considered as representing the general properties of ten electron shell compounds in which one electron pair of the central atom is not shared.

Summary

A method for the preparation of pure tellurium tetrachloride is described.

The melting point and boiling point of tellurium tetrachloride are determined to be 225 and 390°, respectively.

The vapor density of tellurium tetrachloride is measured from above the boiling point to 600°.

The vapor pressure of liquid tellurium tetrachloride is measured.

The heat of vaporization is determined to be 18,400 calories per mole.

The vapor of the compound is concluded to consist of single molecules of $TeCl_4$ from the melting point to about 500°, where dissociation begins.

The density of liquid tellurium tetrachloride is determined from the freezing point to above the boiling point.

The surface tension of tellurium tetrachloride is determined over the same range.

Tellurium tetrachloride is concluded to have a ten electron shell surrounding the central atom, four pairs of these being shared with the chlorine atoms.

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[CONTRIBUTION FROM THE PEARSON CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE STANDARDIZATION OF A MODIFIED OSTWALD VISCOMETER

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A viscometer conforming essentially to Washburn and Williams,[1] modification of Ostwald's viscometer has been used by one of us[2] to determine the viscosities of several aqueous solutions, without attempting to determine how accurately the instrument reproduced true viscosities. The viscosities were calculated both by the simple law of Poiseuille and by assuming a value of 1.12 for m, the coefficient of the correction term which has been variously called the kinetic energy, Hagenbach, or inertia correction. Washburn and Williams reported experiments on changing time of flow with changing pressure, to support the conclusion that the law of Poiseuille, without a correction, should be used, but their method of calculation has since been questioned.[3] Since the magnitude of m is thought to be dependent upon the shape of the terminal of the capillary as well as

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[1] Washburn and Williams, THIS JOURNAL, **35**, 739 (1913).

[2] Chadwell, *ibid.*, **48**, 1912 (1926).

[3] Dorsey, *J. Opt. Soc. Am.*, **14**, 45 (1927).

upon the velocity of flow,[3] the present investigation was undertaken to determine how nearly an instrument of this type reproduced absolute viscosities.

At least two methods of standardizing a viscometer are available. The method usually adopted is to vary the time of flow of a standard substance by varying the pressure by known amounts. The necessary apparatus is complicated.[4] The second method is based on the measurement of times of flow for liquids of known viscosity. Of the data for the various liquids recommended as reference materials, those for water are the most trustworthy. A variation in time can be obtained by varying the temperature.

This paper reports the use of three viscometers, similar to one another in size of capillary and general construction, but differing in the shape of the ends of the capillary tube, ranging from a decided trumpet to the square end of a fractured tube. The dimensions of these viscometers were measured carefully, and the time of flow of water was measured at seven temperatures ranging from 15 to 30°. The resulting data are compared with the viscosity of water as given by previous investigations. The viscosities of aqueous solutions of urethan, determined at 20 and 25°, are given to provide standard solutions to be used as reference materials for future calibration.

Apparatus and Results for Water.—The three viscometers were all of the same type and constructed of pyrex glass, similar to that used before by one of us.[2]

Viscometer I had its capillary sealed into the instrument in such a way that its ends were decidedly trumpet shaped. The capillaries of Viscometer II and III were taken from the same piece of tubing. The capillary in Viscometer II was not sealed into the instrument, but connected by ground joints, sealed on the outside with de Khotinsky cement. Its ends were the square fractures obtained by breaking the tubing. Viscometer III had its capillary sealed in, but with more abrupt endings than Viscometer I, instructions being given to the glass-blower to make the endings as abrupt as possible. The inside diameter of the tubes into which the capillaries delivered the liquid was 8 mm.

Each viscometer was mounted on a brass frame in such a way that the capillary was held in a vertical position in the thermostat. Each frame had three brass reference points that fitted into corresponding small conical cups inside the thermostat.

The thermostat was made from a deep glass jar, insulated as usual, and was fitted with a copper cooling coil, a stirrer and an automatic electrical heating unit. The temperature remained constant to within ±0.002° at all temperatures except 15°, where the variation was slightly larger. Into the jar was built a superstructure of brass to hold the frame of the viscometer in a rigid and definite position. It was found convenient to construct a frame outside of the thermostat with the reference points in similar positions to facilitate the measuring of the dimensions of the instruments. Windows through the packing of plumber's wool were provided so that the movements of the liquid past the scratches could be viewed easily.

The temperatures which the thermostat maintained were obtained with a series of

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[4] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, 1922.

Beckmann thermometers that were used as secondary standards, each one being compared with a platinum thermometer. The platinum thermometer had been calibrated by the Bureau of Standards and has been described in THIS JOURNAL.[5] Each comparison with the platinum thermometer was made within 0.01° of the desired temperature, so that any corrections to the Beckmann were eliminated. It is believed that these temperatures were accurately reproduced within a few thousandths of a degree.

