The temperature coefficients of these groups at 18° were 0.000265, 0.000285, and 0.000290. From these results it is obvious that the temperature coefficient of the electromotive force of the combination changes very little with the concentration of the solution, although the voltages obtained are much higher than in the case of the saturated element.

Summary.

The possibility of employing calomel as depolarizer in the construction of precision standard cells has been established. Ordinary calomel, when suitably modified so as to contain finely divided mercury, giving the material a gray color, forms a depolarizer for cells, gives constant and reproducible electromotive forces, and this preparation should give better results in calomel electrodes.

Saturated and unsaturated cells of composition $Hg \mid HgCl_2 \mid CdCl_2 \mid Cd$ amalgam have been constructed, their E. M. F.'s measured and their temperature coefficients obtained.

The thermodynamics of the saturated combination has been investigated and satisfactory agreement between the heat of the reaction as calculated from the electromotive force data and that obtained from thermo-calomel measurements has been established.

PRINCETON. N. J.

SOME SOURCES OF ERROR IN VISCOSITY MEASUREMENT.

BY EUGENE C. BINGHAM. H. I. SCHLESINGER AND ARTHUR B. COLEMAN.[1]

While using the viscometer recently described by Bingham,[2] it was observed that the viscosities (η) when calculated by the now generally accepted formula

$$\eta = Ctp - C'\rho/t \tag{1}$$

were not constant, but varied considerably when the applied pressure p was varied. In the above formula t is the time of flow, ρ the density, and C and C' are constants. As the instrument differed in what were at first considered minor details from the instrument originally successfully used by Bingham, it was thought that by its use some errors had been made apparent which might have been masked in the original viscometers and that these errors might be of such a nature as to require corrections for all viscosity measurements made in similar types of apparatus. The instrument differed from the original one in that the capillaries were rather wide so as to make possible the measurement of liquids of relatively low fluidities and, for the convenience of the manufacturer, was

provided with rather long bulbs for containing the liquid and with capillaries having ends which were somewhat trumpet-shaped. The length of the bulbs led us to examine critically the customary assumption[1] that the average pressure under which the measurement is made is one-half of the sum of the initial and the final pressures; and the presence of the trumpet-shaped openings of the capillaries seemed to demand an investigation of the kinetic energy correction which is derived on the assumption that the capillaries have square ends.[2]   Finally, while vertical capillaries have frequently been used where relative viscosities have been determined it was thought best to make some measurements to confirm the belief that the position of the capillaries is of no importance.

As the first of the possible sources of error just named is one that can readily be investigated mathematically and which, if found to be of importance, can easily be eliminated, it will be discussed first.

While it is ordinarily assumed that the average pressure to be substituted in the viscosity formula is to be regarded as one-half the sum of the pressures at the beginning and conclusion of the viscosity measurement, a moment's reflection will make it clear to the reader that this cannot be strictly true. Thus suppose the external manometer pressure to be constant and equal to p_0 and that the hydrostatic head at the beginning is $h\rho$ and at the end $-h\rho$. Accepting the customary procedure, the average pressure would be p_0 but, as we shall see, it must strictly be less than p_0. It is evident that when $p_0 \leq h\rho$ the flow cannot complete itself and the average pressure is not p_0 but zero. To find out to what extent the customary method of estimating the average pressure may be a source of error in viscosity measurements, a viscometer was made with a horizontal capillary having uniform bore and square ends, but the bulbs were considerably longer than those used in the ordinary form of the apparatus. The wide part of the bulbs had an estimated length of about 5.5 cm. while the constricted portions added a further 3 cm. to the distance between the marks used in estimating the volume. Measurements were made with pressures differing as widely as possible. The values given in the third column of Table I show that the product Cpt first falls slowly and then increases rapidly as the pressure becomes quite small. The viscosity, as calculated by means of Equation 1 and given in Column 5, is

---

[1] Cf. Brillouin, *Lecons sur la viscosité*, p. 118, *et seq.* Since this work was completed, the papers of Meissner (*Chem. Rev. Fett- u. Harz-Ind.*, **17**, 202 (1910)) and Simeon (*Phil. Mag.*, **27**, 95 (1914)) have come to the attention of the authors, in which they develope an approximate expression for the true average pressure. Neither has applied the correction except to the simplest case nor tested out the expression experimentally with fluids of varying viscosities and specific gravities. In ordinary viscometry it is important to obtain a method for making a suitable correction when the bulbs of the instrument are not simple cylinders as assumed by them.

