

PHYSICAL CHEMISTRY

ON THE CALCULATION OF THE MEAN EFFECTIVE PRESSURE
HEAD FOR CAPILLARY VISCOMETERS

BY

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SUMMARY

When capillary viscometers are used for measurements at different rates of shear, accurate evaluation of the mean effective pressure head is required for calculation of the rate of shear. At high pressure heads an arithmetic mean value of the heads at the beginning and end of the experiment may be used, but for low pressure heads this procedure is incorrect. The situation is examined theoretically and formulae are obtained which enable the mean effective pressure head to be calculated from viscometer dimensions and measurements of the pressure head at the beginning and end of flow from the index bulb. The main case examined is for flow from a spherical bulb into a cylinder.

In measurements of liquid viscosity using capillary viscometers of the Ostwald type, the pressure head forcing the liquid through the capillary is usually taken as the excess gas pressure (if any) applied to the measuring bulb plus the pressure head of liquid in the viscometer. During an experiment, as liquid falls in one side of the viscometer and rises in the other, the pressure head is varying and for any calculations involving this a mean value must be taken. For the measurement of viscosity by comparison with a standard liquid in the viscometer it is unnecessary to know the hydrostatic head since it is the same in both cases. However, when capillary viscometers are used for measurements of viscosity at different rates of shear, the average rate of shear, $D \text{ sec}^{-1}$, can be defined by the expression:

$$(1) \quad D = \frac{\bar{H} \rho g r}{3l\eta}$$

where \bar{H} is the mean effective hydrostatic head, ρ and η are the density and viscosity of the liquid respectively, g is the gravitational constant and r and l are the radius and length of the capillary. Thus the computation, or measurement, of the mean effective pressure head \bar{H} becomes an essential feature of such experiments.

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Many authors have assumed that the mean effective pressure head can be taken as the arithmetic mean of the two extreme pressure heads, that is the pressure at the beginning and end of liquid efflux from the index bulb. It was pointed out, as early as 1881, by KOCH [1], that this assumption is, under many conditions, incorrect, the error only being negligible when the total applied head is large. Following KOCH several other authors [2-7], have also deduced formulae for the calculation of the mean effective pressure head.

In some recent work on the electroviscous effect in concentrated sols of silver iodide [8], a modified Ostwald viscometer of the type devised by FOX, FOX and FLORY [9] was employed for measurements at rates of shear over the range 200-2000 sec^{-1} ; this is illustrated in Fig. 1. In

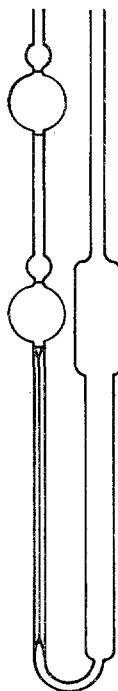


Fig. 1. Ostwald viscometer based on the design of FOX, FOX and FLORY [9].

the calibration procedure it was found that at low rates of shear, when the calibration constants were plotted against the arithmetic mean of the pressure heads the points diverged from the linear plot for pressure heads of less than 10 cm of water. Thus under these conditions it was no longer permissible to use the arithmetic mean value. Moreover, it is difficult to measure the mean effective pressure head of a viscometer experimentally, since this depends upon factors such as the length of time spent by the liquid in the lower half of the bulb in relation to that spent in the top half, although the two extreme heads can be measured accurately. Thus it is evident that the most easily accessible method is to use these measurements to compute the mean effective pressure head from a formula derived for the type of viscometer employed. The necessary

equations for this calculation, for the flow of liquid from a sphere to a cylinder, however, do not appear to have been published. The situation was therefore examined theoretically, and during this examination it became clear that a general solution could be derived, in terms of viscometer constants, which was applicable to most types of capillary viscometer. The solutions for several types of viscometer have been worked out, and in one case, flow of liquid from a sphere to a cylinder, they have been tested experimentally.

