NBS MONOGRAPH 55

NBS Viscometer Calibrating Liquids And Capillary Tube Viscometers

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Contents

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R. C. Hardy

Most measurements of viscosity are made with relative viscometers. These instruments must be calibrated with liquids whose viscosities are known. NBS provides a series of 10 oils for this purpose. Their viscosities range from 0.02 to 450 poises and their temperature coefficients of viscosity range from 2.1 to 9.4 percent per degree C. When properly stored the oils may remain usable for from two months to one year but prompt use is recommended. The less viscous oils are more stable. Representative types of glass capillary tube viscometers and their use are discussed briefly. Contrary to common belief, it is not necessary to calibrate these instruments at the temperature of use since the temperature cofficients of the instruments are small and correction if necessary can be calculated. Instruments in which the effective volume of charge is not adjusted at the test temperature may require adjustment of their calibration constants to compensate for thermal expansion of the test liquid. Correction formulas for this and other errors or conditions are presented.

1. Introduction

For many years the National Bureau of Standards has supplied oil samples of known viscosity to other laboratories for use in calibrating their viscometers. The need for a publication describing this service and its purpose has been evident from time to time. This paper is intended to fulfill that need and to supply general information on the calibration of capillary tube viscometers. Although some of the errors and corrections discussed are small and may be inconsequential even in rather precise work, it seems worthwhile to mention them so that if they are disregarded it can be on the basis that due consideration warrants it rather than on the basis of oversight. Also, it is to be expected that continuing advances in technology will require improved precision in viscosity measurements for commercial purposes and more precise information on the viscosity of materials may permit refinements in our concepts of molecular relations in the liquid state.

The following discussion is limited to consideration of Newtonian or simple liquids and to determinations of their viscosities. A Newtonian or simple liquid is a true liquid, i.e., a substance which will flow under the influence of any finite shearing stress, for which the rate of shear at any point is proportional to the shearing stress at that point, and for which the ratio of shearing stress to rate of shear (commonly referred to as the viscosity of the liquid) is determined solely by its composition, temperature, and pressure. Although we may speak of a material as being Newtonian or non-Newtonian as though this were a fixed characteristic, it should be remembered that its behavior may change with changes in its temperature and pressure. To illustrate, one need only point to the freezing of water or the gradual liquefaction or solidification of butter. The effects of pressure are not readily apparent to the senses but may be demonstrated in the laboratory.

All measurements of viscosity are based on Newton's hypothesis relative to laminar flow of liquids. Broadly stated, this hypothesis is that at any point in a liquid undergoing laminar flow, the shearing stress causing flow is proportional to the rate of shear at that point. The constant of proportionality in this relation is known as the coefficient of viscosity or merely as the viscosity of the liquid.

The generally accepted equation for laminar flow through cylindrical tubes of circular section is

$$Q = \frac{\pi r^4 P'}{8 \eta l'}, \tag{1}$$

where Q is the volume rate of flow, r the radius of the tube, η the viscosity of the liquid, and P' is the pressure drop through a portion of the tube of length l' in which the flow is not modified by the nearness of the ends.

This relation was derived from Newton's hypothesis relative to laminar flow after Poiseuille had established the empirical relation

$$Q = K \frac{P D^4}{l}, \tag{2}$$

where D is the diameter of the tube, P the pressure drop through the tube of length l, and K a constant for a given liquid at a given temperature. This equation was based on the results of an extensive series of very careful observations of the rate of flow of water through fine glass capillaries at various temperatures and pressures. In most of this work the tubes were long in relation to their diameters so that the effects of the ends were negligible and differences between P and P' and between l and l' were negligible. Under these conditions, the equivalence of the two equations is evident if we note that

$$16r^4 = D^4 \text{ and set } K = \frac{\pi}{128\eta}.$$

However, some of Poiseuille's observations were made with relatively short tubes or with high rates of flow and the results did not support eq (2) as well as would be expected in view of the precision of the work. It should be noted that eq (2) considers only the viscous resistance of the liquid and ignores the fact that some of the pressure drop between the ends of the tube represents conversion of potential energy to the kinetic energy of the stream issuing from the capillary. Hagenbach was the first to point this out in a published paper and to propose a correction for it.

Subsequently, Couette proposed a correction to account for the viscous resistance in the supply reservoir and the increased viscous resistance in the entrance portion of the tube where the central portions of the stream are being accelerated with respect to the peripheral portions as the velocity distribution in the stream is changing from the more or less uniform distribution at the entrance to the theoretical parabolic distribution in portions of the tube remote from the entrance. Couette proposed that this correction be made as a hypothetical increase, λ, in the length of the tube. The magnitude of this correction is usually considered to be proportional to the radius of the tube, i.e., $\lambda = nr$, where n is known as the coefficient of the Couette correction.

The change in potential energy of a volume, V, of liquid as it flows from the entrance reservoir to the exit reservoir is PV. Part of this is converted to thermal energy in overcoming viscous resistance to flow in the tube and supply reservoir, and the remainedr is converted to the kinetic energy of the stream issuing from the tube. Then we may write the following energy equation:

$$PV = \frac{8\eta(l + nr)Q}{\pi r^4} V + \frac{\rho Q^2}{\pi^2 r^4} V, \qquad (3)$$

where $\frac{\rho Q^2}{\pi^2 r^4} V$ is the kinetic energy of the liquid passing any cross section of the capillary where the distribution of velocities is parabolic, in time t. Solving eq (3) for η, we get

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

where an empirical factor m has been inserted in an attempt to account for unknown conditions of flow near the ends.

This factor m is known as the coefficient of the kinetic energy or Hagenbach correction. Equation (1) is commonly referred to as Poiseuille's equation and eq (4) as the corrected Poiseuille equation.

Dorsey [1][1] maintains that it is incorrect to refer to the term containing m as the Hagenbach or kinetic energy correction and suggests that the term is much more properly described as an inertia correction. However, by a somewhat different line of reasoning he arrives at the same relation expressed in eq (4). From published data he concluded that for the ideal case[2] $n = 1.146$ and $m = 0$ when the flow is characterized by a Reynolds number $\left(R_e = \frac{vd\rho}{\eta}\right)$ of 10 or less. But where $R_e > 10$, $n = 0.573$ and $m = 1$. Dorsey recognized that in a real instrument slight departures from ideal conditions may require modification of these values and that there is not an abrupt change at $R_e = 10$.

Various values for n and m based on theory or experiment have been proposed. Most of these fall in the range zero to a little more than unity, although some experimental values several times as great have been reported. It is usually assumed that n is a constant for a given viscometer and a similar assumption is often made for m although there is experimental evidence that such is not true and that the value of m is variable and a function of R_e. It may be noted that for a parabolic distribution of velocities the value of m would be unity and for uniform velocity, 0.5. Uniform velocity across the stream would, of course, require slippage at the wall to account for all relative motion between the tube and the liquid. Transition from more or less uniform velocity at the entrance to the theoretical parabolic distribution some distance within the tube is easily visualized and would account for values of m between 0.5 and 1. Experimental values outside this range might find explanation in an inadequate correction for the Couette effect or distortion of the parabolic distribution due to temperature gradients resulting from the conversion of potential to thermal energy, or to deviations from the theoretic shape of the tube as a right circular cylinder.

Heating in the peripheral portion of the stream is greater than in the central portion because the velocity gradients are greater in this region. This would tend to reduce the viscosity in the peripheral region and permit the

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[1] Figures in brackets indicate literature references on page 20.

[2] The ideal case considered by Dorsey is the flow of a liquid from a large reservoir, through a cylindrical capillary of circular cross section, into a second large reservoir, the free liquid surface in each reservoir being great in comparison with the sectional area of the capillary, which is sharp-edged with large terminal faces normal to its axis.

central portion to "slip through" in somewhat plug fashion, leading to abnormally high kinetic energy in the stream and requiring use of a value for m somewhat greater than unity.

The assumption that the velocities are uniform, or virtually so, at the entrance to the tube simplifies theoretical estimation of the entrance effect and may be reasonably appropriate for tubes with widely flared (trumpet shaped) mouths fed from large reservoirs. However, this leads to considerable uncertainty in the values for l and r of the tube. It appears that appropriate values for n and m for any given instrument might be influenced somewhat by the sizes and shapes of the terminal reservoirs as well as the shapes of the ends of the tube.

Because of the uncertainty as to the proper values for n and m, it is necessary either to make careful estimates based on experimental evidence of appropriate values for each instrument or to choose an instrument and test conditions such that the corrections will not have significant magnitude.

Using the relations expressed in eq (4) it is possible to design and construct a capillary tube viscometer and to measure the viscosity of a liquid without reference to any standard for viscosity. In such a case, the instrument would be classed as an absolute viscometer and the method would be referred to as an absolute method.

It is very difficult to make accurate absolute measurements of viscosity because of the difficulties of selecting a suitable capillary tube, measuring its dimensions with suitable accuracy, and then determining suitable values for n and m. On the other hand, it is relatively easy to make accurate comparisons of the viscosities of two liquids. Instruments used for making such comparisons are called relative viscometers but they may be used to determine absolute viscosities as well as relative, specific, or kinematic viscosities. To avoid confusion it may be well to point out that absolute viscosity[3] means merely viscosity, the modifier "absolute" being used only for emphasis and to point out that reference is not being made to one of the ratios involving viscosity, which for brevity are often referred to as "viscosity." Relative or specific viscosity is the ratio of the viscosity of a liquid at some temperature and pressure to the viscosity of the same or another liquid at the same or different temperature and pressure. Kinematic viscosity is the ratio of the viscosity of a liquid to its density at the same temperature and pressure. Absolute viscosities, i.e., true viscosities, are measured in terms of units having the dimensions $ml^{-1}t^{-1}$ or $Fl^{-2}t$, e.g., 1 poise = 1 gram per centimeter-second or 1 reyn = 1 pound(wt)-second per square inch, etc. Relative or specific viscosities are dimensionless numbers. Kinematic viscosity is stated in terms of units having the dimensions l^2t^{-1}, e.g., in the cgs system, 1 stoke = 1 square centimeter per second.

2. Viscometer Calibrating Liquids

Most viscosity measurements are made with relative viscometers, the use of which rests on the availability of suitable reference standards for viscosity. To be suitable for such use a liquid should be Newtonian, have the desired viscosity, and be reasonably stable with regard to aging.

A Newtonian liquid is one for which, at a given temperature and pressure, the ratio of shearing stress to rate of shear is constant, i.e., independent of the rate of shear. It is very important that a reference liquid be Newtonian since, in general, for any given liquid, temperature, and pressure, not only will the rate of shear be different in different instruments but in most instruments the rate of shear will be different at different points in the liquid, and in kinematic viscometers the rate of shear at any given point will vary somewhat during a measurement.

The viscosity of freshly distilled water at 20 °C has been determined accurately by an absolute method [2] and found to be 0.010019± 0.000003 poise, the second number indicating the estimated accuracy of the first. The proposal to use the rounded off value 0.01002 poise has been generally accepted and freshly distilled water at 20 °C is widely used as the primary reference standard for calibrating relative viscometers. Since many viscometers are not suitable for use with liquids as fluid as water, it is necessary to calibrate them with other liquids whose viscosities have been determined by direct comparison with water at 20 °C or by indirect comparison through one or more intermediate liquids and instruments.