[2] See Applebey, *J. Chem. Soc. (London)*, **103**, 2169 (1913).

nearly constant while the pressure is large but increases rapidly as the pressure becomes small. It is apparent therefore that the difference between the assumed average pressure and the true average pressure may be the cause of the discrepancy. Our next step will therefore be to discover a method for calculating the true average pressure in order to learn how far that change will serve to correct the discrepancy.

TABLE I.—WATER AT 25° IN VISCOMETER HAVING SINGLE CAPILLARY OF UNIFORM BORE, BUT WITH BULBS APPROXIMATELY 6.0 CM. LONG.

The lack of constancy in the fifth column shows that the viscosity as ordinarily calculated (Equation 1) may be seriously in error at low pressures, but this danger may be avoided by making the proper correction (Equation 6), as shown by the constancy in the sixth column.

Press. g. per sq. cm.	Ave. t in sec.	$Cpt \times 10^8$.	$C'p/t$.	η (Eq. 1).	η (Eq. 6). $h_1 = 6.0$.
243.68	48.5	9167	236	0.00893	0.00896
201.62	58.3	9117	196	0.00892	0.00894
130.22	89.9	9080	128	0.00895	0.00897
64.57	180.1	9020	64	0.00896	0.00896
43.84	265.4	9024	44	0.00898	0.00895
26.34	446.1	9114	25	0.00909	0.00896
18.97	629.1	9256	19	0.00924	0.00895

Av., 0.008955

To Find the Average Pressure during the Time of Flow.—Let two vertical cylinders, Fig. 1, having the same radius r_1 be connected by means of a capillary tube of length l and radius r. A liquid whose density is ρ_1, not corrected to *in vacuo*, stands originally at the level a in one cylinder and at d in the other. After the time t_0 has elapsed, the liquid level falls a distance h_1 from a to c in one cylinder and rises correspondingly in the other from d to f. In deriving the well-known viscosity formula

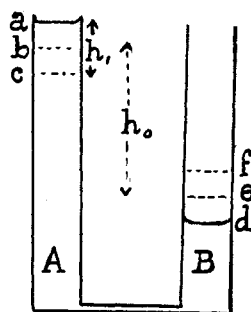$$\eta = \frac{\pi g r^4 p t}{8vl} - \frac{mn\rho_1 v}{8\pi t l}, \qquad (2)$$

it is assumed that the pressure is constant during the time of flow. Obviously this is not the case under ordinary conditions of measurement, but as a result of experiments by Poiseuille,[1] it is generally assumed that a pressure p_0 may be employed in the formula which is equal to the pressure of a column of liquid from the level b, midway between a and c, to the corresponding level e. If this height is h_0 the applied pressure would be $h_0 \rho_1$.

But it may be noted in passing that this assumed constant applied pressure may quite as well be applied either wholly or in part outside of the viscometer. It is almost wholly external in the viscometers of Brück-

Fig. 1.

[1] *Mem. présent. par divers savants à l'académie Roy. des Scienc de l'Inst. de France*, 9, 433 (1846); cf. Brillouin, *Loc. cit.*

ner, Thorpe and Rodger, Übbelohde and others. It is entirely internal in the viscometers of Ostwald, Engler, and others. In any case the assumed constant applied pressure is

$$p_o = h_o\rho_1 + h_o'\left\{\rho_0 - \rho_0'\left(1 + \frac{h_o'}{2066}\right) + \frac{h_o''\rho_0'}{1033}\right\} \qquad (3)$$

where h_o' is the head of liquid of density ρ_0 outside of the viscometer, and h_o'' is the head of air under pressure between the mean level of the liquid in the viscometer and the mean level of liquid in the manometer,[1] it being positive in value when the viscometer is below the middle of the manometer and negative when it is above, while ρ_0' is the density of the air outside of the viscometer and the normal atmospheric pressure is taken as 1033 g. per sq. cm.

We observed in Table I that the discrepancy which we are investigating occurs only when the applied pressure is small. Under these circumstances, the loss of pressure due to the kinetic energy is small, and since the correction which we desire to obtain is but a small part of the total pressure, the kinetic energy correction may be disregarded altogether in obtaining this correction. If we let x represent the distance which the liquid level has fallen after any time t, the pressure at that moment will be $p_o + h_1\rho_1 - 2 x \rho_1$.[2] Equation 2 may be written

$$\pi r_1^2 dx = \frac{k}{\eta}(p_o + h_1\rho_1 - 2 x \rho_1)dt, \qquad (4)$$

where

$$k = \frac{\pi g r^4}{8l},$$

$$t = \frac{\pi r_1^2 \eta}{2k\rho_1} \ln \frac{p_o + h_1\rho_1}{p_o - h_1\rho_1 - 2 x \rho_1}.$$

The time required for a complete transpiration T is

$$T = \frac{\pi r_1^2 \eta}{2k\rho_1} \ln \frac{p_o + h_1\rho_1}{p_o - h_1\rho_1} \qquad (5)$$

where ln is the natural logarithm.

