The values in the third column are in each case those experimentally determined. Where the data of other observers have been employed, the most satisfactory value has been given in the table; the others have been given consideration in the construction of the initial diagram and the isotherms. The values given in this table are plotted in Fig. 1. They are not entirely concordant but sufficiently so to justify the construction of this type of figure. Owing to the limited number of measurements, the data above 100° cannot be considered as accurate as those at temperatures below the boiling point.

Summary

1. An apparatus has been developed with which equilibrium measurements in systems composed of two salts and water may be made at temperatures above the boiling point of the solution.
2. The literature relating to the system magnesium sulfate–sodium sulfate–water has been reviewed and presented along with new data obtained at temperatures between 67 and 210°.
3. The invariant point, löweite-hexahydrate-astrakanite-solution, has been found dilatometrically to lie close to 59.5°; and the invariant point, löweite-kieserite-vanthoffite-solution, to lie between 180 and 210°.
4. It has been shown that the disagreement in the previous data on this system between temperatures of 60 and 100° was probably caused by the extreme slowness with which the stable double salts come to equilibrium with their solutions.
5. The indentification of the salts occuring in this system by optical means has been discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RUTGERS UNIVERSITY]

THE VALUE OF THE HAGENBACH FACTOR IN THE DETERMINATION OF VISCOSITY BY THE EFFLUX METHOD

BY WILLIAM RIEMAN III

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Historical Introduction

For a more complete outline of the history of viscosity and in particular the value of the Hagenbach factor "*m*" in the kinetic energy correction, the reader is referred to Bingham's "Fluidity and Plasticity."[1] It is necessary to emphasize here only the following points. Numerous investigators have attacked the problem from the theoretical point of view, and have derived results identical in all respects except that the value of the constant *m* differs. None of the authors (prior to Bienias and Sauer-

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[1] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, **1922**, pp. 1–21.

wald) have obtained experimental data to support their conclusions. Knibbs'[2] work in this field is unique. He devised an excellent mathematical treatment whereby m can be derived from experimental data, but instead of performing the necessary measurements himself he used Poiseuille's[3] data. The average value for m for 14 tubes is 1.135, with a mean deviation of ± 0.153. Because of the large probable error this result cannot be regarded as an indisputable confirmation of Bousinesq's[4] theoretical value of 1.12.

For years the science of viscosimetry has been handicapped by lack of definite knowledge concerning this constant. Some scientists use Bousinesq's value, others prefer Couette's[5] value of 1.00. As Bingham suggests, the best method of avoiding serious error is to select a viscometer of such dimensions that the kinetic energy correction is only 1 or 2% of the entire viscosity. Then a small error in the constant will cause only an insignificant error in the final result. Recently N. E. Dorsey[6] has studied the configurations produced by a stream of colored liquid flowing from a circular capillary with smooth, square edges directly into the clear water contained in a reservoir. "All the distances from the terminus to the walls of the reservoir are severally so great that the distribution of the flow of the liquid is essentially the same as if they were infinite." His own observations and the data of W. N. Bond[7] led him to draw the following conclusions. The value of m is zero and the value of the Couette correction, λ, is 1.146 R when Reynolds' number[8] is less than 10. When Reynolds' number is greater than 10, two situations are possible; in one m is still zero and λ is 1.146 R; in the other m is a constant, probably 1, and λ is 0.573 R. When Reynolds' number exceeds 700, m decreases and approaches the value of 0.735. These values apply only to the ideal conditions; variations in the shape of the capillary or its ends or in the shape of the reservoirs may cause variation in the value of m and λ.

Dorsey also calculated the value of m from Poiseuille's data and found a value of 1.04. This is at wide variance with Knibbs' result. The author's calculations of Poiseuille's data agree with those of Knibbs.

The problem of the Hagenbach factor has been attacked recently from a new angle by Bienias and Sauerwald.[9] These authors are primarily

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[2] Knibbs, *J. Proc. Roy. Soc. N. S. Wales*, **29**, 77 (1895).

