ON THE SURFACE TENSION OF MERCURY.

By Charles Kemball.

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There still exists considerable uncertainty as to the exact value of the surface tension of mercury. This is a matter of some importance both for the comparison of the surface tension of metals and for the investigation of metal-vapour and metal-liquid adhesions. Again, the best method for determining such adhesions is as yet undecided. It is clear that some method avoiding a contact angle is desirable. The sessile drop method of measuring surface tension avoids this difficulty and has been employed extensively in the past, although the results of different workers have differed greatly. The present paper describes an apparatus for the measurement of the surface tension of mercury in vacuo or in the presence of vapours by the sessile drop method. Particular attention is paid to all possible sources of error.

The type of apparatus used by Burdon, in which mercury was distilled around a circuit in a high vacuum and the surface tension measured by the sessile drop method, was both accurate and clean. Even so the

value obtained (488 dynes/cm. at 25° C.) cannot be regarded as certain to within 1%. Other workers using similar methods obtained values ranging from 438-4 dynes/cm. at 12.5° C. (Kernaghan) to 515 dynes/cm. at 31° C. (Cook). Both Burdon and Porter agreed on the reliability of the sessile drop method and confirmed Worthington's equation (1) for drops over 4 cm. in diameter.

\[ \gamma = \frac{1}{2} \rho g h^2 \left( \frac{1}{r} - \frac{1}{4} \right) \]  

(1)

where \( \gamma \) = surface tension, \( \rho \) = density of mercury, \( R \) = maximum diameter of the drop and \( h \) = height from the maximum diameter to the vertex of the drop. Burdon suggested that the discrepancy between the results of different workers might be due to the difficulty in detecting the vertex of the drop. However, it seems unlikely that this cause alone could give rise to such great undetected errors.

The uncertainty in the surface tension of mercury has meant that there has been no criterion for judging the cleanliness of the mercury used in adsorption experiments with vapours. The extensive work of Cassel and Salditt on this subject, using the drop weight method, must be regarded with suspicion, as the surface tension recorded for their mercury was only 455 dynes/cm. at 50° C. Bosworth, using the same method for measuring the adsorption of fatty acid vapours, recorded a value over 20 dynes/cm. higher. For an accurate study of the adsorption of vapours on mercury it seemed therefore necessary to convert the Burdon apparatus into a form suitable for use with vapours, and to examine all possible sources of error. This might lead to the origin of former discrepancies and would give a datum line for further experiments on adsorption at a mercury surface.

The Apparatus.

Mercury from the distilling flask B was distilled through the asbestos lagged column C, and passed via the tube D and U-tube E to the cup A, which had a carefully ground rim slightly over 5 cm. in diameter. The...
temperature of the mercury was measured by a thermocouple placed in the recess in the bulb F, and after spilling from the cup the mercury completed the circuit by returning to the flask B. The entire apparatus shown in Fig. 1 was constructed of Pyrex, and sealed into one piece. The vacuum line entered the apparatus behind the mercury drop at G, and also at H (cf. Fig. 2; side view). The Pyrex window I, which was just over 3 cm. in diameter, was sealed with the minimum of heating into the tube J. The faces of the window had been ground optically flat. At K a tungsten electrode was sealed through the Pyrex to earth the mercury, which acquired a positive potential of as much as 2000 volts on rapid distillation. An air thermostat (indicated by the dotted line in Fig. 1) surrounded the mercury vessel, and a small heating coil was placed beneath the window I to prevent condensed mercury impairing observation. The portion of the tube D outside the thermostat was well lagged, as was the U-tube E which could be used to cool the mercury.

