is an orthoquinone, there is no steric restriction on forming these bonds. In a paraquinone, however, the two bonds can be formed only by putting the planes of the two six-carbon rings flatly one upon the other. This will be easily possible in benzoquinone, but in duroquinone the voluminous side chains prevent a sufficiently close approach. It may be briefly and preliminarily mentioned that the ease with which a solid quinhydrone is formed by mixing a quinone with the corresponding hydroquinone, decreases with the number of CH_3 groups which substitute the H atoms. In the tetramethyl compound, duroquinone, no quinhydrone is formed at all at room temperature.

The authors are deeply indebted to Columbia University for the use of their facilities.

Summary

Duroquinone in a strongly alkaline solution forms a free paramagnetic semiquinone radical of brown color as intermediate step of the reduction. There is no dimeric form of this radical; in other words, no compound corresponding to the ordinary crystalline benzoquinhydrone, which is a dimeric diamagnetic molecule, is formed from duroquinone and durohydroquinone either from alkaline or acid solutions. Solid benzoquinhydrone is a compound formed from quinone and hydroquinone by two hydrogen bonds. These bonds cannot be formed in duroquinone due to steric hindrance.

The maximum percentage of the duro-semiquinone radical in equilibrium with its parent substances continuously increases with increasing *p*H. At *p*H 13 this maximum is about 50%, a result which is the same whether derived from potentiometric or magnetic observations.

NEW YORK, N. Y. RECEIVED MAY 2, 1938

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Influence of Surface Tension on the Measurement of Viscosity
The Viscosity of Methanol

BY GRINNELL JONES AND HOLMES J. FORNWALT

Introduction

In recent years many measurements of viscosity of solutions of salts in water and in methanol have been carried out in this Laboratory by an improved technique.[1] The various sources of experimental error in determining the measurement of the viscosity of dilute solutions have been studied and discussed in an earlier paper. When measurements were extended to concentrated solutions and especially when the viscosity of methanol was compared with that of water it became apparent that the possibility of two additional sources of error which are negligible for relative measurements of dilute solutions should be considered, namely, errors due to unequal drainage and errors due to surface tension. The drainage error has recently been studied by Jones and Stauffer[2] with results which show that this source of error may be disregarded safely in measurements on methanol.

Surface tension can influence the measurement of viscosity by the Ostwald viscometer because the effective hydrostatic head which drives the liquid through the capillary is not solely determined by the dimensions and mounting of the instrument and the volume of liquid contained therein but is influenced by the capillary rise of the liquid in the two arms of the viscometer. Since this capillary rise is a function of the surface tension divided by the density, it will be different for the solutions and for the pure solvent.[3]

In this paper is given a mathematical analysis of the problem that has led to the development of a method of estimating the magnitude of the correction which should be applied to the results obtained with the Ostwald viscometer. This analysis guided the design of another instrument in which the error due to surface tension was minimized as much as other considerations of design permitted. The viscosity of methanol was then measured with reference to water in both the old and new instruments. The results are compared

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[1] Grinnell Jones and co-workers, THIS JOURNAL, **51**, 2950 (1929); **55**, 624, 4124 (1933); **57**, 2041 (1935); **58**, 619, 2558 (1936); **59**, 484 (1937); *Physics*, **4**, 215 (1933).

[2] Grinnell Jones and R. E. Stauffer, THIS JOURNAL, **59**, 1630 (1937).

[3] M. P. Applebey [*J. Chem. Soc.*, **97**, 2013 (1910)] has applied a correction for the effect of surface tension by a method which is a rough approximation.

before and after applying the computed corrections for surface tension.

Experimental

The source of the methanol was the same as that previously described[4] and the treatment similar except that it was more thorough. Lund and Bjerrum's method[5] of dehydration by distillation from magnesium methylate was carried out twice on each batch and in some cases there was an additional treatment with metallic sodium. The methanol was distilled through a good fractionating column 75 cm. long. The maximum range in the boiling point of the portions collected and used was only 0.04°. The four different batches which were used for the viscosity measurements gave the following densities, respectively: d^{25}_4, 0.786527, 0.786523, 0.786527, 0.786525. These results are slightly lower and more consistent than had been obtained with many batches which had been given a single treatment with magnesium methylate. The average density of these earlier batches was 0.786545. A comparison with the best results which have been found in the literature is given in Table I.

TABLE I

DENSITY OF METHANOL AT 25°

	d^{25}_4
E. C. McKelvy and D. H. Simpson, THIS JOURNAL, **44**, 110 (1922)	0.78658
F. K. Ewart and H. R. Raikes, *J. Chem. Soc.*, 1907 (1926)	.78641
H. Lund and J. Bjerrum, *Ber.*, **64B**, 213 (1931)	.78651
J. A. V. Butler, D. W. Thompson and W. H. Maclennan, *J. Chem. Soc.*, 675 (1933)	.78643
R. E. Cornish, R. C. Archibald, E. A. Murphy and H. M. Evans, *Ind. Eng. Chem.*, **26**, 399 (1934)	.78656
Grinnell Jones and H. J. Fornwalt, this paper	.78652$_5$

The freezing point of this methanol was determined by Mr. Edwin E. Roper in this Laboratory by the use of a platinum resistance thermometer to be −97.68 ± 0.02° (see the succeeding paper).

The first viscometer (designated herein as instrument T) was originally built for and used by S. K. Talley. The quartz-blower was instructed to make the surfaces connecting the constrictions and the cylindrical part of the upper bulb as nearly conical with a 60° angle as possible. Except for some necessary rounding at the line of contact with the cylinders above and below, he accomplished this objective approximately. In the calculations given below, the conical form is assumed. The values used for the angles are based on measurements made on the finished instrument. The lower reservoir was a vertical cylinder of much larger radius than the upper bulb. This larger radius was chosen in order to minimize the error due to variations in the working volume.

In the new instrument (designated here as F) there were three changes in design for the purpose of minimizing the surface tension correction: (1) the lower reservoir was made a cylinder of the same radius as the cylindrical part of the upper bulb; (2) the hydrostatic head was increased; (3) the quartz blower was instructed to make the upper dome and lower bowl as nearly hemispherical as he could. It is easier to meet this specification than to make the surfaces conical. The essential dimensions in centimeters which were used in the calculations are given below. The significance of the symbols will be understood by reference to Fig. 1.