Properly selected petroleum oils have been found suitable for use as intermediate or secondary reference standards if they are considered to be only temporary standards. They are multicomponent solutions of unknown composition and the viscosity of each lot or batch must be determined. If for any reason—age or possible contamination—the applicability of this determined value is questioned, confidence can be restored only by redetermining the viscosity of the sample, since there is no process of repurification which can be relied upon to restore the sample to its original composition and viscosity.

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[3] Use of the phrase "dynamic viscosity" to denote absolute viscosity is deprecated as unnecessary and undesirable in view of (a) the longstanding usage of the adjective "absolute" in this and other fields to signify pure or fundamental and (b) the established usage of the phrase dynamic viscosity in connection with the flow resistance of materials which exhibit frequency-dependent response to a shearing force whose direction is reversed periodically.

The use of pure chemical compounds as reference standards for viscosity has been suggested, the underlying thought being that once the viscosity of the pure compound had been determined, the material could be prepared independently in other laboratories, or that if a sample of the material became suspect because of age or possible contamination, full confidence in the sample could be restored by a suitable routine purification process. However, at present, pure liquid chemical compounds suitable for the purpose are not available in sufficient quantities and techniques for preparing them or for checking their purity are too specialized for most laboratories. Some use has been made of aqueous solutions of sucrose [3] and other substances, but for various reasons these solutions do not provide suitable reference standards for general use, chiefly perhaps because of the difficulty of determining the concentrations of the solutions with sufficient accuracy and of maintaining the desired concentration sufficiently constant. Silicone fluids are somewhat less sensitive to temperature changes than petroleum oils, but this advantage is generally overbalanced by the difficulty of cleaning the viscometers after use of the silicone fluids.

Since the primary reference standard, freshly distilled water, can be prepared readily in any well-equipped laboratory and used as a basis for calibrating viscometers and a series of secondary reference standards covering a wide range of viscosity, it seems obvious that the Bureau has no unique advantage in this field over other well-equipped laboratories.

3. NBS Viscometer Calibrating Oils

Somewhat over 30 years ago the Bureau undertook a program to assist other laboratories in the measurement of viscosities by obtaining a series of capillary tube viscometers, calibrating them with reference to water, and using these instruments to measure the viscosities of a series of oils, samples of which were sold to other laboratories for use in calibrating viscometers. Originally six or seven oils were provided. The current series of oils, which was started in 1938, consists of 10 hydrocarbon oils with viscosities ranging from about 0.02 to 450 poises. A descriptive list of these oils is given in table 1. The spacing of members of this series was arranged to provide a substantially continuous spectrum of viscosity values over this range by varying the temperature of each oil over the range 20 to 40 °C. Viscosity values at other temperatures in the range 20 to 100 °C (30 to 100 °C for Oil P) are determined and reported as a special service for which an additional charge is made. Strict adherence to the plan for spacing of the oils would require Oils A, B, and C with viscosities intermediate to Oil D and water at 20 °C and Oils E, F, and G with viscosities intermediate to Oils D and H. No real need for these six oils has appeared and they have not been prepared. Due to the relatively high sensitivity of the more viscous oils to temperature, their spacing seemed rather wide and Oil OB was added between Oil O (designation changed to Oil OA) and Oil P. The material used for Oil O (OA) subsequently proved unsuitable and it was discontinued.

As the original lots of these oils became exhausted, they were replaced with similar oils of approximately the same viscosity and assigned the same letter designation with a numercial suffix indicating the number of replacement lots, e.g., D, D–1, D–2, etc. Later, to minimize some misunderstanding that these were actually different oil standards, the designations were changed to indicate the situation more clearly, e.g., Oil D, lot 10; Oil D, lot 11, etc.

Oils D through L of the series are prepared from stocks of three commercial "white" oils. Oils M and N originally were high quality, nonadditive, commercial motor oils of SAE 30 and 70[4] grades, respectively. With changing conditions, these oils became unsuitable for use as viscometer calibrating liquids. Currently Oil N is a Pennsylvania bright stock and Oil M is a blend of this and the most viscous of our white oil stocks. Oils OB and P are polyisobutenes.

TABLE 1. *NBS viscometer calibrating oils*[a]

Oil	Absolute viscosity, in poises, at					Kinematic viscosity, in stokes, at				
	20 °C	25 °C	100 °F	210 °F		20 °C	25 °C	100 °F	210 °F	
D	0.020	0.018	0.014	0.006		0.026	0.023	0.019	0.008	
H	.074	.063	.044	.013		.091	.078	.055	.017	
I	.12	.10	.066	.017		.14	.12	.081	.022	
J	.21	.17	.11	.023		.25	.21	.13	.028	
K	.41	.32	.18	.032		.48	.38	.22	.040	
L	1.0	.74	.37	.049		1.1	.84	.43	.060	
M	3.0	2.1	1.0	.099		3.4	2.4	1.1	.12	
N	14	9.6	4.0	.25		16	11	4.6	.30	
	20 °C	25 °C	30 °C	40 °C	50 °C	20 °C	25 °C	30 °C	40 °C	50 °C
OB	300	200	------	55	------	350	210	------	60	------
P	------	------	450	200	95	------	------	510	220	100

[a] Oils SB and SF are not listed because they are intended only for use with Saybolt Universal and Saybolt Furol viscometers, respectively. These instruments are not considered in this discussion.

3.1. Newtonian Character

As stated above, it is important that viscometer calibrating liquids be Newtonian. This statement appears simple enough until we try to apply it practically. Since some materials may deviate only slightly from Newtonian behavior, our classification will depend upon the

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[4] The SAE classification has been revised and grades 60 and 70, discontinued.

sensitivity of our method for detecting non-Newtonian behavior. This reduces to the precision of viscosity determinations at different rates of shear and the range of shear rates which can be covered.

For the low rates of shear attainable with the glass capillary tube viscometers used for determining the viscosities of the NBS viscometer calibrating oils, there appears no basis for questioning their Newtonian character. Tests of the more viscous oils with instruments of somewhat less precision but usable over a wide range of shear rates have indicated Newtonian behavior could be expected at shear rates up to 1,000 sec^{-1}.

In this connection it should be pointed out that all viscosity measurements involve the transformation of mechanical to thermal energy with the development of temperature, and hence viscosity, gradients in the liquid.

This inherent heating error is difficult to assess because of the interdependence of the various factors involved, such as rate of shear and design of the instrument, the thermal capacity and conductance of the liquid, as well as its temperature coefficient of viscosity, and the thermal properties of the instrument and its surroundings.

Although proper design and operation can reduce the effects of heating due to shear, more uncertainty must attach to measurements made at the higher shear rates. When high accuracy is required, calibrations and measurements should be made at shear rates low enough that the heating effect will be negligible.

Oils OB and P are polybutenes. In view of the ample evidence in the literature that many polymers are non-Newtonian, it may be pointed out that although this behavior may be quite pronounced and typical in very high molecular weight polymers, it apparently is not typical of low molecular weight polymers. Porter and Johnson [4] report that polybutenes with molecular weights below some critical value of about 17,000 are Newtonian. The molecular weights of Oils OB and P have been estimated to be about 1,500 to 2,100, respectively. Some qualitative tests for the development of stress in a direction normal to that of shear have indicated that Oils OB and P are not strictly Newtonian, although the deviations from Newtonian behavior apparently are too slight to be demonstrated by variation of their viscosities with rate of shear.

3.2. Temperature Coefficient of Viscosity

Approximate values for the temperature coefficient of viscosity of these oils at various temperatures are given in table 2. Table 3 presents this information in a reciprocal form, i.e., the changes in temperature which would cause a change of 0.1 percent in viscosity. The higher temperature sensitivity of the more viscous oils often raises the question as to the possibility of replacing these oils with liquids having lower temperature sensitivity. While some improvement in this may be possible, it does not appear likely that this difference in sensitivity between the low and high viscosity oils can be eliminated, since all experimental data appear to indicate a general rule that liquids having high viscosity have high temperature coefficients of viscosity and that for any given liquid the temperature coefficient of viscosity is high at temperatures where the viscosity is high. It appears inevitable that when working with high viscosity liquids we must use closer temperature control to obtain viscosity measurements with an accuracy comparable to that obtained with lower viscosity liquids or be satisfied with lower precision and accuracy.

TABLE 2. *Percentage change in η per 1 °C*

Liquid \ Temperature	20 °C	25 °C	100 °F	100 °C
Water	2.44	2.27	1.94	1.04
Oil D	2.11	1.99	1.74	1.08
H	3.42	3.20	2.69	1.43
I	4.02	3.68	3.10	1.54
J	4.61	4.19	3.53	1.71
K	5.45	5.09	4.15	1.96
L	6.38	5.84	4.87	2.28
M	7.27	6.80	5.72	2.62
N	8.03	7.39	6.32	3.13
OB	9.41	9.05	7.6	4.12
P		(8.72 at 30 °C)	(7.03 at 50 °C)	4.52

TABLE 3. *Approximate temperature change causing change of 0.1% in η*

Liquid \ Temperature	20 °C	25 °C	100 °F	100 °C
Water	0.041	0.044	0.058	0.096
Oil D	.047	.050	.057	.092
H	.029	.031	.037	.070
I	.025	.027	.032	.065
J	.022	.024	.028	.058
K	.018	.020	.025	.051
L	.016	.017	.020	.044
M	.014	.015	.017	.038
N	.012	.013	.016	.032
OB	.011	.011	.013	.024
P		(0.11 at 30 °C)	(.014 at 50 °C)	.022

3.3. Precision

Until about 1954 all viscosity values for the NBS oils were determined with one of a series of Bingham variable pressure viscometers. After completion of a careful study of the calibration of the Bingham viscometers and of the Cannon Master viscometers [5] it was decided to use the latter type instruments for determining viscosity values lower than about 30 poises, which appeared to be the upper limit of the useful range of our series of Cannon Master viscometers. We have continued to use the Bingham instruments for determining higher viscosity values. The Cannon Master viscometers yield measurements of the ratio of viscosity to density or kinematic viscosity. The densities of the oils at several temperatures in the range 20 to 100 °C are determined with a dilatometer and values at other temperatures determined by interpolation or extrapolation. Values for absolute viscosity are obtained by multiplying the value for kinematic viscosity by the density at the appropriate temperature.

A statistical analysis of data obtained in the most recent recalibration of our Cannon Master viscometers indicated that the coefficient of variance in the water calibrations was 0.015 percent for the average of three observations by one of three operators chosen at random. For the calibration of the whole series of instruments, only one operator was used and in some instances several fillings of an instrument were made with the same oil and sometimes more than three observations of the flow time for a filling were made. The coefficient of variance for the instrument constants varied from 0.002 percent for the water-calibrated instrument to 0.032 percent for the instruments with the highest range. The coefficient of variance for the viscosity values of the calibrating oils ranged from 0.016 percent for Oil D to 0.031 percent for Oil N and another oil with kinematic viscosity of 25 stokes. A similar statistical study has not been made with the Bingham viscometers, but in the work reported in reference [5] viscosity values obtained with the two types of instruments agreed within 0.05 percent.

