74. *The Drainage of Viscometers and Pipettes.*

By GRINNELL JONES and EDNA FERRELL.

The drainage of liquids in viscometers and pipettes has been studied as a function of the time of outflow, the shape and size of the glass surface, and the properties of the experimental liquid. It is shown that for a given surface and volume, the total volume of after-drainage multiplied by the time of outflow is a constant for any given liquid, and that this constant is proportional to the kinematic viscosity, and independent of the surface tension of the liquid. The error due to incomplete drainage in viscometers and pipettes is discussed. Pipettes having the shape of a double cone are superior to cylindrical and spherical pipettes.

THE drainage of liquids from viscometers and pipettes and burettes is never complete. The volume of liquid retained on the inner walls may be influenced by the shape and the area of these walls, the temperature, the time of outflow, the viscosity, the density, and perhaps also the surface tension of the liquid. Viscometers, pipettes, and burettes are commonly calibrated with water and then used with solutions or other liquids. If the volume of the other liquid retained on the walls under the actual conditions of use differs from the volume of water retained during the calibration there will be an error due to this difference in drainage. Some aspects of this error in volumetric analysis have already been studied (Schloesser, *Z. anal. Chem.*, 1907, **46**, 392; *Z. angew. Chem.*, 1908, **21**, 833; *Chem. Ztg.*, 1906, **30**, 1071; Stott, *J. Soc. Glass Techn.*, 1921, **5**, 307; 1923, **7**, 169; Osborne and Veazey, *Bull. Bur. Stand.*, 1908, **4**, 553). Our own interest in the problem had its origin in concern as to the magnitude of the drainage error in precision viscometry. The existence of such an error has been recognised (Bingham and Young, *J. Ind. Eng. Chem.*, 1922, **14**, 1130; Herschel, *J. Opt. Soc. Amer.*, 1922, **6**, 875; Cannon and Fenske, *Oil and Gas J.*, 1935, April 11, p. 52; McCluer and Fenske, *Ind. Eng. Chem.*, 1935, **27**, 83; Broom, *J. Inst. Petr. Techn.*, 1936, **22**, 23; Ubbelohde, *ibid.*, 1933, **19**, 413; *Ind. Eng. Chem., Anal.*, 1936, **9**, 88), but the data in the literature were nearly all obtained with heavy oils many times more viscous than water, and the conclusions reached by different investigators are somewhat contradictory. A number of improvements in the technique of viscometry have recently been made in this laboratory (Grinnell Jones and collaborators, *J. Amer. Chem. Soc.*, 1929, **51**, 2950; 1933, **55**, 624, 4124; 1935, **57**, 2041; 1936, **58**, 619, 2558; 1937, **59**, 484, 1630; 1938, **60**, 1683; *Physics*, 1933, **4**, 215) which have substantially increased the precision attainable by means of the Ostwald viscometer. This has made it desirable to reconsider the question of drainage error in viscometry.

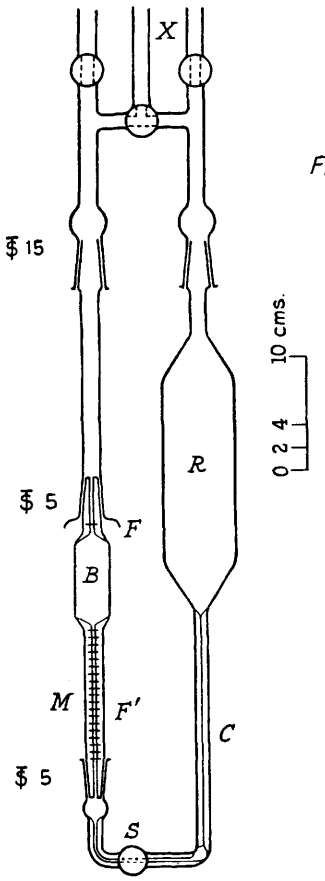
The absolute drainage error is the total volume between the upper and the lower fiducial mark on the measuring bulb of the viscometer (or pipette) minus the volume of the liquid actually delivered under the conditions of the experiment, divided by the total volume. The relative drainage error is the difference between the absolute drainage of the liquid under investigation and that of the water (or other standard of reference) used for calibration. The absolute drainage error can be determined most conveniently in two parts: (*a*) the " after-drainage," which will drain out from the measuring bulb during a protracted period following the passage of the meniscus, and (*b*) the " wetting film," which remains on the inner surface even after protracted drainage. A preliminary paper on this subject (Grinnell Jones and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 1630) described an improved technique for determining the magnitude of the error and included some data on the effect of variations in the time of outflow, water and three solutions being used, but only one pipette. The purpose of the present investigation is to extend this work in several directions to determine (1) the effect of much more rapid efflux such as is commonly used in pipettes, (2) the influence of variations in shape of the bulb, and (3) the magnitude of the error when other liquids differing appreciably from water in viscosity, density, and surface tension are used.