The diameters of the capillary tubes were determined by measuring the length of a small drop of mercury at a known temperature. The mercury was later weighed on an assay balance with weights that had been compared with weights certified by the Bureau of Standards. The measurements of length were made with a "Universal Reading Microscope," manufactured by P. W. G. Pye & Co. The screw with micrometer head read to 0.005 mm. The larger scale, 18 cm. long, could be read with a vernier to 0.05 mm.

In the determination of the radius of the capillaries the mercury used had been purified by washings with nitric acid followed by distillation. The readings of the length of the thread of mercury were made at points equally distributed along the capillary. The results of these measurements are given in Table I.

TABLE I

MEASUREMENTS DETERMINING THE RADIUS OF THE CAPILLARIES

Corrected weight of mercury	No. of settings	Mean length, cm.	Density of mercury	Radius, cm.
		Viscometer I		
0.05593	3	2.2695	13.539	0.024068
.06617	4	2.6814	13.539	.024087
.06253	6	2.5311	13.541	.024099
			Mean	.024085
		Viscometer II		
0.30874	1	13.380	13.537	0.023293
.27087	1	11.765	13.543	.023262
.28076	1	12.170	13.538	.023290
.09614[a]	3	4.150	13.540	.023337
.28042	1	12.155	13.540	.023289
.06282	6	2.7248	13.538	.023283
			Mean	.023283
		Viscometer III		
0.20906	3	9.117	13.524	0.023232
.28815	2	12.565	13.520	.023236
.35810	1	15.600	13.533	.023236
			Mean	.023234

[a] Omitted in the calculation of the mean because of evident irregularity.

In the values of the "mean length" and the "radius," the last decimal place is significant only in determining the next figure. The "No. of settings" refers to the number of measurements of the length of each drop of mercury as it appeared at different positions in the capillary.

In calculating the radius of each capillary from the weight of mercury and the length of the drop, a correction was applied for the meniscus.

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[5] Chadwell, THIS JOURNAL, **49**, 2795 (1927).

This correction was calculated by measuring the height of the meniscus with a microscope having a magnification of 100 and fitted with a micrometer eyepiece. The latter was calibrated by a Bausch and Lomb test plate graduated in 0.01 mm. It was assumed that the meniscus was a spherical segment.

The values of the radius given above are calculated on the assumption that the bore is cylindrical. Formulas[6] have been advanced for capillaries which do not conform with this condition. If the capillary is elliptical

$$\frac{2B^3C^3}{B^2 + C^2} \tag{1}$$

is substituted for R^4 in the formula for viscosity, where B and C are the major and minor semi-axes of the cross section. If the capillary is a frustum of a circular cone, R^4 is replaced by

$$\frac{3R_1{}^3R_2{}^3}{R_1{}^2 + R_1R_2 + R_2{}^2} \tag{2}$$

where R_1 and R_2 are the radii at the two ends. If the capillary is a frustum of an elliptical cone, R^4 is replaced by

$$\frac{3R_3{}^3R_4{}^3}{R_3{}^2 + R_3R_4 + R_4{}^2} \times \frac{(1 - E^2)^3}{1 + E^2} \tag{3}$$

where R_3 and R_4 are arithmetical means of the major and minor axes at their respective ends, and $E = (B - C)/(B + C)$. B and C have the same meaning as in (1).

To determine how great an assumption was introduced in using the simplest method of calculating the radius, the individually determined radii of Viscometer I were plotted against the position of the drop of mercury and the curve extrapolated to give the radii at the ends. The results were 0.02430 and 0.02388. If these data are substituted in expression (2), the corrected value for R^4 comes out equal to 0.0_633669, while that used in the calculations was 0.0_633650, a difference of 0.06%.

A short section of the capillary used in Viscometers II and III was examined under a microscope fitted with a micrometer eyepiece and previously calibrated with a Bausch and Lomb test plate. This showed the cross section to be circular within the accuracy of the examination (between 1 and 2%). If there was a difference in the semi-axis of 2%, the difference in the value of R^4 would be only 0.04%. As a consequence of these measurements, it was felt that the first values for the radius could be used with safety.

The other dimensions of the instruments were determined in the usual way, with corresponding accuracy. They are summarized in Table II.

In the determination of the time of flow of water the usual precautions were taken in regard to cleanliness and absence of dust. The water was

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[6] See Bingham, Ref. 4, p. 69.

