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A CALCULATIONAL METHOD FOR THE DETERMINATION OF
SURFACE TENSIONS FROM PHOTOGRAPHED
MENISCI -- WITH APPLICATION TO WATER AND MERCURY*

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ABSTRACT

A method was developed to calculate surface tensions from menisci in cylindrical tubes. A modified form of the Laplace-Young differential equation was numerically integrated to generate meniscus curves for assumed values of surface tension and tangent angle at the outer edge of the meniscus. The best values of surface tension and tangent angle were obtained by a minimization technique. This calculation method generated surface tensions of mercury and water within 0.5% of the published values.

INTRODUCTION

In plutonium systems any experimental physical measurement is made with great difficulty. For instance, surface tension measurements of liquid plutonium alloys by the standard methods of capillary rise, pendent drop, sessile drop, and bubble pressure require expensive and difficult experimental programs. However, many experiments with plutonium alloys are run in capsules which are later sectioned in order to obtain photomicrographs. The alloys in the sectioned capsules exhibit well formed concave menisci. The analysis herein described was initiated in an attempt to develop a calculational procedure to obtain the surface tensions directly from the experimentally observed menisci. Thus, if successful, relatively inexpensive and less time consuming calculational effort might produce the desired surface tensions from already existing experimental data.

The basic analysis as developed includes a mathematical procedure for calculating the meniscus curve and a method for comparing the computed and experimental curves in a manner to produce the best surface tension value and to throw out the badly distorted menisci. The meniscus curve is generated by numerically solving a modified form of the Laplace-Young equation. As a test of the basic procedure, surface tensions of water and mercury held in glass tubing were determined from photographed menisci.

MATHEMATICAL DEVELOPMENT

The basic differential equation used in this analysis is derived by forming a force balance on a small element containing a **segment of meniscus surface**. The force balance is pictorially presented in Fig. 1.

Let P_0 be defined as the pressure in Fluid 2 at the interface and on the centerline of the tube. Then for any given shell element, the pressure, P_t , in Fluid 2 immediately above the interface and the pressure at the zero curvature datum plane are given below.

$$P_t = P_0 - \rho_2 g (z + dz - z_0) \quad (1)$$

$$P_{\text{datum}} = P_0 + \rho_2 g z_0 \quad (2)$$

Equation 2 actually defines the position of the datum plane. It states that the datum plane is that level at which the pressures in Fluid 1 and Fluid 2 are equal. The height, z_0 , from the datum plane to the bottom of the meniscus is actually the distance of capillary rise above a reservoir of Fluid 1 which has no surface curvature and is covered with a continuous blanket of Fluid 2. One of the problems of the analysis is to determine z_0 when the infinite reservoir does not exist.

The vertical force balance on a differential element, $2\pi r dr dz$, is given as Eq. 3.

$$2\pi r dr (P_b - P_t) + F_{2n} - F_{1n} = 0 \quad (3)$$

$$F_{1n} = 2\pi r \gamma \sin\theta \quad (4)$$

$$F_{2n} = 2\pi r \gamma \sin\theta + \left[\frac{\partial (2\pi r \gamma \sin\theta)}{\partial r} \right] dr \quad (5)$$

$$F_{2n} - F_{1n} = \left[\frac{\partial (2\pi r \gamma \sin\theta)}{\partial r} \right] dr \quad (6)$$

$$P_b = P_{\text{datum}} - \rho_1 g z \quad (7)$$

FIGURE 1

FORCE BALANCE ON ELEMENT OF FLUID IN MENISCUS

EXPANDED VIEW OF ELEMENT

With the substitution of Eqs. 1 and 2, the pressure difference $P_b - P_t$ becomes Eq. 8.

$$P_b - P_t = P_o + \rho_2 g z_o - \rho_1 g z - P_o + \rho_2 g (z + dz - z_o) = g z (\rho_2 - \rho_1) + \rho_2 g dz \quad (8)$$

The combination of Eqs. 8 and 6 with Eq. 3 produces the desired meniscus equation, Eq. 9. In forming Eq. 9, the limit is taken so that the term with dz goes to zero.

$$z = \frac{1}{rg (\rho_1 - \rho_2)} \frac{\partial}{\partial r} (r \gamma \sin \theta) \quad (9)$$

If the surface tension does not vary with r , then γ can be brought outside the partial derivative.* The result, Eq. 10 is an equation which is equivalent to the Laplace-Young equation for capillary rise.¹ This correspondence can be

$$z = \frac{\gamma}{rg (\rho_1 - \rho_2)} \frac{\partial}{\partial r} (r \sin \theta) \quad (10)$$

shown by performing the differentiations, and then substituting for $\sin \theta$ and $r \frac{\partial}{\partial r} \sin \theta$ in terms of $z'(r)$ and $z''(r)$ where $z = z(r)$ is the meniscus curve. These equivalence relations and the final result are given below.

$$\sin \theta = z'(r) / (z'(r)^2 + 1)^{1/2} \quad (11)$$

$$r \frac{\partial}{\partial r} \sin \theta = r z''(r) / (z'(r)^2 + 1)^{3/2} \quad (12)$$

$$z = \frac{\gamma}{rg (\rho_1 - \rho_2)} \left(\frac{z'(r)}{(z'(r)^2 + 1)^{1/2}} + \frac{r z''(r)}{(z'(r)^2 + 1)^{3/2}} \right) \quad (13)$$

The Laplace-Young equation as shown in Eq. 10 will be the form utilized in the subsequent numerical work.

In the work of Adamson² it is shown that the net weight of liquid in the capillary tube between the meniscus and the datum plane is equal to the vertical surface tension force at the perimeter of the tube. This result is also easily shown by direct integration of Eq. 9.

*This assumption may not be valid if Fluid 1 contains two or more components and if the concentration of these components varies along the meniscus in order to minimize the surface energy in the interface.

$$2\pi \int_0^r (\rho_1 - \rho_2) g z r dr = 2\pi \int_0^r (r \gamma \sin\theta) d(r \gamma \sin\theta) \quad (14)$$

$$(\rho_1 - \rho_2) g V_r = 2\pi r \gamma \sin\theta \quad (15)$$

The result in Eq. 15 is true for any radius, r , less than or equal to the radius of the tube.

