

# THE DETERMINATION OF SURFACE TENSION BY SESSILE DROP MEASUREMENTS, WITH APPLICATION TO MERCURY

By G. M. ZIESING\*

[Manuscript received October 24, 1952]

## Summary

The error in the Worthington (1885) sessile drop equation, as an approximation to the exact equation from which it was derived, is found to be of the order of experimental errors in recent surface tension determinations. The source of error and origin of the optical band system observed when parallel light is used to define the summit of a sessile drop have been investigated. The band system is shown to originate in an interference phenomenon from the curved surface of the drop. Detailed descriptions are given of the cleaning and testing methods necessary for the preparation of mercury and glassware involved in the determination of the surface tension of mercury as  $484.9 \pm 1.8$  dyn./cm. A lower limit to the temperature coefficient of the surface tension was set at  $0.20$  dyn./cm. °C.

## I. INTRODUCTION

The determination of the surface tension of a liquid from observations made on a large (sessile) drop resting on a horizontal surface has the advantage that readings are taken only on the liquid surface and do not involve angles of contact of liquid and solid. The method depends on a very precise measurement of  $h$ , the vertical distance between the summit of the drop and the horizontal plane of maximum section (Fig. 1), and a reading of the diameter,  $2R$ , which enters into the correction factor to be applied to the well-known formula for a drop of infinite diameter (i.e.  $\gamma = \frac{1}{2}\rho gh^2$ ).

Workers applying this method to mercury and claiming a high degree of accuracy for their work have obtained values ranging from  $436.3$  to  $515$  dyn./cm. Apart from surface contamination of the mercury and the use of inadequate formulae these variations are probably due to errors in measuring  $h$ , caused firstly by the difficulty of setting on a highly reflecting surface such as the summit of the drop, and secondly by the fact that the microscope must be moved a distance  $R$  horizontally between setting on the "equator" and on the summit. Burdon (1932) discussed these points and values for the surface tension of mercury in more recent papers have been in much closer agreement. In his work, as well as the author's, the mercury drop rested on a slightly concave quartz disk enclosed in an apparatus made of clear silica (Fig. 3) having plane circular windows for illumination and observation. The plane of maximum section is defined precisely by the highly astigmatic reflection in the drop of a

\* Department of Physics, University of Adelaide; present address: Department of Supply, attached to Royal Aircraft Establishment, England.

distant small light on the same horizontal level, as used by Richards and Boyer (1921).

To define the summit Burdon set up a small light at the focus of a large lens of good quality at some distance on the far side of the apparatus so that the drop was silhouetted in the horizontal beam of parallel light. The reading microscope, resting on an accurately plane and horizontal slab of glass, was set on the equator and then pushed forward to focus on the summit. For the present work the apparatus has been modified to include a pointer fixed just above the position of the centre of the drop, so that the reading on the top of the drop is taken by setting midway between the point and its image in the surface,

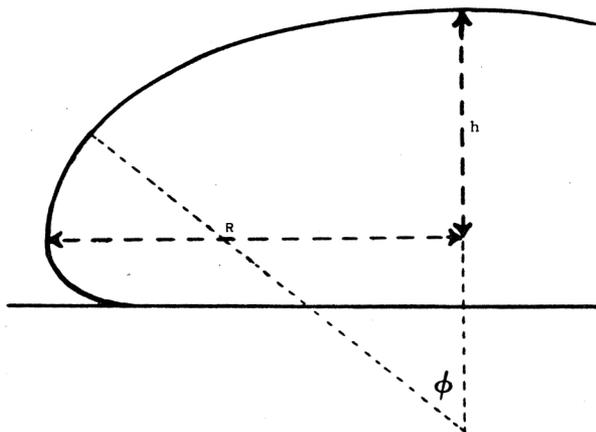


Fig. 1.—Section through sessile drop on horizontal plate.

as in the work of Bradley (1934) and Kemball (1946). Finding  $R$  to the required accuracy offers no difficulty. The present paper shows that modern technique warrants the use of a formula more accurate than the approximation used by previous workers in calculating the surface tension from their measurements. It also deals quantitatively with the optical interference fringes seen above the drop in the parallel beam of light and made use of by Burdon in setting on the summit. An account is given of a redetermination of the surface tension of mercury and its temperature coefficient.