TABLE II

DIMENSIONS OF THE VISCOMETERS IN CENTIMETERS

	w	*r*	*R*	*J*	*a*	*b*	*c*	*e*	*f*
T	0.05	0.90	3.58	24.3	23.8	22.3	18.5	17.5	16.5
F	.05	.848	0.848	28.5	27.43	26.59	21.95	21.1	20.7

T: Upper dome, tan $\theta = -0.567$; $\theta = -29°30'$: lower bowl, tan $\psi = +0.85$; $\psi = +49°38'$.

F: Radius of hemisphere, $r = 0.848$.

The first erratic results for the relative viscosity of methanol obtained with the new instrument were traced to the fact that variations in working volume have a greater effect on the hydrostatic head and, therefore, on the time of flow in the new instrument owing to the narrow lower reservoir. It was found by suitable independent experiments that in the old T viscometer a variation of 0.01 ml. in the working volume of methanol will cause an error of 0.007 second in the total time of 417 seconds; in the new F viscometer a variation of 0.01 ml. causes an error of 0.191 second in 682 seconds. The usual practice of delivering the working volume from a special pipet and determining the weight delivered by the loss of weight of the pipet is adequate when using water even with the F viscometer. However, due to the greater volatility of methanol the results with the old technique were erratic. A technique of transferring by distillation in a vacuum was developed. The methanol was placed in a suitable flask provided with a stopcock and a ground joint beyond the stopcock, and weighed. The flask and the viscometer were then connected by means of their ground joints to the same wide tube, which was also connected to a vapor trap and a stopcock leading to a good mechanical vacuum pump. The ground joints were not greased but were made vacuum tight by an external mercury seal. The vapor trap was chilled with a mixture of solid carbon dioxide and ether, and then the entire system was evacuated through the trap without losing any methanol. After a good vacuum had been established the stopcock to the pump was closed, the viscometer chilled by solid carbon dioxide and ether, and the weighing flask and trap warmed gently, thus distilling the methanol completely into the vis-

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[4] Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, **57**, 2041 (1935).

[5] H. Lund and J. Bjerrum, *Ber.*, **64B**, 210 (1931).

cometer. The empty flask was then weighed, which gave the amount of methanol transferred to the viscometer. This method of transfer by distillation in a vacuum gave more consistent results with methanol and was used in all of the experiments recorded in Table III. With water there was no significant difference between the results obtained by the old and new methods of transfer to the viscometer.

TABLE III

VISCOSITY OF METHANOL RELATIVE TO THAT OF WATER AT 25° UNCORRECTED FOR SURFACE TENSION EFFECTS

Batch	d^{25}_4	Relative Viscosity T	F
35	0.786527	0.60554	0.60831
		.60539	
36	.786523	.60571	.60798
		.60567	.60849
37	.786527	.60562	.60877
		.60584	
38	.786525	.60576	.60794
		.60582	
Average	0.786525	0.60567	0.60830
Probable error of mean		± .00004	± .00010
Ratio F/T = 1.0043			

This table shows that the two instruments give results which differ in the ratio of 1.0043. This difference is substantially greater than the "probable error" of the mean for each instrument, which proves that there is a systematic error in the results obtained with one or both instruments.

The next step is to attempt to compute the correction which must be applied for the error due to surface tension in order to determine whether or not it is large enough to account for the systematic difference.

Computation of the Error in Viscosity Measurements with the Ostwald Viscometer Due to Surface Tension.—The effective hydrostatic head in the Ostwald viscometer will be the geometric head minus the capillary rise in the upper bulb plus the capillary rise in the lower bulb. The capillary rise will depend on the liquid used, and will also depend on the shape of the upper and lower bulbs. The effective hydrostatic head will vary continuously during the flow. It will, therefore, be necessary to derive a differential equation for the time of flow and integrate it over the total volume.

Poiseuille's law of flow may be put in the form

$$\mathrm{d}t = \frac{8l\eta \mathrm{d}V}{\pi s^4 g\rho H} = \frac{A\eta \mathrm{d}V}{\rho H} = \frac{B\mathrm{d}V}{H} \qquad (1)$$

where s is the radius and l the length of the capillary, g the acceleration of gravity, η the viscosity, ρ the density, and H the effective hydrostatic head (geometric head minus the capillary rise) and $\mathrm{d}V$ is the differential volume which flows in the time $\mathrm{d}t$; and for the sake of abbreviation we write $A = 8l/\pi s^4 g$; and $B = A\eta/\rho$. A will have a definite numerical value for any given instrument. B will depend both on the instrument and on the viscosity and density of the liquid used, but will be independent of the surface tension. H will depend on the dimensions of the instrument and the ratio of surface tension to density σ/ρ, but will be independent of the viscosity.

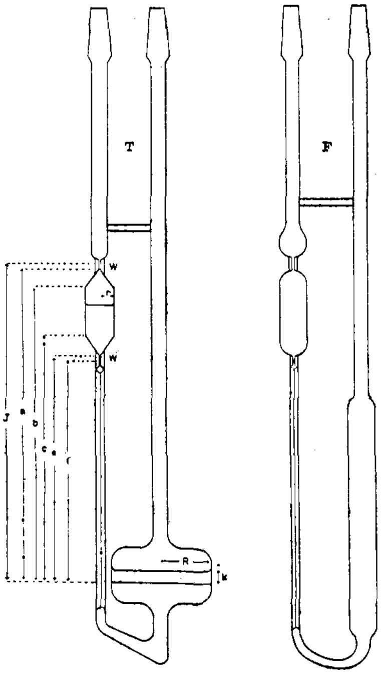

Fig. 1.

The definite integral obtained from Equation (1) should express the time of flow as a function of the instrumental constants which determine A and influence H, and the viscosity, density and surface tension of the fluid. The total time is determined experimentally and the density is also determined independently as a routine part of the viscosity measurements. The surface tension can be measured independently and therefore in mathematical theory may be regarded as a known quantity. However, if it can be shown that with a suitable design of the viscometer the surface tension correction becomes negligible or can be estimated sufficiently well without a precise knowledge of the surface tension, then the precise measurement of viscosity will be greatly simplified.

The absolute measurement of viscosity is an experimental problem of great difficulty. However, for the many theoretical purposes values of the viscosity of solutions relative to that of pure water are sufficient. By making measurements of the total time of flow of water in the same instrument, the instrumental constant A may be eliminated, thus making it unnecessary to measure the length and radius of the capillary.