EXPERIMENTAL.

Fig. 1 shows the special viscometer which permits the liquid under investigation to be forced from the bulb, *B*, through the cock, *S*, and the capillary, *C*, into the reservoir, *R*, by apply-

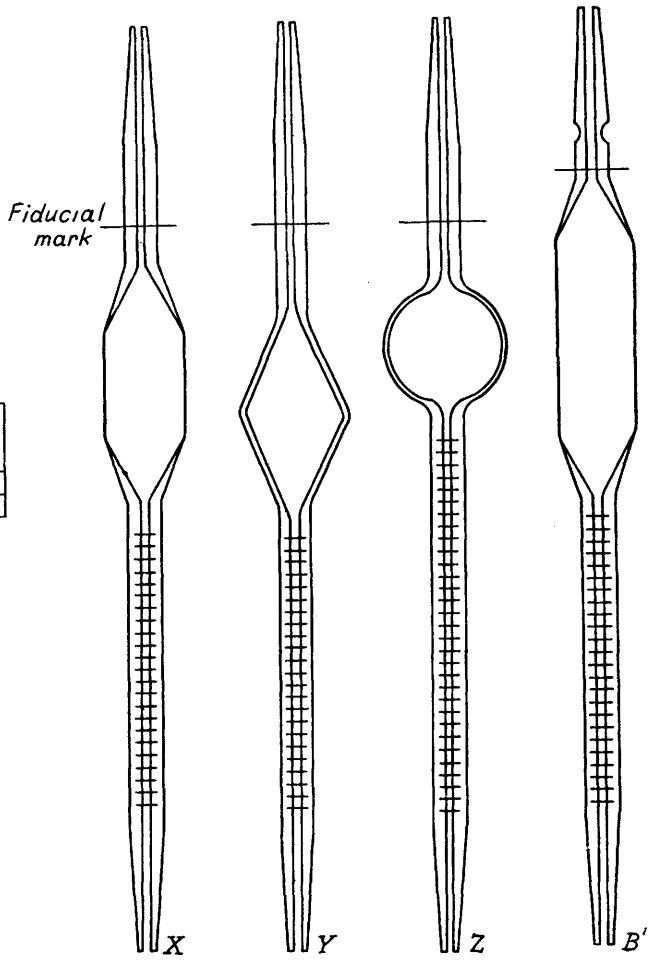
ing any desired pressure. Auxiliary equipment not shown in the figure consists of (1) a tank of compressed air with pressure regulator and manometer attached to the cross head; (2) a coil-spring mechanism with electromagnetic release which opens or closes the cock, *S*, whenever an electric contact key is closed; (3) a chronograph which records the time whenever a key is touched; (4) a thermostat to maintain a temperature of 25°; (5) a cathetometer with a cross-hair, adjustable vertically by a micrometer screw for observing the meniscus. At the beginning of the experiment the liquid to be studied was placed in the instrument from the upper mark, *F*, to the lower part of the reservoir, *R*, with the cock, *S*, closed, and the desired pressure

FIG. 1.



Special viscometer for study of drainage.

FIG. 2.