EXPERIMENTAL DATA PREPARATION

Experimental data for surface tension determinations from menisci can be obtained from photographs of liquids in glass tubes, for photographs of mounted sections of frozen menisci, and from radiographs of liquids in tubes at elevated temperatures. The photograph or radiograph of the meniscus is enlarged from the original diameter of 1/2 to 1 inch to approximately 10 to 12 inches. The meniscus shape is then traced onto graph paper and the differential heights, $z'_{m-\frac{1}{2}}$, in the center of N equal radial increments from the center to the outside are picked off the graph. The meniscus curve is then replotted on an expanded scale, and a smooth curve is fitted to these points. The final points, $z'_{m-\frac{1}{2}}$, are read from the smoothed curve, and these are the data points which are read into the computer for comparison with computed curves. The smoothed height values can be read from the graph to within 0.0003 cm. The scatter of the original points around the smoothed curve is within a band of ± 0.0015 cm.

In calculating a meniscus curve $\sin\theta$ at the outside of the last increment is required as a boundary condition. An estimate of this value can be obtained by calculating experimental sines, $\sin\theta_{\text{exp}}$, at the outside of each increment from the experimental heights, $z'_{m-\frac{1}{2}}$. A short program was used to calculate these values with Eq. 17. The values so calculated have considerable scatter because of the relatively large error that can develop from subtracting two numbers of

approximately the same size. The $\sin\theta$ as calculated with N equal to 25 and meniscus radius equal to 0.5 cm had an error of $\pm \frac{0.0003}{0.020} = \pm 0.015$ just from reading the graph. Also, the uncertainty of ± 0.015 cm of the smoothed height curve gives a total over-all possible deviation in the $\sin\theta_{\text{exp}}$ curve of ± 0.075 .

The plotted sine curve gives a very good indication as to whether or not the experimental meniscus is distorted. The sine curve should be smooth with a monotonic increasing slope. Any bulges or depressions in the curve indicate minor distortions. If the curve is distorted, a smooth curve can be drawn through the data in an attempt to make some use of the curve. Experience in drawing these curves indicates that the curve should start with the initial slope of the data, should pass through the geometric center of the bulges, and then close to experimental points 22 and 23. A critical test of the correct location of the curve is whether or not the calculated surface tensions are approximately the same value when determined with the use of these sine values as boundary conditions at each of the outside five increments. The curve so positioned is called the "adjusted" experimental sine curve.

NUMERICAL TECHNIQUES USED IN DETERMINING SURFACE TENSIONS FROM MENISCI

The calculation method generates surface tensions by comparing computed meniscus curves with the experimentally determined curves. The computed curve is obtained by numerically integrating the Laplace-Young equation, Eq. 10.

The Laplace-Young equation has been numerically integrated previously by Bashforth and Adams,³ Blaisdell,⁴ and others to produce tabular relationships describing the meniscus shape, capillary rise, and capillary volume beneath the meniscus. A possible approach in this present analysis would be to utilize these tables in an attempt to produce the exact meniscus shape for given physical conditions. This method was not followed because of the cumbersome interpolations

involved, the dependence upon hand calculated data that could contain errors, and the possible limited range of conditions covered. Instead, with the use of high speed computers of today, the Laplace-Young equation can be integrated directly for each set of assumed conditions. The directly computed curve can then be compared by the method of least squares with the experimentally determined curve. The numerical methods and comparison techniques are described below.

The computed meniscus curve is obtained by numerically integrating Eq. 10 with a relaxation technique. The distance across the radius of the tube is divided into N increments,* and a first order finite difference form of the equation is written at the center of each increment. This form is shown as Eq. 16.

$$z = \frac{\gamma}{\Delta r (\rho_1 - \rho_2)g} \left[\frac{m}{m - \frac{1}{2}} \sin\theta_m - \frac{m-1}{m - \frac{1}{2}} \sin\theta_{m-1} \right] \quad (16)$$

$$\sin\theta_m = \frac{z_{m+\frac{1}{2}} - z_{m-\frac{1}{2}}}{(\Delta r^2 + \Delta z^2)^{1/2}} \quad (17)$$

$$\sin\theta_{m-1} = \frac{z_{m-\frac{1}{2}} - z_{m-1\frac{1}{2}}}{(\Delta r^2 + \Delta z^2)^{1/2}} \quad (18)$$

The boundary conditions for the above set of equations are as follows:

$$\sin\theta_0 = 0 \quad \text{and} \quad \sin\theta_N = \sin\theta \quad (19)$$

As the equations are set up, no calculation of z is made at r=0. Since this value of z is desired because it is the actual capillary rise, Eq. 10 was modified with L'Hôpital's rule to find the limit at r=0. This form is presented as Eq. 20, and its finite difference counterpart is Eq. 21.

$$z_0 = \frac{\gamma}{(\rho_1 - \rho_2)g} \frac{\partial^2(r \sin\theta)}{\partial r^2} \quad (20)$$

$$z_0 = \frac{\gamma}{(\rho_1 - \rho_2)g} \frac{2 \sin\theta_1}{\Delta r} \quad (21)$$

These equations apply to any symmetrical section of the meniscus bounded by any radial position. Many calculations can be made on one meniscus by including progressively fewer radial increments of the meniscus being studied. With N

*N in general was set equal to 25.

equal to 25, useful data were obtained when as few as 21 increments were included. At each radial position the boundary condition, $\sin\phi$, must be adjusted to best fit the data.

