SURFACE TENSION OF MERCURY

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Abstract

Consistent values for the surface tension of mercury in a high vacuum (air pressure less than 1.2×10^{-5} mm Hg throughout the period of experimentation), ranging from 438.4 ± 0.3 dynes per cm at 12.5°C to 423.9 ± 0.6 dynes per cm at 67°C, have been found by a modified flat-drop method. In evaluating them Worthington's equation

$$\sigma=\frac{(K-k)^2\rho}{2}\cdot\frac{1.641\,L}{1.641\,L+(K-k)}$$

was used. The temperature gradient, determined from the best mean straight line through the experimental points, is 0.3015 dyne per cm per degree. Hence the average value of k, in the Eötvös relation, was found to be 1.82. Reproduction of concordant results at intervals during a period of four months affords ample evidence of the thorough outgassing of the apparatus and is attributed to the great care used in securing relative perfection of details.

Introduction

Within the last decade many publications (between one and two on an annual average) have been concerned with the surface tension of mercury[1–21] and the greater number have dealt with its measurement in a vacuum. Hogness[9] and later Bircumshaw[2] have given excellent summaries of

[1] L. L. Bircumshaw, Phil. Mag. **2,** 341–350 (1926).
[2] L. L. Bircumshaw, Phil. Mag. **6,** 510–525 (1928).
[3] R. C. Brown, Phil. Mag. **6,** 1044–1055 (1928).
[4] R. S. Burdon and M. L. Oliphant, Trans. Faraday Soc. **23,** 205–213 (1927).
[5] S. G. Cook, Phys. Rev. **34,** 513–520 (1929).
[6] W. D. Harkins and E. H. Grafton, J. Am. Chem. Soc. **42,** 2534–2538 (1920).
[7] W. D. Harkins and W. W. Ewing, J. Am. Chem. Soc. **42,** 2539–2547 (1920).
[8] J. Hartman, Phys. Rev. **20,** 728–744 (1922).
[9] T. R. Hogness, J. Am. Chem. Soc. **43,** II, 1621–1628 (1921).
[10] T. Iredale, Phil. Mag. **45,** 1088–1100 (1923).
[11] T. Iredale, Phil. Mag. **48,** 177–193 (1924).
[12] T. Iredale, Phil. Mag. **49,** 603–627 (1925).
[13] M. L. Oliphant, Phil. Mag. **6,** 422–433 (1928).
[14] E. Perucca, Atti. Acc. Torino **57,** 81 (1921).
[15] E. Perucca, Atti. Acc. Torino **57,** 541 (1922).
[16] E. Perucca, Phil. Mag. **7,** 418–419 (1929).
[17] M. J. Popesco, Comptes Rendus **172,** 1474–1476 (1921).
[18] M. J. Popesco, Comptes Rendus **175,** 148–149 (1922).
[19] M. J. Popesco, Ann. de Physique **3,** 402–464 (1925).
[20] T. W. Richards and S. Boyer, J. Am. Chem. Soc. **43,** I, 274–294 (1921).
[21] Sauerwald and Drath, Zeits. Anorg. Chem. **154,** 79 (1926).

the work done in that line since 1898. Hence another summary just now is unnecessary. Suffice it to say that in spite of the great variety of methods painstakingly tried by eminent experimenters, the final results continue to be discordant even in single experiments, the values obtained ranging from "340 to 575 dynes per cm."[9] The true value of the surface tension of mercury cannot be as erratic as the above quoted discordant values would make it. Since the modified flat-drop method, used in finding the surface tension of sodium in a vacuum,[22] gave perfectly consistent results, it was decided to try it out on mercury. Some of its marked advantages are: a high degree of accuracy, perfect control of temperature conditions, facility in the production of fresh and uncontaminated surfaces, possibility of maintaining a high vacuum during a long interval of time, and independence of the contact angle.

Apparatus

The apparatus (Fig. 1) though similar in general outline to that used in the experiment on sodium,[22] differed in several details. The chief difference lay in the shape and size of the surface tension chamber *C* (Fig. 1). It was

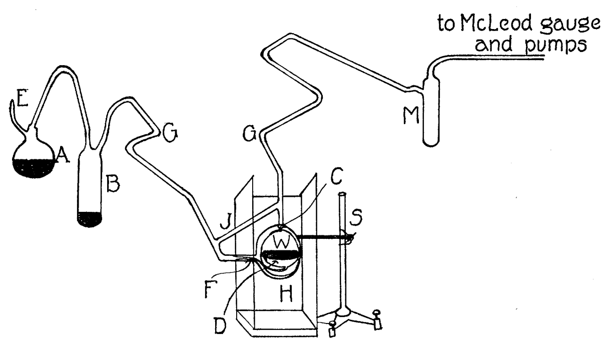

Fig. 1. Diagram of apparatus.

