

Electric Moments of the Methyl and Ethyl Alcohol Molecules

J. D. Stranathan

Citation: *J. Chem. Phys.* **6**, 395 (1938); doi: 10.1063/1.1750275

View online: <http://dx.doi.org/10.1063/1.1750275>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v6/i7>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIPAdvances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

Electric Moments of the Methyl and Ethyl Alcohol Molecules

J. D. STRANATHAN

Department of Physics, University of Kansas, Lawrence, Kansas

(Received April 11, 1938)

The dielectric constant of methyl alcohol vapor has been measured at 14 temperatures between 25.0°C and 206.0°C. At each temperature measurements were made at an average of 23 different pressures ranging from zero to near saturation. The slope, obtained by least squares, of the resulting $(K-1)/(K+2)$ versus pressure curve gives one point on the Debye line. The 14 such points fall accurately on a straight line whose equation as obtained by least squares, and after making proper allowance for probable errors of calibration, is: $[(K-1)/(K+2)]RT/p' = (7.72 \pm 0.15) + (17,730 \pm 71)/T$. Using recently established values of the Boltzmann gas constant and Avogadro's number, this yields a value $(1.706 \pm 0.005) \times 10^{-18}$ e.s.u. for the electric moment of the methyl alcohol molecule. Taking the sum of the electronic and atomic

polarization as 8.6 leads to an electric moment of $(1.688 \pm 0.006) \times 10^{-18}$. The mean $(1.698 \pm 0.005) \times 10^{-18}$ is taken as the electric moment of the methyl alcohol molecule. Data on ethyl alcohol previously published by Knowles have been recalculated, using a least squares treatment throughout, and making a minor correction to the value used for the absolute zero of temperature. The data conform to the equation $[(K-1)/(K+2)]RT/p' = (13.06 \pm 0.20) + (17,725 \pm 87)/T$, wherein probable errors of calibration have again been allowed for. This yields a moment $(1.706 \pm 0.006) \times 10^{-18}$. Taking the sum of electronic and atomic polarization as 13.6 leads to a moment $(1.696 \pm 0.008) \times 10^{-18}$. The mean $(1.702 \pm 0.007) \times 10^{-18}$ is taken as the electric moment of the ethyl alcohol molecule.

CONTINUING an earlier reported¹ effort to fix more definitely the values of the electric moment of several of the lighter alcohol molecules, the author has made extensive dielectric constant measurements on methyl alcohol vapor. Dielectric constants were measured by the heterodyne beat method, using apparatus previously described.² The vapor condenser with quartz insulators, and the vapor system, were the same as those used in previously reported work on water vapor³ and isopropyl alcohol vapor.¹ Dielectric constants were measured at 14 different temperatures between 25.0°C and 206.0°C. At each temperature, measurements were made at an average of 23 different pressures, ranging from the lowest measurable up to near saturation when such saturated vapor pressure did not exceed one atmosphere. Two different samples of methyl alcohol were used, each of the highest purity obtainable and carefully dried.

Values of $(K-1)/(K+2)$ for a given temperature were plotted to a large scale against p' , where p' represents the pressure the vapor would exert were it an ideal gas; the quantity p' is obtained from the observed pressure p and the van der Waals constants a and b , thus:

$$p' = p[1 + (p/RT)(a/RT - b)].$$

At the higher temperatures, for which the highest pressures used were far below saturation, the resulting curves are accurately linear over their entire range. At lower temperatures, slight curvature is apparent at the higher pressures, though a large scale plot is necessary to detect it except very close to saturation. The only use made of such plots was to determine the extent of linearity. Barely perceptible curvature became apparent at pressures approximately two-thirds saturation. For each temperature the slope of the best least squares line through all points on the linear section was found; the average number of points on these linear sections was 19. The several advantages of securing extensive data and of the least square treatment of these data have been discussed previously.¹

The molecular polarization is given by

$$(K-1)M/(K+2)d \\ = (K-1)RT/(K+2)p' = A + B/T,$$

the last equality being a result of the Debye theory. The molecular polarization at each temperature was obtained from the slope of the $(K-1)/(K+2)$ versus p' curve for that temperature. The accuracy of the data can be judged from the calculated molecular polarizations and their probable errors as shown in Table I.

Figure 1 shows the products of molecular polarization and absolute temperature plotted

¹ Stranathan, J. Chem. Phys. 5, 828 (1937).

² Stranathan, Rev. Sci. Inst. 5, 315, 334 (1934).