To get the average pressure P, we must get the mean of the pressures during all of the equal intervals of time during which the pressure may be considered as constant. This value is

$$P = \frac{\int_0^T(p_o + h_1\rho_1 - 2 x \rho_1)dt}{T} = \frac{2h_1\rho_1}{\ln \dfrac{p_o + h_1\rho_1}{p_o - h_1\rho_1}} = \frac{2}{2.303} \cdot \frac{h_1\rho_1}{\log_{10} \dfrac{p_o + h_1\rho_1}{p_o - h_1\rho_1}}. \qquad (6)$$

[1] Bingham, Loc. cit., p. 243.

[2] p_o is the apparent applied pressure as defined in the preceding paragraph.

Substituting the value of T we obtain the viscosity formula of Equation 2,

$$P = \frac{v\eta}{kT} \tag{7}$$

which proves that the average pressure may be substituted into the viscosity formula. As p_0 approaches $h_1\rho_1$, the value of P approaches zero while the value of T approaches infinity. Thus is explained the peculiar increase in the viscosity as the applied pressure is lowered, as already observed in Table I. If, on the other hand, p_0 is large in comparison with $h_1\rho_1$, the average pressure P tends to approach identity with p_0. In practice, the difference becomes less than 0.05%, i. e., negligible for ordinary measurements, as soon as p_0 is thirty times as great as $h_1\rho_1$.

Where the two limbs of the viscometer are no longer cylinders, the case is not so simple. But if we conceive of the instrument as made up of a series of cylinders of varying radii as shown in Fig. 2, we can get a value for the average pressure. Let ab and ef be two narrow cylinders whose height is h_1 and whose radius is r_1, let bc and fg be two wide cylinders whose height is h_2 and whose radius is r_2, and let cd and gl be two narrow cylinders of height h_3 and radius r_3. Let the difference in level between the centers of the wide cylinders be h_0. For the

Fig. 2.

sake of brevity, we assume that the flow is caused by the head of liquid within the instrument solely, and as shown in the figure, i. e., $p_0 = h_0\rho_1$. During the flow through each cylinder the average pressures and the times of flow are:
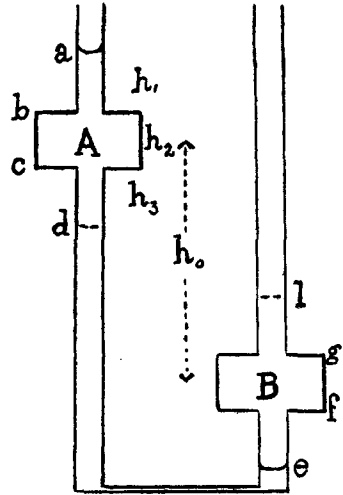
$$P_1 = \frac{2h_1\rho_1}{\ln \dfrac{h_0 + 2h_1 + h_2}{h_0 + h_2}}, \qquad T_1 = \frac{\eta\pi r_1^2}{2k\rho_1} \ln \frac{h_0 + 2h_1 + h_2}{h_0 + h_2},$$

$$P_2 = \frac{2h_2\rho_1}{\ln \dfrac{h_0 + h_2}{h_0 - h_2}}, \qquad T_2 = \frac{\eta\pi r_2^2}{2k\rho_1} \ln \frac{h_0 + h_2}{h_0 - h_2},$$

$$P_3 = \frac{2h_3\rho_1}{\ln \dfrac{h_0 - h_2}{h_0 - h_2 - 2h_3}}, \qquad T_3 = \frac{\eta\pi r_3^2}{2k\rho_1} \ln \frac{h_0 - h_2}{h_0 - h_2 - 2h_3}.$$

Since by Equation 7

$$P = \frac{\eta \pi (r_1^2 h_1 + r_2^2 h_2 + r_3^2 h_3)}{k(T_1 + T_2 + T_3)}$$

we have

$$P = \frac{2\rho_1(r_1^2 h_1 + r_2^2 h_2 + r_3^2 h_3)}{r_1^2 \ln \dfrac{h_0 + 2h_1 + h_2}{h_0 + h_2} + r_2^2 \ln \dfrac{h_0 + h_2}{h_0 - h_2} + r_3^2 \ln \dfrac{h_0 - h_2}{h_0 - h_2 - 2h_3}}. \qquad (8)$$

The average pressure becomes zero when $h_2 + 2h_3$ becomes equal to h_0, and Equation 8 approaches identity with Equation 6 as the values of h_1 and h_3 or r_1 and r_3 becomes very small. Since Equation 8 contains the product of h times the square of r, the effect of the narrow cylinders will be especially small if both their heights and their radii are made as small as possible. Our theoretical investigation proves therefore that the bulbs of the viscometer should be as short as convenient but with a large radius. The constricted portions should be both narrow and short. These objects may be best achieved without sacrificing good drainage by having each bulb shaped like two filtering funnels placed with their wide ends together.

