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THE INFLUENCE OF MOLECULAR STRUCTURE UPON THE INTERNAL FRICTION OF CER-TAIN ISOMERIC ETHER GASES.[1]

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THE following investigation of the coefficients of friction of a group of isomeric ether gases, was undertaken with a view of determining whether the differences in molecular structure which are believed to exist in these isomeric compounds, are accompanied by differences in such a physical property as their internal friction.

It has been demonstrated [2] that the coefficient of friction of a gas

$$\eta = \frac{MG}{4\pi s^2}$$

where M is the mass of a molecule, G the mean value of the velocity as deduced from the mean kinetic energy, and s equals the distance between the center of two molecules at impact, or the diameter of the sphere of action. In isomeric compounds M is constant, and if the temperature is constant, G is also constant, so that if a difference in friction is observed, this difference must be due to a change in s, and, therefore, to a change in the size or the shape of the molecules owing to their different internal structure.

Investigations along this line were made by Meyer & Schumann,[3] in 1881. They determined the coefficient of internal friction by the well known transpiration method. Their apparatus consisted

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[1] A paper read before the American Physical Society, March 2, 1907.
[2] O. E. Meyer's Kinetic Theory of Gases, 1899, p. 179.
[3] Wied. Ann., 1881, Bd. 13, p. 1.

essentially of a capillary nearly 1.5 meters in length coiled into a helix and fastened into the upper part of a boiling flask. The lower end of the capillary passed through the neck of the flask into a condenser. The substance to be examined was boiled at a regulated pressure, the vapor evolved surrounding the capillary and raising it to the same temperature. Part of the vapor which was, of course, saturated, entered the upper end of the capillary and passed through it into an air-free, cooled space where it was condensed and measured as a liquid. The volume of the vapor transpired was calculated from the amount of the liquid collected in the condenser.

Their method is open to criticism for several reasons. Objection might be made against the coiling of the capillary into a small helix because its bore may have thus been deformed and the curved path of the gas may have caused additional resistance. The vapor at the boiling point of the liquid can also hardly be regarded as a true gas, and should have been tested at several degrees above boiling. The expansion of the saturated vapor as it passed through the capillary probably also changed its state. Furthermore, the great length of time, several hours, needed for transpiration made it difficult to keep conditions constant.

TABLE V.

Esters $C_n H_{2n} O_2$ $\eta \times 10^6$.

Acid Radical.	Alcohol Radical.				
	Methyl.	Ethyl.	Propyl.	Isobutyl.	Amyl.
	$n = 2$	3	4	5	6
Formic acid.	173	156	159	172	160
	$n = 3$	4	5	6	7
Acetic acid.	152	152	160	155	
	$n = 4$	5	6	7	8
Propionic acid.	150	158	153	164	158
	$n = 5$	6	7	8	9
Normal butyric acid.	159	160	164	167	155
Isobutyric acid.	152	151	153	158	155
	$n = 6$	7	8	9	10
Valerianic acid.	163	165	167	154	

Two capillaries were employed, one 1427 mm. long and 0.31 mm. in diameter; the other 1404 mm. long and 0.3328 mm. in diam-

eter.   The second capillary gave values 3 per cent. higher than the first.   Above is the table of their results for esters :

They conclude that all esters at their boiling points and at the same pressure transpire very nearly equal volumes of vapor, which, however, because the boiling points are different, do not contain the same number of molecules.

They found η for the corresponding acids considerably smaller than for their esters.   They believed that the differences of η are partly too small and partly too irregular to draw any sure conclusion of the dependence of η on the molecular constitution.   They point out, however, some differences which seem quite regular.

The esters of acetic, propionic and isobutyric acids show almost always a smaller η than those of formic, normal butyric and valerianic acids.   This difference is especially noticeable in the two butyric acids.   The influence of the alcohol radical cannot be seen so clearly.   Among the isomeric esters, those of formic, acetic, propionic and isobutyric acids have the greater η with the greater alcohol radical.   The isomeric esters of normal butyric and valerianic acids do not follow this rule but have the same friction.

The number of carbon atoms in a molecule also seems to have a certain influence on η.   The esters for which $n = 2, 5, 7$ or 8 show a larger η than those with 3, 4 or 9 carbon atoms.   The cause of these differences they were unable to explain.

On calculating the relative molecular volumes they found them only about half those given by Kopp's rule.   L. Meyer tried to account for this by advancing the hypothesis that by Kopp's method the empty space is included which is open to the atoms for their motion, while from the coefficient of internal friction only the volume of the gas particles themselves is determined.

Steudel[1] continued the work of L. Meyer and Schumann, using the same apparatus with the second capillary, the first having been broken.   He investigated several homologous lines of organic compounds, viz.: alcohols up to four atoms of carbon per molecule, and their halogen derivatives, also some substitution products of ethane and methane.

He found the transpiration time increased with the molecular

[1] Wied. Ann., 1882, Bd. 16, p. 369.

weight. Of isomeric compounds at the boiling points, the normal, *i. e.*, those that boil at the highest temperature transpire the slowest and the tertiary the fastest, with the exception of isopropyl alcohol which transpires noticeably slower than the normal. Unsymmetrical low boiling compounds have a smaller transpiration time than the symmetrical. The only exception he found to the rule that the transpiration time increases with the molecular weight is methyliodide whose time was 1,037 minutes, which is almost the same as 1,056 minutes taken by isobutyliodide.

He points out that the coefficients of friction of each line of homologous compounds are nearly alike or only slightly different. The values for the primary alcohols vary from .000135 to .000143 ; for three of them they are almost exactly alike. The isopropyl gave a considerably larger figure, also the tertiary butyl. The chlorides seem to all have the same friction. The greatest differences exist in the iodide column.

TABLE OF $\eta \times 10^6$.

Radical.	Alcohol.	Chloride.	Bromide.	Iodide.
Methyl.	135	116[1]		245
Ethyl.	142	105[1]	183	216
Normal propyl.	142	146	184	210
Isopropyl.	162	148	176	201
Normal butyl.	143	149		202
Isobutyl.	144	150	179	204
Tertiary butyl.	160	150		

He found a considerable difference in η with a change in pressure. With a greater pressure than 10 to 15 cm. of mercury the formula seemed to lose its validity for vapors. This agrees with what L. Meyer had noticed with benzole.

Steudel also gives tables of molecular velocities, mean free paths, combined cross-section of molecules and cross-sections of an equal number of molecules. He points out that the cross-sections of molecules of isomeric compounds are not the same. For the butyl compounds the areas for the normal substances are the largest, the tertiary the smallest, with the iso compounds between. Propyl and isopropyl alcohol, as also both chlorides show the same relation.

[1] Calculated from Graham's results.