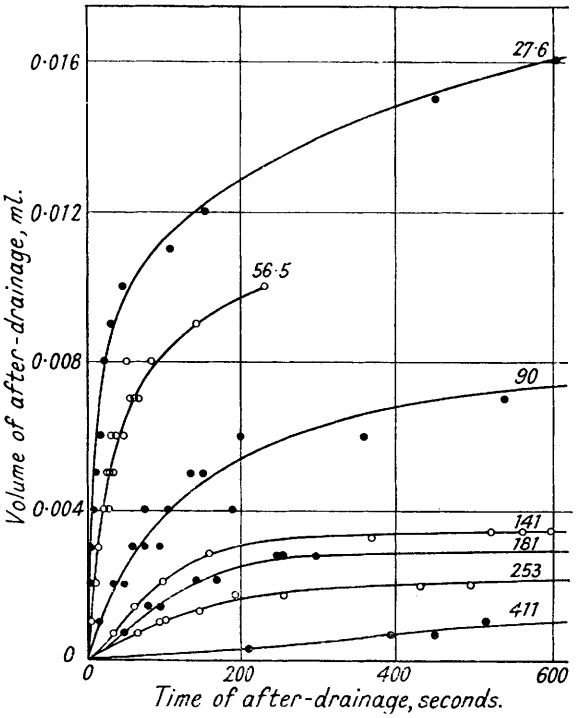


Special pipettes for study of drainage.

applied. The flow was then started by touching the contact key which opened the cock, *S*, and recorded the time on the chronograph. When the bulb had become empty and the meniscus had reached some predetermined mark in the tube, *M*, the contact key was touched, thus closing the cock, *S*, and stopping the flow and recording the time. The lowest position of the meniscus was observed and recorded, and then the rise of the meniscus in the tube, *M*, due to after-drainage from the walls of the bulb, *B*, was observed as a function of time. The instant the meniscus was observed to become tangential to the cross-hair, the time was recorded on the chronograph; the cross-hair was then raised a known amount by means of the micrometer screw, and the record of the time at successive heights repeated until drainage ceased, which often required about $\frac{1}{2}$ hour. The viscometer was then removed from the thermostat, dried

externally, separated at the ground joints, then the few drops in the tube, M, removed by touching with a piece of dry filter-paper, the ends capped, and the entire pipette weighed. The excess of weight over that of the instrument when dried internally gives the wetting film. The entire experiment may then be repeated with a different pressure, thus changing the time of outflow, or with a different liquid. For the present work with other liquids and at greater speeds of flow, two additional instruments were constructed which were similar and interchangeable except that the capillaries, C, were approximately 0·08 and 0·09 cm. in diameter severally, instead of 0·05 cm. as in the original viscometer, thus permitting more rapid outflow, without requiring a driving pressure so great as to be troublesome. Also another pipette, B', 16 c.c. in volume was provided which was made as nearly as possible identical with the original

FIG. 3.



Rate of after-drainage of water with various periods of outflow.

pipette, B, except that the graduated tube below the bulb was smaller in bore and therefore the volume of after-drainage could be read with greater precision. In order to determine the effect of the shape of the bulb on the drainage, three new pipettes were constructed, each having a volume of 10 c.c. (see Fig. 2). The pipette, X, had cylindrical side walls but the upper and the lower part of the bulb were made as nearly conical as possible.

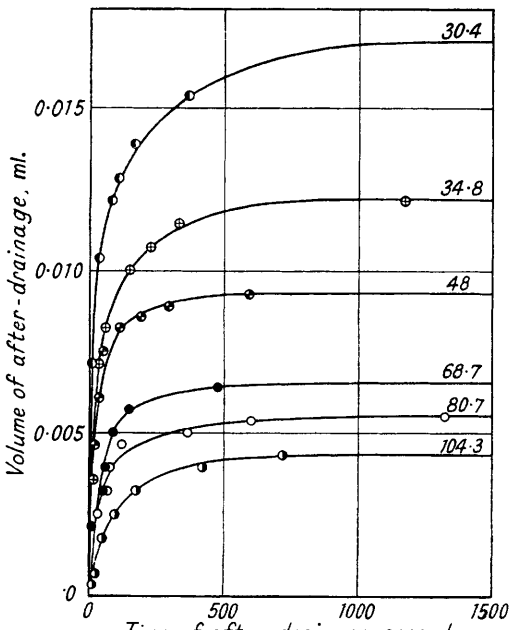
The conical pipette, Y, was designed to give the most favourable conditions for drainage. It was assumed that the amount of liquid, E, retained on the inner walls at the instant when the pipette has emptied itself would be proportional to the surface, S, and also to the secant of the angle, θ, between the wall and the vertical axis (the semi-vertical angle of the cone); *i.e.*, $E = kS \sec \theta$. Then it can be computed that for a given volume the amount of liquid retained on the walls would be a minimum if $\tan \theta = \sqrt{0{\cdot}2}$, or $\theta = 24°$. This most favourable angle is the same for the upper and the lower cone and is independent of the volume desired. To give a volume of 10 c.c., the internal diameter at the widest part should be 2·6 cm. and the height 5·7 cm. The glassblower was instructed to meet these specifications as closely as he could. Of course, the upper and the lower cone should not and do not meet at a sharp angle because the liquid meniscus which would be formed in such an angle would increase the liquid retained. However, the operations of glassblowing eliminate this sharp angle. No extra liquid will be