3.4. Stability

The viscometer calibrating oils supplied by the Bureau are not permanent standards; hence changes in their physical and chemical properties may be expected with age. Results of a recent statistical analysis of available data on the stability of these oils are summarized in table 4. The raw data consisted of the viscosity values determined at three temperatures for various lots of each oil at known (but irregular) time intervals. Complete sets of data were not available for all lots.

The indicated or apparent changes of viscosity with age and the precision were determined for each lot at each temperature. These values were expressed as a percentage of the viscosity in order that values at the different temperatures could be averaged to obtain single values for rate of change and precision for each oil. The results were consistent with the assumption that for any given oil the percentage change in viscosity and the precision would be independent of temperature.

TABLE 4. *Change of viscosity with age*[a]

Oil	Decreases	Increases	Rate	Precision[b]	Uncertainty after issue[c]	
			%/Mo	%	*Mo*	%
D	18	12	----------	0.021	12	0.10
H	16	14	----------	.033	12	.10
I	11	23	----------	.029	12	.10
J	22	10	----------	.022	12	.10
K	18	20	----------	.017	12	.10
L	25	33	----------	.033	12	.10
M	2	16	+0.0051	.065	6	.25
N	2	30	+ .0137	.041	6	.25
OB	2	35	+ .0251	.072	2	.30
P	3	35	+ .0137	.055	6	.30

[a] For Oils M, N, OB, and P deviations for each temperature were taken from the line $\eta = a + bt$ where t is age when measurement was made.

[b] Mean of average for each of three temperatures of $100\,\frac{s}{\eta}$ for each lot.

[c] Based on indicated mean rate of change with age and including an allowance of three times the standard deviation for random errors of measurement.

Columns 2 and 3 of table 4 show a tally of the indicated decreases and increases of viscosity with age. For Oils D through L, the preponderance of changes in one direction over the number of changes in the other direction is not statistically significant at the 5 percent level. That is to say, the data do not constitute convincing evidence that the viscosities of these oils change with age. The 1:2 and 2:1 ratios for Oils I and J may appear significant when not considered statistically; but the possible significance disappears if we consider further that Oils I, J, and K are mixtures of the same two base oils in different proportions and note the lack of correlation between ratios and composition. The combined tally for the three oils is 51 and 53.

For Oils M, N, OB, and P there is an obvious and statistically significant preponderance of positive rates over negative rates and it is clear that the viscosities of these oils do increase with age. The rates of increase shown in column 4 are based on the slopes of the least squares lines representing change of viscosity with age. A least squares line was computed for each lot of oil at three temperatures insofar as data were available. The precision of the measurements (i.e., 100 times the estimated standard deviation, S, divided by the viscosity, η) are shown in column 5. For Oils M, N, OB, and P, the estimates of precision are based on deviations from the least squares lines. Columns 6 and 7 show the uncertainties which attach to the reported viscosity values at stated ages after shipment. These estimates include an allowance of three times the standard deviation for random errors of measurement. It is assumed that the samples have not been opened and have been stored in the dark at normal room temperature. It should be noted that while the data did not present convincing evidence that Oils D through L change with age, they are too few and cover insufficient time intervals to warrant the assumption that these oils will not change if aged sufficiently. Further, the estimates in column 7 are based on the composite picture presented by at least several lots of each oil and any given lot may be expected to deviate somewhat from the average. Consequently it is recommended that the oils be used as soon as convenient after they are received. In no event should oils which have been on hand for periods significantly greater than those listed be considered as standards with accuracies comparable to those of reasonably current standards.

4. API and ASTM Oil Standards

The viscometer calibrating liquids supplied by the Bureau are not absolute standards and similar series of calibrating liquids or working standards may be prepared independently in other laboratories. A number of the petroleum companies have facilities for this. The American petroleum industry through the American Petroleum Institute has for many years supplied a few oil standards for calibrating or checking the calibration of viscometers. These standards were intended primarily for use in petroleum laboratories and originally were calibrated only in terms of the Saybolt viscosity scales. Later, in cooperation with the American Society for Testing Materials, the viscosities of these API oils were reported in terms of kinematic viscosity. Recently this series has been expanded to provide a range almost as wide as the NBS series and the sponsorship transferred to ASTM. These oils are now being supplied by a commercial laboratory under contract with ASTM and under the supervision of an ASTM Committee which through a cooperative test program checks the viscosity values determined by the commercial laboratory. NBS has had representation on the API or ASTM committees for most of the time since inception of the program. During this period the requirements for precision and accuracy of viscosity measurements have grown more exacting, along with a more widespread understanding of the means by which greater precision in measurements can be achieved.

The present series of ASTM oils was designed to meet the needs of petroleum testing laboratories, particularly with respect to the information supplied with the samples. It is expected that some slight modification and extension of the series and amplification of the data reported for each oil will result in a series of calibrating oils which will meet the needs of laboratories in other industries and may make possible discontinuance of the NBS series.

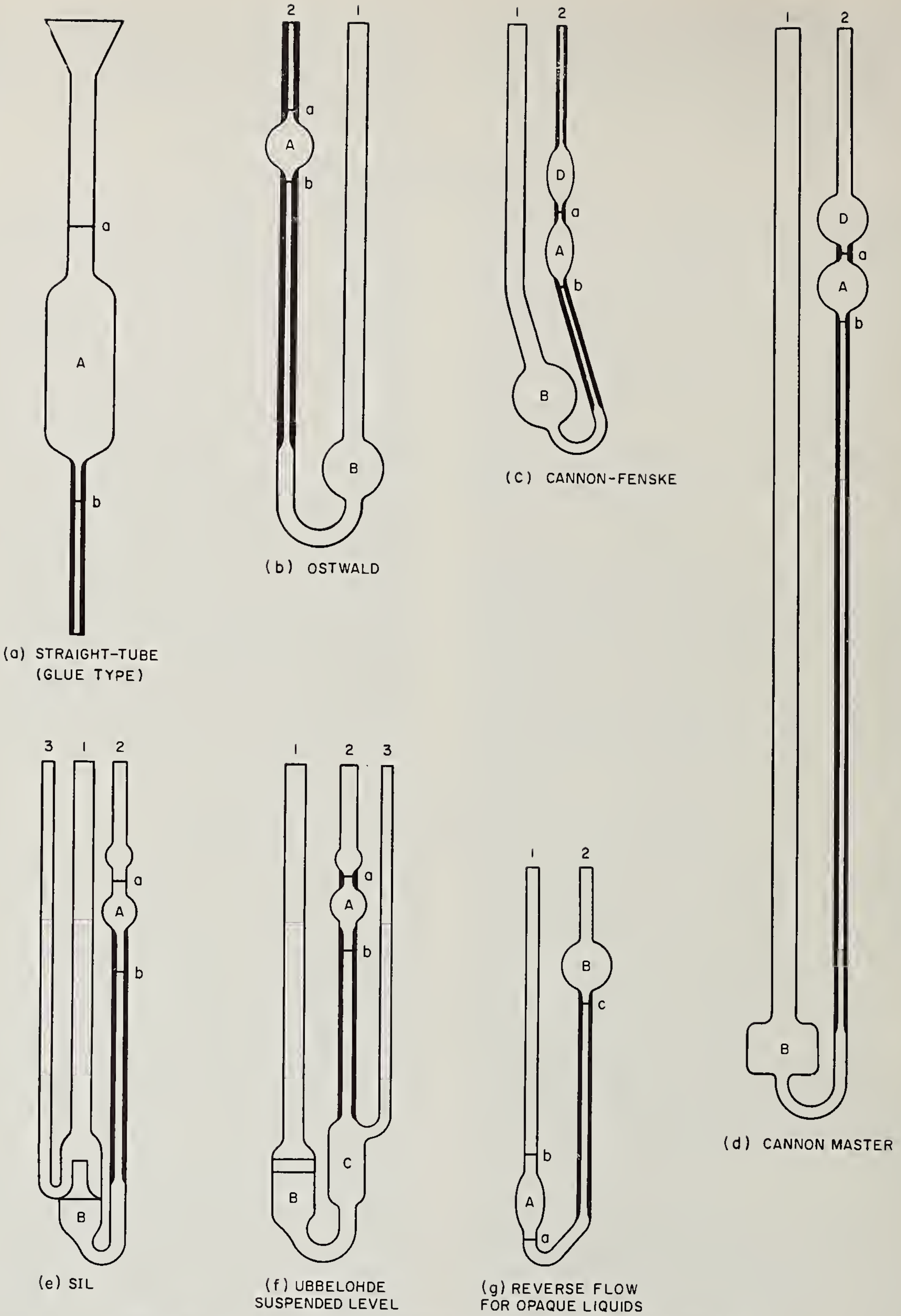
5. Relative Capillary Tube Viscometers

No attempt will be made to consider all the various forms of capillary tube viscometers which are or have been used for relative measurements.

A few types are shown in figure 1 and a brief description of the method of using these may be helpful in pointing out some of the errors and means of correcting them. Several other forms of capillary tube viscometers are described and instructions for their use published in the appendix of ASTM Method D 445 [6] and still other types or forms will be found in the literature.

Perhaps the simplest form is the straight-tube pipet viscometer, which closely resembles the ordinary transfer pipet modified to provide a capillary tube below the bulb and two fiducial lines, one above and one below the bulb. The instrument may be mounted in a vertical position in a thermostat with the lower end extending through the bottom of the bath. The instrument is filled to a point somewhat above the upper fiducial line by holding the sample container below with the viscometer tip submerged and applying suction to the top. The liquid is held in the viscometer by closing one end for awhile to allow it to come to test temperature, then opening the end and allowing the liquid to flow from the instrument, observing the time for the meniscus to fall from the upper to the lower mark. The glue-type viscosity pipet, figure 1a, is a special form with a relatively large diameter tube above the bulb and a funnel top. In using this instrument, the sample is preheated to slightly above test temperature before pouring into the viscometer. The lower end is closed with a finger and the temperature of the sample may be checked with a thermometer inserted through the large upper tube. The thermometer must be removed before starting the run.

Various other modifications of the straight-tube pipette viscometer have been used, but the most widely used glass capillary tube viscometers are of the Ostwald U-tube type or modifications of it. The Ostwald instrument, figure 1b, is charged with a known amount of liquid, either by use of a suitably calibrated pipet or by weighing the instrument (or pipet) before and after charging the instrument or by filling to a mark on the large tube 1. To operate, pressure is applied to tube 1 or suction to tube 2 to cause the liquid to rise in the left limb to a point slightly above line *a*. The pressure (or suction) is released and the time for the meniscus to pass from *a* to *b* is observed. The measurement may be repeated at the same or different temperatures without refilling the instrument.



(a) STRAIGHT-TUBE (GLUE TYPE)

(b) OSTWALD

(C) CANNON-FENSKE

(d) CANNON MASTER

(e) SIL

(f) UBBELOHDE SUSPENDED LEVEL

(g) REVERSE FLOW FOR OPAQUE LIQUIDS

FIGURE 1. *Representative types of capillary tube viscometers.*

Obviously the hydrostatic head causing flow is dependent upon the volume of the charge at the test temperature and for any given filling will vary with the temperature of test. One modification (not shown) of this instrument has a filling mark on tube 1 just above bulb *B* and bulbs *A* and *B* are cylindrical with conical ends.