On the other hand, isopropyl-bromide has a greater molecular area than the normal compound. In the substitution products of ethane the symmetrical ones have a larger area than the unsymmetrical.

Steudel also calculated the relative molecular volumes from SO_2 according to the method of L. Meyer, with whom he agrees in finding the volumes about one half as large as those calculated according to Kopp's rule. The ratios of molecular volumes of the different substances, however, are almost the same as the ratios of the volumes according to Kopp.

L. Meyer,[1] summing up Steudel's and his own previous results, gives the following :

TABLE OF $\eta \times 10^6$.

Alcohols	$C_nH_{2n+2}O$	142 average
Chlorides	$C_nH_{2n+1}Cl$	150 "
Esters	$C_nH_{2n}O_2$	155 "
Bromides	$C_nH_{2n+1}Br$	182 "
Iodides	$C_nH_{2n+1}I$	210 "

Cases in which $n = 1$ and some few unaccountable variations are omitted from the above. When $n = 1$ the variations are great but he could see no law of the influence of molecular constitution on the friction.

On the other hand the influence of the nature of the atom is very clearly seen ; friction of iodine > bromine > chlorine.

The molecular volumes do not agree with those of L. Meyer[2] calculated from Graham's results. He points out that this one fact seems certain, viz.: the molecules of a tertiary butyl compound are smaller than those of a secondary which are smaller than those of a primary. This is in agreement with the universal view taken of the concatenation of these compounds. Those of the tertiary are grouped around a single atom of carbon, hence are more spherical in shape. Propyl and isopropyl compounds on the other hand do not show the same regularity. The alcohols and iodides deviate in opposite directions, which is unexplained. He further points out that the sphere of action of a liquid molecule increases with the temperature, while that of a gaseous molecule diminishes with rise of temperature.

[1] Pogg. Ann., 1882, Vol. 16, p. 394.
[2] Liebig's Ann., 1867, Suppl. Bd. 5, p. 129.

Method Employed in this Investigation.

Owing to the difficulty of getting capillaries of perfectly uniform bore, and of determining with the greatest accuracy the shape and size of their cross-section, and also owing to the possible formation of eddies at the beginning and end of the flow, and to the possible slipping of the gas on the capillary walls, probably the oscillation method is the better for absolute measurements, provided a solid body is employed of such a shape that the mathematical treatment is rigorously correct. It seems certain however that the transpiration method has been growing in favor of late years, and that it is more convenient for comparative measurements than the other method. As my object was more to get comparative than absolute values of the greatest accuracy, the transpiration method was decided upon for this experimental investigation.

General Description of Apparatus.

The form of apparatus as well as the subject of this research was kindly suggested to me by Professor Morris Loeb, then of N. Y. University, under whose guidance these experiments were made. The apparatus consists essentially of a U-shaped tube (see Fig. 1), one limb of which is capillary, while the other is not, but serves as a cylinder of known capacity, down which is forced by gravity a piston consisting of a column of mercury, which drives the gas under it up through the capillary limb. The capillary, *A*, does not begin at the bend of the U, but some distance above it. The distance between the limbs is only 3 cm., so that the apparatus can be placed inside of a glass tube 5 cm. in diameter which serves as a steam jacket (see Fig. 3), the steam being introduced through a side tube, *S*, near the top and passing out freely at the bottom, *O*. A cork, *C*, through which both limbs of the apparatus pass is on a level with the top of the capillary, and serves to close the steam jacket at the top. The mercury limb above the cork is provided with a special stop-cock, *H*, bored out to the same diameter as the tube below it. Above the stop-cock is a continuation of the tube terminating in a small funnel, *F*, for convenience in introducing ether and mercury. An ordinary thistle funnel with horizontal bottom will not answer ; the bottom of the funnel must be inclined

about 45° to the axis of the mercury tube, otherwise the mercury will not so readily descend in one unbroken column when released by turning the stop-cock. Two marks, M_1 and M_2, are etched on the mercury tube a convenient distance apart, the lower one, M_2, being near the bend at the bottom, the volume of the tube between
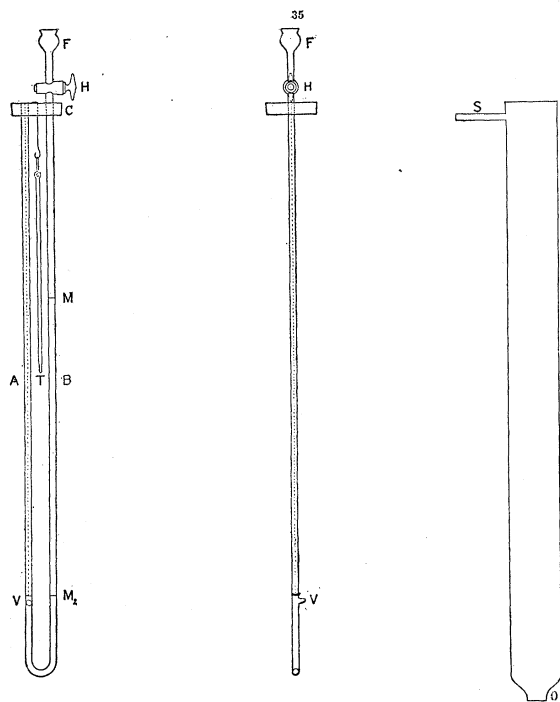

Fig. 1.
View perpendicular to the
plane of the two limbs.

Fig. 2.
View in the plane of
the limbs.

Fig. 3.
Steam Jacket.

the marks being accurately determined by calibration with mercury. The bore of this tube being slightly conical instead of truly cylindrical, its calibration was also carried far enough above the upper mark, M_1, to cover the space passed over by the mercury column during an experiment, so that the average height of the mercury column during an experiment could be calculated.

The method of making an observation on ether gas is essentially as follows: The steam jacket being cold and filled with air the ap-

paratus is placed in it.   The stop-cock is opened and about 1 c.c.
of ether is poured down the mercury tube.   By means of an aspira-
tor the ether is sucked up the other limb close to the base of the
capillary.   The small hermetically closed tube seen at V in Figs.
1 and 2 serves as a reservoir for ether at the base of the capillary.
Care was always taken to fill this tube completely with ether so that
it could not act as an air pocket.   Steam is then led into the jacket
and of course vaporizes the ether, driving surplus liquid violently
out through the top of the mercury tube.   The stop-cock is then
closed and after equilibrium has been established, a weighed amount
of mercury is introduced into the funnel and allowed to flow down
until it is arrested by the stop-cock, which is not quite air tight,
because no grease can be used in it for fear of soiling the mercury.
The stop-cock is then suddenly turned and the mercury descends
in a single column.   When its lower meniscus passes the upper
mark on the tube a stop watch is started, which is stopped as the
same meniscus passes the lower mark.   The barometer is read when
the mercury has covered half the measured distance.   A thermome-
ter, T, Fig. 1, hanging from the cork at the top of the steam jacket
indicates the temperature of the steam, and serves as a plumb line.
The readings of this thermometer were corrected by comparison
with a standard thermometer.   The coefficient of friction of the gas
is calculated by the following formula given by O. E. Meyer:[1]

$$\eta = \frac{\pi g d r^4}{16 L V} \frac{P^2 - p^2}{P} t,$$

in which d = density of mercury at $0°$ C.

   g = acceleration due to gravitation.

   r = radius of capillary in cm.