## II. FORMULAE APPLIED TO SESSILE DROPS

In recent determinations (Cook 1929 ; Kernaghan 1931 ; Burdon 1932 ; Bradley 1934 ; Kemball 1946) of the surface tension of mercury by measurements of sessile drops it has been customary to use the equation

$$\gamma = \frac{1}{2}[\rho g h^2 \times 1.641R / (1.641R + h)], \quad (R > 2 \text{ cm.}) \quad \dots \quad (1)$$

where  $\gamma$  = surface tension in dyn./cm.,

$\rho$  = density of mercury in g./cm.<sup>3</sup>,

$g$  = acceleration due to gravity,

$h$  = height of the drop measured above the plane of maximum section,

and  $R$  = radius of the drop at the plane of maximum section (Fig. 1).

The equation originally given by Worthington (1885) is

$$\gamma = \frac{1}{2}\rho gh^2 + 2\gamma h(1/b - 1/3 \cdot 282R), \dots\dots\dots (2)$$

where  $b$  = radius of curvature at the summit of the drop.

The Worthington equation is itself an approximate form of the exact equation

$$\gamma = \frac{1}{2}\rho gh^2 + 2\gamma h/b - \gamma \int_0^h (\sin \varphi/x) dx, \dots\dots\dots (3)$$

where  $\varphi$  is the included angle between the axis of revolution and the normal to the surface (Fig. 1). Calculation shows that, for a drop of mercury 5.0 cm. in diameter, neglecting the value of  $1/b$  causes an error of 0.04 per cent. and that equation (1) gives a value differing by 0.23 per cent. from that given by equation (3). The total effect is that values calculated using equation (1) are 0.27 per cent. (or 1.2 dyn./cm.) lower than those derived from (3). Nevertheless recent workers (Kemball 1946), whose measurements warrant the claim of 0.3 per cent. as their maximum error, have in fact used equation (1) thus involving a constant error approximately equal to the total estimated error.

It would appear that all results of workers using the sessile drop should be increased by at least 1 dyn./cm.

### III. OPTICAL FRINGES OBSERVED ABOVE SESSILE DROPS

The method of using parallel light to define the summit introduces an error of 0.001 cm. due to the presence of what Burdon (1932) called "diffraction bands" above the liquid surface when viewed through the reading microscope. The nature of these diffraction bands and the magnitude of the resultant error in definition of the summit are discussed below.

Preliminary comparison of the parallel light method and the pointer reflection method of setting on the summit showed that the bands did not originate from the true summit of the drop, but from some vertical plane either on the near side or the far side of the summit. The plane of origin could be controlled by small variations of the angle of incidence of the parallel light on the drop, but, in spite of a fine control of movement, it was impossible to find a band system originating from the vertical plane through the summit of the drop.

Since a similar dependence on the angle of incidence was observed when the parallel light was replaced by light from a pinhole source, the phenomenon is attributable to the small departure from true parallelism which occurs with any optical system. The resultant error in  $h$  depends on the size of the drop on which the setting is made.

Apparently the origin of the unequally spaced optical fringes has not hitherto been described, apart from Burdon's reference to "diffraction fringes". The fringes are characteristic of a liquid surface. The band spacing varies with variation of drop size, increasing as the drops become larger, which is contrary to measurements on diffraction fringes carried out by Arkadiew (1913)

and repeated in this laboratory. The fringe spacing should be independent of change in radius of curvature of the object if the fringes are due to diffraction. A sharp edge, such as that of a razor blade placed normally to the beam in place of the mercury drop, produced no fringes if the microscope was correctly focused on the edge.

The knowledge that the bands or fringes being observed were actually formed in the same plane as the observed summit of the drop, a fact not explainable on normal diffraction theory, prompted further investigation.

