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Exchange of Deuterium Between Methanol and Water: Vibrations of the Hydroxyl Group in Methanol and Methanol-d: The Entropy of Methanol

J. O. HALFORD AND B. PECHERER

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

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New measurements of the equilibrium in the exchange reaction between methanol and heavy water, in conjunction with data in the literature, are considered in relation to the vibrations of the hydroxyl group, including the torsional degree of freedom. An interpretation is presented which allows for a torsional frequency of 250 cm^{-1}, a value which is shown to be in reasonable agreement with the entropy from thermal data.

THROUGH the courtesy of Professor E. F. Barker of the Physics Department, new data on the infra-red absorption of methanol and methanol-d have been made available in advance of publication. In addition to frequencies which can be ascribed to motions of the methyl and methoxy groups, they include the OH and OD valence vibrations at 3683 and 2720 cm^{-1} and the distortion of the $C-O-D$ angle at 863, but the corresponding distortion of the $C-O-H$ angle unaccountably fails to appear. The torsional motion produces a broad complicated band system which is spread over a large part of the low frequency region.

The data are not adequate to permit a calculation of the equilibrium constant of the reaction,

$$CH_3OH + DOH = CH_3OD + HOH,$$
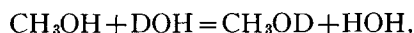
by the statistical method. However, the constant can be obt..ined experimentally to a good degree of accuracy, and it is the purpose of this paper to determine its value and apply it toward the search for the missing deformation and torsional frequencies. The exchange constant turns out to be insensitive to variations of the torsional

frequency. For this reason, little specific information about the torsional motion is obtained, but the deformation frequency is consequently quite closely determined.

EXPERIMENTAL

A recent measurement by Okamoto[1] gives the distribution ratio of deuterium between methanol and water as 1.00 ± 0.01 at $0°C$, corresponding to an equilibrium constant for the exchange reaction of 0.50 ± 0.005. This result was obtained from two sets of experiments, in which H_2 or D_2 was brought to equilibrium with water or methanol with the aid of platinum black, so that no use was made of water-alcohol solutions, and consequently any peculiar activity effects which such solutions might introduce were eliminated.

In our measurements, equilibrium solutions were made by mixing equimolar quantities of methanol and dilute deuterium oxide, and the alcohol and water were separated by fractional

[1] G. Okamoto, Sci. Papers Inst. Phys. Chem. Research (Tokyo), **31**, 211 (1936).

TABLE I. *Methanol exchange equilibrium at 80°C.*

DOH INITIAL	DOH FINAL	DIFFER-ENCE	MOLES WATER / MOLES ALC.	$\frac{CH_3OD}{CH_3OH} \times 100$	$\frac{DOH}{HOH} \times 100$	$K(l)_{353}$
2.644	1.798	0.846	0.982	0.848	1.811	0.468
7.610	5.086	2.524	0.990	2.575	5.194	.496
7.610	5.116	2.494	0.985	2.529	5.225	.484
9.844	6.762	3.122	1.027	3.322	6.955	.478
17.44	11.90	5.54	1.005	5.91	12.52	.472
17.44	11.86	5.58	0.990	5.85	12.47	.469
24.90	16.92	7.98	1.012	8.79	18.20	.483
24.90	16.74	8.16	1.005	8.94	17.99	.496

Mean value, $K(l)_{353} = 0.481 \pm 0.015$.

distillation, using a 90 cm vacuum-jacketed fractionating column. The equilibrium constant was calculated from the decrease in density of the water, as shown by the balance temperature of a glass diver. Initial D_2O concentrations from 1.3 percent to 12.5 percent were employed. The conversion of balance temperatures to D_2O percentages assumes that there is no significant volume change upon mixing D_2O and H_2O, and that the density difference between the two kinds of water is constant in the working temperature range. The second assumption might introduce an error which would appear as a trend in the resulting constant, such that the equilibrium quotient would be a function of the total deuterium content. No trend was observed, and the error introduced is therefore within the limits imposed by the total experimental error. The temperature measurements upon individual samples of water were reproducible to within $\pm 0.02°$, corresponding to an uncertainty of ± 0.006 percent D_2O at the highest concentrations. The spread of the results is somewhat larger than this figure would allow, probably because of differences in the completeness of separation of the water from the alcohol, and because of fractionation of the water during the distillation so that the sample analyzed was not quite representative.

The fact that the separation was not isothermal was not serious because the heat of reaction is very small. The result is assumed to be correct at 80°C. In the calculation of the equilibrium quotient, the ratio of H_2O to DOH was obtained for each concentration from the constant $K = 3.37$ for the reaction,

$$D_2O + H_2O = 2DOH.$$
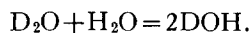
The ratio is not sensitive to the selected value of this constant, but since the constant is a property of the vapor equilibrium, it should be remembered that its application to the liquid phase reaction assumes that the partial pressure of DOH is the geometrical mean of the partial pressures which D_2O and H_2O would have at the same concentration.