The above equations allow a relaxation procedure to be used. An initial set of meniscus heights, $(z_{m-\frac{1}{2}})_1$, are selected for startup. These heights can be set to zero, or, in order to speed convergence, they can be set equal to the experimental meniscus profile heights, $z'_{m-\frac{1}{2}}$, plus some assumed z_0 . If the meniscus is well shaped and the proper guess of z_0 and γ are made, this initial input into the program allows a rapid determination of the meniscus profile. From the initial heights, $(z_{m-\frac{1}{2}})_1$, a corrected set of meniscus heights are calculated with Eqs. 16, 17, and 18, and z_0 is calculated with Eq. 21. The above equations tend to overcorrect the heights, and, therefore, the next values, $(z_{m-\frac{1}{2}})_2$, are formed with a weighted average of the initial and calculated heights according to Eq. 22.

$$(z_{m-\frac{1}{2}})_n = \frac{(z_{m-\frac{1}{2}})_{n-1} (W-1) + (z_{m-\frac{1}{2}})_{\text{calc}} d}{W} \quad (22)$$

With the proper choice of W , the relaxation calculated profile converges toward the correct profile. The calculation of z_0 is made directly from $(z_{m-\frac{1}{2}})_n$ with no weighting of the previously calculated value. Interestingly, z_0 converges to its final value much sooner than does the rest of the profile. This rapid convergence of z_0 gives one indication of convergence of the total profile. The total convergence is satisfactory when $(z_0 - z_{1/2}) < 10^{-4}$ cm.

The above procedure calculates accurately and rapidly the meniscus profile if the physical parameters and boundary conditions are known. However, the purpose of the procedure is to calculate one of the physical parameters, γ , and in most cases the angle, ϕ , at the outer edge of the surface is not known accurately. Therefore, guesses of the surface tension and ϕ have to be made to perform the above calculation. The following section describes the methods used to determine the best values of γ and ϕ .

The calculation of the net weight of fluid beneath the meniscus gives one method of determining the best surface tension for a given value of ϕ . The net weight between the experimental meniscus and a plane tangent to the bottom of the meniscus can be calculated from Eq. 23. To this value

$$W'_{\text{exp}} = g(\rho_1 - \rho_2) \sum_{m=1}^N 2\pi z'_{m-\frac{1}{2}(\text{exp})} r_{m-\frac{1}{2}} \Delta r \quad (23)$$

must be added the net weight of fluid between the tangent plane and the datum plane. For the given assumed values of γ_{as} and ϕ_{as} , a z_0 is found by the numerical integration, and the net weight associated with this z_0 is then added to W'_{exp} according to Eq. 24. From W_{tot} a surface tension, γ_{cal} , can be calculated from Eq. 25. If γ_{cal} equals γ_{as} , then γ_{as}

$$W_{\text{tot}} = W'_{\text{exp}} + \pi (\Delta r M)^2 z_0 (\rho_1 - \rho_2) g \quad (24)$$

$$\gamma_{\text{cal}} = W_{\text{tot}} / (2\pi (\Delta r M) \sin \phi_{\text{as}}) \quad (25)$$

is the "optimum" surface tension that best fits the experimental curve for the assumed angle, ϕ_{as} . If γ_{cal} is greater than γ_{as} then γ_{as} must be increased. Also, if γ_{cal} is less than γ_{as} then γ_{as} must be decreased. A plot of $(\gamma_{\text{cal}} - \gamma_{\text{as}})$ versus γ_{as} is almost linear. Therefore, from two calculations with two values of γ_{as} , a fair estimate of the correct value of γ_{as} can be made by a linear interpolation or extrapolation.

A second method of determining the best γ for a given ϕ is to find the minimum in a plot of the standard deviation as calculated from Eq. 26. In general, this technique gives approximately the same

$$s = \frac{\sum_{n=1}^N [z'_{n-\frac{1}{2}(\text{exp})} - z'_{n-\frac{1}{2}(\text{num})}]^2}{(N - 1)} \quad (26)$$

answer as the method utilizing the net weight beneath the meniscus. However, the standard deviation technique does not lend itself to interpolation or extrapolation, and usually more values of γ_{as} have to be chosen to develop a complete plot than have to be chosen in the net weight method. The standard deviation method

required at least five values while the net weight method required two to three computations for a given value of ϕ .

In the final determination of γ , the optimum values of both γ and ϕ must be found to produce the best fit between the experimental and calculated curves. Therefore, $\sin\phi$ must be set at a value which is judged to give the best physical answer. The best method for making this determination is to allow $\sin\phi$ to vary until the minimum in the standard deviation curve as a function of $\sin\phi$ is obtained. This minimum is effectively a minimum in a trough of a surface formed by the standard deviation as a function of both γ and $\sin\phi$. Actually, for each value of ϕ , the best γ is found by the net weight technique previously described, and ϕ is varied until the absolute minimum standard deviation is obtained.

For each radial position a function of "optimum" γ versus $\sin\phi$ can be plotted as the minimum in standard deviation is being located. This plot allows the positioning of the "adjusted" experimental sine curve. The "adjusted" experimental sine curve is drawn to give a smooth fit of the $\sin\theta_{\text{exp}}$ points and to produce the same value of γ at the outside 3 to 5 radial positions. By trial and error a smooth curve is drawn, and the surface tensions at the desired radial positions are determined from the γ - $\sin\phi$ plots. The curve is slightly repositioned until a constant value of γ is obtained.*

When applying the minimum standard deviation method to distorted menisci, in many instances the distortion is significant enough not to allow a minimum in the standard deviation to be formed or to move the minimum into an unreasonable region. To test the acceptability of the results from a given meniscus, $\sin\phi_{\text{min}}$ is compared with the "adjusted" experimental sine curve.

As explained in the experimental section, a smoothed experimental sine curve has some uncertainty because in calculating the sines small differences of large numbers are utilized. The uncertainty of the sine curve is in the range of

*No proof exists that only one such curve can be drawn. However, in the experience of this investigation only one curve could be found in each case.

± 0.015 . * Therefore, if $\sin\phi_{\min}$ as determined from the minimum standard deviation does not fall within this range of uncertainty about the "adjusted" experimental $\sin\theta$ curve then the result is discarded as being unacceptable due to distortion. In addition, to be acceptable the minimum s has to be less than 0.0020 cm.

In the standard deviation method, a second kind of standard deviation was, also, used. With frozen menisci many times the center of the meniscus is distorted from expansion or contraction during freezing. Therefore, since the true shape of the experimental curve near the center has to be estimated, a sum of squares was formed only with the outside seven increments. This standard deviation is shown in Eq. 27. In many cases with frozen menisci the s_7 curve gave a more acceptable

$$s_7 = \sum_{m=N-6}^N \left(z'_{m-\frac{1}{2}}(\text{exp}) - z'_{m-\frac{1}{2}}(\text{num}) \right)^2 \quad (27)$$

minimum than was produced with s . However, if distortion were present in the outside increments as might be the case in photographed water and mercury menisci in glass tubing, then the over-all s could give better results than s_7 . Therefore, in all calculations both s and s_7 were formed, and a minimum of either one was accepted if $\sin\phi_{\min}$ was in the ± 0.015 range of the "adjusted" sine curve and if their values were less than 0.0020 cm.