The definite integral of Equation (1) may be expressed

$$t_c = B_c \int_0^V \frac{\mathrm{d}V}{H_c} = A\,\frac{\eta_c}{\rho_c} \int_0^V \frac{\mathrm{d}V}{H_c}$$

for methanol or for the solution of concentration c, and

$$t_0 = B_0 \int_0^V \frac{\mathrm{d}V}{H_0} = A\,\frac{\eta_0}{\rho_0} \int_0^V \frac{\mathrm{d}V}{H_0}$$

for water. Hence the relative viscosity is given by the expression

$$\frac{\eta_c}{\eta_0} = \frac{t_c\rho_c}{t_0\rho_0}\,\frac{\int_0^V \frac{\mathrm{d}V}{H_0}}{\int_0^V \frac{\mathrm{d}V}{H_c}} \qquad (2)$$

It has been commonly assumed in this and other laboratories that $\int_0^V \frac{\mathrm{d}V}{H_0} = \int_0^V \frac{\mathrm{d}V}{H_c}$, which amounts to the assumption that the effect of surface tension is negligible. The magnitude of the error caused by this assumption will be considered in the succeeding pages.

In order to integrate the equation $\mathrm{d}t = B\mathrm{d}V/H$ it is necessary to know the shape and dimensions of both the upper and lower bulbs. To facilitate this integration it is practically necessary to assume that the geometric form is a comparatively simple one. It is assumed that the working part of the lower reservoir, the upper and lower constrictions where the transits are timed at the beginning and end of the flow, and the central part of the upper bulb are all right circular cylinders having the internal radii R, w and r, respectively, and that the axes of these cylinders are vertical. The upper dome (from a to b) and the lower bowl (from c to e) of the upper bulb may be assumed to be either cones or hemispheres. Although a good quartz blower can make these portions of the instrument approximately hemispherical or conical as desired, the actual geometrical form of the instrument will not correspond exactly to the assumed geometrical form, especially near the lines of contact with the cylindrical parts of the instrument, and, therefore, these assumptions unavoidably introduce some error in the resulting calculations. Moreover, there will be some experimental error in the measurement of the essential dimensions after the instrument has been constructed. The calculations are, therefore, at best only approximations and they are so laborious that they are entirely impractical as a regular part of the routine of viscosity measurements.

In the integration of the fundamental equation $\mathrm{d}t = B\mathrm{d}V/H$ the geometrically distinct parts of the instrument must be treated separately and the definite integrals for the several parts added together.

In the operation of the viscometer a standard working volume of the liquid is added. The liquid is sucked above the mark in the upper constriction and then allowed to fall under the influence of gravity. The timing is started at the instant the meniscus passes the upper mark. The origin from which all vertical or horizontal distances are measured is in the axis of the upper bulb and at the level of the liquid in the lower reservoir when the instrument contains the standard volume and the upper meniscus is at the reference mark on the upper constriction assuming that there is no distortion of the surfaces by surface tension effects. Let J represent the height of the upper mark above this base level. J as thus defined depends solely on the dimensions of the instrument and the standard working volume and is independent of the liquid used.

Now consider a particular instant of time when the meniscus has passed the upper mark and is flowing downward through the upper constriction at a height y above the base level. We may then write

$$\mathrm{d}V = -\pi w^2 \mathrm{d}y \qquad (3)$$

and

$$H = +y - h + j - k \qquad (4)$$

where

$$h = 2\sigma/gw\rho \qquad (5)$$

is the capillary rise in the upper constriction; and

$$j = 2\sigma/gR\rho \qquad (6)$$

is the capillary rise in the lower reservoir; and

$$k = \frac{w^2}{R^2}(J - y) \qquad (7)$$

is the increase in height of the liquid in the lower reservoir, because a volume of liquid equal to that in the constriction between the initial mark and the height y has entered the lower reservoir.

When

$$y = a \qquad k = k_a = \frac{w^2}{R^2}(J - a) \tag{7a}$$

The correction, j, must be applied even if the lower reservoir is so wide that it has a flat portion at its center because the instrument is filled with a standard volume of liquid and the withdrawal of a part of this volume into the meniscus lowers the effective hydrostatic level in the reservoir and thus increases the effective head.

Substituting these values in (1) gives

$$\mathrm{d}t = \frac{B\mathrm{d}V}{H} = \frac{-\pi Bw^2\mathrm{d}y}{y - \frac{2\sigma}{gw\rho} + \frac{2\sigma}{gR\rho} - \frac{w^2}{R^2}(J - y)} \tag{8}$$

Now integrate between the initial limit of $y = J$ and the final limit $y = a$, which gives

$$t_J^a = \frac{B\pi w^2}{1 + w^2/R^2} \ln \frac{J - \frac{2}{g}\left(\frac{1}{w} - \frac{1}{R}\right)\frac{\sigma}{\rho}}{J - \frac{2}{g}\left(\frac{1}{w} - \frac{1}{R}\right)\frac{\sigma}{\rho} - \left(1 + \frac{w^2}{R^2}\right)(J - a)} \tag{9}$$

It is evident from this equation that in order to minimize the effects of variations in σ/ρ, J should be made large, and $(J - a)$ and w small. Since $\frac{2}{g}\left(\frac{1}{w} - \frac{1}{R}\right)\frac{\sigma}{\rho}$ is small in comparison with J and with $J - (1 + w^2/R^2)(J - a)$, the error due to the neglect of the surface tension will be almost a linear function of σ/ρ.

The upper dome of the upper bulb may be constructed so that it may be treated either as a cone or as a hemisphere. We have not found an equation for the capillary rise in a conical tube in the literature. An exact solution of this problem would require an exact knowledge of the shape of the meniscus expressed as an equation for the surface. The problem of finding such an equation has not been fully solved even for cylindrical tubes, much less for conical tubes. However, we have succeeded in deriving an approximate equation for the capillary rise in conical tubes which is sufficiently good for the present purpose by a method which is similar to that commonly used to derive the equation for the rise in a cylindrical tube. The details of this derivation are omitted for the sake of brevity. Assume that a conical tube open at both ends is dipped with its axis vertical into a large surface of liquid (see Fig. 2), then the rise of liquid inside the cone above the free surface will be approximately

$$h = \frac{2\sigma(1 - \sin\theta)}{gx\rho\cos\theta} \tag{10}$$

where x is the radius of the circle formed by the intersection of the cone with the horizontal plane at the height h above the free surface, and θ is the angle between the vertical axis of the cone and the sides. By substituting $\theta = 0$ this reduces to the correct form for a cylinder. If the narrow end of the cone is upward the angle θ must be taken as negative and therefore will have a negative sine and a positive cosine, therefore

$$0° > \theta > -90°$$
$$1 > \frac{1 - \sin\theta}{\cos\theta} > +\infty$$

The capillary rise in the cone with the tip upward is greater than in a cylinder of the same effective diameter.