retained at this junction if the curvature of the glass surface at the junction is less than the curvature of the meniscus which would be formed.

Pipette *Z* had a bulb which was as nearly spherical as a skilled glassblower could make it, with a radius of about 1·34 cm.

The earlier work indicated that the drainage is a simple function of the kinematic viscosity, or viscosity divided by the density, η/d, but is independent of the surface tension. Water, methanol, *n*-butanol, and 1·46N-potassium chloride solution were selected for investigation and comparison to test the generality of these conclusions (see Table I). The last solution was selected because it has the same viscosity as water (Grinnell Jones and Talley, *J. Amer. Chem. Soc.*, **1933**, **55**, 4124), but a different density and surface tension. Methanol and butanol are nearly alike in density and surface tension, but differ five-fold in viscosity. Both have a surface tension approximately one-third of that of water. Both these alcohols were the best quality that could be purchased, and were carefully dehydrated, distilled through a good fractionating column 75 cm. long, and stored in such a manner as to protect them from atmospheric moisture. The portions collected for use boiled at 64·65° ± 0·02° and 117·57° ± 0·02°, respectively.

FIG. 4.



Rate of after-drainage of methanol.

Figs. 3, 4, and 5 depict the rate of after-drainage for water, methanol, and butanol. The time of outflow in seconds (which depends on the driving pressure applied) is shown at the upper end of each curve. In comparing these curves due allowance must be made for the differences in scale. The great difference in the rate of after-drainage for these liquids is apparent. The rate of after-drainage is evidently closely related to the viscosity of the liquid. Similar curves have been obtained with 1·46N-potassium chloride in the same pipette, and with water in pipettes of different shapes, but these curves and the actual numerical data on which they are based are omitted for the sake of brevity since they have revealed nothing not apparent from the figures shown. These curves resemble those found by Osborne and Veazey (*loc. cit.*) in experiments on the drainage of water from pipettes and burettes.

However, in the measurement of viscosity it is impossible to wait for the after-drainage; and in the use of pipettes, although it would be possible to wait for the after-drainage, it is inconvenient and not customary to do so. Therefore the total volume of after-drainage plus

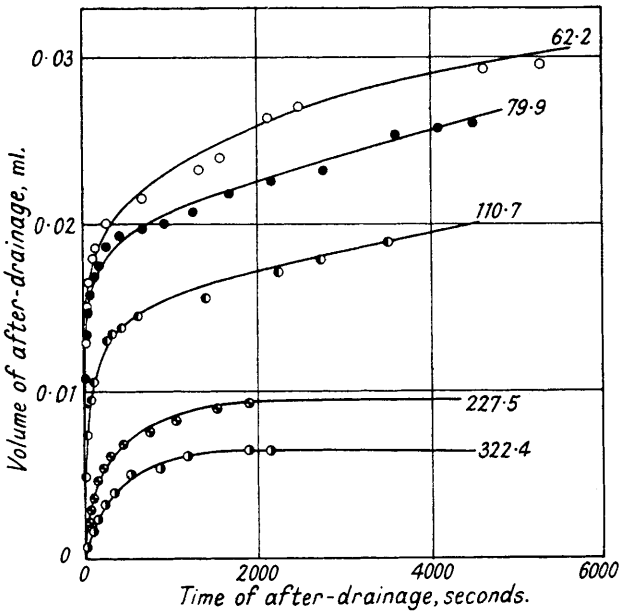
TABLE I.