³ Stranathan, Phys. Rev. 48, 538 (1935).

against T . The data fall accurately on a straight line, no point being off by more than 0.4 percent. Previous data by Miles⁴ and by Kubo⁵ are also shown. In calculating the best straight line through the 14 points of the present work, the question arises as to how the individual points should be weighted. While the author doubts that all variations are truly accidental, he feels that the largest are. Under such circumstances it appears advisable to weight each point inversely proportional to the square of its probable error. With such weighting, a least square solution for the best straight line through the author's data gives:

$$(K-1)RT/(K+2)p' = (7.72 \pm 0.15) + (17,730 \pm 59)/T.$$

Giving all points equal weights results in essentially the same equation, the constants so obtained being (7.55 ± 0.13) and $(17,797 \pm 52)$.

According to the Debye theory, the permanent electric moment u is given by:

$$u = (9kB/4\pi N)^{1/2},$$

where k is the Boltzmann gas constant per molecule and N is Avogadro's number. Recent work of Bearden,⁶ Kellström,⁷ and many others on a new value for the electronic charge leads to new values of N and k . These works have been so numerous and so convincing that there appears no reason for delaying longer the use of these new values in calculations of electric moments. Taking the gas constant per mole as $(8.3136 \pm 0.0010) \times 10^7$ ergs per C°, and N as $(6.0230 \pm 0.0005) \times 10^{23}$ mole-

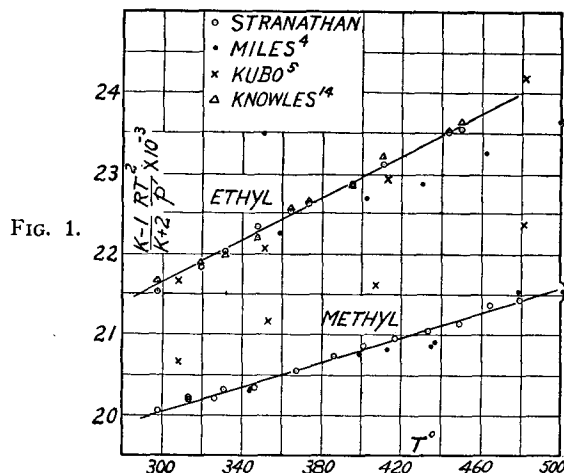


Fig. 1.

cules per gram mole,⁹ then $k = (1.3803 \pm 0.0002) \times 10^{-16}$; hence,

$$u = (1.2811 \pm 0.0002) \times 10^{-20} B^{1/2}.$$

This is larger than the value based upon constants previously accepted⁸ by a factor 1.0069; hence all previous moments obtained from dielectric studies should be increased by this factor. While the difference is not great, it is definitely larger than the probable errors associated with a number of moments. The electric moment of the methyl alcohol molecule obtained from the present data is $(1.7058 \pm 0.0039) \times 10^{-18}$ e.s.u.¹⁰

The probable errors quoted above are those calculated from accidental variations of observed data. Two other appreciable errors enter in the calibration of apparatus. Numerous and varied measurements of the effective capacity of the evacuated vapor condenser indicate that 1 part per 1000 would be a reasonable estimate of the probable error associated with this measurement. Similarly, an allowance of 2 parts per 1000 might be associated with the intercalibration of the large (1500 μmf) condenser used in measuring the effective capacity of the evacuated vapor condenser and the small (15 μmf) condenser used in measuring the increase in capacity occasioned by the presence of the vapor. Error introduced through measurement of temperature is negli-

TABLE I. Methyl alcohol. Experimental values of molecular polarization, with associated probable errors. Values of T are absolute temperatures in C°.

TEMPERATURE T	MOLECULAR POLARIZATION	TEMPERATURE T	MOLECULAR POLARIZATION
298.2	67.29 \pm 0.25	386.5	53.633 \pm 0.073
313.7	64.39 \pm .12	401.7	51.934 \pm .063
313.7	64.47 \pm .11	417.1	50.235 \pm .037
326.6	61.86 \pm .12	433.4	48.565 \pm .035
331.2	61.32 \pm .18	449.0	47.055 \pm .039
346.7	58.684 \pm .083	464.2	46.007 \pm .029
367.4	55.927 \pm .097	479.2	44.735 \pm .030

⁴ Miles, Phys. Rev. **34**, 964 (1929).