A 3 in. optical flat, plane within  $\lambda/15$ , was set up horizontally with its upper surface in the position formerly occupied by the summit of the mercury drop, and with similar lighting it gave rise to an equally spaced system of fringes as in the arrangement known as Lloyd's single mirror (Fig. 2). In such an arrangement the centre of the optical pattern is displaced from the plane of the optical

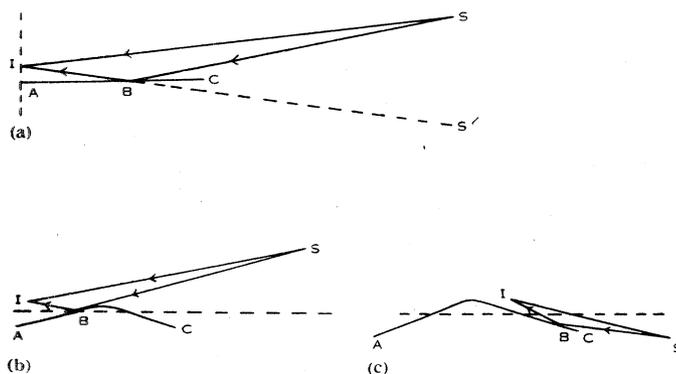


Fig. 2.—Interference occurs at *I* between the incident and reflected rays from *S*, either a distant pinhole, or with imperfectly parallel light.

- (a) From truly horizontal and flat surface (Lloyd's mirror);
- (b) From far side of curved surface;
- (c) From near side.

flat due to the phase reversal of the reflected ray. The plane of the optical flat is thus indefinite, as it has become the centre of a dark band. If the plane of the flat is taken as the edge of the dark band, an error of half a bandwidth (0.0008 cm.) is involved. The occurrence of the fringe system in the plane of the observed summit of the drop still required elucidation.

Since the upper surface of a sessile drop is not plane but has a large radius of curvature dependent on the drop size, the possibility of interference fringes from a curved reflecting surface was investigated.

In a paper entitled "The diffraction of light by cylinders of large radius", where the maximum value of the radius was 1.5 cm., Basu (1918) considered the explanation of fringes formed when the focal plane of the observing instrument

coincided with the edge of the cylinder. A simple interference theory satisfactorily accounted for his observed fringe spacing, which obeyed a law

$$x = \frac{3}{4}(2R)^{1/3}(n\lambda)^{2/3}, \quad n=1, 2, 3 \dots$$

where  $x$ =fringe spacing from minimum to minimum,

$R$ =radius of the cylinder,

and  $\lambda$ =wavelength of the light used.

If the liquid drop is considered as a cylinder of radius  $b$ , the radius of curvature at the summit, reasonable agreement between predicted and measured values of fringe spacings was obtained as shown in Table 1.

TABLE 1  
RESULTS USING A WATER DROP OF RADIUS 3 CM.  
Temperature=25 °C.,  $h=0.3996$  cm.,  $b=R=940$  cm.\*

Fringe number ..	1	2	3	4	5
Actual spacing.. ..		0.0070	0.0058	0.0046	0.0042
Predicted spacing ..	0.0141	0.0082	0.0072	0.0062	0.0051

\* Calculated by the formula of Laplace (1806) or Mathieu (1883).

The accuracy was limited as the fringe system did not originate exactly at the summit, which would itself give a lower value for  $R$  ( $b$ ) and hence better agreement. Again, as  $R$  becomes very large the theory underlying the above equation becomes inapplicable as the finite size of the source limits the definition of a point as the edge of the cylinder. The formula predicted the increase of band spacing with increase of drop size, since the radius of curvature increases as drop size increases.

The fact that the fringes originated in an interference phenomenon and not in diffraction was further confirmed by the effect of small vibrations on the pattern. Minute ripples on the surface, insufficient to cause noticeable movement of the liquid plane, caused the outer fringes to pulsate quite noticeably, owing to the rhythmic variation of angle of the reflected light as the disturbance crossed the surface.

The two errors in the parallel light method were in opposition, the fringe error giving a constant high value to  $h$ , while the error due to the plane of origin of the fringes varied with drop size. In the present experiments, for a water drop of radius 3 cm., the effects cancelled out and no error existed between the parallel light method and the pointer reflection method. For smaller radii the error involved was negative, while at larger radii the error was positive, the exact amount being uncertain to a degree determined by the accuracy of the theory applied above. The direction and magnitude of the error were experimentally confirmed. Thus the parallel light method is unreliable for accuracy beyond 0.001 cm. in measurement of  $h$ .

When using the pointer reflection method the error in definition of  $h$  is limited to observational error. Several papers (Taylor and Alexander 1944; Wheeler, Tartar, and Lingafelter 1945) have been published in which the technique applied in the pendant drop camera has been used for sessile drops within the range of Bashforth and Adams's (1883) five figure tables of calculation.