The location of the vertex of the drop was a matter of some difficulty because of the high coefficient of reflection of mercury. Therefore to a stout tungsten wire sealed through the glass at L was attached a fine tungsten spring carrying a small iron cylinder and tungsten pointer (see diagram). The pointer was controlled externally by a magnet on a screwed rod. The beautiful method of Richards and Boyer\textsuperscript{10} was used to determine the plane of the maximum diameter of the drop. A small source of light, level with, and 2.5 m. from the drop, gave by astigmatic reflection at the mercury surface two images, due to the two different radii of curvature at the maximum diameter. The small horizontal line image, which was formed in front of the vertical line image, gave exactly the plane of the maximum diameter, and the distance between this plane and the vertex of the drop was measured by a travelling microscope reading to 0.0001 cm. The microscope could be moved bodily backwards and

\footnote{Richards and Boyer, \textit{J. Amer. Chem. Soc.}, 1921, \textbf{431}, 274.}
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The remainder of the apparatus is shown in Fig. 3. The source of vapour, the reservoir M, was separated from the rest of the apparatus by a mercury cut-off. N was a greaseless seal consisting of a ground joint sealed with mercury. The cut-off O which separated the grease-free part of the apparatus from the taps, etc., was never lowered unless there was liquid air around the nearest trap Q. P was a cut-off designed to allow the changing of the liquid in the reservoir without letting air into the measuring vessel. An enlarged view of P including the dimensions is given in Fig. 4. The normal mercury cut-off cannot take a pressure difference of an atmosphere between the two sides without the use of compressed air in the lower chamber. By diminishing the volume of this chamber and shortening the distance from it to the U-tube, the act of letting air into one side of the cut-off could be made to compress the air in the lower chamber sufficiently to prevent the mercury level being driven down to the bottom of the U-tube. In Fig. 4 A shows the level of the mercury after admitting air to the lower chamber, and B the levels after allowing an atmosphere into the left-hand side of the cut-off. R, in Fig. 3, was a qualitative MacLeod gauge, working on a ground joint. The reservoir M could be thermostated by means of a mush in a thermos flask, and temperature measured to 0.1°C. by a copper-constantin thermocouple. The whole of the grease-free part of the apparatus could be warmed by means of a resistance wire enabling the use of vapour pressures up to saturation at 25°C.

Preparation of the Mercury and the Possibility of Oxide Formation.

The mercury was freed from readily oxidisable metals and other impurities by treatment with air in the presence of concentrated sulphuric acid and ferrous sulphate. This process of aeration was continued for two to three hours. The mercury was washed with water and dried at 115°C for one hour. After filtration to remove the mercuric oxide formed, the mercury was distilled slowly under reduced pressure. The whole procedure was repeated. The mercury was then transferred to the apparatus where the process of cyclic distillation could be maintained for as long as necessary to remove the final traces of grease.
Another matter of some importance was the question of oxide formation. It was known that most clean metal surfaces become oxidised extremely rapidly on exposure to air even at room temperature. The formation of a visible oxide film occurred rapidly on mercury at temperatures slightly above room temperature in air. The question arose, therefore, as to whether the surface tension of pure mercury or of a film of mercury oxide was being measured. Taylor and Hulett investigated the equilibrium between mercury, oxygen and mercuric oxide at higher temperatures and by means of the heat of reaction in the reaction

$$2\text{Hg} + \text{O}_2 \rightleftharpoons 2\text{HgO}$$

they gave the dissociation pressure of mercuric oxide at other temperatures. An extract from their results is given in Table I, column 2. From their data and from the vapour pressure of mercury, the critical pressure of oxygen for the formation of mercury oxide was calculated from the equation

$$[P_{O_2}][P_{Hg}]^2 = K_P.$$

Thus provided the pressure of oxygen was below $10^{-4}$ mm. all mercuric oxide present would decompose at temperatures up to the boiling point of mercury. It was important that conditions should favour the decomposition, not only at 25°C but at 200°C because the establishment of equilibrium would be so much faster at 200°C. This was the approximate temperature at which the mercury was distilled in the apparatus and unless conditions at this stage favoured the decomposition of the oxide, it would have been impossible to rid the mercury of oxide.