[3] Poiseuille, *Mém. prés. par divers savants à l'acad. Roy. des Sci. de l'inst. de France*, **9**, 433 (1846).

[4] Bousinesq, *Compt. rend.*, **113**, 49 (1891).

[5] Couette, *Ann. chim. phys.*, [6] **21**, 433 (1860).

[6] Dorsey, *Phys. Rev.*, [2] **28**, 833 (1926).

[7] Bond, *Proc. Phys. Soc. London*, **33**, 225 (1921); **34**, 139 (1922).

[8] $2\rho IR/\eta$, where I is the average velocity of the liquid in the capillary. See *Trans. Roy. Soc. London*, **174**, 935 (1883).

[9] Bienias and Sauerwald, *Z. anorg. allgem. Chem.*, **161**, 51 (1927).

interested in the viscosity of molten metals. Their viscometer was designed especially to meet the difficulties peculiar to this type of work and is not capable of as high a degree of accuracy as the instruments of Thorpe and Rodger,[10] or Bingham or other modern investigators. It consists essentially of a vertical capillary whose lower end is immersed in a bath of the metal contained in a carbon crucible. The upper end of the capillary is expanded into a bulb and is connected to a vacuum system and to a manometer. The determinations are made by applying suction and measuring the time required for the liquid to fill the bulb between two electrical contacts.

The dimensions of the apparatus are such that both the kinetic energy correction and the correction for varying hydrostatic head within the instrument must be applied. As Bingham[11] has demonstrated, when the hydrostatic pressure within the viscometer is greater than one-thirtieth of the pressure applied externally, it is not sufficiently accurate to consider the mean of the initial and final internal hydrostatic heads. We must consider the "chronological mean."[12] This value is greater than the mean of the initial and final values. In most viscometers the kinetic energy correction is necessary only at high velocities, whereas the correction for varying internal hydrostatic head is necessary only at low velocities. The necessity, encountered by Bienias and Sauerwald, of applying both corrections to the same measurement is unusual.

The procedure of Bienias and Sauerwald for the determination of m was as follows. Mercury at room temperature was sucked up into the viscometer and the time measured. Since the viscosity of mercury was known, all terms in the equation

$$\eta = \frac{\pi g P R^4 t}{8VL} - \frac{m\rho V}{8\pi L t}$$

were known or could be measured readily except m and P. The term P represents the pressure used to drive the liquid through the capillary. It is the difference between the manometer pressure, P_m, and the chronological mean internal hydrostatic pressure, P_h,

$$P_m - P_h = P$$

By assigning values to m we can calculate the value of P and hence of P_h. Dividing P_h by density, ρ, we get H, the chronological mean hydrostatic head.

The value of the chronological mean head was also determined by direct observation. The level of the mercury in the tube was measured at noted intervals of time. A curve between time and hydrostatic head was plotted and graphically integrated to obtain the chronological mean. This value ought to check the value calculated by the first method, pro-

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[10] Thorpe and Rodger, *Trans. Roy. Soc. London*, **185A**, 397 (1894).

[11] Bingham, THIS JOURNAL, **38**, 27 (1916).

[12] Bienias and Sauerwald call it "mittlere zeitliche Höhe."

vided the proper value of m was used in the calculation. The results of Bienias and Sauerwald are given in Cols. 1, 2, 3 and 4 of Table I.

TABLE I

RESULTS OF BIENIAS AND SAUERWALD

No.	Chron. mean head, cm. $m = 1$	$m = 1.12$	Chron. mean head by direct obs.	Probable error of calcd. value
1*	12.58	12.56	12.58	±0.02
2	12.29	12.24	12.29	± .04
3	12.18	12.10	12.17	± .05
4*	12.62	12.60	12.62	± .02
5*	12.30	12.24	12.28	± .04
6*	12.52	12.50	12.52	± .02
7	12.33	12.26	12.31	± .04
8	12.27	12.16	12.24	± .05
9*	12.81	12.78	12.80	± .02
10*	12.49	12.44	12.48	± .04
11	12.40	12.31	12.30	± .05
12	11.06	10.97	11.04	± .04
13	11.04	10.92	11.02	± .05
14	11.04	10.87	11.03	± .06

From these results Bienias and Sauerwald conclude that the correct value of m is unity.

