on the surface tension at the interface water-benzene, as given in Table IV, where the variation amounts to 8% of the maximum value.

TABLE IV.—ANTONOW'S DETERMINATIONS OF THE SURFACE TENSION AT THE BENZENE-WATER INTERFACE BY THE USE OF EXTREMELY SMALL TIPS.

Radius in mm.....	0.13	0.175	0.350	0.630
$\alpha_{18°}$ corrected.....	34.93	36.04	37.97	35.40

The value obtained by the writers with larger tips is 34.18 dynes.

The correction curve is now most accurately known between the values of r/a from 0.3 to 0.8, since that is the more common range for the tips which have been available for work on the liquid-liquid interface. Seven new tips are now available for use and the corrections from 0.8 to larger values of r/a will be made more accurate by further work.

The writers wish to express their indebtedness to the American Academy of Sciences, Arts, and Letters for a grant of three hundred dollars from the C. M. Warren Fund. The grant will be used in a continuation of this research. The work described in papers II, III, and IV of this series has been accomplished by the use of this fund.

CHICAGO, ILL.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

APPARATUS FOR THE DETERMINATION OF THE SURFACE TENSION AT THE INTERFACE BETWEEN TWO LIQUIDS.

(SURFACE TENSION II.)

BY WILLIAM D. HARKINS AND E. C. HUMPHERY.

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The surface tension at the interface between two liquids has been determined by a number of different methods,[1] but of these only two, the method of the falling drop, and the capillary-tube method, seem well adapted for general use. The importance of the interfacial tension in work in colloidal chemistry and in biological research, makes it essential that the apparatus for the determination of the surface tension should be of better design than that which has been used in most of the research work on this subject.

The Drop-Weight Apparatus.

The most essential features of a drop-weight apparatus are that the tip shall be ground almost perfectly round, with very sharp edges, and that the diameter of the tip shall be of the proper magnitude to give a ratio between the radius of the tip (r) and (a) the square root of the capillary constant, such that the Lohnstein correction[2] for the particular value

[1] For a critical account of twenty methods see "A critical paper by Ferguson," *Science Progress*, Jan., 1915, p. 428.

[2] For an explanation of the Lohnstein correction see the paper which precedes this one.

of r/a may be one which has been accurately determined, and also such that this correction shall not vary rapidly with the radius. The neglect of these essential conditions has been so general that this method in practically all of the previous work on interfacial tension has been very inaccurate. Thus Antonow in his fundamental work on the relation between the tension at the interface and that of the separate phases, evidently in the endeavor to make the correction factor close to unity, chose tips with very small diameters. This does, as a matter of fact, make the factor much closer to unity than if larger tips were to be used, but it also makes the correction vary greatly as the value of r/a changes. Thus the correction factor changes its value from 1.000 for $r/a = 0$ to 0.741 for $r/a = 0.2$, or a variation of 25.9% over a range of 0.2. On the other hand, when larger tips are taken a variation of r/a from 0.9 to 1.2 changes the correction by only 0.2% as a maximum for a change of 0.3 in the values of r/a. For dropping water into other liquids the tip which has been used most largely has a diameter of 9.5 mm., which is very satisfactory, though when dropping water downward into other liquids, the diameter should be somewhat greater if it is desired that the correction factor shall be as constant as possible for different liquids. This is, however, not necessary, since the correction curve has a slight slope and is well determined in the range where this tip is used.

The apparatus, but not its supporting stand, is shown in Fig. 3. It consists of a pipet of a capacity of 10 cc. which for convenience should be made smaller if much smaller drops are to be obtained, either on account of the use of a smaller tip, or because of a greater difference of density between the two liquids. Above and below the bulb of the pipet the stem is graduated to 0.1 cc. so that readings may be made to 0.01 cc. In order to give a better control of the drop the long vertical capillary tube at the right is made as small as a diameter of 0.3 mm.