⁵ Kubo, Inst. Phys. Chem. Res., Tokyo, Sci. Papers **26**, 242 (1935).

⁶ Bearden, Phys. Rev. **48**, 385 (1935).

⁷ Kellström, Nature **136**, 682 (1935); Phil. Mag. **23**, 313 (1937).

⁸ Birge, Rev. Mod. Phys. **1**, 1 (1929).

⁹ Birge, Nature **137**, 187 (1936).

¹⁰ This moment was reported as 1.694×10^{-18} at the Indianapolis Meeting of the Am. Phys. Soc. (1937). When corrected to the new values of constants used here this corresponds exactly to the value here reported.

gible. Error due to adsorption of material on the insulator surfaces³ may not be completely eliminated even by the procedure used here, though the residual must be small. Some evidence¹¹ indicates an appreciable error due to failure of the van der Waals gas law to represent accurately the density of the vapor in terms of its pressure. As far as is known, however, this error is quite small for measurements made at low pressures. If allowance is made for the probable errors of calibration, it is found

$$(K-1)RT/(K+2)p' \\ = (7.72 \pm 0.15) + (17,730 \pm 71)/T$$

and $u = (1.7058 \pm 0.0048) \times 10^{-18}$. The present results are compared with those of other extended works on vapors in Table II. While results of dilute solution studies are in general agreement with those on vapors, they are not as reliable; therefore they are not included.

The term A should be the sum of the electronic and atomic polarizations. A fair estimate¹² of this sum is a value 5 percent greater than the molecular refraction for the Na D line. Hence, one expects a constant term A about $(1.05 \times 8.23) = 8.6$, whereas the experimental value found here is (7.72 ± 0.15) . The difference may be experimental error, though it is considerably larger than one would suspect from the associated probable error. As Groves and Sugden¹³ point out, it may be preferable in the calculation of moments to use the

TABLE II. Comparison of results. A , B , and moments under (1) are calculated entirely from dielectric data. Moments under (2) are calculated by taking $A = 8.6$ for methyl alcohol and 13.6 for ethyl alcohol. All moments are on the basis of the new values of Avogadro's number and Boltzmann's gas constant.

AUTHOR	A	B	(1) $u \times 10^{18}$	(2)
<i>Methyl Alcohol</i>				
Stranathan	7.72 ± 0.15	$17,730 \pm 71$	1.706 ± 0.005	1.688 ± 0.006
Miles ⁴	8.13	17,430	1.691	1.684
Kubo ⁵	9.54	17,710	1.705	1.724
<i>Ethyl Alcohol</i>				
Stranathan	13.06 ± 0.20	$17,725 \pm 87$	1.706 ± 0.006	1.696 ± 0.008
Knowles ¹⁴	13.6	17,550	1.698	1.697
Miles ⁴	11.80	17,780	1.708	1.675
Kubo ⁵	14.25	17,200	1.680	1.691

¹¹ Stuart, Zeits. f. Physik **51**, 490 (1928).

¹² Sugden, Trans. Faraday Soc. **30**, 738 (1934).

¹³ Groves and Sugden, J. Chem. Soc. London, 158, Jan. (1937).

term A estimated from optical data. If A is taken as 8.6, then statistical weighting of data at different temperatures leads to a value $B = (17,354 \pm 11)$ and $u = (1.6877 \pm 0.0008) \times 10^{-18}$. This appears much better determined, and the method is probably preferable for comparison of moments where calibration errors cancel out. However, if the same allowance as before is made for calibration errors, together with an allowance of 2 percent in the value chosen for A , we find $B = (17,354 \pm 80)$ and $u = (1.6877 \pm 0.0055) \times 10^{-18}$. This moment is smaller than that found entirely from dielectric data by about twice the sum of the probable errors. The mean of these $(1.698 \pm 0.005) \times 10^{-18}$, may be taken as the most probable value for the moment of the methyl alcohol molecule. Results of similar calculations from data of other workers are shown in Table II.

The data of Knowles¹⁴ on ethyl alcohol vapor appears sufficiently extensive and reliable to warrant a least squares treatment. Knowles obtained data at 10 different temperatures between 24.55°C and 177.1°C. Observations at an average of 17 widely different pressures were made at each temperature. An average of 14 of these points fell on the straight line section of each curve. The author, having the original data available, has therefore made a recalculation, using least squares throughout, and making a minor correction for the previous use of the approximate value -273.0°C for the absolute zero of temperature. The resulting molecular polarizations with their associated probable errors are shown in Table III.

