6} Torr was used as a compromise between narrow peaks and low pressures. The separator was kept at ambient temperature to minimize contamination in the mass spectrometer.

The separator was silanized to prevent adsorption. Prior to silanization the separator was cleaned in a chromic acid solution; it was then silanized with a 4:1 mixture of dichlorodimethylsilane and hexamethyldisilazane in pyridine.

The mass spectrometer was operated under computer control. Mass-to-charge ratios were selected using a 14-bit digital-to-analog converter (Model 14 QM, Analog Devices, Norwood, Massachusetts). The selection of the picoammeter sensitivity (10^{-5} to 10^{-12} A) was made through an 8-bit input/output latch previously described (*18*). The output of the multiplier was digitized using a 100 kHz voltage-to-frequency converter (Hewlett-Packard Co., Palo Alto, California). Individual chromatograms were stored on DECtape (Digital Equipment Corp., Maynard, Massachusetts).

Data Acquisition

The data were acquired under computer control using a multiple-ion-monitoring approach (*20*). As the peak eluted from the column, 240

readings of intensity vs time were alternately taken for each mass. The picoammeter sensitivity for the ^{18}O species was set at 100 times the sensitivity of the ^{16}O species. Standard deviations shown in the tables are for 12 runs at each temperature for CH_3OH and 20 runs at each temperature for CD_3OH. For the CD_3OH samples, both before and after the 20 runs, a mass spectrum from m/e of 28 to 38 was recorded as a peak eluted from the column so as to be sure that CD_3OH, not CD_3OD, was being measured.

Calculations

The retention times were based upon the peak maximum. Grams polynomials (*21*) were used to least-squares fit the top of each peak to a second degree polynomial. Once the coefficients of the polynomial had been determined, the expression was differentiated to obtain the peak maximum. Thirty-five data points were used in the smooth.

The corrected retention time was calculated by subtracting the retention time of a nonretained species, nitrogen, from the retention time of the solute. The relative retention, α, was calculated from

$$\alpha = t_{R_2}/t_{R_1} = K_2/K_1 \tag{3}$$

where t_{R_2} and t_{R_1} are the corrected retention times for the ^{18}O and ^{16}O species and K_2 and K_1 are the corresponding distribution ratios. The values of α were calculated from the same chromatogram so as to utilize an internal standard approach. For values of α close to 1, it is more convenient to express relative retention in terms of ε, where

$$\varepsilon = \alpha - 1 \cong \ln \alpha \tag{4}$$

where $\alpha \cong 1$.

The temperature dependence of the relative retention is given by the expression

$$\varepsilon T = A/T - B \tag{5}$$

which is identical to Eq. (1). The values of A and B were determined by a linear least-squares line for εT vs $1/T$.

The differential standard molar free energies were calculated from the expression

$$\Delta(\Delta G^0) = -RT \ln \alpha \tag{6}$$

where R is the gas constant and T is the absolute temperature. The values of $\Delta(\Delta H^\circ)$ and $\Delta(\Delta S^\circ)$ were obtained from a least-squares fit of $\ln \alpha$ vs $1/T$.

$$\ln \alpha = \frac{-\Delta(\Delta H^0)}{RT} + \frac{\Delta(\Delta S^0)}{R} \tag{7}$$

RESULTS

Preliminary Studies

Initial studies were carried out in the temperature range 55 to 75°C on the 2.7 m Porapak T column. A measurable fractionation, about a 1-sec difference in the peak maxima of $CH_3{}^{16}OH$–$CH_3{}^{18}OH$, was observed. As expected from the results of Borowitz and Klein, the ^{16}O species eluted first followed by the ^{18}O species. It was not possible to measure accurately the fractionation of the ^{13}C isotope because the fragmentation pattern of methanol did not yield a m/e value corresponding to only a ^{13}C species. However, it was possible to observe qualitatively that the ^{13}C species eluted before the ^{12}C and that the separation was much smaller than that observed for the ^{18}O species.

When CD_3OD was injected onto the glycerol column, the mass spectrum of the eluting peak was that of CD_3OH, indicating that the hydroxyl deuterium was being exchanged as the sample passed through the column. To insure that the exchange was occurring rapidly, a sample of CD_3OD was injected onto a 2.2 mm i.d. × 6 cm column of glycerol and the mass spectrum of the eluting species was recorded. The spectrum was that of a 3:1 mixture of CD_3OH, and CD_3OD, indicating that the exchange was rapid and occurred in the initial part of the column.