The short arm H at the right which has the tip at its lower end is sealed into a large glass stopper, E. The glass beaker F, which is used to hold the lighter liquid, is fastened to the glass stopper by means of a ground joint which is made with a very slight slope, and a longer line of contact than is shown in the figure. The apparatus is supported by a thick sheet of aluminium used as a back, and on the top of this rests a platform which supports a level. The level is set on adjusting screws, so that the end of the tip may be set horizontal. The back and the platform are supported by heavy horizontal rods which are clamped to a vertical 30 mm. rod. This is fitted into a heavy tripod with three leveling screws.

The lighter of the two liquids used in the determination is not usually put directly into the beaker F but into a smaller glass cylinder which rests on the bottom of the beaker, since the beaker is so large that it re-

quires a large amount of liquid. The apparatus is supported in a thermostat with the water level at L. The tube G is used to connect the beaker with the apparatus used for the production of a sufficient decrease of pressure so that the drop may be drawn over. This apparatus, while extremely simple, should be such as to give perfect control of the drop. It consists of a buret with two connecting tubes sealed on at the top. Each of these connecting tubes is fitted with a glass stopcock.[1]

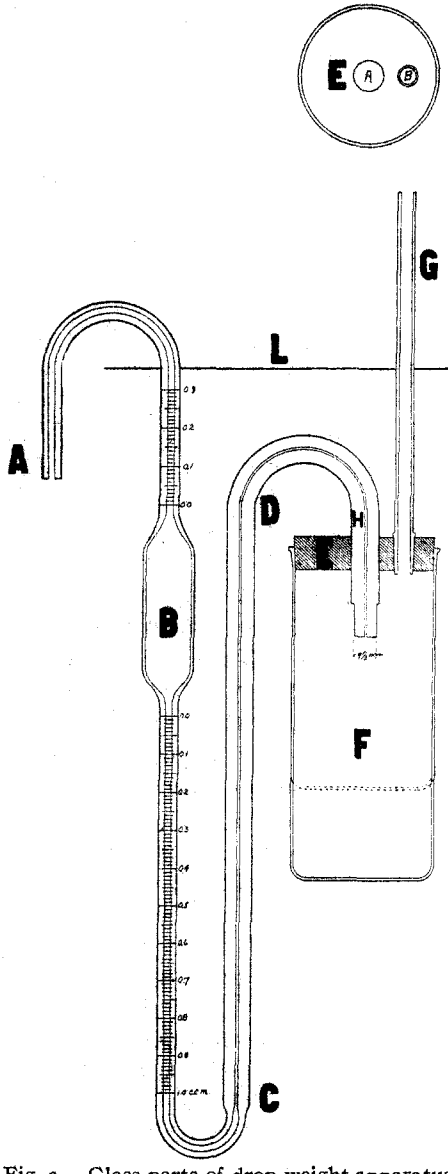

Fig. 3.—Glass parts of drop weight apparatus, for determinations at a liquid-liquid interface.

The procedure used in making the determination is to first fill the pipet by suction until the liquid rises to the 0.2 or 0.3 mark on the upper graduation, the liquid is then allowed to run out until it stands at about the 0.0 cc. mark, when a clamp on the rubber tube fastened on the glass tube at A, is closed.

Then the cylinder containing the lighter liquid is adjusted in the beaker F and the metal shelf on which the beaker rests is lifted to hold it. Care should be taken that a sufficient amount of the liquid is used to raise its level about 1 cm. above the lower edge of the tip when the beaker is placed in its final position.

The apparatus is then lowered into the thermostat, and allowed to stand from 35 to 50 minutes before beginning the run. When the liquids have come to constant temperature the clamp at A is opened and the heavier liquid sucked back into the pipet until its surface is just beginning to enter the mouth of

[1] For a description of this apparatus see paper by Harkins and Brown, p. 250.

the tip. The height of the liquid in the upper graduated tube is read off. The tube G is then connected by a rubber tube with the suction apparatus, which is filled with mercury, and enough mercury is at once run out so that the drop will fall in from 3 to $3^1/_2$ minutes. This causes the drop to form rapidly at first, and with extreme slowness just before the drop falls. If it is seen toward the end of the formation of the drop that the suction is insufficient to cause it to fall, the stopcock at the bottom of the suction buret is rotated quickly, thus allowing a very small amount of mercury to escape. The tube at the bottom of this buret is drawn down to a capillary in order to help keep this amount of mercury small. These precautions are taken so that the liquid in the drop, just before its fall, may be as free from currents, and from motion as a whole, as is possible. It is, of course, impossible to reduce the actual dropping of the drop to a static phenomenon.