A consideration of the errors involved in the work, however, reveals that their conclusion is not well established. They state that the probable error of their viscosity determinations is 1%. The same error would be attached to the determination of P by the method described above. Since P_h is obtained by subtracting P from P_m, an error of 1% in P does not necessarily involve the same percentage error in P_h; but the probable error of P_h and H can readily be calculated. The results of these calculations are given in Col. 5, Table I. (The error in measuring the manometer pressure was assumed to be negligible.)

It is now obvious that the six results marked with an asterisk are meaningless, since the observed hydrostatic head (Col. 4) agrees with both calculated values (Cols. 2 and 3) within the limit of error of the latter values. In the majority of the remaining cases the probable error is so large, compared with the other differences, that very little dependence can be placed on the results. In one case (No. 11) the value, $m = 1.12$, gives the better agreement.

From these considerations it is evident that the conclusions of Bienias and Sauerwald concerning the value of m are drawn from meager, inaccurate and, in part, contradictory data. Apparatus designed for use with molten metals is not suitable for an accurate determination of the Hagenbach factor.

Apparatus

The work described herein had as its sole objective an accurate and reliable determination of m under experimental conditions similar to those generally used by modern investigators in the determination of viscosity.

The apparatus, in general design, is so similar to that recommended by Bingham,[13] that a detailed description is not necessary.

The viscometer, however, is somewhat different. Since it is desirable to change the capillary it was not fused into the viscometer but attached in a horizontal position to the two limbs of the instrument with stout rubber tubing. Since no change in working volume of liquid could be detected during use, we can feel certain that no appreciable leak occurred at the joints. In all other respects, such as traps, shape of bulbs, etc., the viscometer resembled Bingham's. It was immersed in a well-stirred water-bath whose temperature was automatically controlled within a few hundredths of a degree.

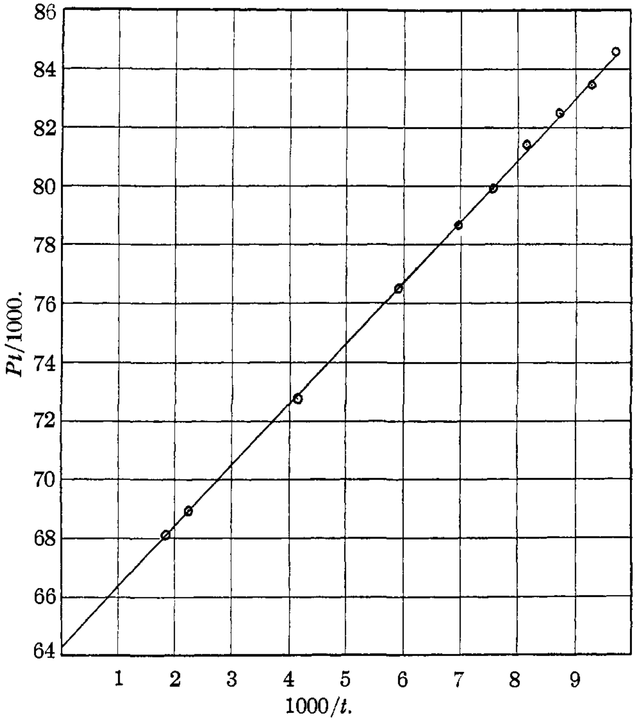

Fig. 1.

The volume of the viscometer and the dimensions of the capillary were selected so that at high pressures the kinetic energy correction, $m\rho V/8\pi Lt$ would be a large fraction, $^1/_7$ to $^1/_4$, of the uncorrected viscosity, $\pi gPR^4t/$-$8VL$. At the same time care was taken to avoid the critical velocity and to avoid the use of apparatus too small to allow accurate measurements.