If the narrow end of the cone is downward the equation has the same form but the angle which is called ψ in Fig. 2 is in the first quadrant and is taken as a positive angle; therefore if

$$0° < \psi < 90°$$
$$1 > \frac{1 - \sin\psi}{\cos\psi} > 0$$

Therefore the capillary rise in a cone with the narrow end downward is less than in a cylinder of the same effective diameter.

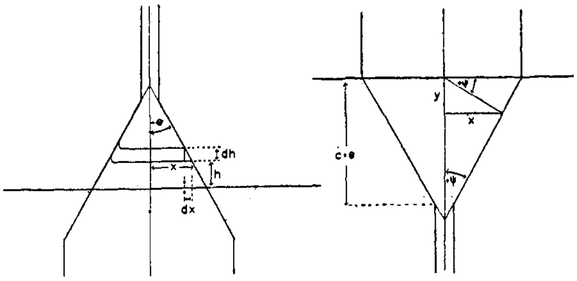

Fig. 2.

The differential equation for the time of flow of the meniscus from a to b in the upper conical dome may now be derived in a manner similar to that given above. The first step is to compute J_a, the geometrical head at the beginning of the conical part of the tube without allowance for surface tension effects. This will be the height, a, above the base level minus the increased level in the lower reservoir, k_a, owing to the transfer of the liquid from the upper constriction to the lower reservoir.

$$J_a = a - k_a = a - \frac{w^2(J - a)}{R^2} \tag{11}$$

Now consider the particular instant of time when the meniscus is in the cone at a distance y above the base level and let x be the radius of the circle formed by the intersection of the cone with a horizontal plane at the height y.

$$H = y - h + j - k - k_a \tag{12}$$

$$(x - w)/(y - a) = \tan\theta \tag{13}$$

here $a > y$ and θ is negative

$$y = a + (x - w)\cot\theta \tag{14}$$

$$\mathrm{d}y = \cot\theta\,\mathrm{d}x \tag{15}$$

$$\mathrm{d}V = -\pi x^2\mathrm{d}y = -\pi x^2\cot\theta\,\mathrm{d}x \tag{16}$$

$$\pi R^2 k = \int \mathrm{d}V = -\pi\cot\theta\int_w^x x^2\mathrm{d}x \tag{17}$$

$$k = -\frac{(x^3 - w^3)\cot\theta}{3R^2} \tag{18}$$

When $y = b$, then $x = r$, and

$$k = k_b = -\frac{(r^3 - w^3)\cot\theta}{3R^2} \tag{18a}$$

h is given by Equation (10) and j by Equation (6) as before, therefore

$$\mathrm{d}t = \frac{B\mathrm{d}V}{H} = \frac{-B\pi x^2\cot\theta\,\mathrm{d}x}{J_a + (x - w)\cot\theta - \frac{2\sigma(1 - \sin\theta)}{\rho g x\cos\theta} + \frac{2\sigma}{gR\rho} + \frac{(x^3 - w^3)\cot\theta}{3R^2}} \tag{19}$$

then an algebraic rearrangement gives

$$\frac{\mathrm{d}t}{3R^2B\pi} = \frac{-x^3\mathrm{d}x}{x^4 + 3R^2x^2 + (3R^2J_a\tan\theta - 3R^2w - w^3)x + \frac{6R\sigma x}{g\rho}\tan\theta - \frac{6R^2\sigma\sin\theta}{g\rho(1 + \sin\theta)}} \tag{20}$$

This equation must now be integrated between the lower limit $x = w$ and the upper limit $x = r$. It has not been found possible to integrate this equation in general terms, but if numerical values are assigned to w, r, R and θ for any particular instrument, and to σ/ρ for any particular liquid, the integration is then possible, although laborious. By a purely algebraic device this equation can be transformed into an equation of the form

$$\frac{\mathrm{d}t}{3R^2B\pi} = \frac{M\mathrm{d}x}{x-m} + \frac{N\mathrm{d}x}{x-n} + \frac{P(2x + p)dx + Q\mathrm{d}x}{x^2 + px + q} \tag{21}$$

with known numerical values for all of the quantities except B. The integral of this equation has the form

$$\frac{t_a^b}{3R^2B\pi} = \Big[M\ln(x - m) + N\ln(x - n) + P\ln(x^2 + px + q) + \frac{2Q}{\sqrt{4q - p^2}}\tan^{-1}\frac{2x + p}{\sqrt{4q - p^2}}\Big]_{x = w}^{x = r} \tag{22}$$

From this equation (22) a numerical value of t_a^b/B can be computed for each special case.

The calculation of t_b^c for the cylindrical part of the bulb between b and c is so similar to that for the cylindrical upper constriction that it is only necessary to write down the equation similar to Equation (9).

$$t_b^c = \frac{B\pi r^2}{1 + \frac{r^2}{R^2}}\ln\frac{J_b - \frac{2}{g}\left(\frac{1}{r} - \frac{1}{R}\right)\frac{\sigma}{\rho}}{J_b - \frac{2}{g}\left(\frac{1}{r} - \frac{1}{R}\right)\frac{\sigma}{\rho} - (b - c)\left(1 + \frac{r^2}{R^2}\right)} \tag{23}$$

where J_b is the geometric head at the beginning of the flow through the cylinder;

$$J_b = b - k_a - k_b = b - \frac{w^2}{R^2}(J - a) + \frac{(r^3 - w^3)\cot\theta}{3R^2} \tag{24}$$