The measurements mentioned above were obtained for the bulk phase decomposition of mercuric oxide. It is possible that the surface phase formation of mercuric oxide proceeds either more readily or less readily. No data on this point appeared to be available. The surface energies of the metal and its oxide would affect the equilibrium, and if the presence of the oxide produced a lowering of the surface tension, the formation of the oxide would occur at very much lower pressures of oxygen. However, until more information about these points is forthcoming, the evidence of the bulk phase thermodynamics, that the mercury prepared at less than $10^{-4}$ mm. of $\text{O}_2$ is free of oxide, stands.

**Experimental Procedure.**

Initially continuous distillation for about fifteen days was required before the mercury would remain at a constant high surface tension for 10-12 hours. At a later stage it remained constant for over 24 hours. Observations were made to see if any decrease in surface tension occurred immediately after the spilling of the mercury from the cup. The surface tension could be measured in 2 minutes, and no decrease occurred after that. When the mercury was exposed to tap grease, the surface tension would remain constant for about half an hour and then would decrease steadily for four or five hours. The initial delay was probably the time taken for the diffusion of the grease to the mercury.

The radius (= 2.52 cm.) of the mercury drop formed by the cup had been determined before the cup was sealed into the apparatus. The gravitational constant was taken as 981.2 cm. per second² and the

<table>
<thead>
<tr>
<th>Date</th>
<th>Values of h uncorrected in cms.</th>
<th>Mean.</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 3rd</td>
<td>0.2804 0.2794 0.2802 0.2798 0.2800 0.2802</td>
<td>0.2800</td>
</tr>
<tr>
<td>May 10th</td>
<td>0.2801 0.2799 0.2803 0.2801 0.2806 0.2799</td>
<td>0.2802</td>
</tr>
<tr>
<td>May 16th</td>
<td>0.2800 0.2795 0.2800 0.2804 0.2801 0.2805</td>
<td>0.2801</td>
</tr>
<tr>
<td>June 7th</td>
<td>0.2799 0.2798 0.2803 0.2802 0.2800 0.2798</td>
<td>0.2800</td>
</tr>
</tbody>
</table>

Sources of Error.

It was important to investigate the sources of error in the above method in detail, because of the great variations in the surface tension of mercury found by different observers.

The most important source of error was the prismatic shape of the window through which the drop was viewed. Before the window was sealed into position, it was carefully tested for distortion and objects showed no change in size when viewed through it. There was, however, a small angle between the two faces of the window. This produced negligible change in the size of an object lying in a plane approximately parallel to the plane of the window. However, it produced considerable alteration in the distance between two points on an object lying in a plane inclined at an angle to that of the window. This led to a considerable error in the measurement of the height $h$ from the maximum diameter to the vertex of the drop. The method of correction will be described in detail as it is extremely difficult to obtain a window in an apparatus of this type with no angle between the faces, and also because it is quite
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Possible that this error has caused some of the observed variation in the surface tension of mercury found by those who have used the sensile drop method.

From Figs. 1 and 2 it can be seen that the two points which mark the limits of the height \( h \) are at different distances from the window, the difference being the radius of the drop. In Fig. 3 the displacement of the point \( O \) when viewed through the wedge of small angle \( \theta \) radians is considered. Let the refractive index of the glass be \( \mu \).

For refraction at a plane surface the equation (2)

\[
\frac{\mu_2}{v} - \frac{\mu_1}{u} = 0 \quad (2)
\]

will relate the distances of the object, \( u \), with the distance of the image, \( v \), and the refractive indices of the two media, \( \mu_1 \) and \( \mu_2 \). The image will lie on the line through the object perpendicular to the surface of the refracting medium.

Let the distance \( OA = d \).

After refraction at the first surface of the wedge, \( O \) will form an image at \( D \) where \( DOB \) is perpendicular to the front surface of the wedge

\[
BOA = \theta/2
\]

\[
\frac{\mu}{DB} = \frac{1}{OB}
\]

\[
\frac{OD}{OB} = \frac{\mu - 1}{1} = \frac{CO}{OA}
\]

\[
\therefore \quad DC = OC \tan \theta/2 = (\mu - 1) \frac{d \theta}{2}.
\]

Similarly after refraction at the second surface \( D \) will give an image at \( E \) on \( DEF \) which is perpendicular to this surface.