The results are summarized in Table I, which shows, in successive columns, the initial and final total deuterium content (expressed as DOH percent of the water content), the decrease produced by reaction, the ratio of total moles of water to total moles of methanol, the ratio of DOH to H_2O, and the equilibrium quotient $K(l)_{353}$ for the liquid phase reaction at 80°C.

The relation between the measured quantity $K(l)$ and the vapor phase constant $K(g)$ must now be considered, since only the latter can be calculated from available data. The transformation would require that $K(l)$ be multiplied by a factor

$$\frac{p^0(HOH) \times p^0(CH_3OD)}{p^0(DOH) \times p^0(CH_3OH)},$$

in which the symbol p^0 refers to the vapor pressure of the pure substance, in order to give the first approximation to $K(g)$. From the vapor pressure of the three kinds of water published by Wahl and Urey,[2] the correction factor to be applied for the HOH/DOH ratio would increase the constant by about 3 percent. It is probable that this correction would be at least partially compensated by the corresponding effect with the methanols. Thus the vapor phase quotient should be slightly greater than the measured quotient $K(l)$. However, the principal error, incomplete separation of the methanol and water, would operate to give a high result. It is known from the spread of the results that the error of measurement is of roughly the same magnitude as the estimated difference between the liquid and vapor quotients. It appears, therefore, that the mean value of $K(l)$ from Table I is probably very close to the correct vapor phase constant.

At 0°C, the temperature of Okamoto's measurements, the HOH/DOH ratio is about 1.1.

[2] M. H. Wahl and H. C. Urey, J. Chem. Phys. **3**, 411 (1935).

If it is assumed that the corresponding ratio for the methanols is nearer to 1.0, say 1.05, the quotient for the vapor equilibrium at the ice point should be 0.525, which differs from the result for the liquid state by about five times the estimated experimental error.

The statistical constant

The calculation of the equilibrium constant of the exchange reaction from the masses, moments of inertia, and fundamental vibration frequencies by the well-established statistical method has been considered in detail by a number of authors.[3] The paper by Urey and Greiff gives the fundamental equation except for the question of the character of the rotational function for molecules with more than three rotational degrees of freedom. This has been treated rigorously by Eidinoff and Aston,[4] who have worked with certain special cases, and has been generalized by Kassel.[5] In addition, the function has been derived for ethane by Mayer, Brunauer and Mayer,[6] and approximate methods of calculation have been employed by Halford[7] and by Wirtz.[8]

The equilibrium quotient is given by the expression,

$$K(g) = \frac{L(\text{alc.})}{L(\text{aq.})} = \frac{f(CH_3OD) \times f(HOH)}{f(CH_3OH) \times f(DOH)},$$

in which f is the quantity frequently called the partition function and L may conveniently be designated as a partition ratio, such that

$$L(\text{alc.}) = \left[\frac{M_D}{M_H}\right]^{\frac{3}{2}} \times \left[\frac{R_D}{R_H}\right]^{\frac{1}{2}}$$

$$\times \prod_i \frac{(e^{-hc\nu_i/2kT})_D (1 - e^{-hc\nu_i/kT})_H}{(e^{-hc\nu_i/2kT})_H (1 - e^{-hc\nu_i/kT})_D},$$

[3] H. C. Urey and D. Rittenberg, J. Chem. Phys. 1, 137 (1933). R. H. Crist and G. A. Dalin, J. Chem. Phys. 1, 677 (1933). D. Rittenberg, W. Bleakey and H. C. Urey, J. Chem. Phys. 2, 48 (1934). H. C. Urey and L. J. Greiff, J. Am. Chem. Soc. 57, 321 (1935). K. Wirtz, Z. physik Chem. B31, 309 (1936); B34, 121 (1936). P. A. Small, Trans. Faraday Soc. 33, 820 (1937). T. Jones and A. Sherman, J. Chem. Phys. 5, 375 (1937).
[4] M. L. Eidinoff and J. G. Aston, J. Chem. Phys. 3, 379 (1935).
[5] L. S. Kassel, J. Chem. Phys. 4, 276 (1936).
[6] J. E. Mayer, S. Brunauer and M. G. Mayer, J. Am. Chem. Soc. 55, 37 (1933).
[7] J. O. Halford, J. Chem. Phys. 2, 694 (1934).
[8] K. Wirtz, Zeits. f. physik. Chemie B34, 121 (1936).