	$d_4^{25°}$.	η.	η/d.	σ.		$d_4^{25°}$.	η.	η/d.	σ.
Water	0·99707	1·000	1·003	71·97	CH_3·OH ...	0·7865	0·6084	0·7736	22·17
1·46N-KCl ...	1·0633	1·000	0·9377	74·4	C_4H_9·OH ...	0·8057	2·902	3·602	24·6

the wetting film, which determines the drainage error, is more important than the rate of after-drainage. Jones and Stauffer found that the total volume of after-drainage, ΔV, multiplied by the time of outflow, t, is a constant for any given pipette and liquid, within the limit of error of the measurements which may amount to 10% owing to the small volume being measured; *i.e.*, $t \cdot \Delta V = K$. Comparing water and two different aqueous solutions of sucrose and one extremely viscous solution of calcium ferrocyanide in the same pipette, they found that this constant was proportional to the kinematic viscosity of the liquid used up to a viscosity double that of water, and at least approximately proportional to the kinematic viscosity for a solution having a viscosity 15 times that of water; or $t \cdot \Delta V = \alpha\eta/d$, where α is a constant for any given pipette independent of the rate of discharge or the liquid used. However, none of these liquids differed appreciably in surface tension. The experimental data given in Table II and

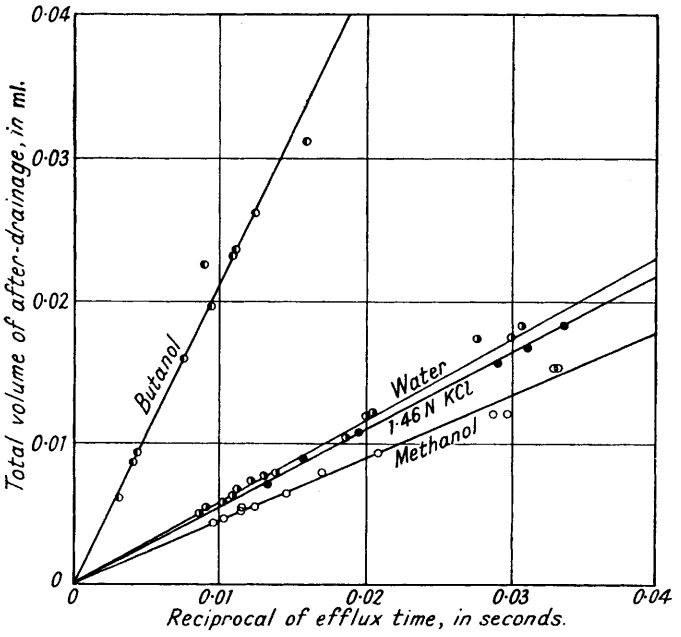
shown in Fig. 6 prove that this same relationship holds for water, methanol, butanol, and for a 1·46N-potassium chloride solution, in spite of substantial differences in surface tension. The

FIG. 5.



Rate of after-drainage of butanol.

FIG. 6.



Drainage of various liquids in the same pipette.

new data also show that this law is valid for rates of outflow nearly 3 times as great as the fastest used by Stauffer. Jones and Stauffer have pointed out that this law leads to an automatic compensation which has the effect of eliminating the error due to after-drainage in relative measure-

TABLE II.

Total After-Drainage at Various Outflow Times for Several Liquids.

Water ($a = td.\Delta V/\eta = 0{\cdot}58$).

Time of efflux, (t), secs.	Total vol. of after-drainage, (ΔV), ml.	$t.\Delta V = K.$	Time of efflux, (t), secs.	Total vol. of after-drainage, (ΔV), ml.	$t.\Delta V = K.$	Time of efflux, (t), secs.	Total vol. of after-drainage, (ΔV), ml.	$t.\Delta V = K.$
				Water.				
8·5	0·0704	0·60	32·6	0·0183	0·60	82·4	0·0073	0·60
10·6	0·0479	0·51	33·3	0·0175	0·58	89·2	0·0067	0·59
11·6	0·0454	0·53	36·1	0·0175	0·63	89·9	0·0063	0·56
13·8	0·0375	0·52	49	0·0121	0·59	91·8	0·0063	0·57
16·2	0·0367	0·59	49·9	0·0119	0·59	97·3	0·0058	0·58
17·7	0·0333	0·59	53·8	0·0104	0·56	110	0·0054	0·60
22·4	0·0267	0·60	72·2	0·0079	0·57	114·9	0·0050	0·57
24	0·0246	0·59	76·5	0·0077	0·59	Mean value for K =		0·58

1·46N-Potassium chloride solution.