   L = length of capillary in cm.

   P = pressure of gas on entering the capillary.

   p = height of barometer at $0°$ C.

   t = time in seconds.

   V = c.c. of gas transpired.

No allowance need be made for the expansion of the mercury at
$100°$ C., for what the column gains in height is compensated for by

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[1] Pogg. Ann., 1866, Bd. 127, p. 269.

loss in density.   No allowance has been made for the expansion of the capillary as it was assumed the expansion of the mercury tube, hence increase of the volume of gas transpired, would counteract this.

The advantages of this apparatus over that devised by L. Meyer are quite obvious and numerous.   In the first place it is much more simple and available.   The capillary is straight instead of coiled into a helix.   The friction of the vapors is taken at a temperature so high above the boiling point that they behave more like true gases than at their boiling points, where they are in a condition of unstable equilibrium.   The length of time required for an experiment is short enough for all conditions to be kept constant, and yet long enough, so that with a stop watch reading to one fifth of a second, the time can be determined to within less than one part in a thousand.

Apparatus No. 1.

The first piece of apparatus was constructed more to test the practicability of the method than for getting accurate results.   It having been determined by experiment, that the largest diameter of tube in which a mercury column would hold together, against a cushion of air, was about .35 cm., this apparatus was constructed with a mercury tube whose mean diameter, where it was traversed by the mercury column was .35104 cm., as shown by the fact that 76.0405 grams of mercury occupied 58.05 cm. at 20° C.   The distance between the two etched marks on the tube was 50 cm. This distance was occupied by 65.5558 grams of mercury at 20° C. The density of mercury at this temperature being 13.5463 the volume between the two marks was 4.8394 cubic centimeters.

The capillary was 34.35 cm. in length which was only about half the length of the mercury tube forming the other side of the U, in other words the capillary formed the upper half of one side of the U.   Its bore was conical as shown by the fact that 9.50 cm. of mercury at the small end occupied 9.05 cm. at the larger end which was made the bottom because O. Reynolds[1] has shown that converging walls tend to a steady instead of a whirling flow of water and presumably also of gas.   The above column of mercury was

[1] Proc. Royal Inst. Grt. Brit., 1884, vol. 11, p. 44.

passed slowly from one end of the capillary to the other and changed its length gradually and steadily, thus showing the absence of abnormal contractions or expansions of the bore. The bore of the capillary was determined from a sample 5.75 cm. long which had been cut from the smaller end. This sample was weighed several times empty and when containing different columns of mercury and the radius of the bore determined in the well-known way. A section was also examined under a microscope with a micrometer eye piece, and found to be so nearly a true circle that it was taken for such. The microscope reading agreed well with the mercury determinations of the radius. After taking the average of the mercury and microscope readings and after allowing for the taper of the capillary its mean radius was found to be .0103908 cm.

TABLE OF THE INTERNAL FRICTION OF AIR.

Apparatus No. 1.

Temp. in C.°	Ht. of Driving Col. in Cm.	Barom. at 0° C.	Press. of Entering Gas.	Time in Seconds.	$\eta \times 10^7$.	Average $\eta \times 10^7$.
15	7.97	76.03	83.09	76.04	1,872	
14.9	7.97	76.03	83.09	75.0	1,862	
14.9	7.97	76.03	83.09	74.8	1,857	
14.9	7.966	76.03	83.09	75.2	1,866	1,863.8 ± 2.57
14.9	7.966	76.60	83.64	75.2	1,860	
15.4	7.966	76.60	83.64	75.4	1,865	
20.4	4.29	75.38	78.87	156.8	1,967	1,972 ± 3.5
20.2	4.29	75.38	78.87	157.6	1,977	
21.4	9.48	75.38	84.01	64.4	1,935	1,932 ± 2.0
21.4	9.48	75.38	84.01	64.2	1,929	
99.9	9.48	75.38	84.01	75.6	2,272.5	
99.9	9.48	75.38	84.01	76.0	2,284.5	
100.3	7.98	76.96	84.00	92.0	2,238.2	
100.3	7.98	76.96	84.00	89.8	2,185.0	2,296.5 ± 15.8
100.3	7.97	76.60	83.64	94.0	2,305.0	
100.3	7.97	76.60	83.64	96.4	2,384.5	
100.3	7.97	76.60	83.64	92.7	2,293.0	
100.3	7.97	76.60	83.64	94.0	2,325.0	

To facilitate the washing of the apparatus the small vent, V, in Figs. 1 and 2, was left about ½ cm. below the base of the capillary. This vent tube, which was only 1 cm. long, was hermetically

sealed off after the apparatus was washed and ready for use. The apparatus, after it was received from the glass-blower, was washed throughout with a solution of potassium permanganate made alkaline with caustic potash, then with a solution of the same substance made acid with dilute sulphuric acid. Later a half and half solution of potassium bichromate and strong sulphuric acid was substituted for the above. Sometimes also strong nitric acid, followed by dilute nitric acid, was used. Then followed many washings with distilled water. The apparatus was then dried, by sucking through it by means of an aspirator, hot air which was filtered through cotton and dried by calcium chloride. A column of calcium chloride was also placed in the connection between the aspirator and the apparatus. The drying was not hastened by the use of alcohol or ether. The mercury was cleansed by shaking with dilute nitric acid, passing through a fine pin hole and drying in a porcelain dish at $110°$ C.

The results of experiments on air with this apparatus are given in the preceding table. It will be noticed they are all rather high, but prove at any rate that the method and apparatus are practicable. The probable errors were calculated by the usual formula

$$0.6745 \sqrt{\frac{\Sigma \, \text{diff}^2}{n(n-1)}} \, .$$

The error for readings at $100°$ C. is large, probably owing to an error of the stop-watch, whose hand showed a tendency to fly forward when stopping near 90 seconds. In one case the hand flew forward 10 seconds. The watch was of course repaired as soon as this defect was noticed. A different and better stop watch was used with apparatus No. 2 and No. 3. In those cases where the mercury was allowed to run back and was used over again the readings were weighted less than independent readings, three readings being converted into two by taking their means, and four into three in the same way.