As soon as the liquid in the pipet falls until its upper surface stands in the lower graduated tube, it is drawn back until it again just begins to enter the mouth of the tip, and the final reading of volume is taken under the same conditions as at the beginning of the determination.

In order that the volume of the drop may be converted into its weight in the lighter liquid, the densities of both liquids must be determined with a degree of accuracy which should be increased as the two approach each other in density. For the more accurate determinations a new form of pycnometer was devised, and this will be described in a later paper.

Apparatus for the Determination of the Surface-Tension at the Interface between Two Liquids by the Capillary-Tube Method.

The apparatus used for the determination of the surface tension at the interface between two liquids by the capillary-tube method, is shown

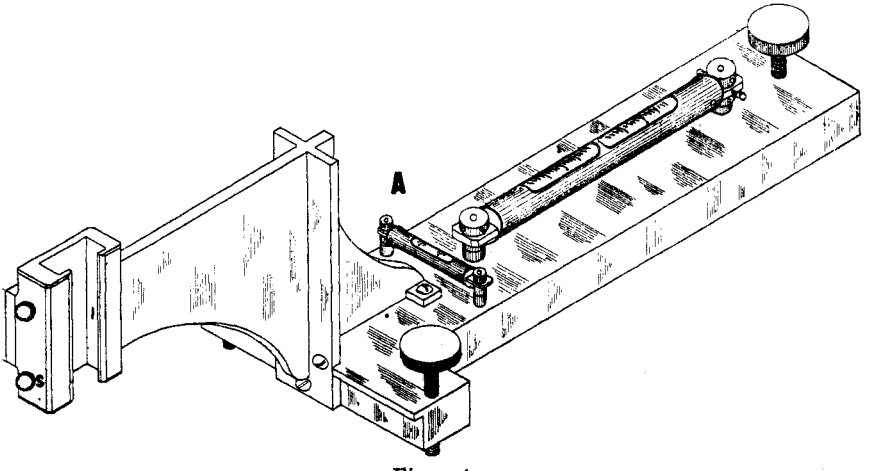

Fig. 4*A*.

in Fig. 4*A*, *B*, and *C*. The base of the stand A is filled with lead so that it may rest upon a supporting pillar and still support the capillary tube in the thermostat. The stand is provided with levels which are adjusted so that when they are level the capillary tube is vertical. The capillary tube is made from Jena capillary tubing and fits through the holes D, D. Its top rests against the stop E. The top of the tube serves only as a support for the lower part and may therefore be replaced by a metal tube or rod. The support B is first fastened in its supporting stand at I, and is fastened by the set screws S, S, against I, which is ground so that both surfaces which come together at I are flat.

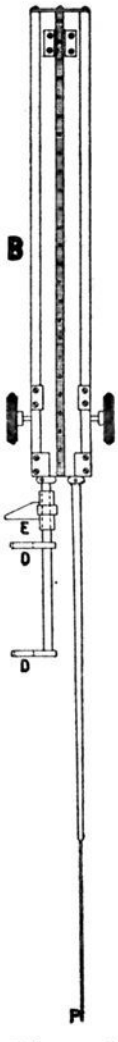

Fig. 4*B*.