Adsorption Chromatography

It was expected from the work of Borowitz and Klein (*13*) that the relative retention would decrease with increasing temperature. The relative retention data for the Porapak T column are summarized in Table 1. The values of α are on the order of 1.002 and were reproducible to about 0.05%. This corresponded to about a 1-sec difference in the peak maxima. A plot of ε vs T is shown in Fig. 1. Initially, up to 64°C, ε decreased with temperature, and the values were roughly 20 to 30% lower than those reported by Borowitz and Klein. For instance, at 64°C Borowitz and

TABLE 1

Relative Retentions on Porapak T as a Function of Temperature for the Fractionation of $^{16}O/^{18}O$ in CH_3OH

Temperature (°C)	α	$\varepsilon \times 10^3$
57.7	1.00260 ± 0.00049	2.60
59.3	1.00255 ± 0.00026	2.55
62.3	1.00194 ± 0.00023	1.94
63.7	1.00195 ± 0.00014	1.95
66.0	1.00283 ± 0.00037	2.83
68.3	1.00507 ± 0.00034	5.07
69.7	1.00357 ± 0.00017	3.57
72.4	1.00245 ± 0.00031	2.45
76.0	1.00155 ± 0.00027	1.55

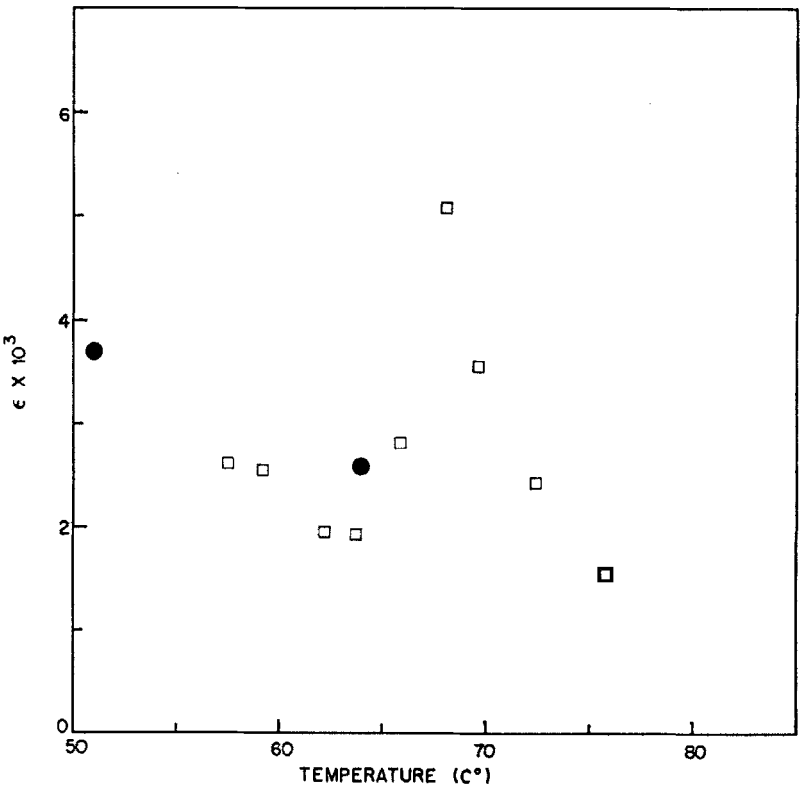

FIG. 1. Relative retention on Porapak T as a function of temperature for the $^{16}O/^{18}O$ pair in CH_3OH. Standard deviations for ε values are given in Table 1. (□) Experimental values; (●) Values of Borowitz and Klein (*13*).

Klein reported an ε of 2.6×10^{-3} compared to our value of 1.95×10^{-3}. However, in the vicinity of the boiling point of methanol, about 65°C, there was a sudden large increase in the value of ε, followed by a rapid decrease. A simiiar discrepancy in the vicinity of the boiling point on Porapak was observed by Patzelova and Valkova (*22*) in the slopes in plots of log retention volume vs $1/T$ for water and methanol. They attributed this change to a breakdown in hydrogen bonding near the boiling point.

Gas–Liquid Chromatography

Since the results at lower temperatures on the Porapak column looked promising, it was decided to try gas–liquid chromatography. Several liquid

TABLE 2

Relative Retentions on Glycerol as a Function of Temperature for the Fraction of the $^{16}O/^{18}O$ Pair in CH_3OH and CD_3OH

Temperature (°C)	α	$\varepsilon \times 10^3$
	CH_3OH	
56.35	1.00263 ± 0.00020	2.63
57.93	1.00240 ± 0.00022	2.40
59.21	1.00237 ± 0.00033	2.37
60.17	1.00242 ± 0.00038	2.42
61.41	1.00231 ± 0.00016	2.31
62.30	1.00205 ± 0.00029	2.05
63.81	1.00225 ± 0.00018	2.25
65.01	1.00215 ± 0.00026	2.15
66.38	1.00197 ± 0.00032	1.97
67.39	1.00205 ± 0.00036	2.05
68.57	1.00194 ± 0.00030	1.94
69.70	1.00168 ± 0.00032	1.68
73.64	1.00161 ± 0.00039	1.61
	CD_3OH	
53.02	1.00251 ± 0.00016	2.57
56.49	1.00182 ± 0.00026	1.82
57.33	1.00211 ± 0.00035	2.11
59.41	1.00219 ± 0.00033	2.19
60.92	1.00220 ± 0.00025	2.20
63.18	1.00160 ± 0.00021	1.60
65.92	1.00163 ± 0.00021	1.63
69.69	1.00128 ± 0.00039	1.28
71.79	1.00053 ± 0.00024	0.53