It is rather difficult to tell what is the true coefficient of the internal friction of air. Landolt and Boernstein[1] give η for air at $15°$ C. $1,784 \times 10^7$. Markowski[2] at $16°$ gives $1,814 \times 10^7$, Kleint[3]

[1] Phys. Chem. Tabellen, Landolt and Boernstein, 1893.
[2] Inaug. Diss. Halle, 1903.
[3] Inaug. Diss. Halle, 1904.

at 14.1 to 14.5° C. gives 1,808 × 10^{7}. According to Landolt and Boernstein, then, my readings are 4½ per cent. too high at 15°, while according to Markowski and Kleint they are about 3 per cent. too high. F. G. Reynolds[1] gives for air at 20.7° .000187, which is 3¼ per cent. lower than my result of .0001932 at 21.4° C.

It was found by repeated trials with di-ethyl ether that the surface tension of the mercury was so much reduced by contact with the ether gas that the mercury would not hold together in one column in apparatus No. 1. It was determined by experiment that the mercury piston could not be used for ether gas in a tube whose diameter was much larger than 2 mm. A second piece of apparatus was accordingly constructed with a mercury tube of about this size, and a finer capillary, so that the transpiration time would be increased and greater accuracy be secured.

Apparatus No. 2.

The capillary selected for this when examined with a simple microscope was at first thought to be circular in cross-section, but the use of a high-power microscope with micrometer eye-piece showed it to be very elliptical, the ratio of the axes being almost exactly as 3 is to 1. The area of its cross-section was determined by mercury several times, and these values averaged with the microscope reading with which they agreed well.

The capillary which was 84 cm. long tapered in its bore, 2.5 cm. of mercury at the large end becoming 2.685 cm. at the small end. The sample whose bore was determined was taken from the small end. After allowing for the taper of the bore the average semi-major axis was found to be .006057 cm. and the average semi-minor axis .002016 cm. The capillary was placed with its larger end downward and reached to within 15 cm. of the bend in the U.

The mean diameter of the mercury tube in that part traversed by the mercury piston during an experiment was .2012 cm. as shown by the fact that 31.3 grams of mercury occupied a length of 72.6 cm. at 16° C. The marks on the mercury tube were made 50 cm. apart, the volume between these marks being found by means of mercury to be 1.5707 c.c.

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[1] Phys. Rev., 1904, vol. 18, p. 419; vol. 19, p. 37.

Because the capillary was elliptical the formula used for calculating the internal friction of gas from this apparatus is, according to Mathieu,[1]

$$\eta = \frac{\pi d g}{8 L V} \frac{a^3 b^3}{a^2 + b^2} \frac{P^2 - p^2}{P} t$$

where a = semi-major axis of ellipse of capillary.

  b = semi-minor axis of ellipse of capillary.

  d = density of mercury at $0°$ C..

  g = acceleration due to gravitation.

  L = length of capillary.

  V = vol. of gas transpired.

  P = pressure of entering gas.

  p = pressure of leaving gas = barom. at $0°$ C.

  t = time in seconds.

The results with air with this apparatus are shown in the next table.

It will be noticed that the values of η are somewhat lower than for apparatus No. 1, and therefore nearer the correct values.

The different lengths of the capillary given in the first column are due to the fact that on several occasions the upper end of the capillary became stopped with dust from the atmosphere and had to be cut off. When not in use the capillaries were kept capped with rubber, the funnels filled with cotton and closed by corks in which were inserted tubes of chloride of calcium.

TABLE OF THE INTERNAL FRICTION OF AIR.

Apparatus No. 2.

Length of Cap.	Temp. in C.°.	Ht. of Driving Col.	Barom. at 0°C.	Press. of Entering Gas.	Time in Seconds.	$\eta \times 10^7$.	Average $\eta \times 10^7$.
81.8	12.5	23.17	75.74	97.92	2,604	1,864.2	
84	18.5	23.17	76.19	98.36	2,721	1,897.4	
84	19.9	23.15	76.26	98.41	2,715	1,892.0 ⎱	1,897.3 ± 3.5
84	19.9	23.42	76.41	98.82	2,700	1,902.5 ⎰	
84	20.9	23.15	76.26	98.41	2,730	1,902.2	
84	26.9	23.16	76.15	98.31	2,810	1,957.1	
84	29.1	23.17	75.90	98.08	2,830	1,973.6	
84	100	23.17	75.91	98.09	3,201	2,233.0 ⎱	
81.8	99.9	23.14	75.70	98.85	3,130	2,237.0 �	2,242 ± 5
81.8	100.2	23.14	76.51	98.65	3,155	2,257.0 ⎰	

[1] Compt. Rend., 1863, Tome 57, p. 320.

Apparatus No. 3.

73.25	10	18.746	76.78	94.56	509.8	1,843.8	
73.25	13.3	18.75	76.78	94.56	516	1,866.9	
73.25	14.4	18.74	76.80	94.58	518.2	1,870.0	
73.25	19.4	18.75	76.00	93.79	524.6	1,894.0	
73.25	20.8	18.74	75.99	93.78	531.2	1,917.2	
70	21.0	18.75	76.99	94.77	509.2	1,923.6	1,909.9 ± 7.2
70	20.8	18.75	76.95	94.74	500.0	1,889.0	
70	100	18.74	75.76	94.50	592.8	2,244.0	
70	100.1	18.74	76.19	94.93	599	2,267.0	2,246.3 ± 7.2
70	100.3	18.75	77.13	94.92	588.8	2,228.0	

PREPARATION OF ETHERS.

The di-ethyl ether used in the following experiments was sulphuric ether, U. S. P. purified by two washings with concentrated sulphuric acid, C. P., each of these washings being followed by one with distilled water. It was then shaken with mercury and dried with sodium wire from which it was distilled into glass tubes which were afterward hermetically sealed. The ethyl-propyl ether, methyl-propyl-ether and methyl-ethyl ether used in this investigation were prepared by me, in the research laboratory of New York University under the personal supervision of Professor Loeb, according to the continuous etherification method described by Norton and Prescott in the Am. Chem. Journal, 1884, Vol. VI., p. 241. They were carefully dried with sodium and kept in sealed tubes.

The other substances, viz.: di-methyl ether, ethyl alcohol, methyl-isopropyl ether, ethyl-isopropyl ether, di-propyl ether, isopropyl-propyl ether and di-isopropyl, I owe entirely to the great courtesy of Professor Loeb, as I had no part at all in their preparation. As far as is known this is the first time that methyl-isopropyl ether has ever been made, while ethyl-isopropyl ether and isopropyl-propyl ether have probably been made only once before.

The internal frictions of the ethers used in apparatus No. 2 are given in the foregoing table on page 239.

