SURFACE TENSION OF MERCURY IN THE PRESENCE OF GAS UNDER VARYING PRESSURES

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Abstract

Quincke's method with Worthington's correction was used. Contrary to the accepted values the maximum surface tension of mercury (515 ± 7 dynes/cm at 31°C) is reached when only mercury vapor is present. A surface freshly created in a gas at 760 mm has a high initial tension approaching that when the surface is created in mercury vapor. The tension falls as the gas is adsorbed until an equilibrium value for a given pressure is attained. As the pressure is reduced the equilibrium value rises to a maximum which depends upon the nature of the gas. For instance, this maximum tension for mercury-hydrogen occurs at the critical pressure of 2.8 mm. If the pressure is lowered to stiction the tension remains unchanged so long as the mercury is not agitated beyond a certain amount. This maximum value for mercury-hydrogen is 441 dynes/cm which is less than the mercury-mercury vapor value of 515 dynes/cm. If the mercury-hydrogen is violently agitated when the pressure has been reduced to stiction the tension approaches 515 dynes/cm, the mercury-mercury vapor tension. Vibrating drop methods tend to give the vacuum value of the surface tension even when a gas is present at atmospheric pressure.

I. Introduction

According to Professor Jauncey of Washington University it has been found that the surface tension of a mercury surface produced in a vacuum (i.e. except for the mercury vapor above the liquid mercury) is greater than the tension of a mercury surface produced in a gas such as air. However, if the surface is first produced in a vacuum and then a gas is admitted the tension does not immediately become that of a mercury surface produced in the gas. On the other hand, Freundlich[1] in his book on "Colloid and Capillary Chemistry" quotes J. Stoeckle[2] as stating that the value of the tension of mercury in a vacuum is less than the initial value of the tension of mercury surfaces created in the presence of gases. Thus there seems to be two distinct experimental findings in regard to the tension of mercury in the presence of gases. Since the experiments quoted by Freundlich were done before 1900 and since vacuum technique has been much improved since then, it seems worth while to investigate this matter anew and hence this present research.

II. Description of Apparatus and Experimental Methods

The apparatus as first used was designed and built by Dr. F. E. Poindexter, who had previously used a similar device in investigating the surface tension of melted metallic sodium.[3] Slight changes have been made as the

[1] H. Freundlich, Colloid and Capillary Chemistry (translated by H. S. Hatfield), p. 82.
[2] J. Stoeckle, Wied. Ann. **66,** 499 (1898).
[3] F. E. Poindexter, Phys. Rev. **27,** 820 (1926).

experiments progressed. A glass cup A, Fig. 1, forms the top of the glass tube B, which tube passes through the wall of the cup chamber C to which it is hermetically sealed. The upper edge of A is ground true and smooth with emery and the inner edge lapped so as to present a truly circular rim free from chipped places caused from grinding the top edge. A plate glass window D, with its center at the level of the top of the drop and vertical in position is sealed to the side of the cup chamber as shown. The cup chamber extends a considerable distance below the cup A forming a catch-well for mercury spilled from A so that the cup may be refilled without disturbing the apparatus. The tube B extends upward outside the cup chamber and reenters it at F. This tube has a constriction at G as shown, the purpose of which will be explained later. Into the vertical part of the tube B the tube H is sealed. This tube H is inclined upward, the higher end leading to the vacuum pumps.

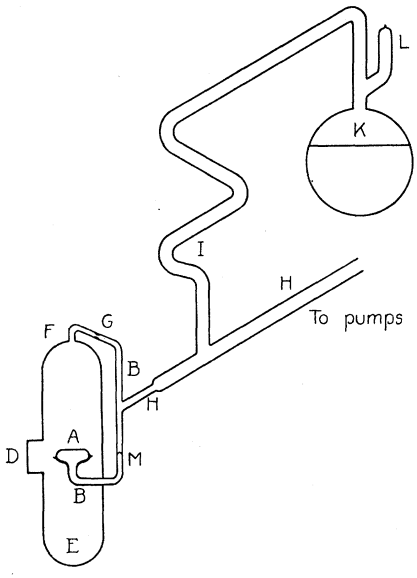

Fig. 1. Diagram of apparatus.

Extending upward from H is a condenser tube I, coiled for compactness, leading from the flask K of 250 cm^3 capacity. A filling tube L enters the flask. This tube is sealed off after filling the flask with mercury. This apparatus as well as the mercury vapor pump and the McLeod gauge are entirely of Pyrex glass all fused together into one piece.