DERIVATION OF AN EXPRESSION FOR THE GENERAL CASE

To derive the general expression we will consider the case where the volumes are symmetrical about mean planes on the efflux and influx sides (Fig. 2a), namely the planes X and Y . Then if h is the arithmetic

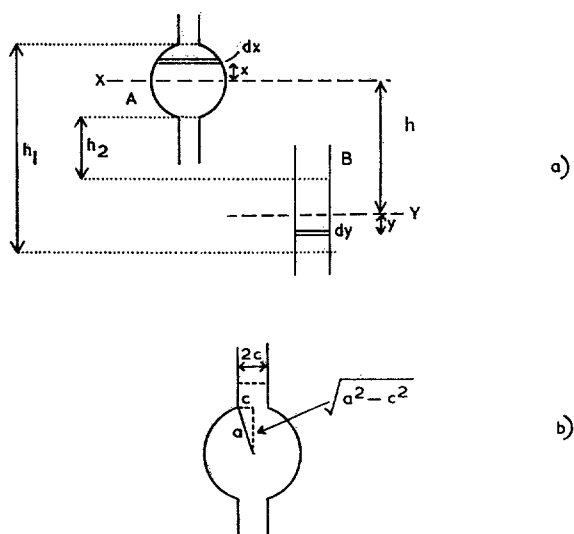


Fig. 2. a) Flow from a spherical bulb to a cylinder;
b) Correction for the volume of the neck.

mean of the pressure heads, i.e. the distance between the planes of symmetry X and Y , $\frac{h_1 + h_2}{2}$, and at an instant of time t the liquid is at a distance x above the mean line X and is at a point where the cross sectional area is A (shape of vessel not defined), then on the influx side the liquid will be at a distance y below the mean line, where the cross sectional area is B . The volumes about the mean lines are equal and hence we may write:

$$\int_0^x A dx = \int_0^y B dy.$$

When the liquid is at a point x above the plane X in the top bulb the pressure head is

$$h + x \div y.$$

Therefore, the rate of flow = $k(h+x+y)$ where k is a constant, neglecting for the moment any corrections for kinetic energy effects and for resistance in other parts of the apparatus. We shall also restrict the arguments to the pressure head of the viscometer remembering that the pressure applied P , will be $(h+x+y)g$. Then if in an interval of time dt , the distance above the mean plane X changes from $x+dx$ to x and the cross sectional area is equal to A , the rate of flow is:

$$-A \frac{dx}{dt}$$

whence

$$-A \frac{dx}{dt} = k(h+x+y).$$

If x changes from d to $-d$ in time t ,

$$(2) \quad - \int_{-d}^d \frac{A}{h+x+y} dx = \int_0^t k dt = kt.$$

Therefore, for a mean effective pressure head \bar{H} , equation (2) can be written

$$- \int_{-d}^d \frac{A}{\bar{H}} dx = kt,$$

giving

$$(3) \quad \frac{\bar{H}}{h} = \frac{\int_{-d}^d A dx}{\int_{-d}^d \frac{A}{1 + \frac{x+y}{h}} dx}$$

Equation (3) is a general relation, which is true even without symmetry, but for the symmetrical case we may write:

$$(4) \quad \frac{\bar{H}}{h} = \frac{\int_0^d A dx}{\int_0^d \frac{A}{1 - \left(\frac{x+y}{h}\right)^2} dx}$$

whence,

$$(5) \quad \bar{H} = \frac{h}{1 + \frac{1}{h^2} \frac{\int_0^d A(x+y)^2 dx}{\int_0^d A dx} + \frac{1}{h^4} \frac{\int_0^d A(x+y)^4 dx}{\int_0^d A dx} + \dots}$$

Thus

$$\bar{H} = \frac{\text{Arithmetic mean of the extreme pressure heads}}{\text{Correction factor}};$$

this is for symmetrical cases a general expression, and it is only necessary to solve the integral

$$(5a) \quad \frac{1}{h^{2n}} \frac{\int_0^d A(x+y)^{2n} dx}{\int_0^d A dx}$$

for the conditions involved, and to determine to what limit n has to be taken.

DERIVATION OF EXPRESSIONS FOR PARTICULAR CASES

Case 1. *Flow from a Cylinder to a Cylinder*

If the cross-sectional area of one cylinder is A and the other B we may write

$$Ax = By$$

whence by substitution in equation (3) for y , we find as A and B are constant:

$$\frac{\bar{H}}{h} = \frac{A \int_{-d}^d dx}{A \int_{-d}^d \frac{dx}{1 + \left(\frac{A+B}{h \cdot B}\right) x}} = \frac{2 \left(\frac{A+B}{B}\right) \frac{d}{h}}{\ln \frac{1 + \left(\frac{A+B}{B}\right) \frac{d}{h}}{1 - \left(\frac{A+B}{B}\right) \frac{d}{h}}}$$