The ethers are arranged in this table in the order of their molecular weights; that of methyl-ethyl ether being 60.064, that of methyl-propyl, methyl-isopropyl, di-ethyl ether being alike 74.08; while that of ethyl propyl is 88.096. It will be noticed the smaller the molecular weight the greater is the internal friction, which
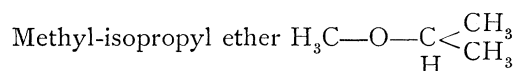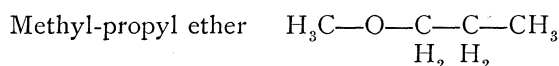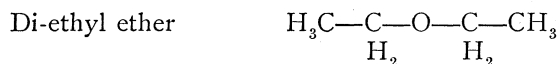
TABLE OF INTERNAL FRICTION OF ETHER GASES.

Apparatus No. 2.

Length Capillary.	Kind of Gas.	Temp. of Gas.	Ht. of Driving Col. at 0° C.	Barom. at 0° C.	Press. of Entering Gas	Time in Seconds.	$\eta \times 10^7$.	Average $\eta \times 10^7$.
81.8	Methyl-	99.9	23.16	75.68	97.85	1,502.0	1,074.5	
81.8	Ethyl	100	23.20	76.09	98.30	1,537.8	1,103	
81.8	Ether.	99.9	23.19	75.87	98.07	1,471.0	1,053.9	
81.8		99.3	23.16	75.44	97.61	1,558.0	1,114.2	1,092.3 ± 6.4
81.8		100	23.06	76.28	98.35	1,550.2	1,105.4	
81.8		100	23.16	76.15	98.32	1,540.0	1,102.8	
84	Methyl-	100	23.90	76.28	99.18	1,380.0	990.9	
84	Propyl	100	23.22	76.23	98.46	1,409.6	985.4	
84	Ether.	100	23.28	76.18	98.47	1,402.2	982.5	
84		100.1	23.14	76.46	98.60	1,461.8	1,018.9	1,004.3 ± 5.5
82.5		99.9	23.13	75.31	97.46	1,440.4	1,021.2	
81.8		99.8	23.11	74.24	96.39	1,439.9	1,027.0	
81.8	Methyl-	100.3	23.15	77.15	99.30	1,481.4	1,061.1	
81.8	Isopropyl	100.3	23.14	77.10	99.24	1,526.0	1,081.1	
81.8	Ether.	100	23.13	76.01	98.24	1,459.6	1,047.3	1,054.8 ± 5.0
81.8		100	23.12	76.00	98.13	1,455 0	1,039.9	
81.8		100	23.14	76.00	98.15	1,460.8	1,044.9	
84	Di-Ethyl	100.1	23.42	76.39	98.81	1,410.0	993.4	
84	Ether.	100	23.42	76.08	98.51	1,404.0	990.6	
84		100	23.16	76.15	98.32	1,416.6	986.8	
84		100	23.17	76.10	98.28	1,417.6	988.6	999 ± 3.3
84		100.1	23.16	76.54	98.71	1,437.6	1,000.6	
82.5		99.9	23.16	75.71	97.89	1,434.6	1,017.8	
82.2		99.9	23.21	75.50	97.73	1,428.0	1,015.2	
84	Ethyl-	100	23.17	76.06	98.24	1,285.0	896.2	
84	Propyl	100	23.17	75.89	98.07	1,296.4	904.6	
84	Ether.	99.9	23.16	75.70	97.87	1,281.2	892.7	
81.5		99.9	23.15	75.58	97.75	1,295.8	930.5	915.2 ± 5.3
81.5		99.9	23.14	75.57	97.73	1,298.8	932.3	
81.5		99.9	23.15	75.57	97.74	1,300.8	934.0	

agrees well with the kinetic theory of gases, according to which the friction increases with diminished size of molecule.

The most noteworthy fact shown in this table is that the three isomeric ethers, di-ethyl, methyl-propyl and methyl-isopropyl have not the same internal friction. Di-ethyl ether and methyl-propyl practically agree, while methyl-isopropyl ether has a friction 5 per cent. higher. According to the generally accepted view of the

concatenation of the molecules of these substances, the first two are simple chain compounds, while the last is a chain compound with two branches :

Di-ethyl ether $\qquad$ H_3C—C—O—C—CH$_3$
$\qquad$ $\qquad$ $\qquad$ H_2 $\qquad$ H_2

Methyl-propyl ether $\qquad$ H_3C—O—C—C—CH$_3$
$\qquad$ $\qquad$ $\qquad$ $\qquad$ H_2 H_2

Methyl-isopropyl ether H_3C—O—C$<^{CH_3}_{CH_3}$
$\qquad$ $\qquad$ $\qquad$ $\qquad$ H

It is easily conceivable how the last arrangement results in a compacter, smaller molecule, and hence shows a higher internal friction.

Although the amount of liquid used varied from $\frac{1}{2}$ c.c. to 1 c.c. as a rule, this small amount seemed sufficient on vaporizing to drive all the air out of the apparatus, as filling the apparatus entirely with ether from the base of the capillary to the stop-cock did not give results different from those obtained using 1 c.c. of ether.

The weight of mercury used in apparatus No. 1 and No. 2 was usually about 10 grams. That in apparatus No. 3 shortly to be described was about 5 grams.

The allowance to be made for the friction of the mercury against the walls of the tube was determined in the following manner. Three readings with air were taken with three very different columns of mercury, under constant temperature conditions. It being known that the internal friction of a gas is independent of the pressure, the values of η from these three readings were equated to each other in pairs, giving, after cancelling out constants of the apparatus, equations of the form

$$\frac{P^2c^2 - p^2}{Pc}t = \frac{P_1^2c^2 - p_1^2}{P_1c}t_1,$$

in which c is a constant reduction factor due to the friction of the mercury against the walls of the tube. The effect of capillarity is probably negligible, because the upper and lower surfaces of the mercury are convex in opposite directions.

In solving the equations for c good agreement was found, the

average c for apparatus No. 1 being .9892.   For apparatus No. 2 $c = .9895$ and for apparatus No. 3 $c = .9894$, all at 100° C.   The pressure of the gas on entering the capillary was calculated by adding the height of the mercury column at 0° C. to the barometer at 0° C. and multiplying by the reduction factor given above.   The mercury and barometer column were reduced to 0° C. by the aid of a table given on page 248 of Kohlrausch's Kleiner Leitfaden der Praktischen Physik.

Apparatus No. 3.

In order to have a second piece of apparatus available for experiments with ether, so that two experiments could be made at the same time, a third piece of apparatus was constructed.   The mercury tube of this apparatus was made a little smaller than that of apparatus No. 2, as some difficulty had been met in the mercury column failing to hold together properly.   The capillary of this apparatus was also elliptical and slightly conical.   The average semi-major axis as determined by the microscope and mercury was .006176 cm. while the minor axis was .002837.   The length of the capillary was 73.25 cm. at first, but was reduced to 70 cm. when the apparatus was repaired after a breakage.