The Cannon-Fenske and the Cannon Master viscometers, figures 1c and 1d, have auxiliary bulbs *D* above the fiducial bulb *A*. The capacity of the instrument above the line *b* serves to measure accurately the volume of charge at ambient temperature. This is accomplished by inverting the instrument, dipping the end of tube 2 in the sample and applying suction to tube 1, drawing the liquid into tube 2 to a point somewhat beyond *b*, raising the instrument from the sample, and quickly closing tube 2 with a finger, taking care to avoid drawing air into tube 2 before closing it. Suction is released and excess liquid removed by easing the finger pressure, then turning the instrument right-side-up and removing the finger with a wiping action to prevent excess liquid on the finger and top of tube 2 from draining into the instrument. After charging, the instrument is placed in the thermostat and the charge allowed to drain down into bulb *B*. Thereafter, operation is the same as for the Ostwald viscometer.

The SIL viscometer, figure 1e, provides for measuring the volume of charge at the test temperature. This is accomplished by drawing the top of bulb *B* to a moderately small diameter and providing a gallery around it. The liquid is poured into tube 1 while the instrument is inclined about 30° from the vertical. Enough liquid is added to fill the lower part of the instrument and the gallery to a point somewhat above the top of bulb *B*, taking care to avoid trapping air in the tube between *B* and the capillary. After the instrument has been in the thermostat a sufficient time for it to come to temperature, the excess liquid is withdrawn by applying suction to tube 3. Thereafter operation is the same as for the Ostwald instrument. Repeat observations may be made on the same specimen at the same or successively higher temperatures, at each new temperature allowing time for adjustment of the working volume by overflow into the gallery.

The Ubbelohde suspended level viscometer, figure 1f, is charged by pouring the liquid into tube 1 while the instrument is inclined about 30° from the vertical. When returned to a vertical position and the liquid drained from tube 1, the instrument should be filled to a level between the two lines on bulb *B*. To operate, tube 3 is closed with a finger and suction applied to tube 2, drawing the liquid into bulbs *C* and *A* and half filling the small bulb above *A*. The suction is released, tube 3 opened, and tube 2 closed immediately with the finger until air entering tube 3 fills bulb *C*. Tube 2 is then opened and the time observed for the meniscus to pass from *a* to *b*. Repeat determinations may be made on the same specimen at the same or different temperatures.

Other modifications of the U-tube instrument include several such as shown at figure 1g, designed for use with opaque liquids. In general, these place the fiducial bulb low in one limb and the capillary with a reservoir bulb above it in the other limb. Various methods, depending upon the detail designs of the instruments, are used to measure the volume of charge. The instrument shown at figure 1g is intended to be filled in a manner similar to that used with the Cannon-Fenske and the Cannon Master instruments. After charging, the liquid is restrained from entering the fiducial bulb by closing one limb with a rubber tube and pinch clamp until the test temperature is attained. In these instruments the time to fill the fiducial bulb is observed. In one form, the sample flows from the reservoir bulb by siphon action which is started when desired by applying suction to the limb containing the fiducial bulb. These instruments for opaque liquids must be cleaned and refilled for repeat measurements, except that one form provides two fiducial bulbs, one above the other, so that the flow is divided into two parts which may be timed separately, thus getting a check measurement with one filling.

6. Calibration of Relative Capillary Tube Viscometers

For all the instruments mentioned as illustrative of relative capillary tube viscometers, the pressure causing flow is due to the difference between the levels of the free surfaces of the liquid, i.e., $P=\rho gh$ where g is the acceleration of gravity and h the mean effective difference between the levels of the liquid surfaces. With this substitution for P, eq (4) becomes

$$\eta = \frac{\pi \rho g h r^4 t}{8V(l+nr)} - \frac{m\rho V}{8\pi(l+nr)t}. \qquad (5)$$

Neglecting minor corrections to be discussed later and with certain reservations as to operating conditions and techniques, the quantities g, h, r, V, and l are constant for a given instrument. The value of n is somewhat uncertain but, based on theory supported by some experimental evidence, is usually considered to be near unity or smaller so that in instruments with reasonably high ratios of l/r, the quantity $(l+nr)$ may be considered constant or substantially so, even though n may vary somewhat for different rates of flow. With these considerations we may now write

$$\frac{\eta}{\rho} = \nu = Ct - \frac{mB}{t} \qquad (6)$$

in which

$$C = \frac{\pi g h r^4}{8V(l+nr)} \text{ and } B = \frac{V}{8\pi(l+nr)}$$

and ν is kinematic viscosity.

Often these instruments are used under conditions such that the kinetic energy correction is negligibly small in comparison with Ct and eq (6) becomes

$$\nu = Ct. \qquad (7)$$

If a suitable liquid for which ν is known is available, the value of C in eq (7) may be determined by observing the flow time, t, for this liquid and dividing ν by t.

When an instrument is used under conditions such that the kinetic energy term is not negligible, but still small, mB may be considered a constant, following the same reasoning as was used for the quantity nr. Calibration of the instrument for such use requires that two calibrating liquids be available and the flow time for each be determined. The known quantities, ν, and t, for each liquid are inserted in eq (6) and the two equations solved simultaneously. This gives the relations

$$C = \frac{\nu_e t_e - \nu_f t_f}{\dfrac{1}{t_f^2} - \dfrac{1}{t_e^2}}$$

and

$$mB = \frac{\dfrac{\nu_e}{t_e} - \dfrac{\nu_f}{t_f}}{\dfrac{1}{t_f^2} - \dfrac{1}{t_e^2}},$$

in which the subscripts e and f refer to values associated with calibrating liquids e and f, respectively. However, since the correction is small, ν is approximately proportional to t and the difference between the two ratios in the numerator of the expression for mB will be small and influenced unduly by minor errors and uncertainties in the values for ν and t. Thus the expression affords a poor measure of the value of mB. A more satisfactory evaluation of mB may result from assuming that $m=1$ and $n=0$, then calculating B from the dimensions of the instrument and the expression

$$B = \frac{V}{8\pi(l + nr)}.$$

Then the value of C may be determined using eq (6) and data for a calibrating liquid having a reasonably high flow time, i.e., a liquid for which mB/t is very small in relation to Ct.

Cannon et al. [7] propose the following relation to replace eq (6):

$$\nu = Ct - \frac{E}{t^2}, \qquad (8)$$

where $E = \dfrac{0.00166V^{\frac{3}{2}}}{l(Cr)^{\frac{1}{2}}}$. They recommend that E be determined experimentally rather than calculated from this expression. On the basis of their work with various instruments, some of special design, they concluded that "E is a constant over the important Reynolds number range."[5]

During calibration, all details of filling and operation should be the same as will be used subsequently in determining the viscosity of an unknown liquid.

Considering the definitions of C and B,

$$C = \frac{\pi g h r^4}{8V(l + nr)} \text{ and } B = \frac{V}{8\pi(l + nr)},$$

it is obvious that these are constants only for certain conditions since the dimensions r, V, and l will change with temperature; g varies with location; and h varies with temperature, the vertical alinement of the instrument, and, in some instruments, with the volume of liquid in the instrument. The pressure difference available to cause flow is also affected by the surface tension of the liquid and the density of the air column in the instrument, or of the ambient air in the case of straight-tube instruments which extend through the thermostat. Also, the temperature and hence the viscosity of the liquid may be expected to vary throughout the volume of liquid in the capillary due to the heating effect mentioned above, and the appropriate value of V may vary due to incomplete drainage from the fiducial bulb.

Apparently many workers assume that it is necessary to calibrate these instruments at each temperature at which they will be used. This is not the case. The effects of thermal expansion on the instruments are largely self-compensating. Any substantial adjustment of the calibration constant as is required with some U-tube instruments when used at different temperatures is due primarily to expansion of the liquid rather than the instrument. Thus, even with an instrument calibrated at the temperature of test, a correction will be required for the difference in thermal expansion between the calibrating and the test liquid.

The following detailed consideration of the various factors mentioned should lead to a better understanding and if desirable to improved precision and accuracy in measurements of viscosity.

6.1. Variation in Value of g

It is obvious that for any given instrument, other factors being the same, the value of C appropriate for use at different geographic locations varies directly with the acceleration due to gravity at the various locations, so that if an instrument is calibrated in one laboratory

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[5] They consider this range to be from 80 to 500 "because all liquid viscosity measurements in present day viscometers that require a significant kinetic energy correction fall within this range."

and used in another, the value of C should be adjusted by the relation

$$C_u = \frac{g_u}{g_c} C_c \tag{9}$$

in which the subscripts c and u indicate, respectively, the values for the calibrating laboratory and the laboratory where used. The correction usually will be small, but should not be overlooked since it may be significant. For example, a correction of about 0.15 percent would be required between Seattle, Wash., and El Paso or Austin, Tex.

6.2. Curvature of the Capillary

All the viscometers in figure 1 have capillaries which are straight. In order to provide instruments of convenient size but having the advantages of a long tube, the suggestion is made from time to time that this be accomplished by bending the capillary, either by extending it around the U-bend in the U-tube instruments or forming it into a helix or otherwise. A few instruments with one or two U-bends in the capillary are in use. Several workers have investigated the flow through bent capillaries and curved pipes. The results of this work, both theoretical and experimental, confirm what might be surmised, that the radial acceleration involved in deflecting the flowing liquid from a straight course disturbs the normal flow pattern and velocity distribution of a straight tube and results in an abnormally high pressure gradient in the curved section. This in itself might not be significant in a relative instrument, since we rely on the calibration with a liquid of known viscosity to yield a properly weighted integration of the effects of variations in bore size and shape, effective length, etc. However, experimental results have indicated that the range of flow conditions in which the flow time is proportional to the viscosity, i.e., conditions for which the equation $\nu = Ct$ is valid, is restricted when the capillary is curved. Thus bending the capillary tends to defeat the purpose of this design feature and, in general, it appears desirable to use straight capillaries and to make necessary bends only in tubing having an inside diameter several times larger than that of the capillary.

6.3. Heating Effect

In capillary tube viscometers used under conditions such that the kinetic energy correction is negligible, the mean temperature rise at the exit of the tube assuming adiabatic conditions is ΔT °C$=2.34\times10^{-5}\ h/c$ where c is the specific heat of the liquid. At the entrance to the capillary, $\Delta T=0$ and the mean temperature increase for the whole tube is of the order of $\overline{\Delta T}=1.17\times10^{-5}\ h/c$. For instruments of the types shown in figure 1 the value of h varies from about 10 to 50 cm. Taking 0.4 as a representative value for c for petroleum oils and many liquids,

$$\overline{\Delta T} = 0.0003 \text{ to } 0.0015\ ^\circ\text{C}.$$

If external pressure is applied, an additional increase in the mean temperature of $\Delta T=0.0003$ °C per 10 cm water pressure is possible. Usually the heating effects will not be significant with instruments of the types shown in figure 1. The above formula is intended only to indicate the possible magnitude of the mean temperature rise and should not be used for correcting measurements made under high shear rate conditions because it does not take into account the temperature gradients along the tube and across the stream which will distort the theoretical parabolic distribution of velocities, nor the heat loss to the walls of the capillary and the thermostat.