TABLE 3

Values of A and B for the $^{16}O/^{18}O$ Pair in CH_3OH and CD_3OH

	CH_3OH		CD_3OH	
	$A \times 10^3$	B	$A \times 10^3$	B
Experimental values	1.91 ± 0.21	-4.9 ± 0.6	3.04 ± 0.63	-8.5 ± 1.9
Literature values	2.2 ± 0.4	-5.6 ± 1.3	4.1 ± 0.4	-11.6 ± 1.6

phases were tested to see if they would give a measurable fractionation of the isotopes on a short packed column. Among the phases tested were glycerol, SE-30, and β,β-oxydipropionitrile. Glycerol was selected as the most suitable because it gave the largest separation and because its chemical similarity to methanol should give results for the vapor-pressure ratio closer to that expected for pure methanol.

The values of α and ε for the $^{16}O/^{18}O$ pair in CH_3OH and CD_3OH were determined on a 14% glycerol column over the temperature range 50 to 75°C. Table 2 shows that the relative retention values for CH_3OH were in the range 1.0016 to 1.0026, while those for CD_3OH showed a larger range from 1.00053 to 1.0025. The standard deviations of the relative retentions on this column were in the range 0.02 to 0.04%, a figure comparable to that reported for high precision gas chromatography using conventional detectors (*23*). Again, the values of ε tended to be 20 to 30% below those reported in the literature for pure methanol. For instance, 2.25×10^{-3} was experimentally observed for CH_3OH at 63.8°C while Borowitz and Klein reported an ε of 2.6×10^{-3} at 64°C.

A least-squares fit of εT vs $1/T$ was carried out on the data in Table 2 to evaluate the constants A and B in Eq. (1). Table 3 shows that for CH_3OH the A and B terms were the same, within experimental error, of the literature values while the values for CD_3OH were lower than the corresponding published values. The uncertainties of the A and B values reported here are better or equal to those previously reported.

Differential Thermodynamic Variables

The values of $\Delta(\Delta G°)$ calculated for the $^{16}O/^{18}O$ pair in CH_3OH and CD_3OH on the glycerol column are given in Table 4. The values of $\Delta(\Delta G°)$ were about -1 cal/mole and became smaller as the temperature increased. The uncertainties in the values of $\Delta(\Delta G°)$ were in the range 0.1 to 0.2 cal/mole, corresponding to about a 10 to 20% uncertainty. The values of

TABLE 4

$\Delta(\Delta G°)$ as a Function of Temperature for the $^{16}O/^{18}O$ Pair in CH_3OH and CD_3OH on Glycerol

CH_3OH		CD_3OH	
Temperature (°C)	$\Delta(\Delta G°)$ (cal/mole)	Temperature (°C)	$\Delta(\Delta G°)$ (cal/mole)
56.35	-1.72 ± 0.13	53.02	-1.63 ± 0.10
57.93	-1.58 ± 0.14	56.49	-1.19 ± 0.17
59.21	-1.56 ± 0.21	57.33	-1.39 ± 0.23
60.17	-1.60 ± 0.25	59.41	-1.44 ± 0.22
61.41	-1.53 ± 0.10	60.92	-1.46 ± 0.17
62.30	-1.36 ± 0.19	63.18	-1.07 ± 0.14
63.81	-1.51 ± 0.12	65.92	-1.10 ± 0.14
65.01	-1.45 ± 0.17	69.69	-0.91 ± 0.15
66.38	-1.33 ± 0.21	71.79	-0.36 ± 0.17
67.39	-1.39 ± 0.24		
68.57	-1.32 ± 0.20		
69.70	-1.14 ± 0.21		
73.64	-1.10 ± 0.27		

TABLE 5

$\Delta(\Delta H°)$ and $\Delta(\Delta S°)$ for the Fractionation on Glycerol of $^{16}O/^{18}O$ Species in CH_3OH and CD_3OH

Sample	$\Delta(\Delta H°)$ (cal/mole)	$\Delta(\Delta S°)$ (eu)
CH_3OH	-12.6 ± 1.2	-0.033 ± 0.003
CD_3OH	-19.0 ± 3.6	-0.053 ± 0.010

$\Delta(\Delta H°)$ and $\Delta(\Delta S°)$ obtained from a least-squares fit of $\ln \alpha$ vs $1/T$ are given in Table 5. The uncertainty in these values was about 10% for CH_3OH and 20% for CD_3OH.