In applying the above restrictions many meniscus were not able to meet the demands imposed. Therefore, a set of less stringent rules were set up to determine whether or not useful data could be determined from the menisci that did not produce acceptable minimum standard deviations. The various methods of restricting the results are summarized below. Three forms of the minimum standard deviation method comprise the first three items.

*This uncertainty of 0.015 in $\sin\phi$ for the outside three radial positions produces a variation of approximately 7-10 dynes/cm in the measurement of water surface tension (72 dynes/cm), and 25-45 dynes/cm in measurement of mercury surface tension (482 dynes/cm).

Fig. 2 Water Meniscus No. 1.

Methods of restricting surface tension values in over-all averages

- Method 1. Average of all surface tension values at minimum s and s_7 where $|(\sin\phi_{\min} - \sin\theta_{\text{adj}})| < 0.015$ and s and $s_7 < 20 \times 10^{-4}$ cm.
- Method 2. Same as Method 1 except $|(\sin\phi_{\min} - \sin\theta_{\text{adj}})| < 0.010$
- Method 3. Same as Method 1 except s and $s_7 < 35 \times 10^{-4}$ cm.
- Method 4. Average of all average surface tensions from the "adjusted" experimental sine curve with all s and $s_7 < 20 \times 10^{-4}$ cm.
- Method 5. Same as Method 4 except all s and $s_7 < 35 \times 10^{-4}$ cm.
- Method 6. Average of all average surface tension values calculated with sines taken from the "adjusted" experimental sine curve where all $|(\sin\theta_{\text{exp}} - \sin\theta_{\text{adj}})| < 0.060$.
- Method 7. Average of all surface tension values calculated with $\sin\phi$ equal to $\sin\theta_{\text{adj}}$ where $|(\sin\theta_{\text{exp}} - \sin\theta_{\text{adj}})| < 0.015$ and s and $s_7 < 20 \times 10^{-4}$ cm.
- Method 8. Average of all surface tension values calculated with $\sin\phi$ equal to $\sin\theta_{\text{adj}}$ where $|(\sin\theta_{\text{exp}} - \sin\theta_{\text{adj}})| < 0.015$.
- Method 9. Same as Method 8 except $|(\sin\theta_{\text{exp}} - \sin\theta_{\text{adj}})| < 0.010$.

The experimental data obtained from the water and mercury menisci were analyzed by each of the above restrictions. The 95% confidence intervals of the results obtained give an indication of each method's usefulness.

DETERMINATION OF SURFACE TENSIONS OF WATER AND MERCURY FROM
PHOTOGRAPHED MENISCI

Water

The first test of the calculational procedure was the determination of the surface tension of water. The experimental procedure consisted of taking five photographs of the water menisci as formed inside thin walled glass tubing. The water was double distilled, and additional water was added to the tube before each photograph was taken. The photograph of Meniscus No. 1 is shown as Fig. 2. The temperature of the water at time of photographing varied between 23 and 25° C.

Because of optical distortion, the shape of the meniscus could not be determined all the way out to the wall. Therefore, even though the water wet the glass and the sine of the outside angle at contact should be 1.0, the maximum sine of the largest useable portion of the meniscus was between 0.50 and 0.65. This maximum useable portion of the meniscus had a radius of 0.6 ± 0.02 cm.

In Table 1 is presented a summary of the properties and measurements of the menisci and the computing times required. The maximum useable height of the meniscus above the bottom tangent plane was approximately 0.14 cm. After four radial increments were removed, this height decreased to 0.09 cm. The computed distance between the tangent and datum planes was 0.09 cm.

To completely analyze one meniscus at five radial positions required from 18 to 32 minutes of computing time on the IBM 7094 computer. Each computation required 1800 iterations to obtain satisfactory convergence. A weighting factor, W , of 400 was necessary to stop oscillatory behavior. An analysis of one radial position was completed with 4 to 8 computations.

In Table 6 in the Appendix are presented the surface tension and computation data obtained from the five photographs. In all cases surface tension calculations were made at radial positions in the center of increments 21 through 25. Included in the table are the surface tensions, $\sin\phi$, s , and s_7 obtained at the minimum s and s_7 and on the "adjusted" experimental sine curve. Also, the deviations of the experimental from the adjusted sines are shown for the outside 5 increments. In only one case, Meniscus No. 1, was the distortion in the photograph small enough to form a minimum in the standard deviation between the calculated and experimental heights and to have $\sin\phi_{\min}$ within ± 0.015 of the "adjusted" experimental sine curve. As an example of the intermediate computational results plots of s and s_7 versus "optimum" γ , "optimum" γ versus $\sin\phi$, and the "adjusted" experimental sine curve for Meniscus No. 1 are shown in Figs. 3, 4, and 5.

TABLE 1
COMPUTATION, PHYSICAL, & MENISCUS DATA FOR WATER

PHYSICAL DATA				MENISCUS DATA			COMPUTATION DATA			
Capsule No.	Differential Fluid Density $\rho_1 - \rho_2$, g/cc	Temperature °C	Maximum Useable Radius of Meniscus, cm	(Computed) z_0 cm	$z'_{21-\frac{1}{2}}$, cm	$z'_{25-\frac{1}{2}}$, cm	No. of Iterations per Computa- tion	Weight- ing Factor	No. of Computa- tions Required per Increment	Time per Computa- tion, Minute
1	0.9965	23-25	0.5950	0.075	0.0760	0.1226	1800	400	4-5	0.923
2	0.9965	23-25	0.6164	0.080	0.0882	0.1492	1800	400	4-7	0.923
3	0.9965	23-25	0.6030	0.092	0.0909	0.1423	1800	400	4-7	0.923
4	0.9965	23-25	0.6170	0.082	0.0876	0.1469	1800	400	4-6	0.923
5	0.9965	23-25	0.5921	0.082	0.0824	0.1338	1800	400	4	0.923

Fig. 3 Meniscus Height Standard Deviation versus "Optimum" Surface Tension for Water Meniscus No. 1.

