303. *The Calibration of Ostwald Viscometers.*

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The object of this note is to describe a convenient method of testing and calibrating an Ostwald viscometer : the disadvantages of previous methods are pointed out.

The time of flow (t) of a definite volume of liquid of viscosity (η) and density (d) through a capillary viscometer can be represented (see, *e.g.*, Barr, " Viscometry," Oxford, 1931, p. 20) by the formula

$$\eta/d = a(h_i + h_e)t - b/t,$$

where a and b are constants characteristic of the instrument, and h_i and h_e are respectively the mean heads of liquid in the viscometer and in a manometer, containing the same liquid that is in the viscometer, which measures an external pressure used to force the liquid through the capillary. Under normal working conditions, no external pressure is used with an Ostwald viscometer (*i.e.*, $h_e = 0$). The second term on the right of the equation is the kinetic, or inertia, correction.

The usual procedure (see, *e.g.*, Applebey, J., 1910, **97**, 2000) is to construct the instrument so that the kinetic correction is negligible, and to prove this by establishing that the product $(h_i + h_e)t$ is independent of h_e, as it should be if the above equation is valid and if b is negligible. The disadvantage of this method is that it involves the measurement of h_i. The method of Grüneisen (*Wiss. Abh. P.T.R.*, 1905, **4**, 151), used by Applebey and by Merton (J., 1910, **97**, 2454), is arduous and hardly affords the necessary accuracy. Washburn and Williams (*J. Amer. Chem. Soc.*, 1913, **35**, 737) stopped the flow of liquid half-way through a run and measured the difference in level of the surfaces in the two limbs with a cathetometer. The quantity measured, however, is not the mean head, though probably not very different from it. For the simplified case of a viscometer, the " bulbs " of which are tubes of uniform bore, it can easily be shown that the quantity measured by Washburn and Williams is $\sqrt{h_1 h_2}$, whereas h_i is $(h_1 - h_2)/\log_e(h_1/h_2)$ (Koch, see Barr, *op. cit.*, p. 74), where h_1 and h_2 are the initial and the final difference in level. In addition, the influence of surface tension was not considered, and refraction by the curved surfaces of the bulbs may cause appreciable error in observing the levels in the two limbs.

Another view is that the kinetic correction can only be made negligible by reducing the rate of flow to such an extent that trouble arises through the tendency of dust particles to choke the capillary at low velocities (Bingham, " Fluidity and Plasticity," 1922, p. 76).

The instrument is therefore designed so that the kinetic correction will be small, and the constant b is calculated from the dimensions of the apparatus by the equation $b = mQ/8\pi L$, where m is a constant—the coefficient of the kinetic energy term—Q is the volume of the bulb, and L the length of the capillary. This procedure assumes that the kinetic correction is applicable to the Ostwald viscometer, a fact which is open to doubt (see Hatschek, "The Viscosity of Liquids," 1928, pp. 22, 28). In addition, the correct value of m is still uncertain, two most used values, 1·00 and 1·12, differing by more than 10%, and the exact length of the capillary of an Ostwald viscometer cannot be determined since it tapers at the ends.

The method now advocated is to find the times of flow for a number of external pressures, as in testing for the constancy of $(h_i + h_e)t$, and to calculate from these the quantity h', defined by the equation $h' = h_e t/(t_0 - t)$, where t_0 is the value of t when $h_e = 0$. On plotting h' against $1/t$, a graph is obtained from which the characteristics of the instrument can be calculated as shown in the following example.

Details of a series of determinations are given in the table. The apparatus was similar in principle to that of Applebey, but modified to give higher external pressures. The capillary of the viscometer used was 10·9 cm. long (approx.) and of radius 0·0245 cm. (calc.), and the volume of the bulb was 7·99 ml. The liquid used was water, and the temperature 25°. On plotting the calculated values of h' against $1/t$, it is found that the points lie, within the limits of experimental error, on a straight line given by the formula $h' = 11{\cdot}49 + 35{\cdot}9/t$ (in cm.). The values given in col. 4 of the table have been obtained from this formula. Now, from the fundamental equation, it follows that $h' = h_i + b/at_0t$. Comparison of these two formulæ shows that $h_i = 11{\cdot}49$ cm. and that $b/at_0 = 35{\cdot}9$ cm./sec. To calculate b from this, the product at_0 can be found with sufficient accuracy from the fundamental equation by assuming that $b = 0$, putting $h_e = 0$, and substituting the known values of η, d, t_0, and h_i. The product ah_i is then found by substituting the known values of η, d, t_0, and b in the equation. The formula for the viscometer was thus found to be

$$\eta/d = 0{\cdot}00001838\, t - 0{\cdot}0278/t.$$

Calculation of b from the dimensions of the apparatus, as described above, putting $m = 1$, gave the value 0·0292. The kinetic correction term amounts to about 0·6% of the total when water is used in the viscometer, and an error of 16% in determining b will not cause an error of more than 0·1% in the viscosity of a liquid provided that t_0 for this liquid be greater than t_0 (water)$/\sqrt{2}$, or 350 secs.

The method has been tested in other series in which (*a*) the working volume of liquid was altered, thereby altering h_i and t_0; (*b*) lower pressures were used, which increases the experimental uncertainty and gives rather erratic results; and (*c*) another viscometer was used.

		h', cm., calc. from				h', cm., calc. from	
h_e, cm.	t, secs.	h_e and t.	linear formula.	h_e, cm.	t, secs.	h_e and t.	linear formula.
—	∞	—	11·49	47·94	97·8	11·91	11·86
0	491·4	—	11·56	54·22	88·5	11·91	11·90
17·02	200·0	11·68	11·67	61·72	79·7	11·95	11·94
20·57	178·0	11·69	11·69	72·70	69·7	12·02	12·00
23·77	162·2	11·71	11·71	81·61	63·2	12·05	12·06
25·10	156·4	11·72	11·72	82·96	62·3	12·05	12·06
34·76	124·3	11·77	11·78	90·41	58·1	12·12	12·11
44·85	102·7	11·85	11·84	92·00	57·0	12·08	12·12
46·42	99·9	11·85	11·85	96·06	55·1	12·13	12·14

There is essentially a greater chance of experimental error in the preliminary examination of a viscometer, either by testing the constancy of $(h_i + h_e)t$ or by the method advocated here, than there is in using it for comparing viscosities, because a second physical measurement—that of a mean external pressure—is involved. There is probably a larger error in estimating this pressure than there is in measuring the time of flow. If a viscometer is tested over a narrow range of velocities, such as is likely to be used in practice, it is easy to overlook a kinetic correction that may not be negligible in use. To compensate for the

lower standard of accuracy attainable, it is essential to test a viscometer over a wider range of velocities than will be used in practice.

In the above treatment, h_i has been regarded as a constant, which is not strictly true (Koch, *loc. cit.*). Neglect of this factor can hardly cause appreciable error, since, for all ordinary Ostwald viscometers, the increase of h_i with h_e is very small.

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