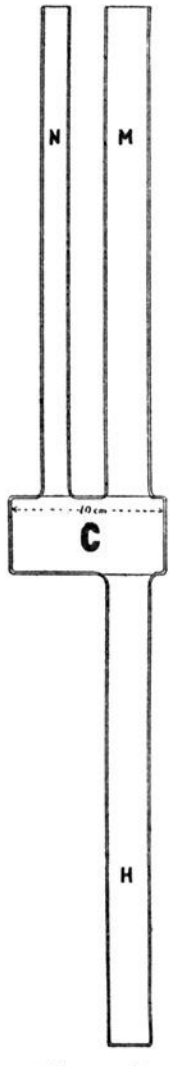

Fig. 4*C*.

The procedure will be described for the case where water is taken as the heavier of the two liquids. In this case the tube C is filled with water until H is completely full and the bulb C[1] is also nearly full, but not so full that the large meniscus which forms strikes the top of this bulb. The capillary tube is steamed out for some time before it is used. This precaution, while seemingly very simple, is essential if the best results are to be obtained, since it puts the surface of the glass in a better condition than cleaning by a cleaning mixture, or the use of acids, alkalies, or organic solvents. Any of these may be used first if it is considered advisable. The capillary tube is then set into the tube M, and lowered by the ratchet screw R, until the top opening in the capillary is underneath the surface of the water, and all of the air is displaced by the water. The upper tubes are then filled with the lighter liquid (*e. g.*, benzene) and after the liquids come to the proper temperature in the thermostat, the capillary tube is raised until the water-benzene meniscus *falls* to one of the graduations on the tube. The point P, which is made of platinum and should be sharp, is lowered until it touches the mirror surface of the benzene-water interface in the bulb C. If the slides in B move with just the right amount of friction this adjustment may be made with extreme accuracy since the point P approaches its image in the interface and the moment the two touch, the water surface gives a slight jump upward. The vertical distance between the platinum point and the graduation on the tube

[1] The bulb C is about 100 mm. in diameter, and has therefore a much larger free liquid surface than has been used in most other work on capillarity.

may then be read off on the millimeter scale by means of the verniers, or a cathetometer may be used to determine the distance. The advantages in the use of this instrument are (1) that it holds the capillary tube firmly in a vertical position, and (2) that the ratchet screws allow the adjustment of the point P to be made with great ease, and also make it easy to lower the capillary tube into the water phase and then raise it until the meniscus is at one of the graduations on the tube. A cathetometer may, of course, be used to measure off directly the distance between the upper and the lower meniscus, and the work recorded here has been checked by measurements made in this way.

The results obtained by the use of this method are much more concordant than the determinations made with a single liquid. This is due largely to the fact that with water-benzene a 1.4 mm. tube could be used and still give a capillary rise of 78 mm., while with water alone in a tube of 2.0 mm. diameter the rise was only about 14 mm., so that, where a considerable height of the capillary column is desirable, a much larger tube may be used for the determination of the interfacial tension. This is advantageous, since not only can the tube be cleaned more readily and the meniscus kept more free from those impurities which easily collect on a small surface and thus vitiate the results, but in addition the diameter of the tube can be determined more accurately.

The Standard Tube.

One difficulty in the determination of the surface tension of a single liquid by the capillary tube method is that the diameter of the tube must, in general, be determined by a mercury calibration, and this is unsatisfactory unless extreme care is taken in the selection of the capillary tube, since it is difficult to find a tube which has the same diameter at different points along its axis, so that the diameter determined by the calibration is usually not that of the tube at the point where the meniscus stands, and in addition the tubes are not round. Two methods of surmounting this difficulty suggested themselves: (1) to use in the place of the tube two plates of optical glass with flat surfaces practically parallel to each other; and (2) to enlarge the hole in a capillary tube by turning it out on a very accurate lathe, and thus make it practically round and of the same diameter for a distance of a few centimeters. This latter alternative, seemingly the more difficult of the two, is the only one which has been used up to the present time. The tube was made in a very skillful way by Captain A. de Khotinsky, the instrument maker for this laboratory, and by whom the eight tips used for the drop-weight method were ground. These tips are sharper and more nearly round than those which may be purchased from the makers of the Morgan drop-weight apparatus, which is, however, used for a different purpose than that described in this paper.

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