TABLE II

SUMMARY OF DIMENSIONS OF VISCOMETERS

	Vis. I	Vis. II	Vis. III
Radius of capillary, cm.	0.024085	0.023283	0.023234
Length of capillary, cm.	17.25	17.225	16.540
Volume of upper bulb, ml.	7.150	5.336	8.874
Volume used in viscometer, ml.	68.53	50.54	60.88
Distance between scratches, cm.	6.065	5.960	5.744
Difference in water levels at start, cm.	24.148	22.285	22.966
Difference in water levels at end, cm.	17.910	16.270	17.010
Mean head (h) by Meissner (Eq. 6)	20.880	19.120	19.841

thrice distilled, from alkaline permanganate and dilute sulfuric acid, using tin condensers. The time of flow was measured, as in the former investigation,[7] by a stop watch having an excellent Swiss movement and recording time to one-fifth of a second. It was verified frequently and kept in a constant state as regards winding and position.

The times of flow for water for the different temperatures, as recorded in Table III, are average results of at least three runs in which the variation was not greater than the accuracy of measuring the time of flow (1/5 sec.). Table III also includes the data for the density of water in air and the viscosity, expressed as poises, as given by the Bureau of Standards[8] and the "International Critical Tables."[9] These data are used in subsequent calculations.

TABLE III

DATA FOR WATER

Temp., °C.	Time of flow Vis. I	 Vis. II	 Vis. III	Density in air	Viscosity B. of S.	 I. C. T.
15.00	523.2	493.3	765.6	0.99790	0.011404	0.011447
18.00	484.4	457.9	709.0	.99741	.010559	.010603
20.00	461.3	436.3	674.7	.99703	.010050	.010087
22.00	439.8	415.6	643.5	.99660	.009579	.009608
25.00	410.6	388.6	600.8	.99589	.008937	.008949
27.00	392.8	371.2	574.5	.99536	.008545	.008551
30.00	368.6	348.5	539.1	.99451	.008007	.008004

Calculation of Results

The viscosity is related[10] to the dimensions of the viscometer by the formula

$$\eta = \frac{\pi r^4 pt}{8V(l + e)} - \frac{m\rho V}{8\pi(l + e)t} \qquad (4)$$

where η is the coefficient of viscosity (in poises), r the radius (cm.) of the capillary assumed to be cylindrical, p the over-all driving pressure, t the

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[7] Chadwell, Ref. 2, p. 1916.

[8] Bingham and Jackson, "Bull. U. S. Bureau of Standards," **14**, No. 298 (1917).

[9] "International Critical Tables," McGraw-Hill Book Co., Inc., **1929**, Vol. V, p. 10.

[10] See, for instance, Dorsey, *Phys. Rev.*, **28**, 833 (1926).

time of flow in seconds for a volume of V (ml.) through a tube of length l cm., e the Couette correction, m a numerical factor usually taken as 1.12, and ρ the density of the liquid.

It follows from this formula that if $\eta/\rho t$ is plotted as ordinates and $1/t^2$ as abscissas for liquids of different known viscosity, the slope of the line to the axis of abscissa is

$$\tan \Theta = -\frac{mV}{8L\pi}$$

where Θ is the angle between the line and the axis and L is the effective length ($L = l + e$). The intercept on the axis of abscissa is π^2r^4hg/mv^2 and the intercept on the axis of ordinates is $\pi r^4hg/8\ VL$ where "h" is the effective height causing the liquid to flow by its own hydrostatic pressure ($p = h\rho g$) and g is the force of gravity. If m is zero, the line will be parallel to the axis of ordinates.

It should be emphasized, in support of this method, that one can conclude whether m has a value other than zero quite independently of any measurements of the dimensions of the capillary. If it is zero, the conclusion depends upon the values of viscosity taken as standard, the density of the liquid and the time of flow; if m does not equal zero, its value is calculated from measurements of the volume of the liquid and length of capillary, not upon the radius.

This method of evaluating m is not new. It is similar to the method of Knibbs[11] where one liquid is used to calibrate a viscometer by allowing it to flow under different pressures, and then plotting pt against $1/t$. Nor is it very dissimilar from that of Herschel,[12] who uses a series of liquids of known viscosity and plots Reynolds' criterion ($R = vd\rho/\eta$ where v, the velocity, is equal to $V/\pi r^2t$, and d is the diameter) against η'/η, the ratio of the viscosity as calculated without the second term of Formula 4 and using the measured length (l), to the true viscosity (η). By this method the intercept on the axis of η'/η is equal to $(l + e)/l$ and the slope of the line gives the value of m by the formula $m = 32\ l/d{\cdot}\tan \Theta$.

Both the method suggested by the authors and Herschel's method of evaluating m presuppose the knowledge of certain viscosities, either of one liquid at different temperatures or different liquids at the same temperature. Since water has been studied more carefully than any other liquid, it was selected as the basis of comparison, and used at different temperatures as described above.

The data for the absolute viscosity of water as determined by various investigators have been recalculated by Bingham, assuming that m has

[11] See Rieman, This Journal, **50**, 46 (1928). Since this manuscript was prepared it has been found that Higgins has used the same method of plotting $\eta/\rho t$ against $1/t^2$, Higgins, *J. Soc. Chem. Ind.*, **32**, 568 (1913).