If sufficient refinement can be introduced to either or both of these experimental arrangements, the order of accuracy will be beyond that of existing measurements and detailed knowledge of the surface tension variation of mercury at higher temperatures than previously measured should become possible.

#### IV. THE SURFACE TENSION OF MERCURY

Following preliminary experiments with a pendant drop camera in which it was not possible to obtain consistently repeatable results owing to the lens in use, the determination of the surface tension of mercury was made by means of large sessile drops in the silica apparatus formerly used by Burdon (Fig. 3). This apparatus was modified by the inclusion of a fixed pointer mounted within 0.001 cm. of the estimated position of the summit of a drop of mercury 5.0 cm.

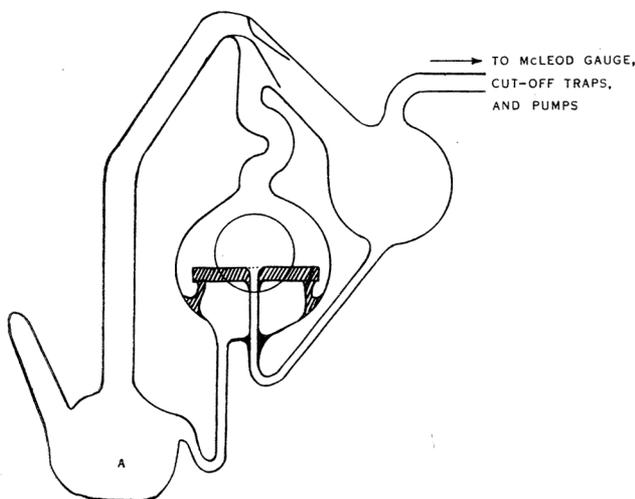


Fig. 3.—The silica apparatus.

in diameter at 25 °C. The vacuum apparatus consisted of a backing pump, mercury diffusion pump, liquid air trap, Pirani gauge, and mercury trap to isolate the greased side of the system from the other side, which comprised a McLeod gauge, charcoal trap, and silica measurement apparatus. A graded Pyrex-to-silica seal was made between the McLeod gauge and the charcoal trap. Provision for the inlet of clean dry gases was made near the diffusion pump such that all gas first passed through the liquid air trap. Each section of the vacuum apparatus was cleaned in chromic acid, washed in conductivity water (conductivity  $< 3 \times 10^{-6}$  mhos), and dried before sealing together. No grease was applied to taps or cone joints until just before final sealing on of the main silica apparatus.

Special attention was paid to the cleaning of all glassware used in either the main or subsidiary operations. The general cleaning of all glassware used in subsidiary operations and not in contact with purified mercury followed the usual procedure of using tongs, washing in hot chromic acid, and rinsing in clean water. Two simple visual tests for cleanliness were applied to all glassware.

For the first, an unbroken water film indicated freedom from gross contamination. In the second test the article was tilted and the absence of an ascending water ridge known as the "Burdon" or "plate" ridge indicated the absence of partial contamination on the water surface covering the article (Burdon 1926; Satterly and Mills 1927; Satterly and Turnbull 1929; Satterly and Collingwood 1931*a*, 1931*b*; Satterly and Stuckey 1932; Satterly and Givens 1933). When apparatus was required to be especially clean, the well-known technique of steaming was used. However, pilot tests had to be maintained on this process to safeguard against the possibility of airborne fatty contamination becoming interdispersed with the steam and coating the apparatus being steamed.

Where rapid drying was required, glassware was suspended on clean glass supports in a small silica oven, a process which was shown to be satisfactory.

The main silica apparatus was washed for 3 hr. in freshly prepared hot chromic acid, with acid being continually rinsed through it. The excess acid was washed off by 25 complete changes of conductivity water (conductivity  $<2.5 \times 10^{-6}$  mhos). The apparatus was steamed for 3 hr., dried in the silica furnace, and attached to the vacuum apparatus, which was then pumped and flamed for 9 hr. to remove as much adsorbed water vapour as possible.