Thus if h_1 and h_2 are the initial and final heads,

$$h_1 = h \left(1 + \frac{A+B}{B} \cdot \frac{d}{h} \right),$$

$$h_2 = h \left(1 - \frac{A+B}{B} \cdot \frac{d}{h} \right),$$

$$h_1 - h_2 = 2 \left(\frac{A+B}{B} \right) d$$

and

$$(6) \quad \bar{H} = \frac{h_1 - h_2}{\ln \frac{h_1}{h_2}}.$$

This is MEISSNER's formula [2], and we note that this equation also applies for discharge from an open cylindrical cup into air; this is also very close to the situation in an Ubbelohde viscometer [7].

Using the general formula, equation (5), we have

$$\int_0^d A dx = Ad$$

and since

$$x + y = \frac{A+B}{B} x$$

the correction factor, considering only the first two terms, is:

$$1 + \frac{1}{dh^2} \left(\frac{A+B}{B}\right)^2 \int_0^d x^2 dx + \frac{1}{dh^4} \left(\frac{A+B}{B}\right)^4 \int_0^d x^4 dx + \dots$$

whence integrating, we have

$$1 + \left(\frac{A+B}{B}\right)^2 \frac{d^2}{3h^2} + \left(\frac{A+B}{B}\right)^4 \frac{d^4}{5h^4} + \dots$$

Thus if the diameters of the cylinders are $2a$ and $2b$, $A = \pi a^2$ and $B = \pi b^2$, giving:

$$(7) \quad \bar{H} = \frac{h}{1 + \left(\frac{a^2+b^2}{b^2}\right)^2 \frac{d^2}{3h^2} + \left(\frac{a^2+b^2}{b^2}\right)^4 \frac{d^4}{5h^4} + \dots}$$

This equation gives the mean effective pressure head in terms of the radii of the cylinders and should lead to the same answer as equation (6). For the case of two cylinders the latter equation is more convenient but as we shall see later, for bulb viscometers simple expressions of this type do not appear and the general solution becomes the more convenient.

Case 2. *Flow from a Sphere to a Cylinder*

This is the case to be considered for an Ostwald viscometer of the type devised by FOX, FOX and FLORY [9]. In the first instance we shall consider the case when the bulb is a perfect sphere, and then extend this treatment to the more practical case; that is, the situation when the liquid initially starts in a cylindrical neck, flows through the spherical bulb and then passes into another cylindrical tube.

2a) *Flow from a Perfect Sphere to a Cylinder*

If the diameter of the sphere is $2a$, and the diameter of the cylinder is $2b$, then following the previous nomenclature with $d=a$ (this means that the index mark coincides with the surface of the sphere) we may write

$$A = \pi(a^2 - x^2) \quad \text{and} \quad B = \pi b^2,$$

whence

$$\pi b^2 y = \pi \int_0^x (a^2 - x^2) dx = \pi \left(a^2 x - \frac{x^3}{3} \right)$$

and

$$(8) \quad x + y = \left(\frac{a^2 + b^2}{b^2} \right) x - \frac{x^3}{3b^2}.$$

Then if we again consider the correction terms given by expression (5A), the coefficient of $1/h^{2n}$ is:

$$\frac{\int_0^a A (x+y)^{2n} dx}{\int_0^a A dx} = \frac{\int_0^a (a^2 - x^2) \left[\frac{a^2 + b^2}{b^2} x - \frac{x^3}{3b^2} \right]^{2n} dx}{\int_0^a (a^2 - x^2) dx}.$$

Substituting $x=au$ and $S = \frac{3(a^2+b^2)}{a^2}$, then the coefficient reads:

$$\frac{\int_0^1 (1-u^2) \left(\frac{a^3}{3b^2} (Su-u^3) \right)^{2n} du}{\int_0^1 (1-u^2) du}.$$