[12] Herschel, *Proc. Am. Soc. Test. Mat.*, **19**, 677 (1919); also Herschel and Bulkley, *Ind. Eng. Chem.*, **19**, 134 (1927).

a value of 1.12. They have been published in several places.[13] When made the basis for evaluating m for Viscometer I by the first method suggested, the values for $\eta/\rho t$ as given in Table IV result.

TABLE IV

VALUES OF $\eta/\rho t \times 10^5$ FOR VISCOMETER I BASED ON THE ABSOLUTE VISCOSITY OF WATER AS DETERMINED BY VARIOUS INVESTIGATORS

Temp., °C.	Poiseuille				Sprung	Thorpe and Rodger	Bingham and White
	A	C	D′	E			
15	2.1807	2.1958	2.1960	2.1942	2.1709	2.1690	2.1784
20	2.1803	2.1901	2.1879	2.1931	2.1694	2.1753	2.1860
25	2.1765	2.1921	2.1926	2.1943	2.1880	2.1766	2.1863
30	2.1708	2.2063	2.2049	2.2093	2.2519	2.1727	2.1798

The columns under "Poiseuille" contain his results for four different capillaries. If m for our viscometers had a value of zero, the term $\eta/\rho t$ should be independent of the time of flow; if m had a positive value, $\eta/\rho t$ would have to decrease with a decrease in time (increase in temperature). It is evident from the data of this table that any conclusion concerning m would be uncertain.

The determinations of the absolute viscosity of water have been critically appraised by two reviewers.[8] The Bureau of Standards has accepted the formula

$$t = A(\varphi + D) + C - \frac{B}{\varphi + D} \tag{5}$$

to define the changes in fluidity with temperature, where t is the centigrade temperature, φ the fluidity and A, B, C and D are arbitrary constants having the values 0.23275, 8676.8, 8.435 and 1.20, respectively. The second set of data were compiled by the editors of the "International Critical Tables."[9] No information is available concerning the basis of their selection. Both sets of values have been included in Table III. They are the basis for calculating the values of $\eta/\rho t$ given in Table V.

The values of $\eta/\rho t$ are remarkably consistent for the Bureau of Standards data. Viscometer II, having fractured ends, is slightly less regular (the value for 15° is evidently in error) but shows no tendencies that can be attributed to the configuration of the terminals of the capillary. *It is to be concluded that viscosities corresponding to the Bureau of Standards data (Bingham and Jackson) could be reproduced by any of the viscometers at the velocities studied, on the assumption that m equals zero, in other words, by calculating the results by the simple Poiseuille formula.*

The values of $\eta/\rho t$ calculated from the "International Critical Tables" data show a decided trend. From them a value of m for each viscometer can be calculated. The data for 15° are so discordant that they are mean-

[13] Bingham and Jackson, *Sci. Paper Bur. Stand.*, No. 298 (1917); Landolt–Börnstein, "Physikalisch-Chemische Tabellen," Erster Ergänzungband, **1927**, p. 83; Bingham, Ref. 4, p. 339.

TABLE V

VALUES OF $\eta/\rho t$ FOR THE THREE VISCOMETERS USING η_{H_2O} ACCORDING TO THE BUREAU OF STANDARDS

	$\eta/\rho t \times 10^5$			% Deviation from average		
Temp., °C.	Vis. I	Vis. II	Vis. III	Vis. I	Vis. II	Vis. III
15.00	2.1843	2.3166[a]	1.4926	−0.04	+0.23[a]	−0.06
18.00	2.1854	2.3119	1.4931	+ .01	− .03	− .03
20.00	2.1851	2.3103	1.4939	± .00	− .04	+ .03
22.00	2.1855	2.3127	1.4937	+ .02	+ .06	+ .01
25.00	2.1856	2.3093	1.4937	+ .02	− .08	+ .01
27.00	2.1856	2.3126	1.4943	+ .02	+ .06	+ .05
30.00	2.1842	2.3103	1.4934	− .04	− .04	± .00
Average	2.1851	2.3112	1.4935	.02	.05	.03

[a] Not included in average.