The cleaning of the experimental mercury started with the preliminary experiments and continued until the vacuum apparatus had been completed. The starting sample was 400 cm.<sup>3</sup> of stock mercury which had been freshly distilled at 200 °C. in a current of air. This was then passed through a series of two nitric acid/mercurous nitrate towers many times, being collected each time in cleaned and steamed glassware. The sample was then agitated in shallow Pyrex dishes under conductivity water to which pure sodium peroxide was continually added in small quantities. This final process occupied 60 hr. The purity of the final sample was tested by the spreading of conductivity water on a newly formed surface as outlined by Burdon (1926).

Since there is no adsorption of mercury by water or vice versa, Antonoff's law for the case of pure water on mercury reduced to the statement that no spreading would occur provided no ions were present in the water to become attached to the mercury surface and act as anchorages facilitating spreading. With water of known purity, the test was very sensitive as regards mercury purity. Conductivity water (conductivity  $<2 \times 10^{-6}$  mhos) did not spread on the initial air distilled sample, nor did it spread on the sample obtained from the acid towers. After 18 hr. under sodium peroxide, limited spreading occurred, becoming a maximum after 60 hr. when water with conductivity  $<1.4 \times 10^{-6}$  mhos spread to cover a circle of diameter 5.9 cm. in 3 min. This drop eventually covered the whole area of the petri dish (except for the curved edge (Burdon 1926)) before evaporating. Exposure of the mercury surface, protected from dust, to the air for half an hour did not alter the rate of spreading. These tests indicated a high standard of purity.

During these tests several observations previously made by Burdon were confirmed. Mercury was very liable to pick up contamination (possibly sodium ions) from dishes which had been thoroughly cleaned and steamed. Quite often conductivity water would not spread on the first mercury surface formed in a

clean dry dish, but the second surface formed in the same dish after rinsing with mercury was perfect, with spreading equal to the best tests performed. As Burdon had shown, adsorbed sodium ions prevented the spread of water on mercury, so that all mercury was stored in silica flasks which did not introduce this contamination.

With this cleaning complete the vacuum apparatus was filled with dry argon, opened, and the clean dry mercury poured into the reservoir chamber (A, Fig.3) from a special flask, constructed so that all mercury delivered came from beneath the free surface in the flask, ensuring absence of contamination. When the apparatus was resealed the argon reduced the risk of mercury oxidation due to the high temperature flame used.

At this stage the error introduced by the observation window not having truly parallel faces, mentioned by Kemball (1946), was finally checked. The wedge angle was  $1.0 \times 10^{-3}$  rad., which for the apparatus in use meant that the measured value of  $h$  was too high by 0.0011 cm.

TABLE 2  
EXPERIMENTAL ERRORS

Type of Error	Error in $h$ (cm.)	Error in $\gamma$ (dyn./cm.)
Height of the lamp defining the equator..	0.0001	0.3
Artificial horizontal plane .. .. .	0.0001(2)	0.4
Diameter of the drop .. .. .	—	0.1
Sum of errors .. .. .		0.8

Mercury was distilled around the apparatus for several days at gas pressures of less than  $10^{-5}$  mm., which, according to the values of Taylor and Hulett (1913), were sufficiently far removed from the critical pressure for oxide formation to avoid the production of an oxide layer. When the final formation of a sessile drop had been made by distilling mercury from the reservoir chamber, with a small bunsen flame, a thermostat chamber maintaining a constant temperature of  $25.0 \pm 0.1$  °C. was placed around the apparatus. Measurement of the surface tension was made when the temperature as registered by a chromel-alumel thermocouple and potentiometer had been constant for 2 hr.

The distillation of mercury within the silica apparatus gave rise to large electrical charges on the sessile drops, which depressed the value of  $\gamma$  by as much as 6 dyn./cm. A small dental X-ray plant was used to restore the original, earth, potential, thus ensuring the normal value of the surface tension. This was always carried out as soon as the drop was at 25 °C.

The value of the surface tension remained constant for 24 hr. The mean of the 42 readings taken was  $483.6 \pm 1$  dyn./cm., when calculated by the Worthington (1885) formula. The experimental errors were as set out in Table 2 so that the final result was  $483.6 \pm 1.8$  dyn./cm. on the Worthington formula, which when corrected for the inaccuracies in that equation became  $484.9 \pm 1.8$  dyn./cm.