Fig. 4 $\text{Sin}\phi$ versus "Optimum" Surface Tension for Water Meniscus No. 1.

Fig. 5 Experimental and "Adjusted" $\sin\theta$ Curves for Water Meniscus No. 1.

In all five samples, the experimental sine curve was adjusted so as to produce a nearly constant surface tension when 21, 22, 23, 24, and 25 radial increments were included. In all cases the adjusted sine curve started with the initial slope of the experimental curve and passed through or near the experimental points in the 22 to 24 increment range. For Menisci 2 and 3 the center portion of the experimental points significantly deviated from the "adjusted" curve. However, Menisci 1 and 5 required only small adjustments from the actual experimental curve to produce "adjusted" curve.

The s values at the minima or at "adjusted" $\sin\phi$ values varied between 6.7 and 9.8×10^{-4} cm while s_7 varied between 6.3 and 15.2×10^{-4} cm. The lowest of these values is only a factor of 2 greater than the uncertainty in reading the smoothed experimental meniscus height data.

Many investigators have determined the surface tension of water in the past 50 years, and the agreement of the results is quite good. In Table 2 are presented data from the International Critical Tables and from Landolt-Börnstein.

Table 2
Surface Tension of Water--Literature Values

Temp. °C	Surface Tension - Dynes/cm	
	I. C. T. ⁵	Landolt-Börnstein ⁶
20	72.75 ± 0.05	72.58
21	72.59 ± 0.05	72.42
22	72.44 ± 0.05	72.27
23	72.28 ± 0.05	72.11
24	72.13 ± 0.05	71.95
25	71.97 ± 0.05	71.81

Recent work substantiates these data fairly well. For instance, Ikeda and Ozaki⁷ in 1950 found the surface tension at 20°C to be 72.6 dynes/cm. From the extremes of these data the observed surface tension in this present work in the 23 to 25°C range should have ranged between 71.81 and 72.28 dynes/cm.

The results of the water surface tension determination from the five photographed menisci are given in Table 3. All of the methods of restricting the data gave 95% confidence intervals* that included or were included in the desired surface tension range. Only one meniscus, No. 1, produced acceptable minima in the s and s_7 curves. The surface tensions at these minima gave an average surface tension of 71.5 ± 2.3 dynes/cm. Of the methods where a minimum in s and s_7 were not required, Methods 4 and 6 gave the best results. Both produced surface tension of 71.9 dynes/cm with confidence intervals of ± 0.64 and ± 0.14 respectively.

Mercury

The surface tension of triple distilled mercury was determined with the same procedure as used on water.** In this case ten photographs of the meniscus were made. The radius of the maximum useable portion of the meniscus ranged from 0.54 to 0.58 cm. The temperatures at which the menisci were photographed were between 23 and 25° C. In Fig. 6 is shown mercury Meniscus No. 7.

In Table 4 are presented a summary of the meniscus physical data and the computational requirements of the various menisci. The $z'_{N-4\frac{1}{2}}$ and $z'_{N-\frac{1}{2}}$ heights were approximately 0.06 and 0.10 cm while the computed capillary depression was approximately 0.026 cm. The number of computation iterations required per meniscus calculation was 1650, and the weighting factor was 400. Between 5 and 11 computations were necessary to find the desired data for each radial position. Thus, for the three radial positions calculated for each meniscus, the computer time on the IBM 7094 ranged from 13 to 28 minutes per meniscus.

*The 95% confidence interval was calculated from the standard deviation of the mean surface tension and the factors from a standard "t" table.

**The meniscus of mercury in glass is inverted, and, as a result, the datum plane is above the meniscus. The same equations apply with z and $\sin\phi$ values being negative. However, the same computational results are obtained if z and $\sin\phi$ are considered to be positive.

TABLE 3
SUMMARY OF WATER SURFACE TENSION DATA

Type of Av	No. of Menisci in Av	No. of Surface Tension Determinations in Av	Range of Surface Tensions in Av, Dynes/cm	Sample Standard Deviation, Dynes/cm	Standard Deviation of Mean Surface Tension, Dynes/cm	95% Confidence Interval for Av Value of Surface Tension, Dynes/cm	Av Value of Surface Tension, Dynes/cm
1	1	8	65.7 - 75.0	2.73	0.97	±2.3	71.5
2	1	8	65.7 - 75.0	2.73	0.97	±2.3	71.5
3	1	8	65.7 - 75.0	2.73	0.97	±2.3	71.5
4	2	2	71.9 - 72.0	0.07	0.05	±0.64	71.9
5	5	5	71.9 - 75.8	1.65	0.74	±2.0	72.9
6	3	3	71.9 - 72.0	0.06	0.03	±0.14	71.9
7	2	6	70.7 - 75.2	1.61	0.66	±1.69	72.1
8	5	13	70.7 - 75.6	1.49	0.41	±0.90	72.5
9	4	7	70.7 - 75.6	1.60	0.60	±1.47	72.4

Fig. 6 Mercury Meniscus No. 7.

TABLE 4

COMPUTATION, PHYSICAL, & MENISCUS DATA FOR MERCURY

PHYSICAL DATA				MENISCUS DATA			COMPUTATION DATA			
Capsule No.	Differential Fluid Density $\rho_1 - \rho_2$ g/cc	Temperature °C	Maximum Useable Radius of Meniscus, cm	(Computed) z_0 cm	$z'_{N-4\frac{1}{2}}$ cm	$z'_{N-\frac{1}{2}}$ cm	No. of Iterations per Computa- tion	Weight- ing Factor	No. of Computa- tions Required per Increment	Time per Computa- tion, Minute
1	13.535	23-25	0.5547	0.0275	0.0581	0.0997	1650	400	11	0.845
2	13.535	23-25	0.5703	0.0274	0.0565	0.0936	1650	400	9-10	0.845
3	13.535	23-25	0.5640	0.0255	0.0589	0.1022	1650	400	8-10	0.845
4	13.535	23-25	0.5591	--	0.0654	0.1015	2100	500	5-11	1.077
5	13.535	23-25	0.5747	0.0262	0.0580	0.0975	1650	400	8-10	0.845
6	13.535	23-25	0.5598	0.0232	0.0573	0.1015	1650	400	9	0.845
7	13.535	23-25	0.5578	0.0277	0.0658	0.1012	1650	400	7-9	0.845
8	13.535	23-25	0.5437	--	0.0563	0.1001	1650	400	-	0.845
9	13.535	23-25	0.5479	0.0201	0.0460	0.0844	1650	400	4-10	0.845
10	13.535	23-25	0.5600	0.0294	0.0610	0.1010	1650	400	8-11	0.845