TABLE II. *Methanol moments of inertia (approximate, $\times 10^{40}$).*

AXIS	CH₃OH	CH₃OD
Transverse, in COH plane	33.16	34.59
Transverse, perpendicular to COH plane	34.55	37.27
Methyl group	5.268	5.268
Hydroxyl group, axis through its C.G., parallel to CO bond	1.344	2.537
Product $= R' \times 10^{156}$	0.811	1.723

M is the molecular weight, R is Kassel's determinant which reduces to the product of the principal moments of inertia if there is no internal rotation, and h, c, k and T have their usual significance. The subscripts H and D refer to the protium and deuterium compounds, respectively. The corresponding ratio for water contains a symmetry factor of two and in this case R is perhaps more conveniently expressed in terms of the principal moments of inertia.

The water partition ratio

The fundamental frequencies of the H₂O and DOH molecules have been taken from a paper by Barker and Sleator.[9] For the ratio of the moment products R it has seemed safer to use the result of a calculation which assumes that the valence angle and the interatomic distances are the same in the two kinds of water. The values of $L(\text{aq.})$ at 0°C and 80°C are, respectively, 70.176 and 35.807. These numbers are somewhat sensitive to the values of the constants h and k, but the effect of the sensitivity upon the equilibrium quotient is negligible. The constants used here have been taken from a table in Pauling and Wilson.[10]

Rotational functions of the methanols

In the evaluation of Kassel's determinant for the methanols, the C−O−H angle has been taken as 105° and the interatomic distances as C−H = 1.09, C−O = 1.42 and O−H = 0.96 angstrom units. The values of R for methanol and methanol-d, respectively, are 0.7989 and 1.6671($\times 10^{-156}$), and the square root of their ratio, which enters directly into the exchange quotient, is 1.444₆.

[9] E. F. Barker and W. W. Sleator, J. Chem. Phys. 3, 660 (1935).
[10] Pauling and Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Company (1935), p. 439.

It becomes desirable to compare this result with one which may be reached by an approximate method, as a partial justification of the ratio used further on in the calculations concerned with the possibility of torsional vibration. In addition to the three principal moments of inertia which the methanol molecule would possess as a rigid body, a reduced internal moment is assigned, such as could be ascribed to a molecule like CH_3CD_3, equal to the ratio of the product to the sum of the moments of two coaxial rotators. Since the sum is equal to one of the principal moments, the quantity calculated as substitute for R in the exact equation becomes the quadruple product of the remaining principal moments and the two internal moments. Table II shows the results of the calculations.

The square root of the ratio of the products becomes 1.457, about one percent higher than the correct value. Consequently, no significant error would be introduced into the exchange quotient by the use of these approximate moments. If the entropy of methanol-d were calculated with the moments of Table II, it would be high by 0.07 unit at 25°C.

The hydroxyl deformation frequency

If free rotation is assumed, the expression for the equilibrium quotient may be put into the form

$$K(g) \cdot L(aq.) = (M_D/M_H)^{\frac{3}{2}} \cdot (R_D/R_H)^{\frac{1}{2}} \cdot V,$$

where $2.303 \log V = (hc/2kT)\sum_i \nu_i.$

The factors $(1 - e^{-hc\nu/kT})$ are omitted because for all the frequencies with which this calculation is concerned they are negligibly different from unity. The one unknown frequency is evaluated by these equations directly from the equilibrium quotient. Numerical solution yields $V_{353} = 11.382$ from the new data presented here and $V_{273} = 23.188$ from Okamoto's data. The same result, 1199 within a wave number, is obtained for $\sum_i \nu_i$ from both values of V, but the close agreement is obviously fortuitous, in view of the probable magnitude of the vapor pressure corrections associated with the low temperature measurement. The algebraic sum of the known methanol frequencies, including a correction for the shift

of ν_5 from 1034 to 1040, is then introduced to give for the missing deformation frequency 1105 cm^{-1}.

This is in very close agreement with the value selected from the Raman spectrum by Bates, Anderson and Halford,[11] and independently by Mizushima, Morino and Okamoto,[12] at 1110.

The spread of the experimental results of Table I corresponds to an uncertainty of ±15 cm^{-1}. Comparison with the observed OD deformation at 863 in conjunction with known isotope shifts for other hydrogen frequencies suggests that the upper limit of 1120 is the most reasonable result. Ratios of protium to deuterium frequencies are: limiting value 1.414, oxygen-hydrogen valence vibration 1.354, carbon-hydrogen valence vibration 1.34, carbon-hydrogen deformation from methane 1.308, oxygen-hydrogen deformation as above 1.280±0.018. The higher value is further indicated by the frequent observation that Raman lines for liquids are a few wave numbers below the correct frequencies.

The above calculation suggests practically unrestricted internal rotation in the methanol molecule. In order to allow for deviation from free rotation, it would be necessary to adopt one of the lower values of the deformation frequency or to increase the equilibrium quotient. However, as will be shown below, a precise independent deformation frequency and a more accurate study of the equilibrium than is feasible at present would be required before this conclusion could be confidently drawn. In order to illustrate this point, an approximation to the equilibrium constant will be derived from the entropy, which is itself different from the free rotation value by about one entropy unit in the ordinary temperature range.