arranged in a horizontal position and though shorter it was wider and more roomy than the first. The plane circular glass window *W* (made to order by the Corning Glass Company) was fused into the end of the tube in preference to the side, in such a way as to render the entire disk optically available. The shallow cup *D* in which the flat drop of mercury was formed was ground with fine emery until all clip scars had disappeared. While similar in general appearance to the cup used for sodium it was wider (average outer diameter 6.04 cm) and deeper (maximum depth 1.2 cm). The difference existing between the various diameters was not more than 0.02 cm. As in the case of sodium, the mercury was introduced into the cup by means of a thick-walled capillary tube *F* which served to prevent too rapid introduction and consequent surging back and forth of the liquid. The tube *J* necessary for outgassing purposes prevented an accumulation of pressure behind the cup. To

[22] F. E. Poindexter and M. Kernaghan, Phys. Rev. **33**, 837–843 (1929).

procure a fine levelling adjustment at any time during the course of the experiment the cup chamber was tightly clamped and exteriorly cemented to a levelling stand S; and coiled tubes G one on either side of C were inserted into the apparatus. The presence of the flask M was merely an added precaution against contamination resulting from any possible overflow of mercury from the McLeod gauge. The entire piece of apparatus, including the McLeod gauge, was constructed of Pyrex glass, having only glass seals throughout.

Redistilled mercury was well shaken with chromic acid solution and then thoroughly rinsed with distilled water. It was next distilled in a current of air, then in a vacuum. This whole process was gone through twice before admitting it into the flask A. After sealing off E and thoroughly outgassing the apparatus the mercury was carefully distilled in a vacuum with a hand burner into the reservoir B from which it was distilled into the cup D as needed. The surface tension chamber was sufficiently roomy to allow the cup to be emptied and refilled without disturbing the apparatus.

The heater of the sodium experiment,[22] adjusted to suit the modification of the cup chamber, was used, hence the temperature conditions were those of the former experiment and hence within one degree of correct values. A frosted glass window arranged in the back panel of the heater made it possible to illuminate the drop from without and thereby get a sharp focus along the meniscus. Once this arrangement was perfected there was no difficulty in determining the exact top of the drop.

The combination of travelling microscope and dividing engine, used as a measuring device in the sodium experiment, was again employed. But instead of locating a number of points on the meniscus of the drop and then graphing the curve, it was decided to use a small carbon filament lamp for locating the top of the meniscus. It was mounted in a manner similar to that described by Richards and Boyer[20] and used by Iredale,[12] Cook,[5] and others. The small lighted lamp, attached to the telescope some distance behind it and on a level with it, was reflected from a spot on the maximum horizontal diameter as a tiny star which could be brought easily to a focus on the cross hairs. The vertical distance from the maximum horizontal diameter to the top of the drop ($K-k$ in Table I) could then be found by direct measurement. The diameter of the drop was measured directly by means of the dividing engine.

Data and Results

A summary of the results obtained from readings taken at intervals during a period of more than four months is given in Table I. The temperatures below 41° (second column) were room temperature in degrees centigrade. The number of separate readings of K (the top of the drop) and of k (the location of the star), from which $K-k$ was in each case determined, may be found in the third column. The values for the density quoted in column 4 have been taken from the Smithsonian Physical Tables.[23] For each set of

[23] Smithsonian Tables, Handbook of Chemistry and Physics, Thirteenth Edition, p. 746 (1928).