Time of efflux, (t), secs.	Total vol. of after-drainage, (ΔV), ml.	$t.\Delta V = K.$	$a = td.\Delta V/\eta.$	Time of efflux, (t), secs.	Total vol. of after-drainage, (ΔV), ml.	$t.\Delta V = K.$	$a = td.\Delta V/\eta.$
29·7	0·0184	0·55	0·58	51·3	0·0107	0·55	0·58
32·1	0·0168	0·54	0·57	63·6	0·0089	0·57	0·60
34·4	0·0157	0·54	0·57	75·5	0·0071	0·54	0·57
					Means	0·55	0·58
			Methanol.				
30·2	0·0154	0·46	0·60	68·7	0·0064	0·44	0·57
30·4	0·0154	0·47	0·61	80·7	0·0055	0·45	0·58
33·7	0·0121	0·41	0·53	86·9	0·0054	0·47	0·60
34·8	0·0121	0·42	0·55	87·4	0·0052	0·45	0·59
48	0·0093	0·45	0·58	97·3	0·0046	0·45	0·59
58·9	0·0079	0·46	0·60	104·3	0·0043	0·45	0·58
					Means	0·45	0·59
			Butanol.				
62·2	0·0311	1·9	0·54	110·7	0·0225	2·1	0·58
79·9	0·0261	2·1	0·59	131·3	0·0159	2·1	0·58
89·1	0·0236	2·1	0·58	227·5	0·0093	2·1	0·59
91·1	0·0232	2·1	0·59	241·9	0·0086	2·1	0·58
105·6	0·0196	2·1	0·58	322·4	0·0061	2·1	0·58
					Means	2·1	0·58

TABLE III.

The Influence of the Shape and Area of the Surface on the Drainage of Water in Pipettes at various Outflow Times.

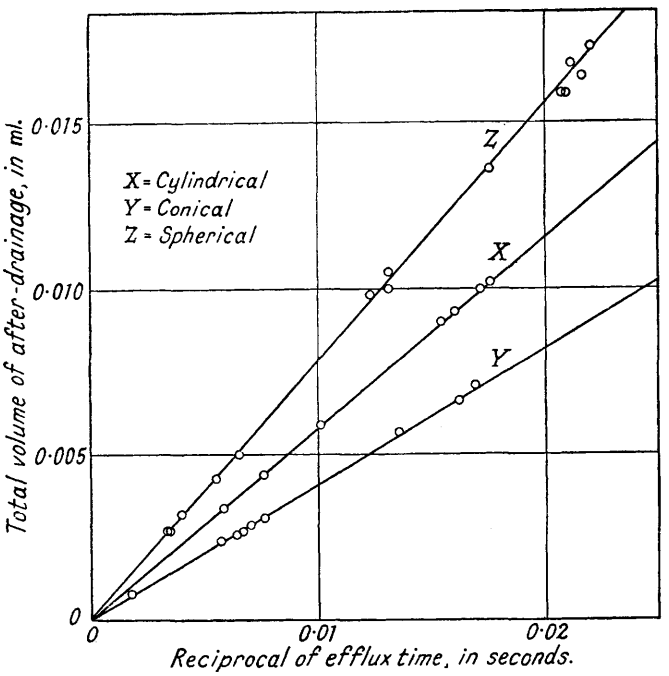
Time of efflux, (t), secs.	Total vol. of after-drainage, (ΔV), ml.	$t.\Delta V = K.$	Time of efflux, (t), secs.	Total vol. of after-drainage, (ΔV), ml.	$t.\Delta V = K.$	Time of efflux, (t), secs.	Total vol. of after-drainage, (ΔV), ml.	$t.\Delta V = K.$
			(i) In cylindrical pipette X.		$a = td.\Delta V/\eta = 0{\cdot}58.$			
56·9	0·0102	0·58	62·5	0·0093	0·58	131·1	0·0044	0·58
58·4	0·0100	0·58	64·9	0·0090	0·59	169·9	0·0034	0·58
			98·6	0·0059	0·58		Mean	0·58
			(ii) In conical pipette Y.		$a = td.\Delta V/\eta = 0{\cdot}41.$			
59·2	0·0071	0·42	130·5	0·0031	0·40	154·2	0·0026	0·40
61·7	0·0067	0·41	141·7	0·0029	0·40	173·4	0·0024	0·41
73·7	0·0057	0·42	148·5	0·0027	0·40	549·4	0·0008	0·42
							Mean	0·41
			(iii) In spherical pipette Z.		$a = td.\Delta V/\eta = 0{\cdot}78.$			
45·2	0·0173	0·78	57	0·0136	0·78	180·7	0·0043	0·78
46·1	0·0164	0·75	76·1	0·0100	0·76	247·9	0·0032	0·79
47·2	0·0168	0·79	76·1	0·0105	0·80	282·8	0·0027	0·77
47·7	0·0159	0·76	81·4	0·0098	0·80	290·8	0·0027	0·79
48	0·0159	0·76	152·9	0·0050	0·76		Mean	0·78