Let the thickness of the wedge at \( F \) be \( t_1 \) cm. then

\[
EG = (\mu - 1)(d + t_1)\theta/2.
\]

\[\because \text{ Total vertical displacement } = CD + EG = \theta(\mu - 1)(d + t_1/2).
\]

Similarly the vertical displacement of an object at a distance \( d + s \), will be

\[
\theta(\mu - 1)(d + s + t_1/2).
\]

\[\therefore \text{ The apparent vertical distance between the two images is }
\]

\[
\theta(\mu - 1) \left( s + \frac{t_1 - t_1}{2} \right).
\]

The distance \( s \) is the radius of the mercury drop \( \approx 2.5 \) cm., and consequently \( t_2 - t_1 \approx 0.001 \) cm. is negligible.

To take an example, suppose \( s = 2.5 \) cm., \( \theta = 0.2 \) degrees, and \( \mu = 1.5 \).

Then displacement = \( (1.5 - 1) \times 2.5 \times \frac{0.2 \times \pi}{180} \)

\[= 0.0044 \text{ cm.}\]

One-fifth of a degree is not a large angle to occur between faces of a piece of glass and therefore the actual correction must be determined for any window unless the faces can be guaranteed parallel to within 0.25 minutes, i.e. correction 0.0001 cm.

It was necessary to determine the wedge angle of the window when sealed on to the apparatus. A satisfactory method of making this determination was to observe the images formed by reflection at the two faces of the wedge, of a source of light. In practice it was simpler to use two objects so adjusted as to give one coincident image, and to determine the angle subtended at the window by the objects. It can easily be shown that this is \( 2\mu\theta \).
The theory of this correction was checked by fixing a wedge on to the outside of the sealed window, and comparing the observed with the calculated change in height of the drop. The observed change was 0.0053 cm., and the calculated 0.0055 cm.

The apparatus as described above was used with a sealed Pyrex window. An earlier modification had had a window of soda glass ground on to the end of the tube and held in position by means of white wax. Details of the correction for both these windows are summarised in Table III. The values of \( \bar{d}, x \) and \( s \) were the mean of three or four determinations and the corrections were probably accurate to 2-3 \( \% \). Not only did the two corrected values corresponding to the highest surface tension of mercury agree, but the corrected value in column 4 with the additional wedge agreed with the uncorrected in column 3. It will be observed that the distance moved by the travelling microscope altered from one apparatus to the next. This was due to difficulty in constructing the glasswork so that the pointer could be brought down exactly on to the vertex of the drop. In the first case the pointer was 2-3 mm. nearer the window and in the second the same distance further away, than the centre of the drop.

<table>
<thead>
<tr>
<th>Description of Window</th>
<th>Soda Glass. Used on first apparatus</th>
<th>Pyrex Glass. Sealed on to second apparatus</th>
<th>Pyrex Glass. The wedge used to test the theory of the correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index ( \mu )</td>
<td>1.516</td>
<td>1.473</td>
<td>1.473</td>
</tr>
<tr>
<td>Distance between objects at 240 cm. ( (= d) ) giving coincident images by reflection at the two surfaces of the window ( (= x ) cm.)</td>
<td>0.64</td>
<td>4.70</td>
<td>3.19</td>
</tr>
<tr>
<td>Angle of wedge ( \theta = \frac{x}{2\mu d} ) radius</td>
<td>0.000882</td>
<td>0.00664</td>
<td>0.00452</td>
</tr>
<tr>
<td>Distance moved by travelling microscope between the two settings ( (= s ) cm.)</td>
<td>2.20</td>
<td>2.60</td>
<td>2.60</td>
</tr>
<tr>
<td>Correction ( (\mu - 1)bs ) cm.</td>
<td>0.0010</td>
<td>0.0082</td>
<td>0.0055</td>
</tr>
<tr>
<td>Observed height, cm.</td>
<td>0.2801</td>
<td>0.2870</td>
<td>0.2923</td>
</tr>
<tr>
<td>Corrected height, cm.</td>
<td>0.2791</td>
<td>0.2788</td>
<td>0.2868</td>
</tr>
</tbody>
</table>

The maximum diameter of the drop was located as described above by the astigmatic reflection of a small source of light at 2.5 metres from the drop. The accuracy with which this light could be adjusted to the height of the drop was about 0.25 cm. The error caused by this was determined experimentally.