Here it should be pointed out that if the instrument is so designed that $r = R$, then the term involving the surface tension drops out entirely so that the time of flow through this part of the apparatus is not influenced by the surface tension regardless of the magnitude of $b - c$. This is because the capillary rise in the upper bulb is exactly compensated by the capillary rise in the lower bulb. The lower bowl, like the upper dome, may be assumed to be either a cone or a hemisphere. If it is assumed to be a cone, the derivation is similar to that given for the dome, except that the half angle, ψ, is to be taken as a positive angle, and of course the initial geometric head J_c is different.

$$J_c = c - k_a - k_b - k_c = c - \frac{w^2}{R^2}(J - a) + \frac{(r^3 - w^3)\cot\theta}{3R^2} - \frac{r^2}{R^2}(b - c) \tag{25}$$

$$H = y - h + j - k - k_a - k_b - k_c \tag{26}$$

$$y = e + (x - w)\cot\psi \tag{27}$$

$$h = \frac{2\sigma}{gx\rho}\,\frac{(1 - \sin\psi)}{\cos\psi} \tag{28}$$

$$k = \frac{(r^3 - x^3)\cot\psi}{3R^2} \tag{29}$$

Making these substitutions followed by a purely algebraic transformation gives the equation

$$\frac{\mathrm{d}t}{3R^2B\pi} = \frac{-x^3\mathrm{d}x}{x^4 + 3R^2x^2 + (3R^2J_c\tan\psi - 3rR^2 - r^3)\,x + \frac{6R\sigma x\tan\psi}{g\rho} - \frac{6R^2\sigma\sin\psi}{g\rho\,(1 + \sin\psi)}} \tag{30}$$

This equation must be integrated between the initial limit of $x = r$ and the final limit of $x = w$. To accomplish this numerical values are substituted and the procedure described above for Equation (20) is carried out.

The equation for the lower constriction is similar to that for the upper constriction. If the dome and bowl are conical

$$J_{\rm e} = e - k_{\rm a} - k_{\rm b} - k_{\rm c} - k_{\rm e} = e - \frac{w^2}{R^2}(J - a) - \frac{(r^3 - w^3)(\cot\psi - \cot\theta)}{3R^2} - \frac{r^2}{R^2}(b - c) \qquad (31)$$

$$t^{\rm b}_{\rm c} = \frac{B\pi w^2}{1 + \frac{w^2}{R^2}} \ln \frac{J_{\rm e} - \frac{2}{g}\left(\frac{1}{w} - \frac{1}{R}\right)\frac{\sigma}{\rho}}{J_{\rm e} - \frac{2}{g}\left(\frac{1}{w} - \frac{1}{R}\right)\frac{\sigma}{\rho} - (e - f)\left(1 + \frac{w^2}{R^2}\right)} \qquad (32)$$

If the upper dome and lower bowl are blown so as to make them as nearly as possible hemispheres instead of cones, the calculation is similar to that for a cone but different in detail. The time of flow through the upper constriction, $t^{\rm a}_{\rm j}$, is computed by Equation (9) just as before. The upper dome is considered to be a hemisphere of radius, r, whose center has the coördinates $y = b$ and $x = 0$ cut by a vertical cylinder of radius w. It is convenient to introduce an abbreviation $z = y - b$. Then $x^2 + z^2 = r^2$ and $\tan\theta = -z/x$; $\sin\theta = -z/r$; and $\cos\theta = x/r$. The minus signs are due to the fact that θ must be taken as a negative angle but z is a positive quantity.

$$\mathrm{d}V = -\pi x^2 \mathrm{d}y = -\pi(r^2 - z^2)\mathrm{d}z \qquad (16')$$

$$H = y - h + j - k - k_{\rm a} \qquad (12)$$

$$h = \frac{2\sigma}{\rho g x}\frac{(1 - \sin\theta)}{\cos\theta} = \frac{2\sigma}{\rho g x^2}(r + z) = \frac{2\sigma}{\rho g(r - z)} \qquad (10')$$

$$\pi R^2 k = \int \mathrm{d}V = -\int_{(a-b)}^{z} \pi(r^2 - z^2)\mathrm{d}z \qquad (17')$$

$$k = \frac{1}{R^2}\left[r^2(a - b) - \frac{(a - b)^3}{3} - r^2 z + \frac{z^3}{3}\right] \qquad (18')$$

When $y = b$, $z = 0$ and

$$k = k_{\rm b} = \frac{r^2(a - b)}{R^2} - \frac{(a - b)^3}{3R^2} \qquad (18'a)$$

$$J_{\rm b} = h - k_{\rm a} - k_{\rm b} = b - \frac{w^2}{R^2}(J - a) - \frac{r^2}{R^2}(a - b) + \frac{(a - b)^3}{3R^2} \qquad (24')$$

$$\mathrm{d}t = \frac{B\mathrm{d}V}{H} = \frac{-B\pi(r^2 - z^2)\mathrm{d}z}{J_{\rm b} + z - \frac{2\sigma}{\rho g(r - z)} + \frac{2\sigma}{\rho g R} + \frac{3r^2 z - z^3}{3R^2}} \qquad (19')$$

Then a purely algebraic transformation gives

$$\frac{\mathrm{d}t}{3R^2B\pi} = \frac{-(r^2 - z^2)(r - z)\mathrm{d}z}{z^4 - rz^3 - 3(R^2 + r^2)z^2 + (3R^2r + 3r^3 - 3R^2J_b)z - \frac{6R\sigma z}{g\rho} - \frac{6R(R - r)}{g}\sigma/\rho + 3R^2rJ_b} \qquad (20')$$

This equation must be integrated between the initial limit of $z = (b - a)$ and the final limit of $z = 0$. This cannot be done except by introducing numerical values. A numerical value of $t^{\rm b}_{\rm a}/B$ can then be computed by introducing the appropriate numerical values for R, r, $J_{\rm b}$ and integrating between the initial limit of $z = b - a$ and the final limit of $z = 0$.[6]

The equation for the time of flow in the cylindrical part of the upper bulb, $t^{\rm c}_{\rm b}$, is the same as Equation (23) above except that J_b is given by Equation (24′) above instead of by Equation (24).

The differential equation for the time of flow in the lower bowl considered as a hemisphere has the same form as Equation (20′) above except that in place of $J_{\rm b}$ we must insert

$$J_{\rm c} = c - k_{\rm a} - k_{\rm b} - k_{\rm c} = c - \frac{w^2}{R^2}(J - a) - \frac{r^2}{R^2}(a - b) + \frac{(a - b)^3}{3R^2} - \frac{r^2}{R^2}(b - c) \qquad (25')$$

The integration must be carried out between the initial limit of $z = 0$ and the final limit of $z = e - c$.