The distance between the marks on the mercury tube was 38.45 cm. and the volume of gas transpired was .742 c.c. since 10.0634 grams of mercury occupied the distance between the marks at 16° C. The average diameter of the mercury tube where the mercury traversed it during an experiment was .158112 cm.

A table of the results obtained with this apparatus for air is given on page 238 underneath those for air with apparatus No. 2.   It will be noticed that the two pieces of apparatus agree very closely in results.

The results obtained for ethers with this apparatus are given in the following table.   The first point worthy of note is that ethyl alcohol which is metameric with di-methyl ether has about three per cent. lower coefficient of friction, showing it to have the larger molecule.
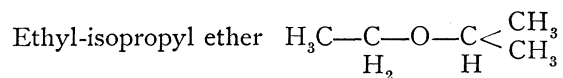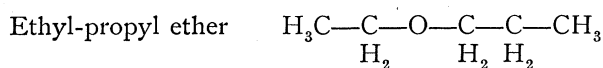
The values for di-ethyl ether, and ethyl-propyl ether agree well with those given on page 239 by apparatus No. 2.

Ethyl-isopropyl ether has a friction 4.6 per cent. higher than that o ethyl-propyl ether, hence a smaller molecule.
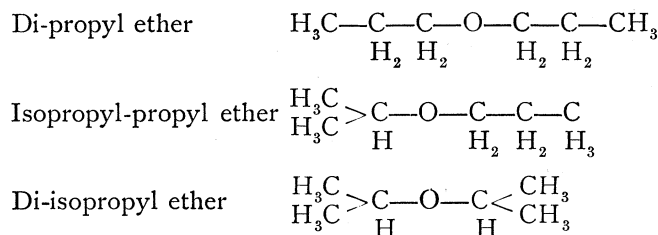
TABLE OF INTERNAL FRICTION OF ETHER GASES.

Apparatus No. 3.

Length Capillary.	Kind of Gas.	Temp. of Gas.	Ht. of Driving Col. at 0° C.	Barom. at 0° C.	Press. of Entering Gas.	Time in Seconds.	$\eta \times 10^7$.	Average $\eta \times 10^7$.
70	Di-methyl	100.3	18.75	77.24	95.03	315.6	1,191.8	
70	Ether.	100.3	18.74	77.32	95.10	314.8	1,188.6	1,190.2 ± 1
70	Ethyl	100.3	18.74	76.98	94.67	303.6	1,145.6	
70	Alcohol.	100.3	18.76	76.99	94.70	308.4	1,164.4	1,155 ± 6.3
73.25	Di-ethyl	100.1	18.78	76.43	94.26	287.4	1,041.8	
73.25	Ether.	100	18.60	76.15	93.81	287.4	1,023.2	
73.25		100	18.79	76.03	93.88	270.4	978.4	1,001 ± 8.15
70		99.9	18.76	75.80	93.61	254.8	963.7	
70		100.1	18.56	76.46	94.07	266.5	998.1	
73.25	Ethyl-	99.9	18.76	75.79	93.61	253.2	914.8	
73.25	Propyl	99.9	18.26	75.74	93.06	267.2	939.3	
73.25	Ether.	100	18.05	76.39	93.50	262.4	921.7	918.4 ± 4.2
73.25		100.3	18.28	76.83	94.16	256.6	902.7	
73.25		100.4	18.05	77.02	94.14	263.2	913.7	
70	Ethyl	100.2	17.74	76.46	93.26	267.7	946.4	
70	Isopropyl	100.2	18.76	76.41	94.22	255.4	966.4	960.7 ± 5
70	Ether.	100.2	18.56	76.34	93.95	258.8	969.3	
70	Di-Propyl	100	18.75	75.95	93.73	222.2	839.5	
70	Ether.	100	18.76	76.02	93.74	222.0	839.3	837.5 ± 1.26
70		100.3	18.75	77.14	94.93	220.8	832.7	
70	Isopropyl-	100.1	18.73	76.19	93.97	230.4	870.2	873.4 ± 2.2
70	propyl Ether.	100.1	18.76	76.22	94.03	231.6	876.6	
70	Di-isopro-	100.3	18.74	77.14	94.92	230.2	869.2	
70	pyl	100.3	18.74	77.14	94.92	230.8	871.5	
70	Ether.	100.3	18.76	77.09	94.89	239.0	902.8	894.3 ± 5.95
70		100.3	18.74	77.13	94.91	236.0	890.7	
70		100.1	18.73	76.23	94.01	241.0	910.5	
70		100.1	18.75	76.23	94.03	243.6	921.2	

Ethyl-propyl ether $H_3C-\underset{H_2}{C}-O-\underset{H_2}{C}-\underset{H_2}{C}-CH_3$

Ethyl-isopropyl ether $H_3C-\underset{H_2}{C}-O-\underset{H}{C}<\overset{CH_3}{\underset{CH_3}{}}$

Isopropyl-propyl ether has a friction 4.3 per cent. higher than that of di-propyl ether, while di-isopropyl ether has a friction 6.8

per cent. higher than di-propyl. This is in accordance with our view of the concatenation of the atoms in these molecules. Di-propyl ether is a straight, chain compound whereas isopropyl-propyl has two branches and di-isopropyl has four branches.

Di-propyl ether
$$H_3C—C—C—O—C—C—CH_3$$
$$H_2\ H_2H_2\ H_2$$

Isopropyl-propyl ether $\begin{matrix} H_3C \\ H_3C \end{matrix}\!>\!C—O—C—C—C$
$$HH_2\ H_2\ H_3$$

Di-isopropyl ether $\begin{matrix} H_3C \\ H_3C \end{matrix}\!>\!C—O—C\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}$
$$HH$$

As already noticed the difference between methyl-propyl and methyl-isopropyl is 5 per cent. due to two branches ; the difference between ethyl-propyl and ethyl-isopropyl due to two branches is 4.6 per cent.; the difference between di-propyl and isopropyl-propyl is 4.3 per cent. due to the same number of branches. The diminishing effect of the two CH_3 branches is probably due to the fact that the molecules of the substances lower on the lists are larger, hence the branches have a smaller relative effect. It would seem that di-isopropyl ether ought to be 8.6 per cent. higher than di-propyl whereas it is only 6.8 per cent. This discrepancy I am unable to explain.

Di-methyl ether, being a gas at ordinary temperatures, had to be handled differently from the other ethers, all of which were put into the apparatus as liquids. The low boiling ethers, methyl-ethyl, and methyl-isopropyl were experimented upon in a room whose temperature was at or very near 0° C.