Each unit of the apparatus before assembling was cleaned in boiling chromic acid, washed with distilled water and dried with heated and filtered air. The mercury was aerated for several hours by drawing air through it by means of an aspirator. It was then treated successively with caustic soda, nitric acid, chromic acid and distilled water. It was then distilled and redistilled directly into the flask K through the tube L which was at once sealed off. The whole apparatus was then thoroughly out-gassed by exhaustion

while a blast flame was played over the entire apparatus including the mercury vapor pump and McLeod gauge. This out-gassing process was repeated frequently during the progress of the experiments.

When it is desired to examine a drop of mercury for its surface tension the apparatus is either exhausted or filled with any gas in the presence of which it is desired to generate the mercury surface to be examined. Heat is then applied to the flask K and mercury distilled over. This condenses in the condenser I, runs down through H into B, then upward into the cup A filling it from the bottom and producing a new surface as the mercury fills the cup and stands above its edge due to its surface tension. In order that there may still be no possibility of this surface being contaminated from contact with the glass it is customary to distill over an excess of mercury allowing it to spill into the well E thus assuring a perfectly fresh and uncontaminated surface on the mercury in the cup.

The drop in A is viewed through the telescope of a cathetometer. Beside the telescope is placed a lamp with a horizontal slit in front of it. This slit

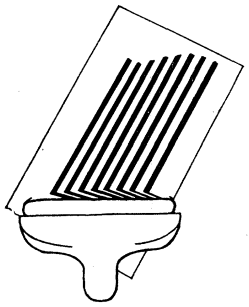

Fig. 2. Mercury drop with background.

is on the same level as the axis of the telescope. When the axis of the telescope, the slit and the point on the curved surface of the drop at which a tangent plane to the drop is vertical are all in the same plane, a bright star is observed at the cross wires of the telescope.

The exact location of the top of the drop is much more difficult. A clean mercury surface is a practically perfect, first-surface mirror, especially when viewed, as in this case, tangentially. For this reason it perfectly reflects any back-ground that can be placed behind it and so, at the extreme top, perfectly blends with the background making the top of the mercury indistinguishable from the background. To overcome this difficulty a background ruled with alternate black and white lines was made and this was placed behind the mercury with the lines inclined at about 30° from the vertical. the angle formed between the parts of the lines visible above the mercury and their reflection is sharply marked as shown on the accompanying Fig. 2, and it was found that the location of the surface of the mercury can be read in the cathetometer within an accuracy of 0.01 mm and these readings can be consistently repeated.

When it is desired to clean all the mercury out of the cup so as to have entirely fresh mercury in the cup all that is necessary is to exhaust the apparatus to a fairly good vacuum and then let in air, or any other gas, rather rapidly. The constriction G prevents the gas from flowing freely into the chamber C through the top, thus producing considerable pressure on the mercury at M, blowing the mercury out of the cup.

III. Calculation of the Surface Tension

Quincke's[4] formula as corrected by Worthington[5] was used. With the approximations suggested by Worthington the formula for the tension, T, is

$$T/\rho = h^2g/2 + (2hTg)/\rho(1/b - 1/3.282L) \tag{1}$$

where ρ is the density of mercury, h is the difference between the equatorial line at the position where the mercury surface is vertical and the top of the drop, L is the radius of the equatorial circle and b is the radius of curvature at the top of the drop and g is the acceleration of gravity. Since in the present experiments $L = 2.4$ cm, we may discard the term containing b so that

$$T = \frac{h^2\rho g}{2(1+2h/3.282L)}. \tag{2}$$

These experiments were done in August with a temperature of 31°C, at which temperature the density of mercury[6] is 13.519 gm/cm³. In St. Louis $g = 980.0$ and the formula becomes

$$T = 6624h^2/(1+0.2538h) \tag{3}$$

As the vernier of the cathetometer reads directly to 0.02 mm and under the microscope can be estimated to 0.01 mm an error of 0.01 mm on each reading is assumed. Since each determination of h requires a reading both of the star and of the top the error in the value of h is twice this amount or ± 0.02 mm which at $h = 2.82$ mm gives an error in surface tension of ± 6.8 dynes/cm.

IV. Surface Tension in a Vacuum

After filling the flask K, Fig. 1, with mercury and sealing off L so that the whole apparatus, including the mercury-vapor pump, is one piece of hermetically sealed Pyrex glass, the pumps were started and when a high vacuum was reached a blast flame was applied to the whole apparatus so as to out-gas it thoroughly as described above. After the apparatus had cooled the vacuum was maintained at "stiction" and mercury distilled over till the cup was filled and overflowed.