Finally, since the pressure $h_1\rho_1$ has no effect upon the calculated value of the viscosity unless its value amounts to one-thirtieth of p_0, it follows that the height h_1 does not need to be known with precision. For practical purposes it seems unnecessary to use Equation 8 and the value to be used for h_1 in Equation 6 may be found by trial in the calibration of the instrument. Of course it is still more desirable to so construct the viscometer that P may be taken as equal to p_0.

Since, as will appear, a modified Ostwald viscometer has been employed for a part of this investigation, a word may be added as to how the correction just discussed affects that instrument, in which the effective pressure is small. Let η_1 be the viscosity of the substance taken as the standard for the calibration of the instrument. Then from Equation 1,

$$\eta_1 = C p_1 t_1 - C' \rho_1 / t_1.$$

In getting the true average pressure, p_1, we use Equation 6 and we find that p_0, cp. Equation 3, becomes simply $h_0\rho_1$, so that the average pressure is

$$p_1 = \frac{2}{2.303} \frac{h_0 \rho_1}{\log_{10} \dfrac{h_0 \rho_1 + h_1 \rho_1}{h_0 \rho_1 - h_1 \rho_1}} = K\rho_1$$

where K is a constant. Similarly, for any liquid whose viscosity, η, is unknown, the average pressure p would be $K\rho$, if ρ is its density. Hence the viscosity of any substance may be written

$$\eta = \frac{CtK\rho - c'\rho/t}{C t_1 K\rho_1 - c'\rho_1/t_1} \eta_1.$$

If the terms $C'\rho/t$ and $C'\rho_1/t_1$ are equal to zero, or if by accident their ratio is equal to the ratio of the other two terms, the equation becomes simply the Ostwald formula

$$\eta = \frac{\rho t}{\rho_1 t_1}\,\eta_1.$$

Any failure of the Ostwald formula is therefore due to not taking into account the loss in kinetic energy and not to any failure to recognize the true value of the average pressure.

In order to test our data, given in Table I, we have calculated the average pressures according to Equation 6 taking h_1 as equal to 6.0 cm. The values of the viscosity are given in the sixth column of the table. The divergences from the mean are less than the experimental error.

While the above test appears to be conclusive, it was noted that ρ_1 has but one value in Table I, therefore it seemed worth while to test liquids having various specific gravities, using the viscometer mentioned at the beginning of this paper as giving abnormal values. Since the two capillaries were rather large and the bulbs were very long, the instrument was well-suited for the purpose, except for the fact that the ends of the capillaries were somewhat trumpet-shaped. In this instrument the time of flow from left to right was the same as the flow from right to left within the experimental error, so that no calculation of the average resultant head was necessary. The equations were tested by measurements on the time of flow of water, 10 and 20% sugar solutions at 25° and of water, 10% sugar solution and formic acid at 18°. A temperature constancy of 0.007° was obtained by placing the instrument in an electrically regulated thermostat.

TABLE II.—WATER AT 18°.

Using water and other liquids with varying known viscosities and specific gravities, it is shown in this table and those following that reliable values of the viscosity can be calculated by means of Equations 1 and 6, since the values of C_A do not vary more than the known experimental error.

$\eta = 0.01059.$ $\rho = 0.9986.$

1. p_0 g. per sq. cm.	2. T_1 sec.	3. T_2 sec.	4. $C_B \times 10^6$.	5. $C_S \times 10^6$.	6. $C_A \times 10^6$.
30.54	282.1	282.4	1.234	1.295	1.279
34.45	248.3	248.6	1.244	1.292	1.279
38.50	221.1	221.4	1.250	1.288	1.277
44.29	191.5	191.5	1.257	1.285	1.278
48.34	175.3	175.1	1.260	1.283	1.277
54.18	156.3	156.4	1.262	1.280	1.276
58.30	144.9	144.9	1.266	1.283	1.277
64.14	131.5	131.5	1.269	1.283	1.278

Av., 1.277

$h = 11.2$ cm., $h_1 = 9.78$ cm.