The computational procedure as previously outlined was followed. As an example of the type of intermediate results obtained, Figs. 7, 8, and 9 are included. These graphs show results obtained for mercury Meniscus No. 7 and include s and s_7 versus "optimum γ ", $\sin\phi$ versus "optimum" γ , and the "adjusted" experimental sine curve plots.

In Table 5 are shown the average surface tensions obtained with the various restrictions on the calculated values. Whereas with water only one of the five menisci produced s and s_7 values with minima, seven of the ten mercury menisci gave such minima. The best average surface tension, 482.8 ± 9.7 dynes/cm, with the smallest standard deviations were obtained when those values of surface tension at the minima were averaged together according to Method No. 1. Interestingly, approximately the same value of surface tension with about the same 95% confidence level was obtained when the sine limit of 0.010 in Method No. 2 was applied. As in the case of the water determinations other averages with restrictions on the size of s and s_7 and $(\sin\theta_{\text{adj}} - \sin\theta_{\text{exp}})$ were calculated and are shown in Table 5. These averages varied from the above value with a maximum deviation of 13 dynes/cm and had larger 95% confidence intervals. A complete tabulation of the surface tensions obtained, values of $\sin\phi_{\text{min}}$, $\sin\theta_{\text{adj}}$, and sine deviations at each increment of each sample is included in the Appendix as Table 7.

An interesting result from the calculations was that the standard deviations, s and s_7 , were in many cases less than a factor of 2 greater than the uncertainty of reading the experimental data from the smoothed meniscus curve. Values of s and s_7 as low as 2.5×10^{-4} cm were obtained. The uncertainty in reading the graph was estimated to be $\pm 3.0 \times 10^{-4}$ cm.

The experimental value for mercury with the smallest 95% confidence limit compares very favorably with that published in the literature. The best values at 25°C in vacuum were obtained by Ziesing⁸ and Kemball⁹. These values are 484.9 ± 1.8 dynes/cm and 484.0 dynes/cm. These investigators also found the temperature coefficient to be -0.20 dynes/cm/°C. Two other investigators,

Fig. 7 Meniscus Height Standard Deviation versus "Optimum" Surface Tension for Mercury Meniscus No. 7.

Fig. 8 $\text{Sin}\phi$ versus "Optimum" Surface Tension for Mercury Meniscus No. 7.

Fig. 9 Experimental and "Adjusted" $\text{Sin}\theta$ Curves for Mercury Meniscus No. 8.

TABLE 5

SUMMARY OF MERCURY SURFACE TENSION DATA

Type of Av	No. of Menisci in Av	No. of Surface Tension Determinations in Av	Range of Surface Tensions in Av, Dynes/cm	Sample Standard Deviation, Dynes/cm	Standard Deviation of Mean Surface Tension, Dynes/cm	95% Confidence Interval for Av Value of Surface Tension, Dynes/cm	Av Value of Surface Tension, Dynes/cm
1	7	31	435 - 545	26.4	4.7	± 9.7	482.8
2	7	23	435 - 539	23.1	4.8	± 10.0	481.2
3	7	31	435 - 545	26.4	4.7	± 9.7	482.8
4	8	8	416 - 515	36.7	13.0	± 30.6	472.4
5	10	10	385 - 555	51.6	16.3	± 36.9	471.9
6	7	7	416 - 515	39.0	14.7	± 36.0	470.1
7	8	16	415 - 517	37.4	9.4	± 19.9	470.6
8	8	16	415 - 517	37.4	9.4	± 19.9	470.6
9	6	11	427 - 517	36.4	11.0	± 24.4	479.2

Burden¹⁰ and Puls¹¹, found that the surface tension of mercury in air was very nearly the same as the value in vacuum if the mercury surface were newly formed. In Burden's work¹⁰ the surface tension dropped from 480 to 475 dynes/cm at 25° C in one half of an hour when the vacuum system was let down to air. If the air was saturated with water vapor, the surface tension dropped from 480 to 430 dynes/cm in one half an hour. However, the surface tension went back to 482 dynes/cm when a new surface was created. Puls¹¹ found the value of surface tension to be 475 ± 2 dynes/cm. His experimental data ranged from 457 to 516 dynes/cm. He also has a summary of other determinations in contact with air. These values ranged from 432 to 547 dynes/cm.

From this investigation the average value of 482.8 ± 9.65 dynes/cm obtained at the s and s_7 minima checks very closely with the most recent values reported. Also, the over-all range of the acceptable values in this average was 435 to 545 dynes/cm which is similar to the range experience by other investigators.

RESULTS AND CONCLUSIONS

The determinations of water and mercury surface tensions from photographed menisci indicate that the meniscus experimental-calculational procedure can produce very satisfactory results. By numerically comparing calculated and experimentally determined menisci, surface tensions of 71.9 ± 0.14 dynes/cm for water and 482.8 ± 9.7 dynes/cm for mercury resulted. (The $\pm$ range is a 95% confidence interval.) These values are within 0.5% of the accepted published values in the 23-25° C temperature range.

In summary the calculational procedure for each meniscus involves the following steps:

- (1) For assumed values of surface tension, γ , and $\sin\phi$, sine of the tangent angle at outer edge of the meniscus, surface tension curves are calculated by numerically integrating a modified form of the Laplace-Young equation. These curves can be computed for any portion of the meniscus out to any desired radial

position. For 25 radial increments calculations were made at the outside 3 to 5 increment positions.