6.4. Drainage Error and Use of External Pressure

Use of eq (5) in connection with viscometers such as those shown in figure 1, except 1g, assumes that the volume of liquid, V, flowing from the fiducial bulb will be the same for liquids having different viscosities. A number of investigations of the validity of this assumption have been made using various techniques. Experiments in this laboratory confirm the findings of some others that, if the rates of flow from the fiducial bulb are proportional to the kinematic viscosities of the liquids, the volume delivered by the bulb is a constant at least for a wide range of viscosities. Consequently, if the instruments shown in figure 1 are used under conditions such that eq (7) is applicable or the value of mB/t in eq (6) is quite small, we may assume that V is a constant although differing from the capacity of the bulb, and that there is no appreciable drainage error in the normal use of the instruments.

However, if the instruments are used with additional air pressure to increase the rate of flow either to extend the range of the instrument or to test the Newtonian character of the liquid, the magnitude of the drainage error must be determined and a correction applied unless the flow is into a clean dry fiducial bulb as might be the case with an instrument such as that shown in figure 1g.

If necessary, the drainage error may be estimated from data obtained by determining the volume of the liquid remaining in a bulb of as nearly as possible the same size and shape as the fiducial bulb, when it is allowed to empty at different rates. The correction factor to account for the reduced volume of flow would be the ratio V/V_P, i.e., the ratio of the volume discharged at the normal rate to the volume discharged at the rate observed when additional pressure is used. It is assumed that this ratio would be the same for two bulbs of about the same size and shape and at the same flow rates. This correction factor should be applied to the observed flow time for the liquid.

For instruments of the Ostwald type (figs. 1b, 1c, 1d, and 1e) the excess liquid remaining on the walls of the fiducial bulb would cause the lower liquid surface to rise more slowly than normal, resulting in a slightly higher than normal mean effective pressure head. An approximate estimate of the correction factor for this effect is $1+\frac{V-V_P}{\pi R^2 h}$ where R is the estimated mean radius of liquid surface in the receiving bulb and h is the normal liquid head. This factor is applied to the instrument constant C, as is the factor H/h needed to account for the direct effects of the increased pressure. In this factor, H is the total pressure causing flow, i.e., normal head, h, plus the applied pressure expressed as a column of the test liquid. All three corrections may be required.

A somewhat inverse situation occurs in the normal use of these instruments when the liquid is forced or drawn up to fill bulb A. If this is done more rapidly than normal, a slight error in the initial head may result from imperfect drainage in bulb B. Although the error due to this may be quite small, it may be minimized by always using the same pressure or vacuum to fill bulb A so that the flow times from bulb B will be approximately proportional to the kinematic viscosity of the liquids.

6.5. Alinement

The vertical distance, h, between the two free liquid surfaces is altered if the axis of the instrument is not vertical. The axis of a capillary tube viscometer may be defined in different ways, but for the purpose of this discussion it is taken to coincide with the vertical line through the center of the upper bulb when the instrument is calibrated. To avoid error due to misalinement, it is usual either to adjust the position of the instrument carefully each time it is used or, preferably, to provide a suitable clamp or holder, or a fixture permanently attached to the instrument which will automatically position the instrument the same each time it is used. The latter procedure, of course, requires that the thermostat cover or other support for the instrument be not easily displaced and that its preferred position be easily checked with a level or plumb line.

For instruments of the type shown in figures 1a, 1c, and 1f, the axis normally passes through the centers of the two liquid surfaces. Misalinement of the instrument, so that its axis deviates from vertical by an angle θ, reduces the effective head by the amount $h(1-\cos\theta)$. For these instruments the change in effective head and the error in the viscosity measurement will not exceed 0.1 percent if θ does not exceed 2°34′.

For instruments shown in figures 1b, 1d, 1e, and 1g, the center of the lower surface is displaced by a horizontal distance d from the axis of the instrument and an additional change in h of $\pm d \sin\theta$ may result from misalinement so that the total error may be $(1-\cos\theta)h \pm d\sin\theta$ or $h(1-\cos\theta \pm d/h \sin\theta)$. If $\theta = 2°34'$ the additional error in h could be as much as $\pm 0.0447d$. The percentage error would depend to some extent on the ratio d/h. If $d/h = 1/10$ and $\theta = 2°34'$, the total error could be as great as +0.35 percent or −0.55 percent. The maximum error occurs when the plane of the instrument lies in the plane of the angle θ and the error could be 0.1 percent if $\theta = 0°33'$. Actually, the d/h ratios for some of the recognized instruments of this type is lower than 1:10 and alinement is more critical than in this example.

The precisely correct alinement of an instrument is that used during calibration, hence it appears probable that closer reproduction of the calibration alinement will be obtained when the instrument is calibrated by the user. If the user's equipment does not provide reproducible alinement, his viscosity measurements will not be reproducible. This would not be corrected or improved by calibration in another laboratory where reproducible alinement, possibly on a somewhat different axis, may be available.

6.6. Effect of Thermal Expansion of the Instrument

If an instrument is calibrated at a temperature T_c and used at a temperature T_u each linear dimension is increased by a factor $F = 1 + \varepsilon(T_u - T_c)$, where ε is the mean linear coefficient of thermal expansion of the material of which the instrument is constructed. The capacity or volume of the fiducial bulb may be considered as the product of three linear dimensions; hence V would be increased by the factor F^3. Indicating these changes in the definitions of C and B, we have

$$C_u = \frac{\pi g (hF)(rF)^4}{8V F^3 (lF + nrF)} = \frac{\pi g h r^4}{8V (l + nr)} F = C_c F$$

and

$$B_u = \frac{V F^3}{8\pi (lF + nrF)} = \frac{V}{8V (l + nr)} F^2 = B_c F^2.$$

Hence $C_u = [1 + \varepsilon(T_u - T_c)]C_c$ and $B_u = [1 + \varepsilon(T_u - T_c)]^2 B_c$. These instruments are usually made of thermal shock resistant glass and the value of ε is of the order of 3×10^{-6} per degree C. If $T_u - T_c = 100$ Celsius degrees, F is approximately 1.0003, e.g., the appropriate value of C for use at a temperature 100° above or below the calibration temperature would be only 0.03 percent higher or lower than the value at the calibration temperature. The change in the value of B would be approximately twice this amount, but this probably would have no significant effect on the viscosity determination since the correction term containing B is small or negligible. In other words, for example, if an instrument is calibrated at 25 °C (77 °F) and used at any temperature in the range from -75 to $+125$ °C(-103 to $+257$ °F) neglecting the correction for the thermal expansion of the instrument would result in a maximum error of only about 0.03 percent.

Discussion of the above factors is intended to call attention to possible errors which can be avoided or minimized, rather than to develop correction factors or formulas, although some were given. The following four corrections relate to adjusting the value of C to compensate for differences between test conditions and the standard reference conditions for which the unadjusted value of C is appropriate. Since the effect of these differences may be expressed in terms of hydrostatic head of the test liquid, it is convenient to compute the corrections as fractions of the head, h. Then the algebraic sum of the fractions increased by one provides a single correction factor for h which may be applied to C, since h is a factor of C. It should be noted that since h does not appear in the kinetic energy term, these corrections do not apply to it.

6.7. Correction for Temperature of Filling

In instruments shown in figures 1a, 1e, and 1f, the effective volume of liquid is adjusted for each run and the temperature at which the instrument was filled is not critical. With instruments shown in figures 1c, 1d, and 1g, the volume of charge is measured at ambient temperature, which in most laboratories is a variable. As a result, the actual volume of charge at a given test temperature is variable. This affects the value of h and hence of C, so that some adjustment of the value of C or correction of the observed time of flow must be made to compensate for the changes in h. With the Ostwald viscometer, figure 1b, the quantity of liquid charged can be adjusted so that h will be a constant, but probably it is more common practice to introduce a fixed volume of charge measured at ambient temperature, in which case a correction for filling temperature is required.

To calculate the correction for filling temperature, temperature of test, air column correction, and surface tension effects, it is convenient to assume some set of standard conditions as a common basis for the calibration and use of the instrument. We have based the calibration constants for our viscometers on the assumption that they were filled and calibrated with water at 20 °C. That these conditions are hypothetical for the instruments with the larger capillaries, which are entirely unsuitable for calibration with water, is immaterial, since the assumption serves only to provide fixed reference conditions.

The capacity of the instrument to the filling mark at the standard temperature, T_c, is $\dot{V}_c$. This is the correct volume of charge. The capacity at the filling temperature T_1 is $\dot{V}_1 = \dot{V}_c [1+\beta(T_1-T_c)]$, which is the measured volume of charge. β is the mean volume coefficient of thermal expansion of the glass of which the instrument is constructed. The volume of the charge $\dot{V}_s$ at T_c when filled at T_1 is $\dot{V}_s = \dot{V}_c \dfrac{1+\beta(T_1-T_c)}{1+\alpha_1(T_1-T_c)}$ in which α_1 is the mean volume coefficient of thermal expansion of the liquid in the temperature interval T_1-T_c, i.e.,

$$\alpha_1 = \frac{\dfrac{\rho_c}{\rho_1} - 1}{T_1 - T_c}.$$

The error in the volume of charge is $\dot{V}_c - \dot{V}_s$ and, assuming that $T_1 > T_c$ for any given position of the upper meniscus, the lower meniscus will be lower than normal by $\dfrac{\dot{V}_c - \dot{V}_s}{\pi R^2}$ where R is the radius of the lower meniscus.[6] Consequently, the value of h is increased to

$$h_u = h + \frac{\dot{V}_c - \dot{V}_s}{\pi R^2}.$$

The fractional change in h due to filling at T_1 instead of T_c is

$$X_1 = \frac{h_u - h}{h} = \frac{\dot{V}_c - \dot{V}_s}{\pi R^2 h}.$$

Substituting for $\dot{V}_s$ and simplifying, we have (see footnote 6)

$$X_1 = \frac{\dot{V}_c}{\pi R^2 h}\left[\frac{(\alpha_1 - \beta)\ (T_1 - T_c)}{1 + \alpha_1\ (T_1 - T_c)}\right]. \quad (10)$$

It may be noted that $\dfrac{\dot{V}_c}{\pi R^2 h}$ is a constant for any given instrument, also, that usually the expression for X_1 may be simplified to read

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[6] For the reverse flow type instrument, figure 1(g), this correction has the opposite sign, since for any given position of the lower meniscus, the upper meniscus will be lower and the value of h decreased.

$$X_1 = \frac{\dot{V}_c}{\pi R^2 h} (\alpha_1 - \beta) \ (T_1 - T_c) \qquad (10a)$$

without introducing appreciable error.