The data for water at 18° are given in Table II. For calculating the value of the constant C, Equations 6 and 1, the viscosity was determined

by means of a quartz viscometer of the type described by Washburn and Williams,[1] and was found to be 0.010585 based on the value of 0.008956 for the viscosity of water at 25°. This value is in good relative agreement with the results of Thorpe and Rodger. For C', we used the value 0.01408, obtained as described by Bingham[2] from rough measurements of the apparatus. The fully corrected pressures are given in the first column of the table and the corresponding times of flow from right to left in the second column, the times in the reverse direction in Col. 3, the values of C^3 according to Equation 1 using the pressure p_0 instead of the true average pressure in the fourth column. The times in each case are the averages of from five to ten readings. The values of C_B are not constant, but rise continuously from the value 1.234×10^{-6} to 1.269×10^{-6}, a change of almost 3% as the pressure rises. Consequently we proceed at once to the calculation of the constant, using in the formula the true average pressure as obtained by means of Equation 6. By measurement the length of each bulb was found to be 11.2 cm. but as already pointed out, this may not be the correct value to use. As a matter of fact, the values in Col. 5, labeled C_S, are calculated using this value for h_1, and they fall from 1.295×10^{-6} to 1.283×10^{-6} as the pressure rises. This shows that 11.2 cm. is too large, as the change in the value of the constants is in the opposite direction from what it was before the correction of the pressure was taken into consideration. In the last column of the table are found the values of the constant calculated with 9.78 cm. as the value of h_1. The values do not vary by more than about 0.2%, which is within the range of the experimental error. The permissibility of using an arbitrary value for h_1 will become clear when it is shown that in all of the cases investigated, far better agreement is obtained with the arbitrary value than with the measured value.

In Tables III, IV, V, VI, and VII are given the data for water at 25°, for 10% sugar solution at 18° and 25° for 20% sugar solution at 25° and for formic acid at 18°. In each table the first column records the corrected pressure p_0, the second column the average time of a large number of readings in both directions, the third column the values of C_B calculated without the use of Equation 6 for obtaining the true average pressure, the fourth column the values of C_S calculated with the use of Equation 6 taking 11.2 cm. for h_1 and the last column the values of C_A taking $h_1 = 9.78$ cm. The values for the viscosity and the density used in the calculations are given at the head of each table. In each case, the viscosity was determined by the Washburn instrument and the density by means of a density flask.

[1] THIS JOURNAL, 35, 739 (1913).
[2] Loc. cit.
[3] For convenience we have called this C_B.

TABLE III.—WATER AT 25°.

t_0 in g. per sq. cm.	$\eta = 0.008956.$ Ave. T in sec.	$C_B \times 10^6$.	$\rho = 0.9971.$ $C_S \times 10^6$. $h_1 = 11.2$ cm.	$C_A \times 10^6$ $h_1 = 9.78$ cm.
34.71	208.6	1.248	1.291	1.280
44.55	161.2	1.259	1.287	1.279
48.50	147.8	1.262	1.284	1.279
54.47	131.5	1.265	1.282	1.280
				Av., 1.279

TABLE IV.—10% SUGAR SOLUTION AT 18°.

	$\eta = 0.01432.$		$\rho = 1.0408.$	
34.62	335.3	1.237	1.286	1.275
38.53	299.3	1.246	1.286	1.276
46.40	247.4	1.252	1.279	1.274
54.33	210.4	1.259	1.278	1.275
58.25	196.1	1.260	1.276	1.275
64.19	177.5	1.264	1.278	1.275
70.25	162.4	1.264	1.275	1.274
				Av., 1.275

TABLE V.—10% SUGAR SOLUTION AT 25°.

	$\eta = 0.01198.$		$\rho = 1.0377.$	
26.77	369.3	1.216	1.302	1.279
30.70	318.6	1.229	1.289	1.280
34.61	280.7	1.238	1.287	1.276
38.57	250.7	1.246	1.284	1.276
44.41	216.6	1.255	1.281	1.276
54.31	176.5	1.258	1.285	1.275
64.20	149.0	1.255	1.276	1.276
				Av., 1.277

TABLE VI.—20% SUGAR SOLUTION AT 25°.

	$\eta = 0.01731.$		$\rho = 1.080.$	
44.66	310.4	1.252	1.285	1.276
54.57	252.5	1.260	1.282	1.275
64.45	213.3	1.264	1.280	1.277
74.52	184.0	1.268	1.280	1.275
84.40	162.4	1.270	1.279	1.276
92.32	148.2	1.272	1.280	1.277
				Av., 1.276

TABLE VII.—FORMIC ACID AT 18°.