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[13] Ref. 1, pp. 67 and 295–311.

Procedure

The volume of the bulb of the viscometer was carefully measured. The capillary was selected and the edges were ground perpendicular to the axis. The length was measured with a micrometer caliper. The capillary was then attached between the limbs of the viscometer with heavy rubber tubing. The viscometer was filled with water and the time of efflux measured under a pressure of about 850 g. per sq. cm. This determination was run in duplicate or triplicate. Then the pressure was reduced somewhat, all other conditions remaining the same, and the time again measured. This process was repeated until a series of about ten readings was obtained for which only the pressure and time varied.

These results were then treated mathematically by the method of Knibbs. The equation is put in the form

$$Pt = \frac{8\eta VL}{\pi g R^4} + \frac{m\rho V^2}{\pi^2 g R^4} \cdot \frac{1}{t}$$

The values of Pt are plotted as ordinates and the values of $1/t$ as abscissas. From the above equation it is evident that if m is constant, the curve should be a straight line. Within the very small experimental error it was found to be such.

The intercept on the Y axis represents the value of Pt when the time is infinite, that is, when the kinetic energy is zero. Then

$$Pt = \frac{8\eta VL}{\pi g R^4}$$

Since the viscosity of water is known, we can use this equation to calculate the value of R. This gives a value of much greater precision than can be attained by microscopic measurement or by weighing a mercury slug.

The slope of the line, s, is equal to the coefficient of $1/t$.

$$S = \frac{m\rho V^2}{\pi^2 g R^4}$$

By use of this equation the value of m can be calculated.

Results

As an example of the method of plotting and calculating the value of m, the complete data for Series 6 are given in Table II.

TABLE II

COMPLETE DATA FOR SERIES 6

Detn. no.	P	t	$Pt/1000$	$1000/t$	Reynolds' number
1	826.3	102.35	84.57	9.770	1013
2	773.7	107.9	83.48	9.268	961
3	718.8	114.8	82.51	8.711	903
4[a]	662.2[a]	123.0[a]	81.45[a]	8.130[a]	843[a]
5	605.8	131.9	79.91	7.582	786
6	548.6	143.4	78.67	6.974	723
7	452.0	169.3	76.52	5.907	613
8	301.0	241.8	72.78	4.136	429
9	160.0	431.0	68.97	2.320	240
10	126.2	539.8	68.11	1.852	192

Temp. = 36° η = 0.007085 V = 10.018

L = 1.9278 g = 980.2 ρ = 0.9937

[a] Reject these values. High value for time, probably because of dust caught in capillary.

The results are plotted in Fig. 1.[14] From the figure we can see that the Y intercept is 64.173.

$$64{,}173 = \frac{8 \times 0.007085 \times 10.018 \times 1.9278}{\pi \times 980.2\, R^4}$$

Solving for R we find that $R^4 = 0.55394 \times 10^{-8}$ or

$$R = 0.0086270 \text{ cm.}$$

From the figure the slope is 2.089.

$$2{,}089{,}000 = \frac{m\, 0.9937\, (10.018)^2}{\pi^2\, 980.2 \times 0.55394 \times 10^{-8}}$$

$$m = 1.122$$

A summary of all the results obtained up to the present time is given in Table III.

TABLE III

SUMMARY OF RESULTS

Series no.	Cap.	L	Temp., °C.	$R\mu$	m
1	1	0.8096	25.00	52.463	1.110
2	1	.8096	22.00	52.498	1.127
3	1	.8096	36.10	52.467	1.134
4	1	.8096	25.00	See below	1.128
5	2	1.9278	34.00	86.278	1.124
6	2	1.9278	36.00	86.270	1.122

$V = 10.018$; av. $m = 1.124$; av. deviation = ±0.006.