The entropy of methanol

The entropy of methanol, as a hypothetical perfect gas at atmospheric pressure and 25°C, based upon free rotation and the new set of fundamental frequencies, is 57.72, as against the value 58.38 recently published by Kassel.[13]

[11] J. R. Bates, L. C. Anderson and J. O. Halford, J. Chem. Phys. **4**, 535 (1936). J. O. Halford, L. C. Anderson and G. H. Kissin, J. Chem. Phys. **5**, 927 (1937).
[12] Mizushima, Morino and Okamoto, Bull. Chem. Soc. Japan **11**, 699 (1936).
[13] L. S. Kassel, J. Chem. Phys. **4**, 493 (1936).

The difference arises primarily from the new frequencies. The third law value obtained by combining the result of Kelley,[14] $S(l)_{298} = 30.26 \pm 0.2$, with the heat of vaporization measured by Fiock, Ginnings and Holton,[15] and the vapor pressure from *International Critical Tables*[16] is $56.6_3 \pm 0.2$. The excess above 55.72 is the contribution of the torsional motion. The harmonic frequency required to bring the entropy to the upper experimental limit of 56.83 is 370 cm⁻¹. If any reasonable smooth curve of entropy against frequency is drawn in such a way as to approach the harmonic oscillator curve at high frequencies and the free rotation contribution of 2.00 entropy units at zero frequency, it will indicate that a frequency not far from 250 cm⁻¹ in the lowest vibrational state corresponds to the harmonic value of 370.

The case of torsional vibration

The statistical expression for the equilibrium constant is rewritten with the contribution of the torsional motion expressed separately as W, so that

$$K(g) \cdot L(\text{aq.}) = (M_D/M_H)^{\frac{3}{2}} \cdot (R_D/R_H)^{\frac{1}{2}} \cdot V \cdot W.$$

Only three rotational degrees of freedom are now included in each moment product R. The factor W is obtained from the torsional frequencies, y for CH₃OH and y' for CH₃OD, by means of two equations,

$$W = e^{hc(y-y')/2kT} \frac{(1 - e^{-hcy/kT})}{(1 - e^{-hcy'/kT})}$$

and

$$y = 1.265 y',$$

in the second of which the quantity y/y' is set equal to the ratio of the square roots of the reduced internal moments of inertia from Table II. Although W is here expressed by means of a function derived from the harmonic oscillator, it appears to depend primarily on the frequency of the ground state. This follows from the fact that it approaches y/y', the ratio for free rota-

tion, as the frequency approaches zero, and becomes equal to $e^{hc(y-y')/2kT}$ for high frequencies, in much the same way as a theoretically correct expression in terms of the actual frequency would be expected to behave.

For this reason the computation of W is based on the value $y = 250$ estimated from the entropy. The introduction of the Raman frequency 1110 for the OH deformation gives $V_{353} = 11.493$ and $V_{273} = 23.480$. For the exchange constant, then, based on the above interpretation of the entropy and the function W, $K(g)_{353} = 0.495$ and $K(g)_{273} = 0.522$. The first of these lies within the spread of the experimental values and the second comes within the range of the vapor pressure correction.

It is evident that the exchange constant would be a good measure of the torsional frequency and the deviation from free rotation only if it were known to three significant figures. Although the accuracy could be improved, it is difficult to see how the required degree of precision could be attained. Agreement between the entropy and the exchange reaction occurs only in the region near the upper limit of the experimental values of both quantities, and then only when the deformation frequency is not too close to the most probable value. This study suggests, but does not prove, that either the exchange constant or the entropy is low.

A minimum potential barrier of 2500 cal. may be estimated for methyl alcohol from the entropy by means of the tables recently published by Pitzer.[17] This is nearly as high as the estimate of 3000 for ethane, and appears to be too high, relatively, for the number of hydrogen atoms involved in the effect. It would be unwise, however, to conclude from this comparison that the entropy is low, because the underlying factors are not well enough understood. In this connection, the surprisingly high potential barriers for ethyl alcohol and isopropyl alcohol, 9000 and 6000 cal., which Schumann[18] and Aston have shown to be consistent with equilibrium data and experimental entropies, are particularly interesting.

[14] Kelley, J. Am. Chem. Soc. 51, 181 (1929).
[15] Fiock, Ginnings and Holton, Bur. Standards J. Research 6, 881 (1931).
[16] *International Critical Tables*, vol. 3, p. 216.

[17] K. S. Pitzer, J. Chem. Phys. 5, 469 (1937).
[18] S. C. Schumann and J. G. Aston, J. Am. Chem. Soc. 60, 985 (1938).