VALUES OF $\eta/\rho t$ FOR THE THREE VISCOMETERS USING η_{H_2O} ACCORDING TO "INTERNATIONAL CRITICAL TABLES"

	$\eta/\rho t \times 10^5$			% Deviation from average		
Temp., °C.	Vis. I	Vis. II	Vis. III	Vis. I	Vis. II	Vis. III
15.00	2.1925	2.3254	1.4982	+0.10	+0.34	+0.08
18.00	2.1946	2.3215	1.4993	+ .20	+ .17	+ .15
20.00	2.1931	2.3208	1.4994	+ .13	+ .14	+ .16
22.00	2.1921	2.3196	1.4982	+ .09	+ .09	+ .08
25.00	2.1885	2.3124	1.4957	− .08	− .22	− .09
27.00	2.1871	2.3142	1.4953	− .14	− .14	− .11
30.00	2.1834	2.3094	1.4928	− .31	− .35	− .28
Average	2.1902	2.3176	1.4970			

ingless, and so are not included. For Viscometers I and III, having the capillaries sealed into the glass and as a consequence having trumpet-shaped openings, the values can be determined graphically (by the method outlined above). Figure 1 shows the plot of $\eta/\rho t$ against $1/t^2$. The slopes of the lines are -0.0355 and -0.0487, leading to values of m of 2.15 and 2.27. The data for Viscometer II (having squarely cut ends) are not close enough to a straight line to insure much confidence in the result. The slope of the most probable straight line was calculated by the method of least squares as -0.0364, which corresponds to values of m equal to 2.93. It would seem that the data from the Bureau of Standards, with the accompanying conclusions, are the most trustworthy.

When Herschel's method is applied to these data, the conclusions regarding m are, of course, the same, but it also produces the Couette correction. This method has been applied to the data for the three viscometers, using the viscosity of water according to the Bureau of Standards. The results are given in Table VI, where R represents Reynolds' criterion. In order for m to have a value other than zero, the data for η'/η would have to show a definite trend, for m is a function of the slope of the line when R is plotted against η'/η.

According to this method the Couette correction (e) is given by the

TABLE VI

HERSCHEL'S METHOD APPLIED TO THE THREE VISCOMETERS USING η_{H_2O} ACCORDING TO THE BUREAU OF STANDARDS

Temp., °C.	Viscometer I R	 η'/η	Viscometer II R	 η'/η	Viscometer III R	 η'/η
15.00	31.61	1.0041	25.88	1.0160^a	27.79	1.0161
18.00	36.85	1.0036	30.10	1.0180	32.40	1.0157
20.00	40.64	1.0038	33.18	1.0187	35.75	1.0152
22.00	44.71	1.0036	36.52	1.0177	39.31	1.0153
25.00	51.29	1.0035	41.84	1.0192	45.10	1.0153
27.00	56.04	1.0035	45.78	1.0177	49.30	1.0149
30.00	63.68	1.0041	51.99	1.0187	56.02	1.0155
Average		1.0037		1.0183		1.0154

^{a} Not included in the average.

expression $e = l(a - 1)$ where a is the intercept on the η'/η axis corresponding to $R = 0$. The calculated corrections are 0.064, 0.315 and 0.255 cm. for the three viscometers. It is not to be expected that these values of the Couette correction would bear the relationship to the radius as derived from theoretical considerations. They really represent a correction to one particular measured dimension of the capillary to counteract inaccuracies in the others. The real Couette correction for these viscometers is almost negligible, for the ratio of l/r is so large, the correction being much smaller than the uncertainty in measuring the length of a capillary terminating in trumpet-like openings.

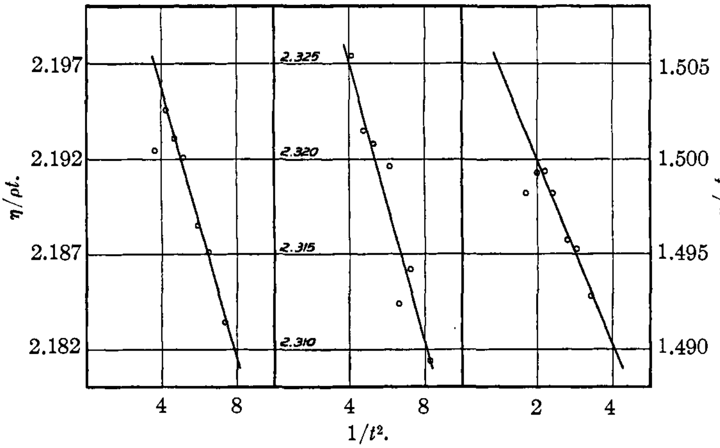

Fig. 1.—The values of $\eta/\rho t$ ($\times$ 10^5), using the data of "International Critical Tables" for the viscosity of water, are plotted against $1/t^2$ ($\times$ 10^6) for the three viscometers. The slopes of the lines give the values of m.

These results are of interest in relation to Dorsey's[14] interpretation of

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[14] Dorsey, *Phys. Rev.*, **28**, 833 (1926); and *J. Opt. Soc. Am.*, **14**, 45 (1927).