(2) From comparisons of the computed and experimental curves, optimum values of γ and $\sin\phi$ are found by computing the surface tension from the net weight of fluid held between the meniscus and the zero curvature datum plane and by minimizing the standard deviation between the heights of the computed and experimental menisci.

Acceptable surface tensions from the above procedure were determined by placing limitations on the size of the height standard deviation and the variation $\sin\phi$ at the minimum standard deviation from an "adjusted" experimental sine curve. Secondary restrictions were placed on results when no acceptable minima could be obtained. For water only one of the five menisci produced acceptable minima; however, the secondary restricting methods produced very acceptable surface tensions. For mercury seven of the ten menisci produced acceptable minima. The average surface tension found at these minima is reported above. The averages from the secondary methods deviated by as much as 13 dynes/cm from the above result, and the 95% confidence intervals for these averages were considerably greater.

The techniques developed for meniscus analysis should be applicable to frozen menisci of alloys, elements, and compounds if they freeze at nearly a constant temperature. The methods of restricting the computational results should throw out menisci that are unacceptably distorted on freezing.

NOMENCLATURE

F_{1n}	Normal component of surface tension force at inside of radial increment, dynes.
F_{2n}	Normal component of surface tension force at outside of radial increment, dynes.
g	Acceleration due to gravity, cm/sec ² .
m	Number of radial increment. $0 \leq m \leq N$.
N	Maximum number of radial increments.
P_0	Pressure in Fluid 2 at meniscus interface with $r = 0$, dynes/cm ² .
P_t	Pressure in Fluid 2 immediately above meniscus at radial position r , dynes/cm ² .
P_{datum}	Pressure at zero curvature datum plane. The pressures in Fluids 1 and 2 are equal at the level of the datum plane, dynes/cm ² .
P_b	Pressure in Fluid 1 directly below meniscus at radial position r , dynes/cm ² .
r	Radial distance, cm.
Δr	Radial increment equal to R/N , cm.
R	Maximum useable radius of meniscus, cm.
s	Sample standard deviation between calculated and experimental heights at all N radial positions, cm.
s_7	Sample standard deviation between calculated and experimental meniscus heights at outside seven radial positions, cm.
V_r	Volume of fluid between meniscus, datum plane, and radial position, r , cm ³ .
W	Weighting factor used in relaxation calculation procedure.
W'_{exp}	Net weight of fluid between experimental meniscus and horizontal plane tangent to meniscus at $r = 0$, gms.
W_{tot}	W'_{exp} plus net weight of fluid between horizontal tangent plane and datum plane, gm.
z	Height of meniscus above datum plane at radial position r , cm.
z_0	Height of meniscus above datum plane at $r = 0$, cm.
$(z_{m-\frac{1}{2}})_n$	n th iterated value of $z_{m-\frac{1}{2}}$, cm.

NOMENCLATURE (continued)

$(z_{m-\frac{1}{2}})_{\text{cal}}$	Values of $z_{m-\frac{1}{2}}$ as calculated directly by the numerical equations before being weighted, cm.
$z(r)$	Surface tension curve, z as a function of r . $z'(r)$ = 1st derivative at r ; $z''(r)$ = 2nd derivative at r .
Δz	Change in meniscus height from position $m-\frac{1}{2}$ to $m+\frac{1}{2}$, $= (z_{m+\frac{1}{2}} - z_{m-\frac{1}{2}})$, cm.
z'	Height of meniscus above horizontal plane tangent to bottom of meniscus at $r = 0$, cm.
$z'_{m-\frac{1}{2}}(\text{exp})$	Experimental meniscus height above horizontal tangent plane, cm.
$z'_{m-\frac{1}{2}}(\text{num})$	Numerically calculated meniscus height above horizontal tangent plane, cm.
ρ_1	Density of Fluid 1, gm/cm ³ .
ρ_2	Density of Fluid 2, gm/cm ³ .
θ	Angle between tangent to surface tension curve and horizontal line at radial position r , radians.
θ_0	Angle of tangent to curve at $r = 0$.
θ_1	Angle of tangent to curve at outside of 1st radial increment, radians.
θ_{exp}	Experimental angles calculated from $z'_{m-\frac{1}{2}}(\text{exp})$, radians.
θ_{adj}	Values of θ on a smoothed curve through $\sin\theta_{\text{exp}}$ points. Values from this curve when used for boundary condition of $\sin\theta$ give approximately a constant value of γ at all radial positions tested.
ϕ	Angle of tangent to meniscus curve at outside of meniscus. This is the boundary condition required in the numerical computation, radians.
ϕ_{min}	Value of ϕ at minimum in s or s_7 , radians.
ϕ_{as}	External tangent angle assumed for a computation, radians.
γ	Surface tension, dynes/cm.
γ_{as}	Surface tension assumed for a computation, dynes/cm.
γ_{cal}	Surface tension calculated by the net weight method, dynes/cm.