The vertex of the drop was located by means of a tungsten pointer. As already mentioned, this pointer did not come down exactly on the centre of the drop, but about 2-3 mm. from the centre. It was possible to show that there was negligible difference in height between a point as far as 0.5 cm. from the centre of the drop and the vertex itself. The difference in height was considered as the sum of two quantities; firstly, the part due to the curvature of the drop at its vertex. This was 2 \times 10^{-4} cm. for a drop 5 cm. in diameter. Secondly the changing curvature of the drop caused a slight vertical displacement between the vertex and the point 0.5 cm. away. The drop was assumed infinitely large in one direction for the purpose of obtaining a relation for the contour of the surface. This approximation introduced an error of not more than 10 \( \% \) in the correction, i.e. an error of the same order as found in the uncorrected relation for the surface tension \( \gamma = \frac{1}{2}gh^2 \). This part of the correction was found to be less than 10^{-5} cm. at 0.5 cm. from the vertex.
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Thus, at any distance from the centre of the drop under 0.5 cm, the total correction was quite negligible.

The height measured was very sensitive to the levelling of the steel plate upon which the travelling microscope was supported. The limit of accuracy of the level used was determined experimentally.

The error in the actual measurement of the height and the error in the correcting of the height for distortion due to the prismatic shape of the window probably amounted to 0.0002 cm. The radius of the drop was known to within 0.02 cm. The equation for the surface tension was not sensitive to small changes in $R$.

### TABLE IV.—SUMMARY OF ERRORS IN THE MEASUREMENT OF SURFACE TENSION.

<table>
<thead>
<tr>
<th>Nature of Error</th>
<th>Magnitude</th>
<th>Error in $h$ cm.</th>
<th>Error in $y$ dynes/cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Setting lamp</td>
<td>0.25 cm.</td>
<td>0.0001</td>
<td>0.3</td>
</tr>
<tr>
<td>Levelling surface-plate</td>
<td>0.0008 cm.</td>
<td>0.0015</td>
<td>0.5</td>
</tr>
<tr>
<td>Measurement and correction</td>
<td>0.0002 cm.</td>
<td>0.0002</td>
<td>0.6</td>
</tr>
<tr>
<td>Radius of drop</td>
<td>0.02 cm.</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>1.5</strong></td>
</tr>
</tbody>
</table>

The error in the absolute value of the surface tension was therefore 1.5 dynes/cm. as can be seen from the data in Table IV. Differences in surface tension can be determined with less error, probably less than 1 dyne/cm.

### Experimental Results.

The reading for the height $h$ in the first apparatus was 0.2801 cm. for mercury at 25°C. and in the second 0.2870 cm. As explained above, both these were subject to corrections for the prismatic shape of the windows used. The corrected values were 0.2791 cm. and 0.2788 cm.

### TABLE V.—SURFACE TENSION OF MERCURY AT DIFFERENT TEMPERATURES.

<table>
<thead>
<tr>
<th>Temp. °C.</th>
<th>Density</th>
<th>Corrected height, cm.</th>
<th>Surface tension, dynes/cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>13.534</td>
<td>0.2790</td>
<td>484.2</td>
</tr>
<tr>
<td>50</td>
<td>13.473</td>
<td>0.2781</td>
<td>479.0</td>
</tr>
<tr>
<td>75</td>
<td>13.412</td>
<td>0.2774</td>
<td>474.5</td>
</tr>
</tbody>
</table>

The corresponding surface tensions were 484.5 dynes/cm. and 483.5 dynes/cm. giving a mean value of 484.0 dynes/cm. at 25°C. The height 0.2790, i.e. 484.2 dynes/cm. was adopted as a working basis, involving the subtraction of 0.0080 cm. from the observed height for all observations made with the second apparatus, and 0.0011 cm. from all made with the first.