TABLE I. *Surface tension of mercury in a vacuum.*

No.	Temp. C	No. of Trials	Density ρ	Radius L cm	K-k cm	Uncorrected σ dynes	Corrected σ dynes	Date
1	12.5°	11	13.5646	2.87	0.2639	462.9±0.3	438.4±0.3	Nov. 26, 1930
2	14.°	20	13.5610	2.87	0.2638	462.4±0.3	437.9±0.3	Nov. 28, 1930
3	18.3°	15	13.5504	2.87	0.2635	461.0±0.3	436.6±0.3	Nov. 26, 1930
4	20.°	9	13.5462	2.87	0.2634	460.5±0.3	436.1±0.3	Nov. 28, 1930
5	21.°	9	13.5438	2.87	0.2633	460.1±0.3	435.7±0.3	Nov. 29, 1930
6	21.5°	15	13.5425	2.87	0.2633	460.0±0.3	435.7±0.3	Nov. 30, 1930
7	22.5°	15	13.5400	2.92	0.2632	459.6±0.2	435.7±0.2	Nov. 2, 1930
8	23.1°	13	13.5389	2.87	0.2630	458.9±0.3	434.6±0.3	Nov. 30, 1930
9	23.5°	11	13.5377	2.87	0.2629	458.5±0.3	434.2±0.3	Nov. 27, 1930
10	23.5°	10	13.5377	2.87	0.2630	458.8±0.6	434.5±0.6	Nov. 30, 1930
11	24.°	10	13.5364	2.87	0.2628	458.1±0.3	433.8±0.3	Nov. 27, 1930
12	25.1°	9	13.5337	2.91	0.2631	459.05±0.2	435.1±0.2	Oct. 12, 1930
13	25.2°	9	13.5335	2.92	0.2631	459.03±0.2	435.1±0.2	Oct. 11, 1930
14	25.8°	9	13.5320	2.91	0.2632	459.3±0.2	435.4±0.2	Oct. 11, 1930
15	26°	8	13.5315	2.84	0.2630	458.6±0.3	434.3±0.3	Sept. 25, 1930
16	28°	10	13.5266	2.84	0.2628	457.8±0.3	433.5±0.3	Sept. 25, 1930
17	31°	11	13.5193	2.89	0.2624	456.1±0.3	432.2±0.3	July 31, 1930
18	31°	12	13.5193	2.89	0.2624	456.1±0.3	432.2±0.3	Aug. 1, 1930
19	32.3°	10	13.5161	2.86	0.2624	456.0±0.3	431.9±0.3	July 29, 1930
20	32.3°	24	13.5161	2.86	0.2624	456.0±0.3	431.9±0.3	July 29, 1930
21	33°	9	13.5144	2.89	0.2624	455.95±0.3	432.1±0.3	July 30, 1930
22	33.3°	12	13.5136	2.85	0.2623	455.6±0.3	431.5±0.3	Aug. 5, 1930
23	34°	10	13.5119	2.91	0.2622	455.2±0.3	431.5±0.3	July 27, 1930
24	34.8°	10	13.5100	2.85	0.2622	455.1±0.2	431.0±0.2	Aug. 6, 1930
25	35°	10	13.5095	2.91	0.2621	454.8±0.2	431.1±0.2	July 26, 1930
26	35°	10	13.5095	2.91	0.2622	455.1±0.3	431.4±0.3	July 27, 1930
27	35°	9	13.5095	2.85	0.2621	454.8±0.3	430.7±0.3	Aug. 4, 1930
28	41°	12	13.4949	2.91	0.2619	453.6±0.2	429.9±0.2	Aug. 1, 1930
29	43°	8	13.4900	2.87	0.2618	453.1±0.3	429.0±0.3	Nov. 30, 1930
30	44°	9	13.4875	2.87	0.2617	452.6±0.3	428.6±0.3	Nov. 30, 1930
31	47.5°	7	13.4790	2.85	0.2616	452.0±0.3	428.1±0.3	Aug. 2, 1930
32	48°	13	13.4778	2.92	0.2615	451.6±0.3	428.1±0.3	July 27, 1930
33	48°	11	13.4778	2.92	0.2616	451.96±0.3	428.4±0.3	Aug. 1, 1930
34	48°	9	13.4778	2.85	0.2615	451.6±0.3	427.7±0.3	Aug. 5, 1930
35	49.5°	10	13.4741	2.85	0.2614	451.2±0.3	427.2±0.3	Aug. 6, 1930
36	54°	10	13.4632	2.85	0.2613	450.4±0.3	426.5±0.3	Aug. 2, 1930
37	57.5°	11	13.4547	2.85	0.2612	449.8±0.4	425.9±0.4	Aug. 6, 1930
38	64°	9	13.4389	2.85	0.2609	448.2±0.5	424.5±0.5	Aug. 2, 1930
39	67°	10	13.4317	2.84	0.2608	447.7±0.6	423.9±0.6	Aug. 2, 1930

readings two values for the surface tension are given. That under uncorrected value (seventh column) was found by means of Quincke's simple formula[24]

$$\sigma = \tfrac{1}{2}h^2\rho\cdot 980 \qquad (1)$$

(where σ and ρ are surface tension and density respectively; 980 cm per sec^2 is the value of the acceleration of gravity in Saint Louis.) The corrected values of σ (eighth column) were determined according to Worthington's equaton[25]

$$\sigma = \frac{(K-k)^2\rho}{2} + 2\sigma(K-k)\left\{\frac{1}{b} - \frac{1}{3.282L}\right\} \qquad (2)$$

[24] G. Quincke, Ann. d. Physik, **105**, 1–48 (1858); **139**, 1–89 (1870); **160**, 337–374 (1877).
[25] A. M. Worthington, Phil. Mag. **20**, 51–66 (1885).