The di-methyl ether gas was kept in sealed glass bulbs of 250 c.c. capacity. The lower end of a bulb was connected by rubber tubing to a reservoir of mercury while the upper end was connected by a rubber tube to the funnel at the top of the apparatus. After the aspirator had created a partial vacuum in the apparatus by sucking the air out through the capillary, the tips of the bulb were broken off inside the rubber tubes and mercury allowed to flow into the bulb gradually from the bottom, driving the ether gas before it into the apparatus, the action being assisted all the while by the suction

of the aspirator. As 250 c.c. was many times the cubic capacity of the apparatus, by the time the mercury had entirely filled the ether bulb, it was judged the apparatus would be filled with pure ether, unmixed with any air. This method of getting the ether gas into the apparatus proved a failure several times for various reasons, but the very close agreement of the two readings which were at length obtained points to their correctness.

MOLECULAR VOLUMES.

L. Meyer[1] gives the following formula for calculating approximate relative molecular volumes, derived from the molecular volume of SO_2 as determined by Andreef at $-8°$ C.

$$V = 3.10^{-6} \left\{ M(1 + at) \right\}^{\frac{3}{4}} \left\{ \frac{1}{\eta} \right\}^{\frac{3}{2}}$$

in which $M =$ molecular weight, $t =$ temperature Centigrade $\eta =$ coefficient of friction.

The values obtained for the substances under investigation are given on the next page. According to Kopp[2] the molecular volume of a liquid composed of carbon, hydrogen and oxygen can be found by substituting in its formula 11 for each atom of carbon, 5.5 for each hydrogen and 7.8 for each oxygen. The values thus calculated are given in the last column. The agreement between the molecular volumes calculated in these two ways is quite good, much better than that obtained by L. Meyer and Schumann.

As both apparatus No. 2 and No. 3 gave values for air about 5 per cent. higher than those given by Landolt and Boernstein as probably the most correct values, it is probable that the values of η for the ethers are correspondingly too high. Accordingly in the second table of molecular volumes the values of η were reduced by multiplying by 2,113/2,244, thus calibrating with air, and the molecular volumes recalculated. A still better agreement with Kopp's values is shown, the disagreement being greatest when the boiling point of the ether approaches the temperature at which η was determined.

[1] Wied. Ann., 1881, Bd. 13, p. 17.
[2] Ann. Chem. Phar., 1855, Bd. 96, pp. 1, 153, 303.

First Table of Molecular Volumes.

Material.	Formula.	Boiling Point in Degrees Centigrade.	$\eta \times 10^7$.	Molec. V. Found.	Molec. V. Calculated According to Kopp.
Di-methyl ether.	C_2H_6O	—23.65	1,190.2	51.62	} 62.8
Ethyl alcohol.	C_2H_6O	78.	1,155.0	55.25	
Methyl-ethyl ether.	C_3H_8O	10. –13.	1,092.3	71.65	84.8
Di-ethyl ether.	$C_4H_{10}O$	34.6–35.	1,000	95.73	
Methyl-propyl ether.	$C_4H_{10}O$	40. –45.	1,004.3	95.16	} 106.8
Methyl-isopropyl ether.	$C_4H_{10}O$	7.	1,054.8	88.37	
Ethyl-propyl ether.	$C_5H_{12}O$	66. –68.	916.8	124.19	} 128.8
Ethyl-isopropyl ether.	$C_5H_{12}O$	54. –57.	960.7	115.77	
Di-propyl ether.	$C_6H_{14}O$	84.5–86.5	837.5	158.90	
Isopropyl-propyl ether.	$C_6H_{14}O$	76.5–77.	873.4	148.86	} 150.8
Di-isopropyl ether.	$C_6H_{14}O$	68.5–69.	894.3	144.06	

Second Table of Molecular Volumes.

Material.	Formula.	Boiling Point in Degrees Centigrade.	$\eta \times 10^7$.	Molec. V. Found.	Molec. V. Calculated According to Kopp.
Di-methyl ether.	C_2H_6O	—23.65	1,121.0	56.46	} 62.8
Ethyl alcohol.	C_2H_6O	78.	1,088.0	59.05	
Methyl-ethyl ether.	C_3H_8O	10. –13.	1,029.0	81.12	84.8
Di-ethyl ether.	$C_4H_{10}O$	36.6–35.	942.0	104.71	
Methyl-propyl ether.	$C_4H_{10}O$	40. –45.	946.0	104.20	} 106.8
Methyl-isopropyl ether.	$C_4H_{10}O$	7.	993.6	96.66	
Ethyl-propyl ether.	$C_5H_{12}O$	66. –68.	863.6	135.84	} 128.8
Ethyl-isopropyl ether.	$C_5H_{12}O$	54. –57.	905.1	126.61	
Di-propyl ether.	$C_6H_{14}O$	84.5–86.5	788.9	173.08	
Isopropyl-propyl ether.	$C_6H_{14}O$	76.5-77.	822.7	163.20	} 150.8
Di-isopropyl ether.	$C_6H_{14}O$	68.5–69.	842.4	157.51	

In this second table η has been reduced by calibration with air.

MOLECULAR MEAN SPEEDS, FREE PATHS AND COLLISION FREQUENCIES.

In Meyer's Kinetic Theory of Gases on page 219 is given the formula $\eta = 0.30967 \, \rho L \Omega$ whence

$$L = \frac{\eta}{0.30967 \rho \Omega},$$

in which $\eta =$ coefficient of internal friction of the gas,

$\rho =$ density of the gas,

$\Omega =$ mean molecular velocity,

$L =$ mean molecular free path.

On page 55 of the same work we find $p = \frac{1}{8}\pi\rho\Omega^2$ whence

$$\Omega = \sqrt{\frac{8p}{\pi\rho}},$$

where p = pressure in absolute measure.

On page 195 we see that the

$$\text{Collision Frequency} = \frac{\Omega}{L}.$$

The values given in the table on this page were calculated according to the above formulæ, at a pressure of 76 cm. of mercury and a temperature of 100° C., the density being calculated from the formula

$$\rho = \frac{1}{2}\frac{(\text{formula weight})\ (0.000089)}{1 + at}.$$

First Table of Mean Molecular Speeds, Free Paths and Collision Frequencies.

Material.	Molecular Weight.	$\eta \times 10^7$.	Mean Molecular Speed Cm. per Sec.	Molecular Free Path Cm. $\times 10^{10}$.	Collision Frequency $\times 10^{-6}$.
Di-methyl ether.	46.048	1,190.2	41,470	61,787	6,711.7
Ethyl alcohol.	46.048	1,155.0	41,470	59,970	6,915.0
Methyl-ethyl ether.	60.064	1,092.3	36,310	49,660	7,312.0
Di-ethyl ether.	74.08	1,000.0	32,695	40,895	7,994.9
Methyl-propyl ether.	74.08	1,004.3	32,695	41,111	7,952.7
Methyl-isopropyl ether.	74.08	1,054.8	32,695	43,180	7,572.0
Ethyl-propyl ether.	88.096	916.8	29,982	34,415	8,711.8
Ethyl-isopropyl ether.	88.096	960.7	29,982	36,063	8,315.5
Di-propyl-propyl ether.	102.112	837.5	27,848	29,201	9,536.6
Isopropyl-propyl ether.	102.112	873.4	27,848	30,454	9,144.6
Di-isopropyl ether.	102.112	894.3	27,848	31,182	8,931.0

Second Table of Mean Molecular Speeds, Free Paths and Collision Frequencies.