The surface tension of mercury was also obtained at 50°C. and at 75°C. The results quoted in Table V were the mean of several determinations. The temperature of the thermostat was maintained constant to a tenth of a degree at 25°C. and to a fifth at 50°C. The observed temperature coefficient was about 0.20 dynes per degree cm. The thermostatic control was not very good at 75°C. and the two lower values were more trustworthy.
Discussion.

As mentioned above, there is considerable discrepancy in the values given by different workers for the surface tension of mercury even in recent years. Adam\(^1\) suggested \(485 \pm 5\) dynes/cm. for the surface tension at \(20^\circ C\). Burdon\(^2\) quoted a list of values which led him to the decision that the surface tension of mercury lies between \(480\) and \(500\) dynes/cm. at room temperature. Puls\(^3\) who measured the surface tension of mercury in air by Bond's flowing sheet method,\(^4\) obtaining \(475 \pm 2\) dynes/cm., gave a comprehensive list of the results of other workers with mercury in air. These combined with the results that have been obtained for the surface tension of mercury in vacuo comprise a formidable list. One or two values obtained in recent years do agree with the value of \(484 \pm 1.5\) dynes/cm. at \(25^\circ C\) found in the present work. Burdon\(^5\) using the sessile drop method in a silica apparatus found \(488\) dynes/cm. at \(25^\circ C\) in vacuo. Bosworth\(^6\) using the bubble pressure method obtained \(484\) dynes/cm. in air at \(20^\circ C\). Owen and Dufton\(^7\) using the capillary rise method in amalgamated copper tubes obtained \(485\) dynes/cm. Another view of the scattered data is obtained by looking at those results giving a value greater than \(488\) dynes/cm. Since 1900 only three results of this type appear to have been found. Two of these were obtained by the sessile drop method. Cook\(^8\) found \(515\) dynes/cm. at \(31^\circ C\) and Bradley\(^9\) \(500\) dynes/cm. at \(16.5^\circ C\). It has been known for some time that the sessile drop method must be used with caution to obtain accurate results. At first doubt centred around the equation used to calculate the surface tension from the shape of the drop. That difficulty can be overcome by using drops of sufficient size (over 4 cm. diameter). Both Cook and Bradley used suitable sizes of drops for accurate calculation of the surface tension. A second difficulty which has been discussed at length by Burdon\(^10\) was the detection of the vertex of the drop. Burdon advanced the opinion that this difficulty may have been the cause of much of the discrepancy in the results obtained with the sessile drop method. Lastly there is the error due to the angle which may be present between the two faces of the window through which the drop is viewed. In the calculations given above it was shown that a window with an angle between the faces of \(0.00664\) radians, i.e. \(0.38\) degrees, gave an error in the height of \(0.0082\) cm. corresponding to a change in surface tension from \(483.5\) to \(511.4\) dynes/cm., i.e. \(28\) dynes/cm. This source of error has not been emphasised sufficiently in previous work and it must have been important, because the usual standard of window offered by technical firms has an angle between the faces of \(\pm 5\) minutes which means an error of \(\pm 7\) dynes/cm. Cook gave no details as to the quality of his window and he only claimed an accuracy of \(0.002\) cm. which meant an error of \(7\) dynes/cm. He located the vertex of his drop by means of a cord ruled with oblique lines which was placed behind the drop. This is one of the methods regarded as satisfactory by Burdon. Bradley used a Bourdon gauge to detect the vertex of his drop which was likewise accurate. Bradley recorded that his window did not alter the distance between two points, but did not say whether the two points were equidistant from the window, i.e. lay in a line parallel to the plane of the window or not. This point is most important because a wedge of small angle will not distort the distance between two points which are equidistant from it. The other value of the surface tension over \(488\) dynes/cm. obtained since 1900 was that found by Satterly and