Poiseuille's and Bond's[15] experiments on the flow of liquids through capillaries. Dorsey maintains that the data show that when Reynolds' number (R) is less than 10, m has a value of zero and the Couette correction (e) is 1.146 r. If R is greater than 10, two regimes are possible if the capillary is long and free from mechanical vibration. In the one case m still remains equal to zero; in the other, and the more likely, m is probably equal to unity and e is half as large as before. A theoretical interpretation of the stability of these regimes is given, based on the premises "that the free surface of the liquid in each reservoir is great compared with the sectional area of the capillary, that the edge at each terminus of the capillary is sharp and smooth, that at each end of the capillary the terminal face is normal to the axis of the capillary, and that the radial extent of this face, in every direction, and all other distances from the terminus to the wall of the reservoir are severally so great that the distribution of the flow of the liquid is essentially the same as if they were infinite." It is further pointed out that departures from these ideal conditions will result in different values of m and e, and probably account for the variations actually found in determined values of m between 1.0 and 2, and averaging 1.12. Variation in the configurations of the terminals of the capillaries are probably the most significant.

The velocities of flow through the three viscometers studied were sufficiently large to allow either of the two regimes to be satisfied, for the values of Reynolds' number were between 25 and 65. Furthermore, Viscometer II had a capillary with terminals which fulfilled the postulated conditions, particularly that of a sharp-edged face normal to the axis of the capillary, while the others had terminals that were trumpet-like, Viscometer III having a more abrupt opening than Viscometer I. Yet there is little or no evidence in the data given above to show that the configuration of the capillary ends in these particular viscometers played a part in determining m.

Equation 4 has been used in various ways to evaluate different dimensions of the viscometer. Reference has already been made to Knibbs' method, which produces the value of m and r, and to Herschel's method yielding m and e. Dryden's equation[16] for the evaluation of the hydrostatic head causing the flow is still another modification, but these methods can hardly be used simultaneously.[17] The value to be used for the over-all driving pressure (p) is particularly hard to evaluate for a viscometer of the Ostwald type, for the hydrostatic head is varying during the flow of liquid. The average head is certainly in error.[18] The chronological average head

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[15] Bond, *Proc. Phys. Soc. London*, **33**, 225 (1921); *ibid.*, **34**, 139 (1922).

[16] Reported in a paper by Herschel, Bureau of Standards Tech. Paper, No. 210, 230 (1922).

[17] See Herschel and Bulkley, *Ind. Eng. Chem.*, **19**, 134 (1927).

[18] See Lidstone, *Phil. Mag.*, [VI] **43**, 354 (1922).

has sometimes been evaluated by an integration method applied to observed changes of head at intervals of time throughout the flow. This pressure is more generally calculated from the approximation formula of Meissner

$$h = \frac{h_1 - h_2}{\log_e h_1/h_2} \tag{6}$$

where h_1 is the initial and h_2 the final hydrostatic head. This latter method when applied to our viscometers produced the values listed under the heading "h" in Table II. To determine how different these values of effective heads are, the correct value to be used to give the mean value of $\eta/\rho t$ in Table IV was calculated from $h = \frac{8VL}{\pi r^4 g}\left(\frac{\eta}{\rho t}\right)_{\text{mean}}$ assuming the Couette correction to be that given by Dorsey. The results are summarized in Table VII.

TABLE VII

HYDROSTATIC HEADS CALCULATED BY VARIOUS METHODS

No. of viscometer	h_a	h_m	h_η
I	21.029	20.880	20.836
II	19.278	19.120	18.805
III	19.988	19.841	19.571

Here the arithmetic average of the initial and final heads is given as h_a, the values by Meissner's formulas as h_m, and the values calculated from the viscosity as h_η. The percentage differences between the last two columns are 0.2, 1.6 and 1.4, respectively, for the three viscometers.

The above comparison should not be interpreted to measure the approximation of Meissner's formula, for all of the inaccuracies in measurements of the dimensions of the capillaries are automatically included. It is rather disconcerting, however, that the capillary for Viscometer II, which was the easiest to measure, shows the largest deviation. Furthermore, it should be remembered that Meissner's formula was derived on the assumption that the two limbs of the viscometer are cylindrical and equal, and these conditions are not satisfied in the design of the viscometers in question.

For an exact determination of m, the length of the capillary tube should be relatively small so that the kinetic energy correction is large. This procedure was followed by Rieman,[19] who concluded that the value of m was 1.12. A Bingham viscometer was used, modified to the extent that the capillary was mounted in rubber tubing and had, presumably, squarely fractured ends. The times of flow under varying pressure were determined and the value of m calculated by the method of Knibbs. The velocities of flow were very different from those reported in the present investigation, Reynolds' number varying from 192 to 1013.

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[19] Rieman, THIS JOURNAL, 50, 46 (1928).

In the standardization here reported, the primary objects were to determine how exactly a viscometer essentially of the Washburn and Williams type reproduced absolute viscosities, and to determine the effect of different configurations in the terminals of the capillary. We believe that the investigation has shown that these viscometers would reproduce viscosities comparable to the values of water accepted by the Bureau of Standards (Bingham and Jackson), and at the velocities used, on the assumption that *m* equals zero. If further investigation changes the absolute viscosities of water, the data determined by these viscometers must be changed. We would emphasize the need of evaluating *m* for a given viscometer, and for a given range of velocities of flow. We do not wish that our conclusions be interpreted to mean that the kinetic energy correction can be neglected in determining viscosity.