In Series 4, methanol was used instead of water. A C. P. sample was further purified by fractional distillation and the portion distilling between 64.46 and 64.51° was collected foruse. Its density was 0.79158 at 20° and 0.78695 at 25° Because of uncertainty concerning the viscosity of methanol and also because of the possibility of impurities in the sample used, no attempt was made to calculate R in this determination. Instead, the average of the three previous values was used for the calculation of viscosity. The viscosity was found to be 0.005508 at 25°. Interpolating the results of Thorpe and Rodger to the same temperature, we find a value of 0.005527. Since Thorpe and Rodger took more care in the purification of their sample, their result is probably more nearly correct. It should be noted, however, that Thorpe and Rodger used 1 for the Hagenbach factor. If they had used the value, 1.12, their result would have been 0.005521.

Microscopic Measurements.—Although microscopic measurements of the capillary radius are not sufficiently precise for use in the calculation of m, they must be used to gain knowledge concerning the shape of the capillary. The two ends of the thermometer tubing, which before break-

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[14] In drawing the line which runs through the points with the minimum error, the graphical method cannot be considered sufficiently accurate. The mathematical treatment given on p. 327 of Mellor's "Higher Mathematics for Students of Chemistry and Physics," 4th edition, Longmans, Green and Co., New York, 1913, was used.

ing were in juxtaposition to the portion used in the viscometer, were used to prepare cross-section slides for the microscope. From these slides the major and minor axes of both ends of the capillary were determined by use of a filar micrometer. It was assumed that the cross section was elliptical, a fact which was supported by the appearance of the slide under the microscope. The formula of Knibbs

$$R = \sqrt[4]{\frac{3R_1^3R_2^3}{R_1^2 + R_1R_2 + R_2^2}\cdot\frac{(1 - e^2)^3}{1 + e^2}}$$

was used to calculate the value of R which should be used in the viscosity equation. In this formula, R_1 is the arithmetical mean of the semi-axes at one end, R_2 is the mean of the semi-axes at the other end; e is $(B - C)/(B + C)$, where B is the mean of the major axis and C is the mean of the minor axis. The results are given in Table IV.

Table IV

Results

	Capillary 1	Capillary 2
End A. Major radius, μ	53.78	95.20
End A. Minor radius, μ	50.82	79.45
End B. Major radius, μ	54.20	95.20
End B. Minor radius, μ	50.46	79.35
R by micrometry	52 26	86.60
R by viscometry	52.476	86.274

The slight differences in the values of R obtained by the two different methods are due to errors in the microscopic measurements or to irregularities in the capillary between the two ends.

Discussion of Results

Precision.—In the individual measurements of length, volume, time and pressure, the precision varied from about 0.01 to 0.1%. Since the maximum internal hydrostatic pressure was less than one-thirtieth of the manometer pressure, the correction for varying internal head is less than the experimental error and can be omitted. The value of R^4 as determined by the viscosimetric method is attended by an error probably not greater than 0.1%. The percentage probable error of m is greater than that of R^4 in about the ratio, kinetic energy correction at high pressures to uncorrected viscosity. That is, the percentage probable error of m is 4 to 7 times that of R^4 or about 0.4 to 0.7%. This agrees with the mean deviation of m.

To the length, as actually measured, some investigators add the Couette end correction, nR, where n is a constant. Couette originally assigned to n a value of 6. More recent investigation indicates that the correction is much smaller, perhaps even zero. The correction has not been applied in our calculations because of the uncertainty of the correct value of n

and because it has only an insignificant effect on the calculated value of m. For example, if we use Dorsey's value ($n = 0.573$) in calculating the data of Table II we find $m = 1.125$, or 0.003 greater than the value calculated without the Couette correction.

Conclusions.—Within the range studied the value of m is 1.124 ± 0.006. This agrees with the theoretical value of Bousinesq, 1.12, within the experimental error. The question arises whether this result may be applied to other tubes and other liquids.

The choice of liquids was restricted to those which do not attack rubber. Although only two were used in this investigation, there is no reason to believe that the value of m depends on the nature of the liquid.