DISCUSSION

By inspection of Eq. (1) it is apparent that the relative retention of two species is determined not only by the vapor-pressure ratio of the pure substances but also by the ratio of the activity coefficients. The activity coefficient is a measure of the deviation from pure solute–solute interactions, and in a dilute solution is not expected to be unity. According to Karger (*15*), the activity coefficient has two components, one a thermal component related to the types of solute–solvent interactions and an athermal contribu-

tion due to size differences between the solute and the solvent. By using a glycerol liquid phase we attempted to minimize the differences in the interactions since the intermolecular forces between methanol and glycerol should approximate those in pure methanol, and the size differential between methanol and glycerol would be small compared to that obtained using polymeric liquid phases. It was hoped that the activity ratio would be kept close to unity by minimizing the individual coefficients.

The values of ε observed in this study both on Porapak T and glycerol columns were consistently lower than those reported by Borowitz and Klein for pure methanol where the activity-coefficient ratio is unity. It is therefore possible to ascribe the observed differences to the activity coefficients.

Using a least-squares fit of the ε values reported by Borowitz and Klein as the correct values of the vapor-pressure ratio, it was possible to calculate the activity-coefficient ratio of the $^{16}O/^{18}O$ species on the glycerol column. Table 6 shows that for CH_3OH the activity-coefficient ratio was fairly constant at all temperatures and very close to unity. The activity-coefficient ratio for CH_3OH was much closer to unity than the vapor-pressure ratio, and in contrast to the vapor-pressure ratio, where the ^{16}O isotope had the

TABLE 6

Ratio of the Activity Coefficients on Glycerol for $^{16}O/^{18}O$ Pair in CH_3OH and CD_3OH

CH_3OH		CD_3OH	
Temperature (°C)	Activity coefficient ratio	Temperature (°C)	Activity coefficient ratio
56.35	0.99936	53.02	0.99954
57.93	0.99925	56.49	0.99928
59.21	0.99930	57.33	0.99967
60.17	0.99942	59.41	1.0000
61.41	0.99939	60.92	1.0980[a]
62.30	0.99919	63.18	0.99985
63.81	0.99949	65.92	1.00019
65.01	0.99947	69.69	1.000239
66.38	0.99938	71.79	0.9923[a]
67.39	0.99952		
68.57	0.99949		
69.70	0.99930		
73.64	0.99947		

[a] Standard deviations were the same as for the rest of the data; the recorded temperature must be in error.

higher vapor pressure, the ^{18}O isotope had the higher activity coefficient. The results for CD_3OH were not as reproducible as those for the CH_3OH, so it was difficult to make any generalizations from them.

As mentioned earlier, the A and B terms in Eq. (1) have physical significance. The A term is related to lattice vibrations while the B term is the contribution from the differences in the zero-point energies of the isotopes. The A value for CD_3OH was larger by a factor of 1.6 than the corresponding value for CH_3OH.

From this and Eq. (2), one can calculate that

$$F^2_{CD_3OH}/F^2_{CH_3OH} = 1.9 \tag{8}$$

which means that the intermolecular forces are greater for the CD_3OH on glycerol than for the CH_3OH. The B value for CD_3OH was larger than the value for CH_3OH by a factor of 1.7. This is again the qualitative agreement with the results reported by Borowitz and Klein that the B term, which reflected intramolecular forces, was always larger for the heavier molecule.

The values of $\Delta(\Delta G°)$, $\Delta(\Delta H°)$, and $\Delta(\Delta S°)$ were of the same magnitude as those observed by Shepard et al. (*16*) for the oxygen isotopes in CO_2. The value of $\Delta(\Delta H°)$ for CD_3OH was larger than that for CH_3OH, again indicating the intermolecular forces in CD_3OH were greater than those in CH_3OH. It is interesting to note that, although the intermolecular forces were greater in the heavier molecule, CD_3OH was more volatile than CH_3OH. This was because the intramolecular contribution to the volatility was greater than the intermolecular contribution for CD_3OH (*13*).

As noted earlier, the elution order was not always determined by the molecular weight, and the elution order was temperature dependent. Crossover temperatures, where the elution order reverses, have been reported by Bruner et al. (*24*) for CH_4–CD_4. The elution order for methanol at the temperatures studied is $^{13}CH_3{}^{16}OH$–$^{12}CH_3{}^{16}OH$–$^{12}CH_3{}^{18}OH$. By linear extrapolation of εT vs $1/T$, one can calculate that for methanol the ^{18}O species will cross over and elute before the ^{16}O species at about 120°C. It was not possible to check this experimentally because, at that temperature, there would have been a significant amount of column bleed.

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