The equation for the time of flow through the lower constriction has the same form as Equation (32) above except that $J_{\rm e}$ is given by

$$J_{\rm e} = e - \frac{w^2}{R^2}(J - a) - \frac{r^2}{R^2}(a - e) + \frac{(a - b)^3 + (c - e)^3}{3R^2} \qquad (31')$$

Table IV gives the results of the numerical calculations carried out by the use of these equations for the instrument T using the dimensions

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(6) There is one disturbing subtlety in these calculations which deserves a footnote: the assumption that the shape of the upper dome is a hemisphere of radius $r = 0.848$ cm., intersected by a vertical cylinder of radius $w = 0.05$ cm., and that the equation (10) holds for values of θ which are near $-90°$ gives a value of $h > J_{\rm a}$ which makes $H < 0$ and the time of outflow infinite. But as a matter of fact the actual instrument does empty itself, which shows that the conditions mentioned above do not prevail. This means that as a matter of practical quartz blowing the vertical cylinder is somewhat flared before it meets the hemisphere, so that there is in effect a short conical tube inserted between the cylinder and the hemisphere so that values of θ which are nearly $-90°$ do not occur in the actual instrument. At the level where the hemisphere starts x is large enough and θ sufficiently different from $-90°$ so that $h < J_{\rm a}$ and $H > 0$. The calculations of the results shown in Table V are based on the assumption that there is a truncated cone with $\theta = -45°$ and a height of 0.07 cm. between the vertical cylinder of radius, $w = 0.05$ cm., and the hemisphere of radius, $r = 0.848$ cm. This makes the initial limit for the integration of Equation 20′, $z = \sqrt{0.848^2 - (0.05 + 0.07)^2} = 0.8394665$, which avoids the mathematical paradox described above. Essentially the same result may be obtained in a much less laborious manner by arbitrarily taking as the initial limit for z a value which is slightly smaller than the value which would make $H = 0$, and $t = \infty$.

TABLE IV

ERRORS IN VISCOSITY MEASUREMENTS DUE TO SURFACE TENSION

Values of the definite integral $\int \mathrm{d}V/H$ for parts of the viscometer T for water, methanol and solutions having values of σ/ρ equal to 0.9, and 0.8 of that of water, respectively.

		Water	Solution	Solution	Methanol
	σ/ρ	72.18	64.962	57.744	28.19
	$\frac{\sigma_c\rho_0}{\sigma_0\rho_c}$		0.9	0.8	0.3906
Upper constriction	t_3^a/B	0.000186	0.000183	0.000181	0.000171
Upper cone	t_a^b/B	.060399	.060295	.060195	.059784
Upper cylinder	t_b^c/B	.482138	.481843	.481548	.480345
Lower cone	t_c^e/B	.050238	.050218	.050197	.050119
Lower constriction	t_e^J/B	.000569	.000558	.000546	.000505
Total	t_3^J/B	0.593530	0.593097	0.592667	0.590924
	$\frac{\int \mathrm{d}V/H_0}{\int \mathrm{d}V/H_c}$		1.0007_3	1.0014_6	1.0044_1

given in Table II. These calculations have been carried out for water, assuming that $\sigma = 71.97$ dynes per centimeter at 25° and $\rho = 0.99707$, giving $\sigma/\rho = 72.18$; and for two hypothetical aqueous solutions for which σ/ρ is taken as 0.9 and as 0.8 of that of water, or 64.962 and 57.744, respectively; and for methanol[7] assuming that $\sigma = 22.17$ dynes per centimeter, and $\rho = 0.78652$, giving $\sigma/\rho = 28.19$.

The experimental data recorded in Table III for methanol with viscometer T give $t_c\rho_c/t_0\rho_0 = 0.60567$ and therefore, according to Equation (3), we have $\eta_c/\eta_0 = 0.60567 \times 1.0044_1 = 0.6083_4$ as the value for the relative viscosity of methanol corrected for the surface tension as determined with the old T viscometer.

Similar calculations have been carried out with the new F viscometer and the results are recorded in Table V. The dimensions used in the calculations are given in Table II.

TABLE V

ERRORS IN VISCOSITY MEASUREMENTS DUE TO SURFACE TENSION

Values of the definite integral $\int \mathrm{d}V/H$ for parts of the viscometer F for water and for methanol.

		Water	Methanol
	σ/ρ	72.18	28.19
Upper constriction	t_3^a/B	0.000377	0.000356
Upper dome	t_a^b/B	.048368	.048125
Upper cylinder	t_b^c/B	.498190	.498199
Lower bowl	t_c^e/B	.078955	.079115
Lower constriction	t_e/B	.000254	.000224
Total	t_3^f/B	0.626153	0.626019
	$\frac{\int \mathrm{d}V/H_0}{\int \mathrm{d}V/H_c} =$	1.0002_1	

A comparison of Tables IV and V shows clearly the effectiveness of the new design in reducing the error due to surface tension. One important result of making the radius of the lower reservoir equal to that of the cylindrical part of the upper bulb is that for this part of the apparatus $\int \mathrm{d}V/H_0 = \int \mathrm{d}V/H_c$, thus completely eliminating the correction for a large fraction of the total time. Moreover, another result is that the effect in the lower bowl partly compensates the effect in the upper dome. For the upper dome $\int \mathrm{d}V/H_0 - \int \mathrm{d}V/H_c = +0.000243$, whereas for the lower bowl $\int \mathrm{d}V/H_0 - \int \mathrm{d}V/H_c = -0.000160$.

The experimental data recorded in Table III for methanol with viscometer F give $t_c\rho_c/t_0\rho_0 = 0.60830$, and, therefore, according to Equation (2), we have $\eta_c/\eta_0 = 0.60830 \times 1.0002_1 = 0.6084_3$.

The values obtained with the two different instruments agree much better after applying the surface tension correction (0.60834 with viscometer T, and 0.60843 with viscometer F) than they did before the correction was applied (0.60567 and 0.60830). Averaging the results, giving greater weight to the F instrument because the correction is so much smaller, gives $\eta_c/\eta_0 = 0.6084$. If the absolute viscosity[8] of pure water at 25° is taken as 0.008949 poise, then the absolute viscosity of methanol is 0.005445 poise.