Since

$$\int_0^1 (1-u^2) du = \frac{2}{3}$$

we have

$$\frac{3 a^{6n}}{3^{2n} b^{4n} 2} \int_0^1 (u^{2n} - u^{2n+2}) (S - u^2)^{2n} du,$$

whence on expansion of $(S-u^2)^{2n}$ followed by integration we obtain the general term

$$\frac{3 a^{6n}}{3^{2n} b^{4n}} \left[\frac{S^{2n}}{(2n+1)(2n+3)} - \frac{{}^{2n}C_1 S^{2n-1}}{(2n+3)(2n+5)} + \frac{{}^{2n}C_2 S^{2n-2}}{(2n+5)(2n+7)} \cdots \frac{1}{(6n+1)(6n+3)} \right],$$

where ${}^{2n}C_1$, ${}^{2n}C_2$, etc. are the binomial coefficients. Thus the mean effective head is given by,

$$(9) \quad \bar{H} = \frac{h}{1 + \frac{a^6}{3b^4 h^2} \left[\frac{S^3}{15} - \frac{2S}{35} + \frac{1}{63} \right] + \frac{a^{12}}{27b^8 h^4} \left[\frac{S^4}{35} - \frac{4S^3}{63} + \frac{6S^2}{99} - \frac{4S}{143} + \frac{1}{195} \right] - \dots}$$

For a typical viscometer the capacity of the bulbs was approximately 5 ml and the measured radii of the bulbs and the cylinder were found to be 0.9 and 0.7 cm respectively, giving $S=4.814$. From these values \bar{H} has been calculated for various values of h using equation (9); the results are recorded in Table 1.

TABLE 1
Comparison between \bar{H} and h for Flow from a Sphere to a cylinder

h cm	\bar{H} cm		
	h	h	h
	$1 + 0.9484/h^2$	$1 + 0.9484/h^2 + 2.056/h^4$	$1 + 1.139/h^2$
30	29.97	29.97	29.97
20	19.96	19.96	19.95
10	9.92	9.90	9.89
7.5	7.38	7.38	7.35
5	4.82	4.80	4.78
3	2.71	2.66	2.66
2	1.62	1.46	1.57

It is evident from Table 1 that for pressure heads greater than 10 cm the correction is insignificant, but below this it is advisable to apply a correction. Between h values of 10 and 3 cm only the coefficient of $1/h^2$

needs to be considered but below this the coefficient of $1/h^4$ must also be included. The values of these corrections suggested that it might be possible to approximate equation (9) even further, for most of the range, and simply write,

$$(9a) \quad \bar{H} = \frac{h}{1 + \frac{a^6 S^2}{45 b^4 h^2}} = \frac{h}{1 + a^2 \left(\frac{a^2 + b^2}{b^2} \right)^2 \frac{1}{5 h^2}}$$

Calculations of \bar{H} using this equation are given in the last column of Table 1; it is apparent that we may use this equation down to an h value of 3 cm without introducing an appreciable error in \bar{H} .

For a viscometer of the Fox, Fox, and FLORY type [9] the kinematical viscosity is given by

$$v = \alpha t - \frac{\beta}{t}$$

where

$$\alpha = \frac{\pi r^4 g \bar{H}}{8 Q (1 + nr)},$$

r is the radius of the capillary, nr is the end correction and Q is the volume of liquid discharged per second; β is a kinetic energy correction term. Thus α as determined experimentally should be directly proportional to the mean effective pressure head \bar{H} . In Fig. 3 a graph is given of α values plotted against \bar{H} and h . With \bar{H} as abscissa a good linear plot results passing through the origin, whilst using h the curve becomes non-linear at values of h less than 10 cm.

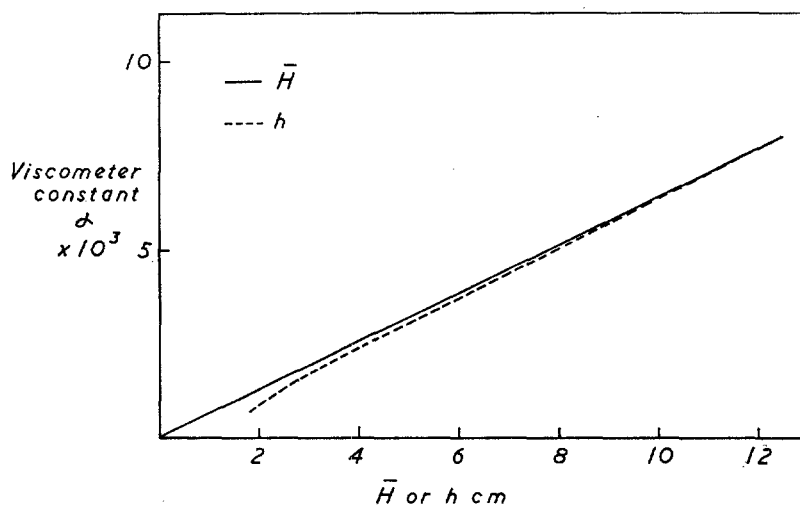


Fig. 3. Viscometer Constant α vs. Pressure head cm; ——— calculated values of mean effective pressure head \bar{H} , ---- arithmetic mean head h .