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APPENDIX

TABLE 6

SURFACE TENSIONS OF WATER

Meniscus No.	No. of Increments Included	At Minimum Standard Deviation								From Adjusted Experimental Sin Curve				
		All $z_{m-\frac{1}{2}}$ Included				Outside $7 z_{m-\frac{1}{2}}$								Deviation of Experimental Sin From Adjusted Curve
		γ d/cm	$\sin\phi$	s cm x 10^4	Within 0.015 Limit	γ d/cm	$\sin\phi$	s cm x 10^4	Within 0.015 Limit	γ d/cm	$\sin\phi$	s cm x 10^4	s cm x 10^4	
1	25	70.6	0.5341	8.1	yes	71.2	0.5328	6.25	yes	72.0	0.531	8.1	6.3	--
	24	71.9	0.4882	7.9	yes	75.0	0.4821	6.8	yes	71.1	0.490	7.9	7.7	- 0.025
	23	71.7	0.4482	7.8	yes	80.0	0.4360	8.5	no	71.2	0.4515	7.8	9.9	- 0.015
	22	65.7	0.4235	7.5	yes	73.1	0.4115	9.75	yes	70.6	0.415	7.7	9.8	+ 0.016
	21	58.7	0.4045	7.2	no	73.0	0.3785	9.2	yes	75.2	0.386	7.9	9.2	+ 0.012
	av	70.0				73.1				72.0				
2	25	~ 96	0.5719	23.2	no	78.0	0.6067	30.6	no	72.9	0.619	26.8	31.2	--
	24	no minimum				83.0	0.5475	22.2	no	73.0	0.567	26.7	32.2	+ 0.120
	23	no minimum				no minimum				73.2	0.523	25.6	33.4	0
	22	no minimum				no minimum				72.8	0.486	24.0	31.8	- 0.040
	21	no minimum				no minimum				71.8	0.452	22.2	31.1	- 0.060
	av									72.7				
3	25	no minimum				no minimum				74.0	0.621	21.6	33.1	--
	24									75.6	0.571	19.0	30.0	- 0.002
	23									75.5	0.530	15.7	24.7	- 0.065
	22									76.1	0.490	12.7	20.1	- 0.049
	21									77.8	0.452	10.3	16.4	- 0.064
	av									75.8				
4	25	no minimum				92.8	0.5790	24.0	no	72.1	0.624	28.4	31.2	--
	24					84.8	0.5472	24.4	no	71.5	0.575	29.0	32.2	+ 0.014
	23					no minimum				71.3	0.530	29.1	36.4	+ 0.012
	22									71.9	0.488	27.0	35.7	- 0.002
	21									72.7	0.451	27.2	35.7	- 0.022
	av									71.9				
5	25	no minimum				no minimum				70.7	0.587	9.8	15.2	--
	24									71.4	0.539	9.7	15.2	- 0.003
	23									71.9	0.496	9.8	16.0	+ 0.004
	22									72.2	0.457	8.2	14.6	- 0.003
	21									73.2	0.421	6.7	12.2	- 0.016
	av									71.9				

-35-

SURFACE TENSIONS OF MERCURY

Meniscus No.	No. of Increments Included	At Minimum Standard Deviation								From Adjusted Experimental Sin Curve				
		All $z_{m-\frac{1}{2}}$ Included				Outside of $z_{m-\frac{1}{2}}$				Deviation of Experimental Sin From Adjusted Curve				
		γ d/cm	Minus Sin ϕ	s cm x 10^4	Within 0.015 Limit	γ d/cm	Minus Sin ϕ	s cm x 10^4	Within 0.015 Limit					
1	26	480	0.5415	7.10	yes	460	0.5520	7.78	yes	488	0.5370	7.20	8.70	--
	25	521	0.4690	5.65	yes	499	0.4780	4.40	yes	488	0.4335	6.00	4.70	+ 0.0755
	24	521	0.4244	5.60	yes	482	0.4380	6.70	yes	487	0.4360	5.90	6.80	- 0.015
	23										0.395			0.000
	22										0.357			+ 0.009
	av	480				480				488				
2	25	512	0.5065	12.85	yes	545	0.4910	10.10	yes	515	0.505	12.9	10.7	
	24	504	0.4600	12.70	yes	539	0.4445	11.00	yes	517	0.453	12.8	11.4	0.000
	23	465	0.4265	12.18	no	515	0.4080	11.45	yes	513	0.409	12.6	11.5	- 0.019
	22										0.373			- 0.018
	21										0.341			- 0.033
	av	508				527				515				
3	25	471	0.5655	3.10	yes	466	0.5675	3.60	yes	454	0.5750	3.60	4.60	--
	24	464	0.5088	2.99	yes	454	0.5140	3.05	yes	455	0.5130	3.10	3.20	- 0.030
	23	469	0.4520	2.90	yes	455	0.4580	3.30	yes	453	0.4590	3.10	3.40	- 0.011
	22										0.4110			+ 0.010
	21										0.3690			+ 0.005
	av	468				458				454				
4	25	no minimum				no minimum				555	0.5650	19.2	33.0	
	24										0.5000			- 0.110
5	25	487	0.5325	10.9	yes	466	0.5451	14.15	no	496	0.5285	14.50	10.60	--
	24	461	0.4895	9.8	no	430	0.5065	13.35	no	499	0.4720	14.50	10.80	- 0.038
	23	449	0.4420	11.0	no	415	0.4595	12.80	no	498	0.4220	14.80	12.45	0.000
	22										0.3800			- 0.001
	21										0.3460			- 0.007
	av	487				----				499				
6	25	451	0.5660	5.00	no	435	0.5755	6.08	yes	426	0.5820	5.90	6.35	--
	24	465	0.4960	4.45	no	446	0.5060	5.75	yes	425	0.5180	5.95	6.65	+ 0.003
	23	489	0.4340	3.80	no	460	0.4460	5.30	yes	427	0.4605	5.75	6.60	- 0.0005
	22										0.4120			+ 0.002
	21										0.3660			- 0.003
	av	---				---				426				
7	24	468	0.5615	5.05	yes	466	0.5620	4.10	yes	477	0.5560	5.20	4.70	--
	23	472	0.4975	5.10	yes	470	0.4935	4.12	yes	478	0.4945	5.20	4.28	0.000
	22	486	0.4370	4.80	yes	497	0.4330	2.58	yes	479	0.4400	4.90	3.20	+ 0.042
	21										0.3930			- 0.019
	20										0.3510			- 0.001
	av	475				478				478				
8	25	no minimum				no minimum				385	0.5790	19.20	23.00	--
9	23	370	0.5255	4.35	no	379	0.5170	5.95	no	416	0.494	6.80	8.80	---
	22	349	0.4745	2.85	no	359	0.4680	3.08	no	416	0.431	7.90	9.55	- 0.014
	21	338	0.4202	2.55	no	350	0.4145	2.45	no	415	0.382	6.10	10.75	+ 0.011
	20										0.338			+ 0.017
	19										0.299			+ 0.026
	av	---				---				416				
10	26	482	0.5558	7.05	yes	495	0.5475	6.05	yes	503	0.546	7.45	6.20	--
	25	460	0.5100	6.75	no	475	0.5019	6.50	yes	503	0.490	7.50	7.25	- 0.010
	24	441	0.4670	6.40	no	470	0.4540	6.95	yes	502	0.442	7.90	8.60	+ 0.003
	23										0.398			+ 0.001
	22										0.360			- 0.007
	av	482				480				503				

-36-