ments of viscosity. These new data indicate that this automatic compensation is also effective with methanol and butanol which differ greatly in surface tension from water, and therefore give a strong indication that the automatic compensation may be relied on in all cases.

The experimental data recorded in Table III and depicted in Fig. 7 show that the value of $t \cdot \Delta V = K$ is substantially influenced by the shape of the pipette. Water was used in these experiments. It is clear that the conical pipette has the smallest after-drainage and the smallest wetting film. It may be inferred from these data that, unless the time of outflow is more than 97 seconds for the spherical, more than 64 seconds for the cylindrical, and more than 82 seconds for the conical pipette, the after-drainage will exceed the wetting film.

In making absolute measurements of viscosity there would be a significant advantage in using a conical pipette, although for relative measurements the automatic compensation referred

FIG. 7.



Influence of shape of pipette on drainage of water.

to above will nullify the advantage if it can be relied on quantitatively and universally. However, as has been pointed out by Jones and Fornwalt (*J. Amer. Chem. Soc.*, 1938, **60**, 1683), the design of viscometers in the cylindrical form with the lower reservoir equal to the upper bulb in radius has the advantage that it minimises the error due to surface tension in viscometry. In view of the automatic compensation which probably eliminates the drainage error, the cylindrical form is to be preferred in the design of a viscometer.

For transfer pipettes for use in volumetric analysis, or for quantitative delivery of a definite volume of a liquid for any purpose, there is a real advantage in the conical form because the automatic compensation is less complete and less reliable. Transfer pipettes, which usually drain rapidly in comparison with viscometers and in which the resistance to flow is mainly in a constricted tip rather than in a long capillary tube, do not obey Poiseuille's law, so the time of outflow is not strictly proportional to the kinematic viscosity. Moreover, to make the automatic compensation effective, it would be necessary for the operator to withdraw the pipette from the receiver as soon as the meniscus reaches the tip (or lower fiducial mark), so that all of the after-drainage is retained in the pipette, both in the standardisation and in use. However, this is not the common practice. Some operators wait for an arbitrary time for the after-drainage and then blow into the pipette to add a portion of the after-drainage to the receiver. The quantitative reproducibility of such a procedure would evidently be improved by a design which favours rapid and effective drainage. The conical form is appreciably better than the

other forms in this regard. The shorter the delivery time the more important this advantage becomes. The specifications of the U.S. Bureau of Standards (Circular No. 9) require that a 10 c.c. transfer pipette shall have a time of outflow of not more than one minute and not less than 20 seconds. The calculated value of the total after-drainage, ΔV, for each of our pipettes is given in Table IV. In the last colum is given the sum of this after-drainage plus the wetting

TABLE IV.

Pipette.	$t \cdot \Delta V = K$.	Wetting film, ml.	ΔV, calc. for 20 sec. outflow.	Total in % of vol. of pipette.
Z, spherical	0·78	0·008	0·039	0·47
X, cylindrical	0·58	0·009	0·029	0·38
Y, conical	0·41	0·005	0·021	0·26

film expressed as a percentage of the volume of the pipette. If the liquid used is a dilute aqueous solution with a kinematic viscosity nearly that of water, then its drainage time will be nearly the same as that of water, and therefore the accuracy in use of the pipette will depend on the reproducibility of the procedure in allowing for drainage. But with a conical pipette the penalty for carelessness or haste may be appreciably less than with the usual forms.

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