2b). Flow from a Sphere with Necks to a Cylinder

Since in viscometry we are usually dealing with a spherical bulb joined to a cylindrical tube at top and bottom, upon which the index marks are

engraved, this situation corresponds to the more practical case. Thus if the diameter of the spherical bulb is $2a$, the diameter of the associated cylinders with the index marks is $2c$ (see Fig. 2b) and the diameter of the inflow cylinder is $2b$, we have:

equations as for case 2a existing from $x=0$ to $\sqrt{a^2-c^2}$ and equations as for case 1 existing from $x=\sqrt{a^2-c^2}$ to d , where d is the distance of the index mark above the centre of the sphere, whence

$$(10) \quad \int_0^d A \, dx = \pi \int_0^{\sqrt{a^2-c^2}} (a^2-x^2) \, dx + \pi \int_{\sqrt{a^2-c^2}}^d c^2 \, dx = \pi [c^2 d + \frac{2}{3} (a^2-c^2)^{3/2}]$$

From the calculations in the previous section it appears that the $1/h^2$ term in the correction factor is the most important and hence we have to evaluate the integral

$$\int_0^d A(x+y)^2 dx = \pi \int_0^{\sqrt{a^2-c^2}} (a^2-x^2) \left(\frac{a^2+b^2}{b^2} x - \frac{x^3}{3b^2} \right)^2 dx + \pi \int_{\sqrt{a^2-c^2}}^d c^2 \left(\frac{a^2+b^2}{b^2} x \right)^2 dx.$$

Thus putting

$$u = \frac{x}{a} \text{ and } S = 3 \left(\frac{a^2+b^2}{a^2} \right)$$

the solution is,

$$\frac{\pi a^9}{3^2 b^4} \left[\frac{S^2 u^3}{3} - \frac{2Su^5}{5} + \frac{u^7}{7} - \frac{u^5 S^2}{5} + \frac{2Su^7}{7} - \frac{u^9}{9} \right]_{u=0}^{u=\sqrt{1-c^2/a^2}} + \frac{\pi c^2}{3} \left(\frac{a^2+b^2}{b^2} \right)^2 [d^3 - (a^2-c^2)^{3/2}].$$

If, as in the previous case, we retain for a first approximation only, the S^2 terms, this becomes,

$$\pi \left(\frac{a^2+b^2}{b^2} \right) \left[\frac{c^2 d^3}{3} + \frac{2}{15} (a^2-c^2)^{3/2} \right]$$

and we find,

$$(11) \quad \bar{H} = \frac{h}{1 + \frac{1}{5h^2} \left(\frac{a^2+b^2}{b^2} \right) \frac{5c^2 d^3 + 2(a^2-c^2)^{3/2}}{3c^2 d + 2(a^2-c^2)^{3/2}}}$$

which when $c=0$ and $d=a$ becomes equal to equation (9A).

For the viscometer employed, with a and b as before, c was found to be 0.28 cm and $d=1.25$ cm and calculations of \bar{H} using equation (11) yielded the values given in Table 2.

Comparison with Table 1 shows that under the conditions employed in this viscometer, i.e. with the index mark on the neck close to the bulb, then for all practical purposes, down to $h=5$ cm, we can neglect the

volume of the neck, and no serious error is introduced if we use the approximate equation (9A).

TABLE 2

Values of \bar{H} after correction for the volume of liquid contained in the neck of the bulb

h cm	$\bar{H} = \frac{h}{1 + 1.5332/h^2}$
30	29.95
20	19.94
10	9.85
7.5	7.30
5	4.71
3	2.56
2	1.45

APPENDIX

An alternative approach to the solution of case 2a can be made by evaluating \bar{H} in terms of the rise in level of the liquid in the cylinder. From Fig. 2a, we obtain that the unit of volume in the sphere dV is given by

$$dV = -\pi(a^2 - x^2) dx = \pi b^2 dy.$$

On integration between a and x , the rise in the cylinder is

$$(12) \quad y = \frac{(x-a)^2(x+2a)}{3b^2}.$$

Note that y is counted upwards from the initial level and thus differs from the y shown in fig. 2a.