The shape of the capillary may affect the value of m. In this investigation an effort was made to secure capillaries which were as nearly as practical right circular cylinders. Therefore, we are not entirely justified in extending the value, $m = 1.12$, to capillaries which deviate from the ideal shape more than the capillaries described here. Let us consider two possible manners of deviation from the right circular cylinder.

In the first place the capillary may be a frustum of a cone, that is, the cross-sectional area may be different in different parts of the tube. In a capillary of uniform cross section the loss of kinetic energy occurs only at the ends. In a conical tube, however, there would also be a loss or gain of kinetic energy inside of the capillary. Consequently, it is possible that the Hagenbach factor may have a different value in conical tubes. The capillaries used in this investigation had almost uniform cross sections.

In the second place, the cross section, although uniform throughout the length of the capillary, may be elliptical rather than circular. Indeed, it is impossible to find thermometer tubing of perfectly circular bore. The capillary cross section of greatest deviation from the circle was end B of capillary 2, with an eccentricity of 0.553.

The shape of the ends of the capillary and the shape and size of the reservoir may also affect the value of m. The exit reservoir of our viscometer differed widely from the ideal conditions described by Dorsey. The liquid leaving our capillary flowed into a trap, provided for the settling of dust particles, then into a bulb, provided to facilitate the adjustment of the working volume, and finally into the larger bulb of measured volume. This difference in reservoirs may account for the difference between our results and Dorsey's.

It should be noted, however, that our viscometer is fundamentally similar to the viscometers used by Thorpe and Rodger and other investigators who are interested in the practical determination of viscosity rather than the theoretical laws of flow under ideal conditions. Therefore, it is very probable that the value, $m = 1.12$, is the correct one to be applied to instruments like those of Thorpe and Rodger and Bingham. Our data do not support Dorsey's view that *m* decreases when Reynolds' number exceeds 700.

Further investigations are being conducted in this Laboratory to determine the value of *m* for capillaries of other shapes.

Summary

1. Within the range of experimental conditions studied, the Hagenbach factor has been found to be 1.124 ± 0.006.

2. The viscosity of methanol at 25° has been determined and a value obtained which agrees with the value of Thorpe and Rodger within 0.3%.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY AND THE METALLURGICAL LABORATORIES OF HARVARD UNIVERSITY]

CHEMICAL AFFINITY IN METALLIC ALLOYS, ESPECIALLY SOLID SOLUTIONS: A STUDY IN COMPRESSIBILITY

BY ROBERT FRANKLIN MEHL[1] AND BEVERIDGE JAMES MAIR[2]

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The study of the properties of solid solutions is one of the chief aims of metallurgical science. Its practical importance is evidenced by the fact that of the alloys useful because of their superior mechanical properties most are wholly or partly solid solutions. Numerous researches[3] have shown that, with one or two exceptions,[4] terminal solid solutions are simple in structure, showing the space lattice of the solvent metal only, the atoms of the solute having simply replaced atoms of the solvent; intermediate solid solutions are more complicated in structure. The behavior, physical and chemical, of the lattice so modified is, therefore, dependent upon the interaction of the different atoms, and this will be intimately related to their different chemical natures, and also to their specific crystallographic tendencies. From a chemical standpoint the chief effect of interest is that of a partial fixing of the valence electrons, an effect to be expected from the normal chemical affinities between the unlike atoms, and indicated by the enormous decrease in electrical conductivity resulting from solid solution formation. From a mechanical point of view the interaction between unlike atoms is presumably intimately related to the large increase in hardness observed.

Such a partial fixing of the valence electrons is of course not stoichio-

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[1] National Research Fellow.

[2] Contributor to the experimental work on compressibility only.

[3] See G. L. Clarke, "Applied X-Rays," McGraw-Hill Book Co., New York, 1926, page 204.

[4] Notably iron-carbon, manganese-carbon and perhaps copper-tin (see page 66).