(where $(K-k)=h=$distance from vertex to maximum horizontal diameter; $b=$radius of curvature at the vertex and $L=$maximum horizontal radius).

According to Worthington[25] for values of L greater than 2 cm the term $1/b$ is negligible. Therefore since in this experiment the minimum value of L was 2.84 cm it was at all times sufficiently large to justify the omission of $1/b$ from the equation, which consequently reduces to the form

$$\sigma = \frac{(K-k)^2\rho}{2}\cdot\frac{1.641L}{1.641L+(K-k)}\times 980. \qquad (3)$$

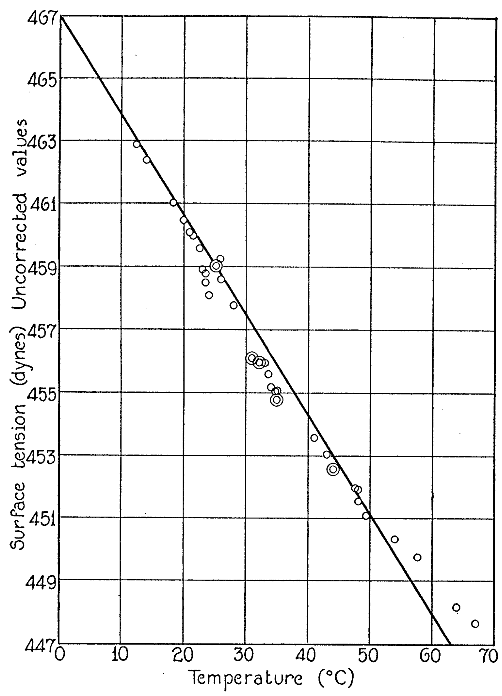

Fig. 2. Surface tension of mercury as function of temperature.

Hence to correct values computed from equation (1) we have only to multiply the result obtained by the correction factor

$$\left(1+\frac{K-k}{1.641L}\right)^{-1}$$

Since there was scarcely any appreciable variation in the size of the drops used, the correction factor reduced to either 1/1.055 or 1/1.056.

From the two surface-tension, temperature graphs (Figs. 2 and 3) it is evident that temperature variations gradually decrease as temperature increases. However, for values of T lower than 65°C the deviation of experimental points from a straight line is slight. Hence from the best mean straight line through the experimental points (Fig. 3) σ at 0° and at 63° was judged to be 442 and 423 dynes per cm, respectively. Hence the temperature gradient is 0.3015 dyne per cm per degree.

Upon differentiating with respect to temperature, the Eötvös relation $\sigma v^{2/3} = k(T_c - T)$ we get,

$$v^{2/3}\left(\frac{d\sigma}{dT}\right)_v + \frac{2}{3}\sigma v^{-1/3}\left(\frac{dv}{dT}\right)_\sigma = -k \quad (4)$$

(σ, v, T represent surface tension, volume of a gram atom, temperature respectively. T_c and k are constants.)

The Eötvös constant, k, was found at 20°C by substituting in Eq. (4) for $(d\sigma/dT)_v$ and for σ experimental values, and for v and $(dv/dT)_\sigma$ values

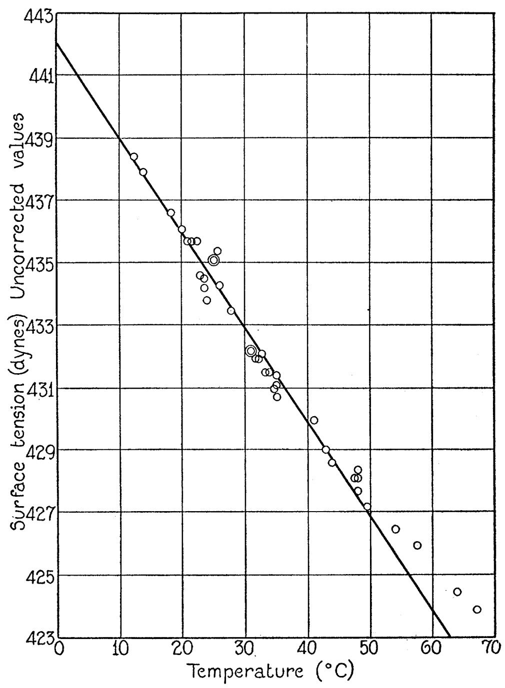

Fig. 3. Surface tension of mercury as function of temperature.

calculated from data given in the Smithsonian Physical Tables, as quoted in the thirteenth edition of Handbook of Chemistry and Physics.[23] The value found is 1.82.