Contrary to the results obtained by J. Stoeckle and G. Meyer,[7] the maximum surface tension was found to be that of mercury in a vacuum, i.e.,

[4] G. Quincke, Phil. Mag. **41,** 245 (1871).
[5] A. M. Worthington, Phil. Mag. **24,** 51 (1885).
[6] International Critical Tables **2,** 458.
[7] G. Meyer, Wied. Ann. **66,** 523 (1898).

mercury-mercury vapor, a value as high as 515 dynes/cm being obtained. It must be remembered, however, that this result is obtained only when all the conditions are at the limit of their perfection. The above is the maximum surface tension obtained during the whole course of these experiments. The measurements were very carefully checked. If less care is taken in outgassing a lower value of the tension is obtained.

V. Surface Tension in Various Gases

In order to obtain consistent results when the mercury was in contact with gases it was found to be very necessary to keep the surface free from vibration and extension. If a fresh mercury surface is generated in contact with a gas the tension is at first high approaching the value in a vacuum. The tension soon falls, as first noticed by Quincke,[8] till it reaches equilibrium with the gas at the existing pressure. If now the surface of the mercury be agitated beyond a certain amount, either by the addition of more mercury from below thereby stretching the surface, or by spilling some thereby rupturing the surface, there will occur an instantaneous rise in the surface tension, the extent of such rise in tension depending upon the kind of gas to

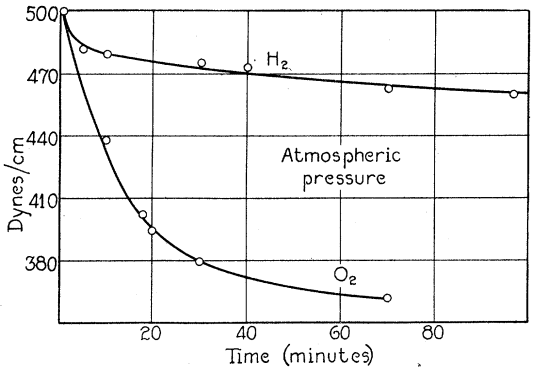

Fig. 3. Variation of surface tension with time from exposure to gas.

which the mercury is exposed and upon the amount of disturbance. This rise in tension is accompanied by the liberation of gas from the mercury in quantities measurable on the McLeod gauge as pointed out by Stoeckle who attributed it to a gas film condensed on the mercury surface. In one case the tension of mercury in contact with hydrogen at a pressure of 0.00015 mm remained constant at 421 dynes/cm over a period of 8 minutes. On spilling a drop from the mercury, however, the tension immediately rose to 473 dynes/cm and remained constant at this value for 14 minutes. Simultaneously the pressure of the hydrogen rose to 0.00048 mm.

After exhausting and thoroughly outgassing the apparatus, purified gas of the desired kind is admitted up to atmospheric pressure. Mercury is then distilled over into the cup A till it overflows, thus creating a fresh mercury

[8] G. Quincke, Pogg. Ann. **105,** 1 (1858).

surface in the presence of the gas. The distillation is then stopped and the surface tension observed as it lowers, approaching equilibrium. The curves of Fig. 3 show how the tension decreases with the time after a fresh surface has been produced in contact with hydrogen or oxygen at atmospheric pressure. During these observations great care was taken to keep the apparatus free from any mechanical disturbance.

The curves of Fig. 4 show the effect of exhausting the gas after the mercury has been standing in contact with the gas at atmospheric pressure for two or three hours. In these curves the readings at the various pressures were taken at intervals of time shorter than the time necessary for the equilibrium tension to be established at each pressure. For this reason no points are shown. The curves merely show the general trend. It will be noticed that reducing the pressure of the hydrogen had no effect on the surface tension till about 10 mm was reached when the tension suddenly began to rise. A similar effect is noticed in the case of CO_2 but the curve has a

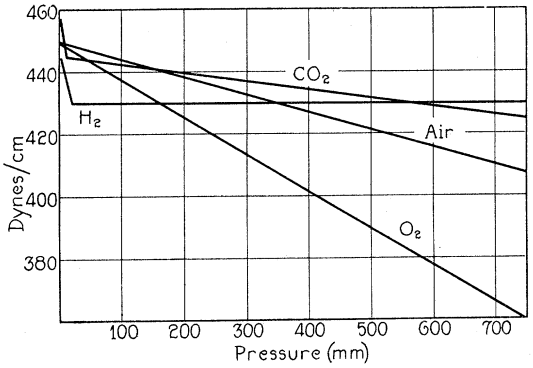

Fig. 4. Variation of surface tension as gas pressure is lowered.

considerable slope before reaching its critical pressure of about 6 mm. The tension when oxygen and air are the gases, on the other hand, begins to increase as soon as exhaustion begins so that if they have a critical pressure of this nature it is greater than 760 mm.