For the purpose of estimating this and other corrections, appropriate values for $\dot{V}_c$, h, and R may be obtained as follows:

The value of $\dot{V}_c$ may be determined by filling bulbs A and D and tube 2 with water or mercury and weighing the quantity discharged or with somewhat less precision by use of a buret to determine the volume of water required to fill these parts of the instrument. To accomplish the first method, a glass stopcock is attached to tube 2 with transparent tubing. The tube on the other side of the cock should be drawn down to form a fairly small tip similar to those on burets. With the instrument in the inverted position, liquid is drawn or forced through the cock to fill the instrument to a point in the capillary. By careful manipulation of the cock, the liquid is drawn down to the fiducial mark b above the bulb (instrument inverted) and then the contents of the instrument drawn into a tared container and weighed. In the second method, the instrument is clamped in the inverted position adjacent to a standard calibrated buret, the tip of the buret connected to tube 2 with trasparent tubing, and the viscometer filled with liquid from the buret, noting the difference between the buret readings when the liquid just enters tube 2 and when the viscometer is filled exactly to mark b.

An approximate value for h may be taken as the head at mean time, i.e., the difference in level of the two liquid surfaces in the instrument when half the flow time for that liquid has passed. A highly accurate value for h is not required since it enters into calculations of correction terms which are small.

The value of R may be estimated from the outside diameter of the bulb corrected for the estimated wall thickness, or the instrument may be filled in the normal way, the liquid drawn up to line a, and the level in bulb B marked accurately. Then allow the liquid to drain down to b and mark the level in B. $R = \sqrt{\frac{V}{\pi S}}$ where V is the capacity of bulb A, and S is the distance between the two marks on B. (V may be determined by an adaptation of one of the methods suggested for determining $\dot{V}_c$). A more precise method, and one which will give some indication of the uniformity of R at different levels in B, is to plug the U-bend with wax, mount the instrument firmly in a vertical position and fill bulb B to a point slightly below the initial level, measure the height of the liquid surface above some reference point with a cathetometer (or measure the depth of the surface below the top of the instrument with a micrometer depth gage), add a known small increment of liquid, and again measure the height of the surface. This is repeated until B is filled somewhat above the final level. The mean value of R_i for the region filled by each increment is $R_i = \sqrt{\frac{V_i}{\pi S_i}}$, where V_i is the volume of the increment and S_i is the change in level of the surface resulting from the addition of the increment. This method assumes that the shape of the meniscus is constant as would be the case if the portion of the bulb B involved is cylindrical.

6.8. Correction for Temperature of Run

As shown above, when these instruments are used at a temperature other than that at which calibrated, thermal expansion of the instrument results in a slight change in the values of the constants C and B, but usually the changes are small enough that they may be ignored, although calculation of an appropriate correction is not difficult. However, in the U-tube type instruments in which the effective volume of charge is not adjusted at the test temperature, thermal expansion of the liquid will change the effective value of h and significant corrections may be necessary.

Assuming that the instrument has been filled at T_c or a correction made for filling at another temperature, the apparent change in volume of charge between T_c and the test temperature, T_u, is

$$\dot{V}_A - \dot{V}_c = \dot{V}_c[1 + (\alpha_u - \beta)(T_u - T_c)] - \dot{V}_c$$

$$= \dot{V}_c(\alpha_u - \beta) \ (T_u - T_c),$$

where $\dot{V}_A$ is the apparent volume of charge at T_u.

The value of h will be reduced[7] by $\frac{\dot{V}_A - \dot{V}_c}{\pi R^2}$ due to thermal expansion of the liquid. This is only partially compensated by the cubic expansion of the instrument and by $\varepsilon(T_u - T_c)h$ due to linear thermal expansion of the instrument.[8] Then the effective value of h at the test temperature is

$$h_u = h - \frac{\dot{V}_A - \dot{V}_c}{\pi R^2} + \varepsilon(T_u - T_c)h.$$

Letting X_u be the fractional change in h, we

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[7] For the reverse flow type instrument, figure (1 g), h is increased by expansion of the liquid and linear expansion of the instrument but decreased by the cubic expansion of the instrument.

[8] The cubic expansion of the instrument reduces the effect of expansion of the liquid and thus tends to increase h; also, the linear expansion of the instrument tends to increase the value of h. This may appear to be making a double correction for expansion of the instrument. However, the point may be clearer if we consider the case of an instrument charged with a hypothetical liquid having the same volume coefficient of thermal expansion as the instrument: a change in temperature would produce no apparent change in the volume of the liquid, but the distance between the two liquid surfaces, h, would change in accordance with the change in temperature and the linear coefficient of thermal expansion of the glass.

write

$$X_u = \frac{h_u - h}{h} = -\frac{\dot{V}_A - \dot{V}_c}{\pi R^2 h} + \varepsilon (T_u - T_c)$$

$$X_u = -\left[\frac{\dot{V}_c}{\pi R^2 h}(\alpha_u - \beta) - \varepsilon\right](T_u - T_c). \tag{11}$$

6.9. Air Column Correction

In developing eq (5) from eq (4) we said that $P = \rho g h$. This neglected the hydrostatic head of air in the other limb of the instrument (or the ambient air in the case of a straight-tube pipet viscometer). The correct expression for P is

$$P = (\rho_{wc} - \rho_{ac}) g h,$$

where ρ_{ac} is the density of the air in the instrument (or the ambient air when a straight-tube instrument is used).

To correct the kinematic eqs (6) and (7) for this, we must multiply the constant C by $1 - \frac{\rho_{ac}}{\rho_{wc}}$. Then under calibration conditions (real or hypothetical)

$$\nu = \frac{\pi g r^4 h}{8 V l}\left(1 - \frac{\rho_{ac}}{\rho_{wc}}\right) t$$

and under test conditions,

$$\nu = \frac{\pi g r^4 h}{8 V l}\left(1 - \frac{\rho_{au}}{\rho_{lu}}\right) t,$$

where ρ_{ac} and ρ_{wc} are the density of air and water at 20 °C, respectively, and ρ_{au} and ρ_{lu} are the density of air and the test liquid at the test temperature. Thus the geometric head, h, is reduced by the factor $1 - \frac{\rho_{ac}}{\rho_{wc}}$ under calibration conditions and by the factor $1 - \frac{\rho_{au}}{\rho_{lu}}$ under test conditions. The fractional change in head is

$$X_a = \frac{h\left(1 - \frac{\rho_{au}}{\rho_{lu}}\right) - h\left(1 - \frac{\rho_{ac}}{\rho_{wc}}\right)}{h\left(1 - \frac{\rho_{ac}}{\rho_{wc}}\right)} =$$

$$\left(\frac{\rho_{ac}}{\rho_{wc}} - \frac{\rho_{au}}{\rho_{lu}}\right)\left(\frac{\rho_{wc}}{\rho_{wc} - \rho_{ac}}\right). \tag{12}$$

The precise values for ρ_{ac} and ρ_{au} will vary with barometric pressure and humidity but the value of X_a is small and use of reasonable average values will not involve serious error. We use values for the density of air at 760 mm of Hg pressure having a dew point of about 15 °C. Thus $\rho_{ac} = 0.001197$ g/cm^3. The density of water at 20 °C is 0.99821 g/cm^3. Using these values,

$$X_a = 0.001200 - 1.0012 \frac{\rho_{au}}{\rho_{lu}}. \tag{12a}$$

6.10. Correction for Surface Tension Effects

Considering the effects of surface tension in a capillary tube viscometer in terms of capillary rise, the driving head is reduced by the capillary rise in the upper bulb and increased by the capillary rise in the lower bulb. Usually the diameters of the bulbs are fairly large and the capillary rise is small except near the fiducial marks. Fortunately the relatively large capillary rise when the liquid surface is near the fiducial marks is effective for only a small fraction of the total flow time.

Instruments (e) and (f) of figure 1 are intended to minimize the effects of surface tension so that they may be used with liquids with widely different values for γ without requiring correction. This requires proper matching of the two bulbs connected to the opposite ends of the capillary. Obviously, other instruments shown in figure 1, except the glue type, could be rendered less sensitive to surface tension effects if proper consideration were given to matching the surface tension effects in bulbs A and B.

Accurate evaluation of the effect of surface tension in altering the mean effective head, h, is difficult because of changing diameters of the liquid surfaces, changing inclination of the bulb walls as flow progresses, and the fact that the simple capillary rise formula, $h_\gamma = \frac{2\gamma}{\rho g r}$, is applicable only to tubes with vertical walls and which are literally capillary in size. The effect usually is small and often it is ignored or a correction applied which is only a rough approximation based on the simple capillary rise formula and estimated mean effective diameters for the bulbs. These procedures may be satisfactory when the instrument is used only with liquids having surface tensions approximately the same as that of the calibrating liquid or when accurate values for viscosity are not required.

A reasonably accurate evaluation of the correction required for a given viscometer and liquid may be made either by calculation or by experiment. Both methods are somewhat tedious.

To estimate the correction by calculation, an accurate vertical profile sketch or photographic silhouette of the interior surface of the bulb is made and divided into a number of horizontal zones (perpendicular to the axis of the instrument). The lengths of these zone boundaries and the angle ϕ between the axis and the normal to the profile at each intersection of the profile and zone boundaries are measured. The angle ϕ is between the normal and the segment of the bulb axis below its intersection with the normal. The measurements give the diameter of the bulb at each zone boundary and the angle ϕ for use with the tables prepared by Bashforth and Adams [8] to obtain values for a quantity b and the volume of the meniscus[9] at each zone boundary.

The capillary rise at each boundary is $h_{\gamma b} = \frac{a^2}{b}$, where $a^2 = \frac{2\gamma}{\rho g}$. If the zones are narrow, the value of $h_{\gamma z}$ for the zone may be taken as the arithmetic mean of the values for $h_{\gamma b}$ at the upper and lower boundaries. The time during which the mean value, $h_{\gamma z}$, for each zone is effective is proportional to the volume of flow and inversely proportional to the mean effective head, h_z, for the zone. The volume of flow is estimated as the volume of the frustrum of a cone (with radii and height equal to those of the zone) decreased by the volume of the meniscus at the upper boundary and increased by the volume of the meniscus at the lower boundary. (For this purpose, the meniscus at a boundary is the meniscus which is tangent to the bulb profile at the boundary—not the meniscus tangent to the zone boundary.) The mean effective head for each zone may be taken as the mean geometric head for the zone h_{gz} increased by the capillary rise in the lower bulb $h_{\gamma B}$ and decreased by the mean capillary rise for the zone $h_{\gamma z}$, i.e., $h_z = h_{gz} + h_{\gamma B} - h_{\gamma z}$. Then, if V_z, $h_{\gamma z}$, and h_z are, respectively, the volume of flow, the mean capillary rise, and the mean effective head for each zone, the total effective capillary rise is

$$h_\gamma = \frac{\sum \frac{V_z\, h_{\gamma z}}{h_z}}{\sum \frac{V_z}{h_z}}.$$

Use of this method is limited by the range of the Bashforth and Adams tables.