	$\eta = 0.01868.$		$\rho = 1.2224.$	
38.49	395.0	1.231	1.287	1.274
42.47	357.0	1.235	1.281	1.271
50.34	299.2	1.244	1.276	1.269
54.21	276.7	1.249	1.276	1.271
64.18	232.9	1.255	1.272	1.270
74.15	201.0	1.265	1.280	1.271
78.14	190.6	1.260	1.273	1.271
84.12	176.7	1.264	1.273	1.273
				Av., 1.272

The sugar solutions were made up to about the desired concentration from a Kahlbaum preparation. They were boiled to prevent the formation of moulds and were filtered until no particles were visible by transmitted light. Thus they probably are not exactly 10 or 20% solutions, nor are we absolutely certain of the purity of the sugar, but since all necessary data were determined with the solutions as used, the exact concentration is not essential. The formic acid was prepared by the method of Schlesinger and Martin[1] and was of good quality as shown by its low conductivity. The relative viscosity of the acid agrees exactly with that found by Thorpe and Rodger.

It will be seen that in no case are the values of C_B constant when calculated in the accustomed manner. On the other hand, the values of C_A obtained for water at 18° and 25° and for the sugar solutions, calculating the true average pressure, agree with one another to within 0.2%. The value obtained for formic acid at 18° is a little low—it differs from the average of the others by about 0.4%. The above data show conclusively that the so-called "applied pressure" cannot be safely used for the true "average pressure" when the change of level of the liquid within the instrument is fairly large compared with the applied pressure. How great an error the use of the latter in these calculations might have introduced is shown by the fact that had we standardized our instrument with water at 25° at a pressure of 54.47 g. per sq. cm. without regard for the correction expressed in Equation 6, the viscosity of the 10% sugar solution at 18°, calculated in the same way would have appeared to be 0.01467 instead of the correct value 0.01432. This involves an error of 2.4% in the viscosity, whereas by the use of the true average pressure in both cases the viscosity of the sugar solution is reproduced to within less than 0.25%, which is about the range of the experimental error.

Finally a short discussion of the slightly discordant value obtained for C_A when this is calculated from the data obtained with formic acid is necessary. The value obtained for this constant from the data for the acid is 1.272 while the average for the other liquids used is 1.2768. This divergency of about 0.37%, while small when compared with the error introduced by the use of the applied pressure instead of the true average pressure, is nevertheless larger than the experimental error should be. A number of possible explanations can be suggested to explain the divergency and in the following the most likely are discussed and tested:

1. The second term in Equation 2 was neglected in the derivation of the value of the true average pressure, but on account of the small relative value of this term this course seems justified.

2. The capillaries in our instrument had trumpet-shaped openings and therefore the kinetic energy correction which we employed in the calcula-

[1] THIS JOURNAL, 36, 1589 (1914).

tions may not have been correct. There are two reasons however for believing that the deviation in question is not due to an error of this sort. In the first place an error in the formula for the kinetic energy correction should have affected the constancy of C_A in the case of each of the liquids as the pressure is varied. But the tables show that no such variation can be observed even in the data for formic acid. In the second place, as will appear below, the correction when the openings of the capillary are trumpet-shaped seems to be smaller than the one we used. As the total correction amounts in maximum to only about 0.5% of the viscosity it seems quite impossible that this can be the source of the error in question.

3. The two capillaries of the instrument are vertically placed. Table IX shows that this is of no importance.

4. The most likely explanation of the difficulty is that the value which we used for the viscosity of the acid is incorrect (relatively). The relative viscosity of the acid was determined by means of a Washburn instrument and was calculated without the use of any kinetic energy correction. Based on the value 0.008956 for the viscosity of water at 25°, that of the acid at 18° was calculated to be 0.01868. This value is identical with that obtained by Thorpe and Rodger as the result of their most painstaking work. But the value which these investigators find for water is not the same as the one we use. They did not actually measure water at 25° but a value can be interpolated for this temperature either by use of their curve or their interpolation formula. The average of the two values thus obtained is 0.00892. The relative viscosity of the acid is therefore 2.094. Based on the value 0.008956 for water at 25°, which we have used as a standard, and assuming that the relative viscosity of Thorpe and Rodger is correct, the viscosity of the acid at 18° would become 0.01875. Had we used this value for the calculations of C_A, we would have obtained the value 1.276, which is in perfect agreement with the values obtained from the other liquids. While this calculation seems definitely to clear up the source of the error, we have nevertheless thought it best to investigate further the second and third points mentioned above because of the striking agreement of the relative value which we obtained with the absolute value of the viscosity of the acid as found by Thorpe and Rodger.