Products of molecular polarization and absolute temperature are shown plotted against absolute temperature in Fig. 1. The 10 points fall accurately on a straight line, no point being off by more than 0.4 percent. The previous points

TABLE III. Ethyl alcohol. Experimental values of molecular polarization, with associated probable errors. Values of T are absolute temperatures in $^\circ\text{C}$.

TEMPERATURE T	MOLECULAR POLARIZATION	TEMPERATURE T	MOLECULAR POLARIZATION
297.7	72.30 ± 0.46	373.3	60.58 ± 0.23
319.7	$68.28 \pm .34$	395.5	$57.84 \pm .11$
332.0	$66.39 \pm .11$	410.9	$56.29 \pm .09$
347.9	$64.21 \pm .17$	443.6	$53.02 \pm .16$
364.3	$61.83 \pm .34$	450.2	$52.33 \pm .34$

¹⁴ Knowles, J. Phys. Chem. **36**, 2554 (1932).

obtained graphically by Knowles¹⁴ from the same data, as well as previous data by Miles⁴ and by Kubo⁵ are shown. If the present points are weighted statistically, a least squares solution for the best straight line through them gives:

$$(K-1)RT/(K+2)p' \\ = (13.06 \pm 0.20) + (17,725 \pm 78)/T.$$

This yields an electric moment $(1.7056 \pm 0.0052) \times 10^{-18}$ for the ethyl alcohol molecule. Giving equal weights to all points leads to constants (13.35 ± 0.23) and $(17,610 \pm 85)$ in the above equation, thus yielding a moment $(1.7000 \pm 0.0058) \times 10^{-18}$. The probable errors of calibration in Knowles work probably approximated those estimated in the present work on methyl alcohol. If the same allowance is made for them, we obtain from a statistical weighting of points:

$$(K-1)RT/(K+2)p' \\ = (13.06 \pm 0.20) + (17,725 \pm 87)/T$$

from which $u = (1.7056 \pm 0.0059) \times 10^{-18}$. These results are compared with other extended works on the vapor in Table II.

The constant term $A = (13.06 \pm 0.20)$ is again

slightly smaller than the value $(1.05 \times 12.93) = 13.6$ which we might reasonably expect. Taking $A = 13.6$, statistical weighting of data at the various temperatures leads to values $B = (17,517 \pm 8)$ and $u = (1.6956 \pm 0.00055) \times 10^{-18}$. If allowance is made for probable errors of calibration, together with a 2 percent probable error in the value chosen for A , then $B = (17,517 \pm 110)$ and $u = (1.6956 \pm 0.0076) \times 10^{-18}$. This moment is smaller than that found entirely from dielectric data by somewhat less than the sum of the probable error. The mean $(1.702 \pm 0.007) \times 10^{-18}$ may be taken as the most probable value for the moment of the ethyl alcohol molecule. Results of similar calculations from data of other workers are shown in Table II.

Judging from the general agreement of results of various workers, together with the probable errors associated with these, it appears that little real improvement can be made in the moments of the methyl and ethyl alcohol molecules until several possible sources of error are eliminated. The author is attempting several improvements in this direction before proceeding to a study of other moments.

The Transference Numbers of Potassium Acetate in Aqueous Solution

D. J. LE ROY AND A. R. GORDON

Chemistry Department, University of Toronto, Toronto, Canada

(Received April 25, 1938)

The transference numbers for aqueous solutions of potassium acetate at 25°C have been determined by the moving boundary method for the concentration range 0.01 *N* to 0.25 *N*. Two different types of cell and two different methods of measuring the number of coulombs were employed. Up to 0.16 *N* the transference numbers can be represented by the Shedlovsky-Longworth equation within ± 0.05 percent, and lead to a transference number for the cation at infinite dilution of 0.6428, in close agreement with that obtained from the limiting ionic mobilities.

IN recent years the determination of the transference numbers of ions in solution by the moving boundary method has been developed (thanks primarily to the work of MacInnes, Longworth and their associates) until it will yield results of the highest precision; combined with accurate conductivity data, such numbers permit the calculation of limiting ionic mobilities

with an accuracy of a part in several thousand. In the course of a study of the transference numbers for several electrolytes, Longworth¹ has determined the transference numbers for solutions of sodium acetate; in this paper we report the numbers for solutions of potassium acetate.

¹ Longworth, J. Am. Chem. Soc. **57**, 1185 (1935).