Then if f is the height between X and the initial level in the cylinder and H is the pressure head at time t ,

$$H = f + x - y$$

and

$$\frac{dV}{dt} = k(f + x - y)$$

giving on substitution for y from equation (12),

$$(13) \quad \frac{dV}{dt} = \frac{k}{3b^2} [(3b^2f - 2a^3) + 3(a^2 + b^2)x - x^3].$$

Further, we can write

$$h = f - \frac{y_{\max}}{2}, \text{ and since } y_{\max} = \frac{4a^3}{3b^2}$$

when

$$x = -a, \quad f = h + \frac{2a^3}{3b^2}.$$

Thus by substitution for f in equation (13) and remembering

$$dV = -(a^2 - x^2)\pi dx,$$

$$\frac{dx}{dt} = \frac{-k}{3b^2\pi(a^2 - x^2)} (3b^2h + 3(a^2 + b^2)x - x^3)$$

whence the total time for flow from $x = a$ to $x = -a$ is

$$T = \frac{b^2\pi}{k} \int_{-a}^a \frac{3(a^2 - x^2)}{(3b^2h + 3(a^2 + b^2)x - x^3)} dx.$$

If the effective pressure head H is assumed to be the mean effective pressure head \bar{H}

$$\frac{dV}{dt} = k\bar{H}$$

and

$$V = \int_0^T k\bar{H} dt = k\bar{H}T = \frac{4}{3}\pi a^3$$

giving

$$\bar{H} = \frac{4a^3/3b^2}{\int_{-a}^a \frac{3(a^2 - x^2)}{3b^2h + 3(a^2 + b^2)x - x^3} dx}$$

or

$$(14) \quad \bar{H} = \frac{\text{Total rise in cylinder in cm}}{\int_{-a}^a \frac{3(a^2 - x^2)}{3b^2h + 3(a^2 + b^2)x - x^3} dx}.$$

Integration of equation (14) leads to the expression,

$$(15) \quad \bar{H} = \frac{\text{Total rise in cylinder in cm}}{\left[(1+2z) \ln(\alpha - x) + (1-z) \ln(x^2 + \alpha x + \beta) - \frac{6\alpha z}{\sqrt{4\beta - \alpha^2}} \tan^{-1} \frac{2x + \alpha}{\sqrt{4\beta - \alpha^2}} \right]_{-a}^a},$$

where

$$z = \frac{b^2}{2(\alpha^2 - a^2 - b)^2}.$$

This follows since the real root, α , of the cubic expression in the denominator of the integral is given by

$$= \alpha \left(\frac{3b^2h}{2} + \sqrt{\left(\frac{3b^2h}{2}\right)^2 - (a^2 + b^2)^3} \right)^{\frac{1}{3}} + \left(\frac{3b^2h}{2} - \sqrt{\left(\frac{3b^2h}{2}\right)^2 - (a^2 + b^2)^3} \right)^{\frac{1}{3}}$$

and for the conditions used,

$$\frac{3b^2h}{2} > (a^2 + b^2)^{\frac{3}{2}},$$

the expression has only one real root, and we may write the cubic as $(\alpha - x)(x^2 + \alpha x + \beta)$ with

$$\beta = \frac{3b^2h}{\alpha}.$$

Thus from equation (15) \bar{H} can be calculated from the rise of liquid in the cylinder, which occurs as the liquid flows from one index mark on the bulb to the other. The rise can be measured accurately using a cathetometer and for the viscometer employed was found to be 1.98 cm. Using the values of a and b previously given the values of \bar{H} were calculated for various values of h ; these are recorded in Table 3. It may be noted that equation (15) gives complete values for \bar{H} and thus enables a direct check to be made of the errors involved in using curtailed series in equations (9) and (9A).

TABLE 3
Values of \bar{H} calculated from equation (15)

h cm	\bar{H} cm
30	29.96
10	9.92
5	4.81
3	2.68
2	1.35

Comparison of these values with those given in Table 1 shows that they are in excellent agreement with those given by equation (9), even down to $h=2$ cm. At values of h greater than 3 cm the more approximate equation (9A) gives equally good results, and since this is much easier to use for computation it can be used in practice without loss of accuracy.

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