On decreasing the pressure below the critical pressures for the respective gases, the tension rises until a second critical pressure occurs below which no further rise in the tension occurs even when the pressure is lowered to stiction and kept at stiction for several hours. These first and second critical pressures together with the corresponding tensions are shown in Table I.

It must be remembered that the apparatus must be kept free from mechanical vibration in order to obtain these critical pressures. The final tension obtained is decidedly lower than that of a mercury surface produced in a vacuum.

Next, the apparatus was thoroughly exhausted and outgassed. While the vacuum is maintained mercury is distilled over from K, Fig. 1, into A till it piles up and runs over, thus creating a fresh mercury surface in a vacuum.

When the apparatus has assumed room temperature carefully purified gas of the desired kind is then admitted, either slowly or rapidly as required and the mercury in A observed through the cathetometer as described above, great care being taken to keep the apparatus free from vibration. The initial

TABLE I. *Critical pressures for mercury in various gases.*

Gas	First critical pressure (mm)	First critical tension (dynes/cm)	Second critical pressure (mm)	Second critical tension (dynes/cm)
Hydrogen	10	430	2.8	441
Carbon dioxide	6	445	3.5	455
Air	—	—	1.0	451
Oxygen	—	—	1.0	451

surface tension before admitting the gas was, as mentioned in section IV under the most favorable circumstances, about 515 dynes/cm but it could easily be brought to 491 dynes/cm with reasonable care. There was never observed the slightest tendency of the surface tension of the mercury to increase, even temporarily, upon admission of hydrogen, dry air, carbon dioxide, or oxygen whether the gas was admitted very slowly or rapidly enough to bring the pressure up to 760 mm in one minute. On the contrary, there set in at once, upon admission of the gas, a decline of surface tension

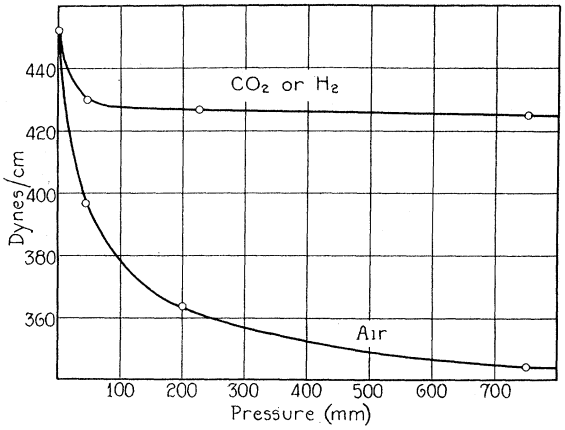

Fig. 5. Variation of equilibrium surface tension with gas pressure.

which varied in rapidity with the kind of gas used. Final equilibrium is reached only after long periods of time and is dependent upon the pressure and nature of the gas. At almost any pressure above stiction and below the second critical pressures of Table I, the tension finally comes to the values given in the last column of this table. At pressures below the second critical pressure for a gas the surface tension decreases from the vacuum value as the time from the instant of admission of the gas increases. The decrease of tension is accompanied by a decrease in the pressure of gas. As an example

the tension in hydrogen decreased from 495 dynes/cm to 484 dynes/cm in 20 minutes while the pressure decreased from 0.0037 mm to 0.0020 mm.

At pressures greater than the critical pressures, the equilibrium values of the tension for various pressures of carbon dioxide, hydrogen and air are shown in Fig. 5. Each point shown was obtained after allowing at least 13 hours for the tension to come to equilibrium at the pressure indicated. Because of these long intervals only few points are shown.

VI. Discussion

Contrary to the findings of Stoeckle the surface tension of mercury is found to be higher when the surface is produced in a vacuum than when the surface is produced in the presence of a gas. The explanation of Stoeckle's results is that even minute traces of gas lower the tension by about 50 dynes/cm below the true vacuum value. Further the vacuum value of 515 dynes/cm which was obtained in these experiments can only be obtained when a fresh surface is created in a vacuum made as perfect as possible by outgassing. The lowest pressure obtained by Stoeckle was 0.0004 mm and this is much too great to be considered as a vacuum. Further it has been found that if mercury has been in contact with a gas and then the gas exhausted the tension will not rise above about 455 dynes/cm no matter how low the pressure is made unless the surface is subjected to mechanical disturbance. If the surface is disturbed violently enough the tension will rise suddenly. Because of this fact, vibrating drop methods of measuring surface tension tend to give a value approaching that of a surface produced in a vacuum even though the vibrating drops are in the presence of a gas.

In conclusion the writer desires to thank Professor G. E. M. Jauncey for suggesting this research and Professor Ward of the Department of Chemistry for much valuable discussion regarding this problem.