We may add a few remarks in regard to the older determinations of viscosity, to which the main corrections here discussed might apply. Concerning the most important work of Thorpe and Rodger, it is impossible to state whether the length of the bulbs in their instrument was small enough to render the correction for the average pressure negligible, but since they used rather large pressures, and since, according to the diagram of their instrument the distance between the marks seems fairly

small, it is very likely that their results are correct. Furthermore they used very nearly the same pressure for almost all of their measurements and the relative values would therefore in most cases be correct. Only for the very fluid substances is there reason to have doubts, because there lower pressures were employed. The results of Hosking for sugar solutions may not be so reliable, although we cannot reach a definite conclusion as his paper also fails to give the necessary data. Nevertheless Hosking's results on sugar solutions do not in the least agree with ours. We realize, to be sure, that we did not take special precautions either concerning the purity of the sugar or in regard to obtaining definitely known concentrations, but Hosking's data differ from ours more than should be caused by the points mentioned. Mr. C. Coleman, who made some measurements on sugar solutions of exactly correct concentrations, made up from an entirely different sample of sugar, obtained data in agreement with ours. It seems advisable to make a more detailed study of the older viscosity data than can be attempted here.

As has been pointed out above, one of the possible sources of error in the data with the viscometer used for the measurements on various liquids might have been due to the fact that the capillaries had trumpet-shaped ends and that therefore the kinetic energy correction may not have been correctly represented by the term $\dfrac{mn\rho V}{8\pi tL}$. This question was experimentally investigated by making a viscometer in sections so that different capillaries in different positions could be used. The different sections were joined by means of short rubber tubing and, when necessary, by glass tubing also. The bulbs were short to eliminate the pressure correction above discussed, being about 1.5 cm. in length and having a capacity of approximately 3.95 cc. In order to secure good drainage, each bulb was made to approximate the shape of two cones placed base to base. The capillary used to investigate the question of the influence of trumpet-shaped ends was made by blowing a series of bulbs in an ordinary capillary tube. In this way the flow is interrupted and any loss of kinetic energy greatly increased over what it is in the ordinary form of the viscometer. The results of measurements with this capillary are shown in Table VIII.

TABLE VIII—THE EFFECT OF TRUMPET-SHAPED ENDS UPON THE KINETIC ENERGY CORRECTION. WATER AT 25°.

The lack of constancy in the values in the sixth column proves that a kinetic energy correction is necessary.

Press. corr.	Time.	$Cpt \times 10^{6}$.	$C'\rho/t \times 10^{6}$.	η (Eq. 1).	η (Eq. 9).
25.14	660.7	9389	319	0.009070	0.008963
33.22	499.4	9378	423	0.008955	0.008952
54.78	303.4	9395	697	0.008698	0.008968
69.37	240.9	9446	876	0.008570	0.009017
130.54	132.9	9807	1592	0.008215	0.009361

The first column contains the pressures in grams per square centimeter after making the necessary corrections. The second column gives the times of flow in seconds. In the third and fourth columns are given the values of the different terms in the equation

$$\eta = Cpt - C'\rho/t. \qquad (1)^1$$

Were the kinetic energy correction zero when the ends of the capillary are trumpet-shaped, this equation would become simply

$$\eta = Cpt. \qquad (9)$$

We have made many measurements similar to those given above with other interrupted capillaries. In every case, the viscosity calculated by means of Equation 9[2] (Col. 6) seems to drop slightly at first and then rise quickly as the pressure increases. We have here used small pressures only, making the conditions advantageous for the use of Equation 9. In spite of this fact, these experiments prove that the kinetic energy correction is not negligible except over a small fraction of the range of pressures here employed. It is especially to be noted however that the viscosity as calculated by means of Equation 1 (Col. 5) is also not constant, as it should be if Equation 1 holds. We have not yet definitely determined the cause of this discrepancy. It might have resulted from the unequal diameters of the capillaries, or from having the bulbs too small to produce the theoretical dissipation of the kinetic energy. Or there remains the possibility that with the trumpet-shaped openings, the kinetic energy correction never attains its full value.

It will be seen, therefore, that our data on this point are as yet not complete. They indicate, however, that the kinetic energy correction is not entirely negligible when capillaries with trumpet-shaped ends are used, as has been suggested by Applebey,[3] but that it may be smaller than when square ends are employed. In judging the deviations from the formulae, it must be born in mind that the experiments on this point were made in an apparatus which enormously exaggerated the value of the kinetic energy correction. It varies from 3.3 to 16.3% of the value of the term Cpt in Equation 1, while in most of the other experiments described herein and in viscometers as actually employed for viscosity determinations the correction seldom reaches 0.5% of the term Cpt. Consequently, even if the kinetic energy correction used in the first experiments on water, sugar, and formic acid had been too large, this error could have had but a small influence on the values of constants obtained. This conclusion, as has been stated, is borne out by the fact that for each liquid the constant was the same over a large range of pressures.