In the experimental method of estimating h_γ, a bulb with two fiducial lines, of the same size and shape as the fiducial bulb of the instrument, is connected to a vertical cylindrical tube of known diameter by a U-shaped glass or flexible connection and mounted in a stirred bath to prevent rapid changes in temperature. The U-shaped connection is filled to the lower fiducial line with water or other liquid of known surface tension and the heights of the menisci in the two arms referred to some common reference level are measured with a cathetometer or equivalent means. A known volume of the liquid is added to the cylindrical tube and the change in the levels of the menisci measured. This is repeated until the fiducial bulb has been filled to the upper fiducial line. The work can be carried out at ambient temperatures provided these do not vary greatly or rapidly. By observing the bath temperature when measuring each pair of meniscus heights, suitable corrections for changes in volume may be made, if necessary. Then if V_i is the volume of the increment, R the radius of the cylindrical tube, and Δh_T the change in level in the cylindrical tube, the volume of liquid entering the bulb is $V_z = V_i - \pi R^2\, \Delta h_T$. The capillary rise in the fiducial bulb for any pair of observations of the menisci heights is equal to the calculated capillary rise in the tube, $h_{\gamma T}$, plus the observed level of the meniscus in the bulb and minus the observed level of the meniscus in the tube. If the values of V_z are small, the arithmetic mean value of the capillary rise in the bulb before and after adding the increment may be taken as the mean effective value, $h_{\gamma z}$, for the portion of the increment entering the bulb, V_z. Then

$$h_{\gamma z} = \frac{\Delta h + \Delta h_i}{2} + h_{\gamma T},$$

where Δh and Δh_i are the differences between the liquid levels before and after adding the increment. The differences must be taken by subtracting the level in the tube from the level in the bulb and may be either positive or negative. The diameter of the cylindrical tube will be too large for use of the simple capillary rise formula and $h_{\gamma T}$ must be computed by use of the Bashforth and Adams tables [8] or by use of Sugden's table [9].

The mean effective value of the capillary rise for the whole bulb is

$$h_\gamma = \frac{\sum \frac{V_z\, h_{\gamma z}}{h_z}}{\sum \frac{V_z}{h_z}},$$

where h_z is the mean effective geometric head for any increment of liquid V_z, calculated as though the bulb were actually the fiducial bulb of the viscometer. Thus, if h is the head at mean time for the viscometer and e is the distance from the upper liquid level at mean time to the lower fiducial mark,

$$h_z = (h - e) + J,$$

where J is the height of the midpoint of the

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[9] The volume of the meniscus is the volume enclosed by the meniscus and the horizontal plane containing the line of tangency between the meniscus and the tube or bulb which is assumed to be symmetrical about its vertical axis.

zone above the lower fiducial line of the experimental bulb.

If this method is applied directly to the viscometer rather than to a separate bulb closely resembling the fiducial bulb of the viscometer, considerable time must be allowed after each addition of liquid to permit the system to reach equilibrium before reading the levels of the menisci.

An inherent error in this empirical method when using a cathetometer results from differences in the optical path at different levels due to differences in the angles of incidence and in the wall thickness of the bulb. This can be minimized by using a test liquid and bath liquid having approximately the same refractive index as the glass of the instrument. The value of h_γ thus determined is for the capillary rise in the fiducial bulb. The capillary rise in the receiving bulb may be estimated in a similar manner or, if this bulb is cylindrical, the capillary rise may be estimated by use of Sugden's table [9]. The driving head in the instrument corrected for surface tension effects is $h - h_{\gamma F} + h_{\gamma R}$ where the subscripts $_F$ and $_R$ indicate the values for the fiducial bulb and the receiving bulb, respectively.

It may be noted that both methods for estimating the surface tension effects are based on static conditions and neglect the effects of distortion of the menisci when in motion. A receding meniscus has a smaller than normal radius of curvature and exhibits a greater than normal surface tension effect. The converse is true for an advancing meniscus. Hence in a kinematic viscometer the motion of the liquid tends to augment the surface tension effect in the upper bulb and to diminish it in the lower bulb. (It is assumed that the liquid wets the walls of the instrument, otherwise the effects of the moving menisci would be opposite to what has just been stated.) In ordinary kinematic viscometers, the motions of the menisci are quite slow except for brief periods at the beginning and end of a determination and it is believed that the distortion of the menisci can be of only academic interest. This effect was neglected also in the discussion of the use of external pressure, although in some instances when considerable external pressure is used with a viscous liquid the distortion of the menisci may be quite noticeable. Nevertheless, the error due to neglecting this effect may well be negligible, since the whole effect of surface tension would be relatively small in relation to the applied pressure.

The fractional change in the effective value of h due to changing from the the standard reference conditions to the test conditions is

$$X_\gamma = \frac{h_{\gamma c} - h_{\gamma u}}{h}, \tag{13}$$

where $h_{\gamma c}$ and $h_{\gamma u}$ are the net effective capillary rise of the calibrating and test liquids, respectively.

On the basis of results of experimental determination of the capillary rise effect for water and three hydrocarbon liquids in an experimental bulb similar to the essentially spherical fiducial bulbs of our water-calibrated Cannon Master viscometers and calculations of the capillary rise effect for water in these instruments using Bashforth and Adams tables, we have found that for our Cannon Master viscometers,

$$X_\gamma = \frac{0.1235 - 0.8346a^2}{h} \tag{14}$$

or, since $h = 46.4$ for the Cannon Master viscometers,

$$X_\gamma = 0.00266 - 0.0180a^2. \tag{15}$$

Calculations of the capillary rise effect with water and three hypothetical liquids in one of our Cannon Master viscometers having a somewhat elongated fiducial bulb indicated that the same relation was a reasonable approximation for this shape bulb and we have used eq (15) for all our Cannon Master viscometers.

These four corrections or adjustments are intended to account for differences in the pressure causing flow, which result from differences between conditions of calibration and use. They have been computed as actual or equivalent fractional changes in h. We do not attempt to measure h accurately and the corrections may be smaller than the uncertainty in h. This is not particularly significant since h is a factor in determining the value of C, which is known (or to be determined) accurately and thus involves an accurate but undetermined value for h. In effect, this accurate but undetermined value for h may be corrected by applying the correction to C. This may be accomplished conveniently by adding the fractional correction to unity to obtain a combined correction factor or multiplier, M, to be applied to C, i.e.,

$$M = 1 + X_1 + X_u + X_a + X_\gamma. \tag{16}$$

Then eqs (6), (7), and (8) become

$$\nu = CMt - \frac{mB}{t}[1 + \varepsilon(T_u - T_c)]^2; \tag{17}$$

$$\nu = CMt; \tag{18}$$

$$\nu = CMt - \frac{E[1 + \varepsilon(T_u - T_c)]^2}{t^2}. \tag{19}$$

The kinetic energy term does not involve pressure and is unaffected by the pressure adjustments effected by use of the factor M. However, as noted above, a correction for thermal expansion of the instrument may be applied, although the effect probably would have no significance. The effects of thermal expansion of the instrument on the value of C are included in the X_u correction.

To calibrate an instrument it is necessary to observe the flow time of water or some liquid of known viscosity and to compute the various corrections X_1, X_u, etc. Then if conditions are such that the kinetic energy correction is negligible, i.e., the Reynolds number does not exceed a value of 10 to 15, $\nu = CMt$ and $C = \frac{\nu}{Mt}$.

If the kinetic energy term is not negligible, it will be necessary to determine the flow times and correction factors for two liquids, e and f, of known viscosity and solve one of the following pairs of simultaneous equations:

$$\text{(a)} \qquad \nu_e = CM_e t_e - \frac{(mB)}{t_e}$$

$$\nu_f = CM_f t_f - \frac{(mB)}{t_f}$$

or

$$\text{(b)} \qquad \nu_e = CM_e t_e - \frac{E}{t_e^2}$$

$$\nu_f = CM_f t_f - \frac{E}{t_f^2}$$

E is said to be much more constant than (mB) so unless the correction term is quite small the equation containing E may be preferred. However, confidence in the accuracy of results obtained with either equation is impaired if the correction is not small.

Some typical values for the various corrections used with our Cannon Master viscometers are shown in table 5. These are intended only to indicate the magnitude of the corrections when the instruments are used with petroleum oils and the calibration constants are appropriate for the conditions associated with operation at 20 °C with water. If the corrections for the oil calibrated instruments were on the basis of reference to calibration conditions with oil at 20 °C, the value of the X_γ correction would be reduced to not more than about 0.02 or 0.03 percent for liquids with values for γ in the range 20 to 32 dynes/cm. However, it should not be overlooked that the percentage corrections would be larger for instruments having bulbs of about the same size but much lower values for h. For example, since the bulb sizes are about the same for the Cannon Master and the Cannon Fenske viscometers but the value of h for the Cannon Fenske instruments is only about 1/5 of that for the Cannon Master viscometers, the values of X_1, X_u, and X_γ for the smaller instruments are about five times as great as for the Master viscometers.

TABLE 5. *Approximate ranges of correction for Cannon Master viscometers*

Correction	Oil D		Oil N	
	at 20 °C	at 210 °F	at 20 °C	at 210 °F
[a]X_1	0 to +0.018	0 to +0.018	0 to +0.014	0 to +0.014
X_u	0	−0.135	0	−0.078
X_a	−0.032	−0.009	−0.015	+0.008
X_γ	+0.144	+0.163	+0.133	+0.153
Total	+0.112 to +0.130	+0.019 to +0.037	+0.118 to +0.132	+0.083 to +0.097

[a] Assume filling temperature between 20 and 30 °C (68–86 °F).

Not all the corrections discussed are necessary with all the types of instruments shown in figure 1. The capillaries are essentially straight, and bends are made only in tubes with diameters considerably larger than the capillary and in which both the fluid velocity and resistance to flow are relatively low. Probably no corrections for curvature, heating effect, or drainage need be applied to these instruments when not used with externally applied pressure. All of the instruments may require correction for changes in the value of g if calibrated and used at different locations and all are subject to alinement error, air column correction, surface tension effects, and thermal expansion of the instrument; however, these corrections may be negligibly small. For types (b), (c), (d), and (g) the correction for expansion of the instrument is included in the correction for temperature of test. Instrument types (b), (c), (d), and (g) may require a correction for the temperature of filling as well as for the temperature of test. The error resulting from misalinement was discussed to point out the need for careful reproducible positioning of the instrument. It is not anticipated that these instruments would be used intentionally with improper alinement, the error of alinement measured, and a correction applied. The SIL and the Ubbelohde instruments are designed so that the capillary effects of the two liquid surfaces will in large measure neutralize each other so that X_γ for these instruments probably is negligible. Also, for these two instruments, as well as for the straight-tube viscometer, the working volume of liquid is adjusted at each test temperature, eliminating the need for corrections X_1 and X_u.

7. Calibration of Viscometers With a Reference Viscometer

The preceding discussion has been written from the viewpoint that relative viscometers will be calibrated with liquids whose viscosities are known explicitly at a specified temperature. This is the usual practice in the United States, although some prefer to calibrate relative capillary tube viscometers by direct comparison with a calibrated viscometer of similar design and range. This direct comparison method is preferred in some countries where viscometer calibrating liquids are not so readily available.

Briefly the method consists of determining the flow times of one or more suitable liquids in a calibrated viscometer and in the viscometer to be calibrated. The determinations are made by the same method that would be used if the purpose were to determine the viscosity of the liquid, except that there is no concern that the measurements be made at a specific temperature—only that both instruments be at the same temperature and that the determinations be made concurrently. Then if eq (7) is applicable,

$$\nu = C_a t_a = C_b t_b$$

or (20)

$$C_b = C_a \frac{t_a}{t_b}.$$

The subscripts a and b refer, respectively, to values associated with the reference instrument and the instrument to be calibrated.