The Viscosity of Aqueous Solutions of Urethan.—In order to have liquids available for standardization of other viscometers, the viscosities of several aqueous solutions of urethan were determined with Viscometer I.

Urethan was selected primarily because of its ease of purification by recrystallization. Other substances have been recommended for standardizing purposes, particularly aqueous solutions of alcohol and of sucrose. The latter was discarded from consideration because of the difficulty of purification and because the solutions were liable to mold. Alcohol is a difficult substance to free from aldehyde and water. At the beginning of this investigation it was thought that alcohol–water mixtures could be used as well as water in the preliminary standardization, but the results in the literature were more discordant than those of water, and several weeks spent in purifying alcohol led to the conclusion that although relatively pure alcohol could be prepared, the sample obtained would not be comparable to those of previous investigators and certainly could not be easily reproduced in the future.

Purification of Materials

Urethan.—Urethan ($NH_2COOC_2H_5$) from a reliable source was crystallized four times from water, the crystals being separated from the mother liquor by a centrifuge. The material was dried and kept in a desiccator over solid sodium hydroxide until the solutions were prepared.

The melting points were determined by immersing a standardized tenth degree thermometer in a mush of the melted urethan, surrounded by an air jacket and immersed in a bath of warm sulfuric acid. The thermometer reading was corrected for emergent stem, zero point and scale deviation. The melting point of the material after four crystallizations was the same as after three, namely, 48.19.° This is slightly higher than the values obtained previously of 47.94 and 47.99°.[20]

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[20] Richards and Chadwell, This Journal, **47**, 2283 (1925). For other values for the melting point, see Ref. 7 in that paper.

Water.—The water was triply distilled as usual and was purified directly before the solutions were prepared.

Preparation of Solutions and Measurement of Viscosity.—The solutions were prepared in 100-cc. graduated flasks, their concentrations being determined by weighing to milligrams on an analytical balance. Precautions were taken to prevent evaporation by adding the water last, and by keeping the bottles sealed with collodion. In a few cases the solution contained small particles of lint, in which event it was filtered rapidly into another flask. Vacuum corrections were not applied for they would have changed the percentage by only 0.01%.

The densities were determined in duplicate in 10-cc. Ostwald pycnometers, weighing against a sealed counterpoise,[21] and corrected to the vacuum standard.

The technique of making a viscosity measurement was the same as with water. All of the runs were made with Viscometer I, the determinations at 25° being completed before the thermostat was changed to 20°. Frequent runs were made with water to ascertain that the apparatus was functioning properly. The time for each solution was the mean of at least two runs, concordant within the accuracy of measuring time.

In Table VIII are given the results of these experiments. In the first column is given a letter to represent the order of runs, in the second the percentage of urethan by weight and in the third the number of moles of urethan (mol. wt., 89.062) per 1000 g. of solution. The values for density are corrected to the vacuum standard. When used in calculating the viscosity they are changed to the density in air by subtracting the weight of 1 ml. of air. The viscosities are expressed as centipoises (the viscosity in poises × 100) and were calculated by the formula $\eta = 2.1851\ \rho t \times 10^{-5}$ based on the results given in Table V. In other words, the viscosities given above are referred to the viscosity of water as given by the Bureau of Standards.[22]

Table IX includes the viscosities (in centipoises) and fluidities (in reciprocal poises) for these urethan solutions obtained by interpolation from the curve of the ratio of change in viscosity to molarity plotted against molarity (η solution $-$ $\eta H_2O/c$ vs. c). The data in Table VIII are consistent with the exception of Solution E, whose viscosities at both temperatures are slightly high.

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[21] Richards and Chadwell, THIS JOURNAL, **47**, 2286 (1925).

[22] These results at 20° are in good agreement with those determined by Richards and Palitzsch [*ibid.*, **41**, 63 (1919)]. Their values for the relative viscosity, which they calculated by the simple Poiseuille formula, are as follows

%........	9.12	16.69	28.62	44.51	50.07	55.65
η.........	1.206	1.398	1.730	2.250	2.471	2.716

By interpolation of our results we get for viscosities at the three lowest concentrations the following: 1.206, 1.402 and 1.730. Our density values are slightly lower than those of Richards and Palitzsch.