Material.	Molecular Weight.	$\eta \times 10^7$.	Mean Molecular Speed Cm. per Sec.	Molecular Free Path Cm. $\times 10^{10}$.	Collision Frequency $\times 10^{-6}$.
Di-methyl ether.	46.048	1,121.0	41,470	58,204	7,125.0
Ethyl alcohol.	46.048	1,088.0	41,470	56,490	7,341.0
Methyl-ethyl ether.	60.064	1,029.0	36,310	46,782	7,762.0
Di-ethyl ether.	74.08	942.0	32,695	38,570	8,477.0
Methyl-propyl ether.	74.08	946.0	32,695	38,725	8,639.5
Methyl-isopropyl ether.	74.08	993.6	32,695	40,682	8,036.7
Ethyl-propyl ether.	88.096	863.6	29,982	32,418	9,248.4
Ethyl-isopropyl ether.	88.096	905.1	29,982	33,976	8,824.3
Di-propyl-propyl ether.	102.112	788.9	27,848	27,507	10,124.0
Isopropyl-propyl ether.	102.112	822.7	27,848	28,685	9,708.0
Di-isopropyl ether.	102.112	842.4	27,848	29,372	9,481.1

In this second table η has been reduced by calibration with air.

It will be noticed that the values are all of the proper order of magnitude, but do not rise and fall in a periodic way while the molecular weight increases, as pointed out for other substances by Meyer on page 196 of his Kinetic Theory of Gases, probably because these ethers are all so closely related.

COMPARISON WITH THE RESULTS OF OTHERS.

The results of my work cannot be compared satisfactorily and exactly with that of others, because I have determined the friction at a temperature higher than most other observers, and the law of its increase with the temperature is not accurately known in each case. Furthermore, air, di-ethyl ether, di-methyl ether and ethyl alcohol are the only substances which I have employed that others have investigated.

Disregarding the results with apparatus No. 1 as being only preliminary, we see that the values of η for air for the other two pieces of apparatus agree closely and are consistent, though both are about 5 per cent. higher than the values which are most probably correct, according to Landolt and Boernstein's tables. That the relative values of η at the different temperatures are correct is shown by calculating η at $0°$ C. by Sutherland's formula[1] and then calculating from that η at $100°$ C. Using the value of the cohesion constant $C = 119.4$ as determined by Breitenbach[2] we get for apparatus No. 2, $\eta_0 = .0001793$ and $\eta_{100} = .00022367$ the latter value agreeing with .0002242 observed within $\frac{1}{4}$ per cent. For apparatus No. 3 we get in like manner $\eta_0 = .0001795$ and $\eta_{100} = .0002239$, the latter value agreeing with .0002246 observed within $\frac{1}{3}$ per cent. This agreement is within the limits of error of the experiments.

Puluj's[3] formula for the coefficient of friction of di-ethyl ether vapor, $\eta = 0.0000689 \ (1 + .0041575 \ t)^{.94}$ gives $\eta = 0.0000935$ at $100°$ C. which agrees with my corrected value of 0.0000942 within $\frac{3}{4}$ per cent. This is good agreement bearing in mind the fact that Puluj's formula was determined from experiments over a small range of temperature, viz. : from $0°$ to $37°$ C.

[1] Phil. Mag., 1893 (5), vol. 36, p. 507.

[2] Drude's Ann., 1901, Bd. 5, p. 166.

[3] Wien. Ber., 1878, vol. 78 (2), p. 279 ; Carls Rep., 1878, vol. 14, p. 573; Phil. Mag., 1878 (5), vol. 6, p. 157.

The coefficient of friction of di-methyl ether is given on page 192 of Meyer's Kinetic Theory of Gases as 0.000092 at 0° C. No one has determined the law of its increase with the temperature. My corrected value is .0001121 at 100° C. which seems reasonable.

Steudel [1] gives 0.000142 as the coefficient of friction of ethyl alcohol at 78.4° C., its boiling point. My corrected value of .0001088 at 100° C. does not agree well with this. Because his value was determined at the boiling point I think it is open to question. My value for ethyl alcohol agrees much better with Puluj's [1] results which are 0.0000827 at 0° C. and 0.0000885 at 16.8° C. He assumes η is proportional to the absolute temperature which gives $\eta = .0001130$ at 100° C., which is nearly 4 per cent. higher than my value of .0001088. I think the assumption that η increases exactly as the absolute temperature is not strictly correct.

Concerning the differences which I have found between the normal propyl and the isopropyl ethers I would point out that Lothar Meyer, Schumann and Steudel found similar differences between many, though not all, of the normal propyl and isopropyl compounds which they examined. They also found that normal butyl, isobutyl and tertiary butyl compounds showed still more regular differences. The weight of evidence gives a larger molecule to the primary, a smaller to the secondary and the smallest to the tertiary compound. My values of the molecular speeds, free paths and collision frequencies being for 100° C. of course do not agree with those calculated for 0° C. by others.

Summary of Results.

1. The coefficients of internal friction of the following eight ether gases which have hitherto not been experimented with, have been determined with considerable accuracy as follows:

Methyl-ethyl ether	0.0001029	at 100° C.
Methyl-propyl ether	0.0000946	" "
Methyl-isopropyl ether	0.00009936	" "
Ethyl-propyl ether..	0.00008636	" "
Ethyl-isopropyl ether......................................	0.00009051	" "
Di-propyl ether	0.00007889	" "
Iso-propyl-propyl ether....................................	0.00008227	" "
Di-isopropyl	0.00008424	" "

[1] Wied. Ann., 1882, Bd. 16, p. 369.

2. The molecular volumes calculated from the friction have been shown to agree fairly well with those obtained by Kopp's rule.

3. A marked and unmistakable difference between the normal propyl and isopropyl ethers has been found, proving that the difference in the molecular structure of these ethers has a very noticeable effect upon their internal friction, and therefore upon the size of their molecules, the molecules having the most numerous branches being smaller than those with fewer or no branches.

In conclusion I wish to express my thanks to Professor Loeb for suggesting both the subject of this research and the form of apparatus, and for his kind interest and help throughout the course of the investigation.   In addition I wish to thank him heartily for his courtesy in supplying me with certain of the necessary ethers.

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