## V. THE TEMPERATURE COEFFICIENT OF THE SURFACE TENSION OF MERCURY

Two series of values of surface tension against temperature were measured using a specially constructed furnace surrounding the silica apparatus. Within the furnace the formation of sessile drops continued by slow distillation, so that the results represent the surface tension of a series of slowly formed new surfaces. However, the electrical charge on the drop was also being continually built up as the distillation proceeded, so that the measurements made were limited in value as exact measurements. They did have value in one sense, for, since the influence of charge was greater at low temperatures where electrical equilibrium was harder to maintain, the values set a lower limit to the temperature coefficient of the surface tension of mercury. The measured value was  $0.20 \pm 0.01$  dyn./cm. °C. over the range 20–220 °C. The uncertainty in this value demonstrates the limitation in measurement of a temperature coefficient by means of sessile drops, since, even under the best conditions, at any temperature the observational error is generally  $\pm 1$  dyn./cm., so that, unless the temperature range can be extended or an improved order of accuracy introduced, the value of the temperature coefficient has a lower accuracy of only 0.01 dyn./cm. °C. The use of a camera is the most promising method in both cases.

## VI. CONCLUSION

The experimental value for the surface tension of mercury was in good agreement with previous work as reviewed by Kemball (1946), especially when all sessile drop measurements in that review were corrected for the inaccuracy in the Worthington equation. The value for the temperature coefficient was a good lower limit to the values quoted by Kemball.

## VII. ACKNOWLEDGMENT

This paper describes part of the work for an M.Sc. thesis and was carried out, under the direction of Dr. R. S. Burdon, in the Physical Laboratory, Department of Physics, University of Adelaide.

## VIII. REFERENCES

- ARKADIEW, W. (1913).—*Phys. Z.* **14**: 832.  
 BASHFORTH, F., and ADAMS, J. C. (1883).—"An Attempt to Test the Theories of Capillary Action." (Cambridge Univ. Press.)  
 BASU, N. (1918).—*Phil. Mag.* **35**: 79.  
 BRADLEY, R. S. (1934).—*J. Phys. Chem.* **38**: 231.  
 BURDON, R. S. (1926).—*Proc. Phys. Soc. Lond.* **38**: 148.  
 BURDON, R. S. (1932).—*Trans. Faraday Soc.* **28**: 866.  
 COOK, S. G. (1929).—*Phys. Rev.* **34**: 513.  
 KEMBALL, C. (1946).—*Trans. Faraday Soc.* **42**: 526.  
 KERNAGHAN, MARIE (1931).—*Phys. Rev.* **37**: 990.  
 LAPLACE, P. S. (1806).—"Mécanique Céleste." 2me Supplém. au livre 10, p. 483.  
 MATHIEU, E. (1883).—"Théorie de la Capillarité." p. 137. (Gauthier-Villars: Paris.)  
 RICHARDS, T. W., and BOYER, S. (1921).—*J. Amer. Chem. Soc.* **43**: 274.  
 SATTERLY, J., and COLLINGWOOD, L. H. (1931a).—*Trans. Roy. Soc. Can.* **25** (3): 205.

- SATTERLY, J., and COLLINGWOOD, L. H. (1931*b*).—*Trans. Roy. Soc. Can.* **25** (3): 215.
- SATTERLY, J., and GIVENS, H. (1933).—*Trans. Roy. Soc. Can.* **27** (3): 145.
- SATTERLY, J., and MILLS, W. J. P. (1927).—*Trans. Roy. Soc. Can.* **21** (3): 277.
- SATTERLY, J., and STUCKEY, E. L. (1932).—*Trans. Roy. Soc. Can.* **26** (3): 131.
- SATTERLY, J., and TURNBULL, R. (1929).—*Trans. Roy. Soc. Can.* **23** (3): 95.
- TAYLOR, G. B., and HULETT, G. A. (1913).—*J. Phys. Chem.* **17**: 565.
- TAYLOR, H. J., and ALEXANDER, J. (1944).—*Proc. Indian Acad. Sci. A* **19**: 149.
- WHEELER, O. L., TARTAR, H. V., and LINGAFELTER, E. C. (1945).—*J. Amer. Chem. Soc.* **67**: 2115.
- WORTHINGTON, A. M. (1885).—*Phil. Mag.* **20**: 51.