At least sixteen different determinations of the viscosity of methanol at 25° are recorded in the literature, but the references and results are not given in detail. In most cases the results are quite discordant because the measurements were incidental to some other purpose and the technique was crude, or the density of the methanol was so high that it is evident that the sample contained water. The best of the previous results are given below.

The data given in Table IV show that the cor-

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(7) "International Critical Tables," Vol. IV, pp. 447–448.

(8) "I. C. T.," Vol. V, p. 10.

TABLE VI

ABSOLUTE VISCOSITY OF METHANOL

	$d^{25}{}_4$	Poises
Dunstan, Thole and Benson, *J. Chem. Soc.*, **105**, 784 (1914)	?	0.00546
H. Goldschmidt and H. Aarflot, *Z. Physik. Chem.*, **122**, 374 (1926)	0.7869	.00544
F. K. Ewart and H. R. Raikes, *J. Chem. Soc.*, 1907 (1926)	.78641	.00545
Grinnell Jones and H. J. Fornwalt, this paper	.78652	.005445

recting factor for viscometer T is very nearly a linear function of σ/ρ so that

$$\int\frac{\mathrm{d}V}{H_0}\Big/\int\frac{\mathrm{d}V}{H_c} = 1 + 0.0074\,\frac{(\sigma_0/\rho_0 - \sigma_c/\rho_c)}{\sigma_0/\rho_0} = 1.0074 - \frac{0.0074\,\sigma_c\rho_0}{\rho_c\sigma_0}$$

However, no systematic attempt will be made at this time to estimate the corrections which should be applied to the viscosity data which have been published from this Laboratory, because the surface tension data are not available in most cases. An improved method of measuring surface tension has been developed[9] and data on a few salts obtained, but it is necessary to postpone a general revision of the data for the viscosity of concentrated solutions until the surface tensions of these solutions have been measured. One illustrative example, in which the correction is exceptionally high, must suffice for the present. Jones and Talley,[10] who used our instrument T, report that the relative viscosity of a 2.962 normal potassium chloride solution at 25° is 1.03211. From the data of Jones and Ray the value of $\sigma_c\rho_0/\rho_c\sigma_0$ may be found by a slight interpolation to be 0.9445. This gives a correcting factor of 1.00041 or a relative viscosity corrected for the effect of surface tension of 1.03253.

The Design of the Ostwald Viscometer

With an Ostwald viscometer, where the liquid depends on its own hydrostatic head for driving pressure, an approximate value for the viscosity relative to that of water is computed by the simple equation $\eta = \eta_c/\eta_0 = t_c\rho_c/t_0\rho_0$, but to obtain the maximum precision it may be necessary to apply one or more of the following corrections unless the instrument can be designed so as to make the corrections negligible. The four corrections are (1) the drainage correction; (2) the working volume correction; (3) the kinetic energy correction; (4) the surface tension correction.

It is obvious that the first requirement for precise viscometry is accuracy in the timing and in the determination of the densities. However, the technique of making these measurements has been developed so that the real precision depends on the reliability of the corrections.

The instrument should be designed so as to make the corrections negligible if possible, or at least to minimize them as much as other considerations of design, such as convenience and speed of operation, permit. Unfortunately, details of design which may be helpful in minimizing one of the corrections may increase some other correction or cause trouble in operation or other errors so that the best design is a matter of compromise.

It has been shown in a recent paper from this Laboratory[2] that if the design is suitable in other respects the drainage correction is negligible except for extremely viscous liquids or for viscometers of a very short time of efflux.

The correction for variations in working volume can be applied with most confidence because its theoretical basis is beyond criticism, and the experimental determination of the magnitude with sufficient precision is easy in the case of aqueous solutions if the lower reservoir is not too narrow.

In the case of the kinetic energy correction there is some doubt, or at least a difference of opinion among the authorities, as to the proper way to compute the correction. Some authorities even deny that the correction should be applied at all. Although we believe that the correction should be applied, we also believe it wise to use every feasible artifice of design to reduce the magnitude of the correction, and thereby reduce the error due to inaccuracy in its computation. In designing the viscometer it is possible to control within practical limits the length and radius of the capillary, the hydrostatic head, the volume and shape of the measuring bulb, and the radius of the lower reservoir. The kinetic energy correction is diminished by any change in design which increases the time of outflow, except increasing the volume of the measuring bulb. The correction in principle always can be made negligible by using an instrument with a sufficiently long time of outflow, but this may cause serious inconvenience and delay in making measurements. Reducing the radius of the capillary and reducing the hydrostatic head both increase

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[9] Grinnell Jones and W. A. Ray, THIS JOURNAL, **59**, 187 (1937).

[10] Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933).

the time of flow and hence reduce the kinetic energy correction proportionally to the increase in time of flow. However, reducing the radius of the capillary has the disadvantage that it may increase the number of erratic results due to dust particles. Reducing the hydrostatic head will increase the error due to surface tension and make the reproducibility of the mounting more critical. The most useful and unobjectionable way to reduce the kinetic energy correction is to increase the length of the capillary. The time of flow increases proportionally with the length but the correction varies inversely as the square of the length. Variations in volume and shape of the upper bulb and variations in the radius of the lower reservoir have no direct influence on the kinetic energy correction.

Similarly, it is desirable to make the surface tension correction negligible by suitable design of the instrument if feasible. Although the theory of the correction as developed above seems to be mathematically logical and the correction clearly should be applied, nevertheless, it has the weakness that (1) the actual instrument does not have the exact shape and dimensions assumed in the calculations; (2) the equation for the capillary rise in conical or hemispherical tubes used in the calculations is an approximation; (3) the surface tension of the solution may not be known with sufficient accuracy; (4) the calculations are so laborious that they can never become popular.

As has been pointed out above the effective way to minimize the surface tension correction is to design the upper bulb so that as large a part of its volume as is feasible is in the cylindrical portion, and to make the radius of the lower reservoir the same as the radius of the cylindrical part of the upper bulb. If this common radius is too small, the correction for the variation of working volume will be troublesome, especially when dealing with volatile liquids, which may make it difficult to determine the actual volume added with sufficient precision. On the other hand, if, in order to avoid this difficulty, the common radius is made larger, the time of outflow may be made inconveniently long. If the attempt is made to remedy this difficulty by increasing the radius of the capillary there will be an increase in the kinetic energy correction. The best radius will, therefore, be a compromise.