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\(^1\) Adam, *The Physics and Chemistry of Surfaces*, 3rd edition, 1941.
\(^2\) Burdon, *Surface Tension and the Spreading of Liquids*.
\(^3\) Puls, *Phil. Mag.*, 1936, 22, 970.
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Strachan, using the observations of stationary waves formed on a vertical jet, and obtaining 562 dynes/cm. at 20° C. The theory of the method is not, however, considered to be accurate because of the possibility that the surface layers of the jet may be moving very much more slowly than the inside. Popesco did obtain a value of 532 dynes/cm. in air, but he was using the uncorrected equation for the surface tension, possibly in error by 20%.

The values usually found for the temperature coefficient of surface tension range from 0.20 to 0.23 dynes/cm. degree. The value of 0.20 found in the present work is of the right order.

Preliminary experiments brought to light some interesting results concerning the adsorption of tap-grease on mercury. Originally the apparatus was built with grease taps in place of the mercury cut-offs shown in Fig. 3. Apiezon L grease having a reputed vapour pressure of 10^(-11) mm. of mercury at room temperature was used, and it was hoped that this would cause no contamination because of its low vapour pressure. It was possible to get the surface tension of the mercury up to 484 dynes/cm. in this apparatus. However, it only remained at this value for about 20 minutes and then gradually fell throughout the next few hours to 460 dynes/cm. When a liquid air trap was inserted between the nearest tap and the mercury and maintained in liquid air the mercury remained at the high surface tension. Within a few hours of the removal of the liquid air the surface tension had fallen by some 25 dynes/m.

It was perhaps surprising that a substance of such low vapour pressure should affect the surface tension of mercury so markedly. However, the figures given by Micheli for the decrease of the surface tension of mercury in the presence of hydrocarbon vapours throw more light on this point. An extract from his results is given in Table VI. Although the vapour pressure is reduced by a factor of three for each additional carbon atom, the adsorption is approximately three times as strong, and the decrease in surface tension is fairly constant. It is not expected that this relationship be maintained accurately for the C₉₆ or C₉₈ hydrocarbons, but the experimental lowering of 25 dynes/cm. for a vacuum grease is reasonable. The period of four or five hours presumably represented the time for the grease to reach its equilibrium pressure throughout the apparatus.

I wish to express my thanks to Professor E. K. Rideal, F.R.S., for his interest and encouragement in the work. The investigations formed part of a programme of research conducted in the Department of Colloid Science and financed by the Ministry of Aircraft Production.

Summary.

I. An apparatus has been designed for the measurement of the surface tension of mercury by the sessile drop method in vacuo or in the presence of vapours. The design embodies a number of features from the researches of earlier workers and an accuracy of 1% was attained. A new type of mercury cut-off, capable of taking differences in pressure of over an atmosphere is described.

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TABLE VI.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Vapour pressure at 20° C. (mm.)</th>
<th>Lowering of S.T. of Hg at 25° C. (dynes/cm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>426</td>
<td>70.3</td>
</tr>
<tr>
<td>Hexane</td>
<td>122.5</td>
<td>63.3</td>
</tr>
<tr>
<td>Heptane</td>
<td>35.5</td>
<td>68.5</td>
</tr>
<tr>
<td>Octane</td>
<td>13.1</td>
<td>67.5</td>
</tr>
</tbody>
</table>

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21 Micheli, *Phil. Mag.*, 1927, 3, 89.
2. The prismatic shape of the window through which the mercury drop was viewed is shown to be an important source of error. Details of the magnitude of this error and the means of correcting for it are given.

3. A value of 484.0 dynes/cm. at 25° C. was found for the surface tension of mercury in vacuo. This is shown to be in agreement with other recent values and a possible explanation of some of the discrepancies in the literature is given.

4. The contamination of mercury by means of high grade vacuum grease was demonstrated and the adsorption is compared with the effect of lower hydrocarbons on the surface tension of mercury.

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