TABLE VIII

THE VISCOSITY OF URETHAN SOLUTIONS

No.	%	c	20° t	20° $\rho_{vac.}$	20° η(cp.)	25° t	25° $\rho_{vac.}$	25° η(op.)
	0	0	461.3	0.9982	1.005_{0}	410.6	0.9971	0.893_{5}
D	5.270	0.591_{7}	511.4	1.0049	1.121_{6}	453.0	1.0033	0.991_{9}
A	10.812	1.213_{9}	567.6	1.0115	1.253_{0}	500.3	1.0097	1.102_{5}
E	14.869	1.669_{5}	611.4	1.0164	1.356_{3}	538.2	1.0143	1.191_{4}
B	20.549	2.307_{3}	674.1	1.0229	1.504_{9}	589.8	1.0205	1.313_{6}
F	24.599	2.762_{0}	721.7	1.0273	1.618_{2}	629.9	1.0247	1.408_{7}
C	28.815	3.235_{4}	774.2	1.0316	1.743_{1}	673.5	1.0290	1.512_{6}
G	41.464	4.655_{6}	946.7	1.0437	2.156_{5}	819.4	1.0403	1.860_{5}

TABLE IX

VISCOSITIES AND FLUIDITIES OF URETHAN SOLUTIONS (FROM SMOOTH CURVES)

c	20° η(op.)	20° φ	25° η(op.)	25° φ
0.0	1.005_{0}	99.50	0.893_{5}	111.92
.5	1.103_{2}	90.65	$.976_{4}$	102.42
1.0	1.206_{7}	82.87	1.063_{6}	94.02
1.5	1.315_{7}	76.01	1.155_{3}	86.56
2.0	1.431_{0}	69.88	1.251_{7}	79.89
2.5	1.552_{5}	64.41	1.353_{3}	73.90
3.0	1.680_{6}	59.50	1.460_{5}	68.47
3.5	1.815_{6}	55.08	1.573_{6}	63.55
4.0	1.958_{2}	51.07	1.693_{1}	59.06
4.5	2.107_{5}	47.45	1.820_{1}	54.94

It might be argued that it was unsafe to assume that the viscometer would reproduce viscosities over a greater range than was used in the standardization, that m might change from its value of zero. If we base a conclusion on Dorsey's analysis, this might very well be the case for greater velocities of flow, but quite improbable for smaller. As a consequence, confidence is felt that these solutions can be used for future standardizations. It would be interesting to see what the viscosities of these solutions would be if determined with an instrument with which it had been demonstrated that m had a value different than zero, and which reproduced the Bureau of Standards data for water.

We are indebted to the Elizabeth Thompson Science Fund for providing a grant to aid this investigation.

Summary

Three viscometers of the Ostwald type as modified by Washburn and Williams have been constructed similar to each other with the exception of the configuration of the ends of the capillaries, which varied from gradual trumpets to squarely fractured ends. The dimensions of these viscometers were determined as accurately as possible.

The times of flow with water were determined with the three instruments

at 15, 18, 20, 22, 25, 27 and 30°. In terms of Reynolds' criterion the velocities of flow varied between 25 and 63.

The resulting data were compared with previously determined viscosities of water in a manner to show any variations in *m*. It was found that any of the three viscometers reproduced the Bureau of Standards data for water on the assumption that *m* was zero. No evidence was found for believing that *m* changed in value due to the configuration of the capillary ends.

These results were discussed in relation to Dorsey's interpretation of *m*.

The viscosities of urethan solutions up to 4.5 moles/1000 g. of solution were determined at 20 and 25° for future use in standardizations. These data were given in reference to the Bureau of Standards data for water.

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[CONTRIBUTION FROM THE PEARSON CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE VISCOSITIES OF SEVERAL AQUEOUS SOLUTIONS OF ORGANIC SUBSTANCES. II

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A study of the compressibilities and volume changes upon solution of several organic substances in water[1] has shown that with these properties, the effect of a change in the polymerization of the solvent is most apparent. The viscosities of these same solutions determined at 25°[2] showed no effect that could be ascribed to such a change in molecular state, for it was found that although the solutes had viscosities very much less than water, the aqueous solutions possessed a viscosity greater than water. If a depolymerization of the solvent was brought about by the presence of solute, the viscosity should be decreased, for the depolymerized water is supposed to possess a lower viscosity.[3] Determinations made at a lower temperature, where the water is supposedly richer in polymer, might show this effect more vividly. As a consequence, one of the viscometers (Viscometer I) whose standardization was described in the preceding paper, was used to measure this property at 10° of aqueous solutions of diethyl ether, methyl and ethyl acetates and urethan.

It has been reported[4] that aqueous solutions of urea show "negative viscosity," or viscosity less than water. Since this seems to be an exception to the general rule that aqueous solutions of non-electrolytes possess a viscosity greater than water, determinations were made at 5, 10,

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[1] Richards and Chadwell, THIS JOURNAL, **47**, 2283 (1925).

[2] Chadwell, *ibid.*, **48**, 1912 (1926).

[3] See, for instance, Tammann and Rabe, *Z. anorg. allgem. Chem.*, **168**, 73 (1927).

[4] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., **1922**, p. 179. The reference to Mutzel seems to be an error.