---

[1] *J. Ind. Eng. Chem.*, **6**, 242 (1914).

[2] The constant in Equation 9 is of course not identical in value with the constant C in Equation 1, but is calculated independently.

[3] *Loc. cit.*

Finally the effect of the position of the capillary was investigated. The instrument used for the experiments just described was employed. But in place of the capillary with the series of bulbs, we used one of uniform bore and square ends. Its length was approximately 12.75 cm. By means of the rubber tubing it could be placed either in a horizontal or in a vertical position at will. The data of Table IX are in each case the averages of several determinations with flow in alternate directions through the instrument. They show that it is immaterial whether the capillary is horizontal or inclined. They show further that where a properly constructed instrument is employed, the constants of the apparatus do not vary with the pressure and that Equation 1 can be satisfactorily used.

TABLE X.—CONSTANT OF VISCOMETER, WITH CAPILLARY HAVING SQUARE ENDS.

Press. corr.	Time.	$C \times 10^{10}$.	Temp.	Position of capill.
251.34	91.4	4011	$25°$	Horizontal
139.47	161.0	4025	$25°$	Horizontal
87.66	255.2	4025	$25°$	Horizontal
65.99	399.0	4020	$25°$	Horizontal
39.64	564.7	4015	$25°$	Horizontal
96.11	234.0	4018	$25°$	Vertical
75.10	185.8	4022	$50°$	Vertical

We reserve for a later paper a discussion of the correction for capillarity in different types of viscometers.

Conclusions.

1. The average pressure to be used in the calculation of a viscosity measurement is not strictly one-half the sum of the initial and final pressures as ordinarily assumed, and the use of this value may lead to considerable error. The method of calculating the correct value has been developed and tested experimentally.

2. In the flow of a liquid through a capillary tube it is immaterial whether the capillary is in a horizontal or in a vertical position.

3. When a liquid flows out from a capillary with a trumpet-shaped opening there is a definite loss of kinetic energy, but whether this kinetic energy correction is the same as in the well-studied case of a capillary with uniform bore, is not proved.

4. The work herein reported leads to some suggestions toward improvements in the construction of viscometers. The capillaries should have ends which are as nearly square as possible so that the kinetic energy correction may be calculable and the bulbs should be as short as possible. The latter may be accomplished by making each bulb approximate the shape of two cones placed base to base.

5. Finally in the opinion of the authors the value of using an instrument for relative as well as for absolute determinations of viscosity in

which the time of flow of any given liquid may be varied by varying the pressure has again been demonstrated by the discovery of the errors discussed.

WASHINGTON, D. C., AND CHICAGO, ILL.

THE SEPARATION OF THE RARE EARTHS GIVING THE MORE SOLUBLE DOUBLE SULFATES FROM BRAZILIAN MONAZITE SAND.

BY C. JAMES AND A. J. GRANT.

The raw material for this work was supplied by the Welsbach Light Co. of Gloucester City, N. J., through the kindness of Dr. H. S. Miner, to whom the authors offer their most sincere thanks. It was prepared by treating the rare earth sulfates with potassium sulfate in a smaller quantity than that required for complete precipitation of the cerium metals. Under these conditions the greater part of the samarium and gadolinium, present, should remain in solution. The solution was then precipitated by oxalic acid.

The oxalates were converted into oxides by ignition. The conversion of oxalates to oxides is very troublesome when working on the large scale. The furnace used for this purpose was made by supporting a large $^3/_4$ inch steel plate in fire-brick. Coke was used as a source of heat.

The oxides were found to contain considerable quantities of lanthanum, cerium, praseodymium and neodymium in addition to samarium, gadolinium and the yttrium earths. Since the oxides dissolved in nitric acid with violence, the cerium content could not be very large.

The fractionation of the double magnesium nitrates is the best method for roughly splitting up such a mixture. The oxides were therefore dissolved in concentrated nitric acid, any ceric nitrate being reduced to the cerous condition by the addition of some of the original oxalates. The warm and somewhat diluted liquid was then filtered through large cloth filters, supported in such a way as to allow the liquid to run into a long trough which drained into a large earthenware receiver. Owing to the presence of so much of the yttrium earths, a quantity rather less than the theoretical amount of nitric acid was neutralized by powdered ignited magnesite. The solution of magnesium nitrate was diluted, and filtered in a similar manner to the rare earth nitrates. The solutions were mixed and evaporated until about half the solid crystallized out on cooling. The crystals were twice recrystallized and then placed aside, while the mother liquor was fractionated until the spectrum of samarium or erbium became intense. When the above condition had been reached the mother liquor was largely diluted and precipitated by means of oxalic acid. The oxalates were filtered off, dried and ignited to oxides. These last opera-