Discussion

Every possible precaution was taken to procure absolute cleanliness. Boiling hot chromic acid solution was used to cleanse not only the entire glass apparatus (including the still used for distilling the mercury in a current of air), but also the beakers and the bottles into which the mercury was poured at any stage of experimentation: Several consecutive days were devoted to a thorough outgassing of the apparatus. During periods of four or five hours each, while the pump was running, the entire apparatus was kept at a high temperature by means of the heater and a hand burner. The thoroughness of the process was proven by the fact that the McLeod gauge registered stiction (a gas pressure less than 1.2×10^{-5} mm Hg) except when filtered air was purposely admitted into the apparatus. Occasionally over night the pressure rose to 4.6×10^{-5} mm Hg, but then the apparatus was again outgassed. No readings were recorded except when the McLeod gauge registered stiction.

The main purpose of this experiment was to get consistent values for the surface tension of mercury in a vacuum hence no perfection of detail that might lead to a higher order of accuracy was overlooked. To eliminate vibration of the mercury drop a special wall table was constructed. The difficulty experienced by Cook[5] in determining the exact position of K (the top of the drop) was obviated by keeping the drop enclosed in the heater, even when working at room temperature, and by illuminating it from without. As previously mentioned, for all readings recorded the top showed as a sharp dark line. The small lamp used for determining the point of vertical tangency was set at the same level as the center of the objective of the travelling microscope, by means of a reading telescope. The utmost care was used to keep it in that exact position for it was noticed that the least deviation from it caused a considerable difference in the readings of K and k. The same is true of the level position of the travelling microscope and the dividing engine.

A tenths thermometer, calibrated by comparison with a standard thermometer was throughout immersed in the heater to the same depth and at the same angle of inclination. Stem correction was, however, found to be negligible for temperatures lower than 70°C, i.e., for temperatures used in this experiment.

No set of readings was recorded until all details were brought to relative perfection. On the other hand no set of readings was discarded after that point had been reached, except in cases of fluctuating temperature.

On two different occasions a set of readings was taken in a vacuum (15 and 16; 19 and 20, Table I) the dish was partially emptied by violent shaking, filtered air was admitted and the apparatus was allowed to stand for a while. When again pumped to stiction the change in surface tension was merely that to be expected from variation in temperature.

Popesco[17,18,19] Iredale[12] and Cook[5] have determined the surface tension of mercury in a vacuum by the flat-drop method. However, the experiments of the first two differed from this experiment in some important details—to mention only a few: the method of forming the drops was essentially different; both used wax seals. Iredale was himself conscious that "the experimental conditions would be very much improved if such adhesives could be done away with." (reference 12, page 607) Both worked on drops too small (Popesco's was about 3.6 cm in diameter; and Iredale's ranged from 1.2 cm to 1.5 cm in diameter) to be considered perfectly flat. The values obtained by Iredale from eleven consecutive drops, at a temperature of 19.5°C, vary from 430 to 472 dynes per cm. Cook's flat-drop method is essentially the same as the one used in this experiment. But he has quoted only one value found for the surface tension of mercury in a vacuum; and that value seems abnormally high even though in the author's words "the measurements were very carefully checked." (reference 5, page 517). The apparatus of this experiment was as completely outgassed as his, but not once was a value any where near as high as his obtained. His readings of K and k were taken with a cathetometer the vernier of which "reads directly to 0.02 mm and under the microscope can be estimated to 0.01 mm" (reference 5, page 516). The travelling microscope used in this experiment records to 0.002 mm.

The dates given in the last column of Table I show how well conditions were reproduced. In turn the consistent values obtained seem to point to the fact that, more than a new theory, we need a high vacuum, uncontaminted surface and utmost care in manipulation.

This work was suggested by and carried on under the guidance of Doctor F. E. Poindexter in the laboratories of Maryville, Corporate College of Saint Louis University. I wish to thank him for his generous cooperation. I wish to thank both him and Rev. Professor James I. Shannon for their many helpful and encouraging suggestions. Thanks are also due to Brother A. Zeller for his kindness in rearranging the heater to fit the remodelled apparatus.