For use with dilute aqueous solutions having a viscosity and surface tension and density nearly the same as water, the compromise can favor the working volume correction by choosing a larger radius for the lower reservoir than for the upper bulb. If the liquids to be studied differ substantially from water, then it will be advisable to make the radius of the lower reservoir the same as that of the upper bulb, to minimize the surface tension correction; and if this common radius is made large in an effort to minimize the working volume correction, then either the kinetic energy correction will be large or the time of outflow inconveniently long.

Similarly, increasing the hydrostatic head will lower the surface tension correction and the working volume correction, but increase the kinetic energy correction by lowering the time of outflow. However, the latter effect can be compensated by a decrease in the radius of the capillary without introducing any other unfavorable result except more trouble from dust particles. Therefore the hydrostatic head should be made as great as mechanical considerations permit without undue inconvenience.

Viscometer T, which was originally designed for dilute aqueous solutions, has proved in the light of our experience to be well designed for this purpose, except that the original specification that ends of the bulb should be made as nearly conical as possible has been found to be unnecessary. Hemispherical ends would be slightly better. Viscometer F, which was designed for methanol, a volatile liquid differing substantially from water in viscosity, surface tension and density, is satisfactory for such liquids and for concentrated aqueous solutions, except that it would have been better to have made the areas of the cross section of the lower reservoir and upper bulb 1.5 or 2 times as great as they actually are.

Summary

1. It is demonstrated by mathematical analysis and by experiments on methanol and water that surface tension effects may influence the measurement of viscosity with the Ostwald viscometer.

2. A method of computing the error due to surface tension for an instrument of known dimensions is given.

3. The viscosity of methanol at 25° relative to that of water is 0.6084.

4. The principles of design of the Ostwald

viscometer to give high precision without unnecessary sacrifice of convenience and speed in operation are discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Freezing Point of Methanol; A Simple Type of Cryostat Applicable to Freezing Point Determinations

BY EDWIN E. ROPER

A very pure sample of methanol had been prepared by Jones and Fornwalt[1] for their work on the relative viscosity and on the density. It appeared desirable to determine some physical constants as accurately as possible. Since a cryostat had been constructed by the author and a standardized resistance thermometer was available, Professor Jones requested a determination of the freezing point of their best samples of carefully purified methyl alcohol. The reported physical constants in the literature for methanol appear to be somewhat erratic and, in view of the difficulty involved in thoroughly freeing this material from water, in all probability the main cause of the discrepancies may be assigned to the presence of this impurity.

Experimental Procedure

Temperature Measurement and Standardization.—The temperature of the alcohol sample was measured by means of a four-lead coiled-filament 25-ohm platinum resistance thermometer.[2] The thermometer resistance was measured by a standardized Mueller type Wheatstone bridge, which was thermostated (25.0 ± 0.1°) in an oil-bath. The reproducibility of the measurements was *ca.* 0.0001 ohm, corresponding to 0.001°. The thermometer was standardized by accepted methods[3] at the sulfur boiling point, the steam point, the ice point and compared against the vapor pressure thermometers of carbon dioxide and of oxygen. The temperatures of the fixed points above 0° were taken as recommended by the International Temperature Scale specifications[3] and below 0° as given by Heuse and Otto.[4] The temperature of the ice point on the thermodynamic temperature scale was taken as 273.16 °K.[5] The thermometer constants fulfilled all specifications[3] for pure platinum. The absolute accuracy at −100° is probably ±0.02° and the precision ±0.001°. A single junction copper–constantan thermel was used as an aid in adjusting the cryostat. This thermel was standardized at the same fixed points as was the resistance thermometer, with the exception that the freezing point of a National Bureau of Standards sample of tin replaced the sulfur boiling point. The e. m. f. of the thermel was determined with a special type K potentiometer to one microvolt. The e. m. f. was converted into temperature by the accepted method of constructing a deviation curve[6] in conjunction with the reference tables of Southard and Andrews.[7] The accuracy is about ±0.05°.

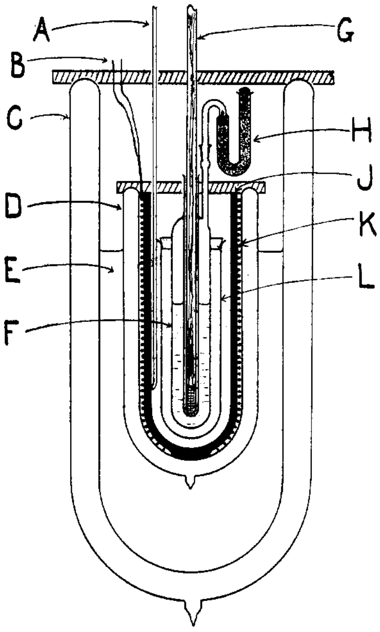

Fig. 1.—Freezing point apparatus showing details of cryostat. A is the environment thermel, B the heater leads, C the outer Dewar containing the refrigerant, D is the inner Dewar, E is the refrigerant, F is the freezing point tube, G the resistance thermometer, H a protective tube of Dehydrite, J is the copper tube, K is the heater wound on the surface of J, L is a glass jacket about the freezing point tube. Not drawn to scale.

Temperature Control.—The cryostat, somewhat similar to the one of Southard and Andrews,[7] is shown diagrammatically in Fig. 1. The copper shell J was 4 mm. wall thickness, 52 mm. outside diameter and 200 mm. long. The outer surface was so machined that after the heater winding was in place, the assembly fitted quite closely

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[1] Jones and Fornwalt, THIS JOURNAL, **60**, 1683 (1938).

[2] (a) Meyers, *Bur. Stds. J. Res.*, **9**, 807 (1932). (b) This thermometer and bridge are the same as were used for the ice point investigation, Roper THIS JOURNAL, **60**, 866 (1938).

[3] Burgess, *Bur. Stds. J. Res.*, **1**, 635 (1928).

[4] (a) Heuse and Otto, *Ann. Physik*, **9**, 486 (1931); (b) *ibid.*, **14**, 181, 185 (1932).

[5] (a) Heuse and Otto, *ibid.*, **2**, 1012 (1929); (b) Roebuck, *Phys. Rev.*, **50**, 370 (1936).

[6] "Inter. Crit. Tables," Vol. I.

[7] Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).