If the instrument is to be used in a range where the end corrections are not negligible, comparisons with two liquids will be required. The two liquids should be chosen so that the end correction for one will be substantial and for the other negligible. If the end corrections for one liquid are negligible in both instruments the value of C_b may be determined as just described using eq (20). Then $(mB)_b$ may be evaluated by use of eq (21) and the flow times for the other liquid. However, if the end corrections for neither of the liquids are negligible for both viscometers, simultaneous equations based on either eq (6) or eq (8) may be written and solved to determine the constants for the instrument to be calibrated. For example, using eq (6) we would write

$$\nu_e = C_a t_{ae} - \frac{(mB)_a}{t_{ae}} = C_b t_{be} - \frac{(mB)_b}{t_{be}}; \tag{21}$$

$$\nu_f = C_a t_{af} - \frac{(mB)_a}{t_{af}} = C_b t_{bf} - \frac{(mB)_b}{t_{bf}}. \tag{22}$$

The advantages cited for this procedure are (a) that errors due to faulty temperature measurement and control are avoided, since it is not necessary to make the comparison at an accurately known temperature and (b) that since the glass capillary tube viscometers are much less subject to change with age than are the calibrating liquids, they may be used as reference standards repeatedly over a long period of time.

Although the first point may be valid with regard to the calibration of an instrument, it should not be construed as in any way suggesting the lack of need for accurate measurement and control of temperature when the instrument is used for measuring the viscosity of a liquid.

The superior stability of the instruments may be utilized in both methods, since after an instrument has been calibrated with a reference liquid (or viscometer) it may be preserved as a reference standard for the laboratory and used to recalibrate the reference liquid or to calibrate new reference liquids as required.

One serious limitation of the direct comparison method is that, in general, it may be used only for instruments of the same or similar design and range. At least, it is not readily apparent how direct comparisons may be effected between capillary tube instruments and various rotational viscometers, falling body viscometers, etc., or even between some glass capillary tube vicometers of different designs.

In using the direct comparison method, the corrections appropriate for each instrument should be applied. If the reference viscometer was calibrated in a different laboratory, the possible need for adjustment of the instrument constant, C_a, for differences in the strength of the earth's gravitational field should not be overlooked. Also, special care should be used to duplicate the instrument alinement and operating procedure used in the calibration of the reference viscometer.

In comparing the merits of the two methods, it should be recognized that the appropriate value for the instrument constant is affected by the temperature, place, and method of use as well as by the design and dimensions of the instrument, and certain properties (surface tension and coefficient of thermal expansion) of the liquid being examined. On the other hand, the viscosity of a reference liquid is affected by its temperature but not by its geographic location or the method by which it was determined, and of course it is more subject to change with age. This statement assumes that Newtonian behavior is an essential characteristic of a reference liquid for viscometry and that, if necessary, the viscosity value has been corrected to the standard pressure of one atmosphere.

Ordinarily when external pressure is not applied, the pressure correction is neglected and in most instances lacks significance. However, when measurements of more than routine accuracy are desired, the correction for barometric pressure may be large enough to warrant consideration if the work is being done in a laboratory situated at a considerable elevation. For example, it is estimated that at Denver, Colo. (elevation 5374 ft, normal barometric pressure 625 mm of Hg) correction of measured viscosity values to account for the effect of ambient pressure less than 1 atm would range from about +0.016 percent to +0.065 percent for petroleum oils with viscosities ranging from 0.01 poise to 100 poises. Such correction would be necessary to account for the pressure sensitivity of the liquid. Changes in barometric pressure would not affect the value of the instrument constant.

These estimates are based on the empirical relation

$$\Delta\eta\% = (3 + 0.91\ \log\eta)10^{-4}\,\Delta p, \qquad (23)$$

where $\Delta\eta$ is the change in viscosity, in poises, resulting from a pressure differing from one atmosphere by Δp mm of Hg. Equation (23) was derived from relationships proposed by Cragoe [9], using 3×10^{-4} mm Hg as a representative value for the pressure coefficient of viscosity of petroleum oils.

8. Precalibrated Viscometers

Formerly the Bureau provided a viscometer calibration service covering a few types of capillary tube viscometers. This service was discontinued January 1, 1958 because of the relatively small demand and the belief that calibrations performed in the laboratory where the viscometers were to be used were to be preferred because the effects of any peculiarities of operating technique and accessory equipment may tend to cancel when they are the same for both the calibration and the measurements on unknown samples.

Since precalibrated viscometers, i.e., instruments which have been calibrated some place other than where used, usually are calibrated with petroleum oils at 100 °F, it may be well to point out to those working with nonpetroleum liquids that some adjustment of the calibration constants may be desirable to account for differences between the surface tension of petroleum oils and the liquids to be measured, as well as for the difference between the temperatures of calibration and use. Probably this will not be necessary with instruments of types similar to (e) and (f) of figure 1 since for these instruments the volume of charge is not critical and the net effect of surface tension is small. As noted above, some adjustment of the instrument constant to compensate for differences in gravity may be necessary when an instrument is used at different locations. The need for such adjustment could be determined by the user of the instrument if the calibration certificate contains a statement as to the acceleration due to gravity in the calibrating laboratory.

For the more common types of U-tube viscometers for which appreciable correction may be required for thermal expansion of the liquid and for surface tension effects, a correction factor[10] M may be determined as indicated above to adjust for differences between conditions when calibrated at 100 °F with petroleum liquid and the hypothetical conditions of filling and calibrating with water at 20 °C. This would be the same factor that would be used if the viscosity of the calibrating oil were being determined in a water-calibrated instrument. Then

$$\nu_o = C_o t_o = CM_o t_o$$

$$C = \frac{C_o}{M_o},$$

where the subscript o indicates the value associated with the calibrating oil and C is the constant applicable to the hypothetical use with water at 20 °C. Using the subscript l to indicate values associated with another liquid, we may write

$$\nu_l = C_l t_l = CM_l t_l;$$

$$C_l = CM_l = C_o \frac{M_l}{M_o}.$$

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10. Symbols

a = capillary constant = $\left(\frac{2\gamma}{\rho g}\right)^{0.5}$.
B = constant factor in kinetic energy correction term.
b = radius of curvature of meniscus at its center.
C = instrument constant applicable under conditions associated with real or hypothetical calibration with water at 20 °C.
c = specific heat of liquid.
D = diameter of capillary tube.
d = horizontal distance between upper and lower bulbs of a U-tube viscometer.
E = constant (approximately) factor in kinetic energy correction term, proposed by Cannon et al.
e = height of meniscus in fiducial bulb at mean time above the lower fiducial mark.
F = factor for adjusting viscometer dimensions for thermal expansion; force.
f = variable ratio ν/t.
g = acceleration due to gravity.
H = total pressure causing flow when external pressure is used, expressed as head of test liquid.
h = difference between the levels of the two free liquid surfaces.
J = height of mid-point of zone above lower fiducial mark of experimental bulb.
K = constant of proportionality in Poiseuille's equation.
l = length of capillary tube; length.
l' = length of a portion of capillary tube where flow is not affected by end conditions.
m = coefficient of the Hagenbach or kinetic energy correction; mass.
M = combined correction factor.
n = coefficient of the Couette correction to length of the capillary tube.
P = pressure difference between ends of capillary tube.
P' = pressure drop through a length l' of tube remote from the ends.
Q = volume rate of flow through capillary.
R = radius of receiving bulb or lower meniscus.
R_e = Reynolds number = $\frac{vd\rho}{\eta}$.
r = radius of capillary tube.
S = change in level of liquid surface in receiving bulb as the fiducial bulb is emptied or filled.
T = temperature.
t = time for liquid to flow from or into the fiducial bulb; time.
V = volume of liquid flowing from or into the fiducial bulb.
$\dot{V}$ = volume of liquid charge in viscometer.
v = average velocity of liquid flowing in capillary.
X = fractional change in effective value of h due to various differences between conditions during calibration and use.
α = mean volume coefficient of thermal expansion of the liquid.
β = mean volume coefficient of thermal expansion of the instrument glass.
γ = surface tension of the liquid.
Δp = difference between 1 atm and the pressure on the liquid.
ε = mean linear coefficient of thermal expansion of the instrument glass.
η = viscosity.
θ = angle between the axis of the viscometer and the line of action of gravity.
λ = Couette correction to length of capillary.
ν = kinematic viscosity = $\frac{\eta}{\rho}$.
ρ = density of liquid or air.
ϕ = angle between the axis of the fiducial bulb and the normal to the bulb profile at the point of tangency between the meniscus and the bulb ($\phi < 90°$ when normal is below horizontal).

Subscript	Indicates value associated with:
$_1$	temperature at which viscometer is filled; value of α for temperature interval $T_1 - T_c$.
$_2$	the second of two or more liquids.
$_a$	reference viscometer.
$_b$	zone boundary; viscometer to be calibrated by direct comparison.
$_B$	lower or receiving bulb.
$_c$	time or place of calibration.
$_{e,f}$	any two calibrating liquids e and f.
$_F$	fiducial bulb.
$_g$	geometry of instrument.

i	increment of liquid.
l	liquid under examination.
o	calibration with petroleum oil at 100 °F.
p	external pressure.
R	receiving bulb.
S	$\dot{V}$ at T_c after filling at T_1.
T	tube used in experiment to determine h_γ.
u	time or place of use; or unknown.
w	water.
z	zone; volume increment in bulb.
γ	surface tension effect.

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U.S. DEPARTMENT OF COMMERCE
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The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D.C.

Electricity. Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics. High Voltage.

Metrology. Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

Heat. Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics.

Radiation Physics. X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

Analytical and Inorganic Chemistry. Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research. Crystal Chemistry.

Mechanics. Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

Polymers. Macromolecules: Synthesis and Structure. Polymer Chemistry. Polymer Physics. Polymer Characterization. Polymer Evaluation and Testing. Applied Polymer Standards and Research. Dental Research.

Metallurgy. Engineering Metallurgy. Microscopy and Diffraction. Metal Reactions. Metal Physics. Electrolysis and Metal Deposition.

Inorganic Solids. Engineering Ceramics. Glass. Solid State Chemistry. Crystal Growth. Physical Properties. Crystallography.

Building Research. Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials. Metallic Building Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

Data Processing Systems. Components and Techniques. Computer Technology. Measurements Automation. Engineering Applications. Systems Analysis.

Atomic Physics. Spectroscopy. Infrared Spectroscopy. Solid State Physics. Electron Physics. Atomic Physics.

Instrumentation. Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

Physical Chemistry. Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Molecular Kinetics. Mass Spectrometry.

Office of Weights and Measures

BOULDER, COLO.

Cryogenic Engineering Laboratory. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Cryogenic Technical Services.

CENTRAL RADIO PROPAGATION LABORATORY

Ionosphere Research and Propagation. Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services. Vertical Soundings Research.

Radio Propagation Engineering. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

Radio Systems. Applied Electromagnetic Theory. High Frequency and Very High Frequency Research. Modulation Research. Antenna Research. Navigation Systems.

Upper Atmosphere and Space Physics. Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

RADIO STANDARDS LABORATORY

Radio Physics. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time-Interval Standards. Millimeter-Wave Research.

Circuit Standards. High Frequency Electrical Standards. Microwave Circuit Standards. Electronic Calibration Center.