as 35% higher than the older ones. The difference in the results is due to a change from the capillary tube to the drop-weight method.

CHICAGO, ILL.

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

A SIMPLE APPARATUS FOR THE ACCURATE AND EASY DETERMINATION OF SURFACE TENSION, WITH A METAL THERMOREGULATOR FOR THE QUICK ADJUSTMENT OF TEMPERATURE.

BY WILLIAM D. HARKINS AND F. E. BROWN.[1]

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The importance of the values of the surface tension of a liquid in connection with work in colloidal chemistry, on molecular association, and such technical work as the testing of soap, makes it important to devise apparatus for the determination of the capillary constant which is at the same time easy to use, and capable of giving very accurate results. The aim of the designers of the apparatus here described has been to construct an apparatus as easy or easier to use than the stalagmometer of Traube, or of Donnan, and also so well designed that it will give results of the highest accuracy.

The new apparatus has the following advantages: The surface tension tips are very perfectly ground, and are made from Jena glass, monel metal, or quartz; no cement is used in setting in the tip, so the danger of contamination is eliminated; the apparatus is very rigid; one tip may be taken out, and another one substituted in less than five minutes; the apparatus is already provided with a leveling arrangement which is extremely easy to set, and it is not fragile. Perhaps the greatest advantage over the Morgan[2] apparatus lies in the substitution of a metal construction for glass, and the consequent elimination of cements, amalgams, linseed oil and plaster of Paris mixtures, and wooden or glass blocks. The setting of these requires a great amount of time, and this is apt to discourage the worker from replacing one surface tension tip by a more suitable one. In the new apparatus the weighing bottles are protected from the water of the thermostat by a nickel plated brass box, fastened to its top by thumb screws, and with a joint made waterproof by a rubber gasket, R (Figs. 1 and 2). In the apparatus as described, monel metal stoppers are used but glass stoppers may be substituted for these if a slight change is made in the design, as indicated in the last part of the paper.

[1] This is the first of a series of papers on surface tension to be presented to the University of Chicago by F. E. Brown as a dissertation in part fulfilment of the requirements for the Ph.D. degree.

[2] THIS JOURNAL, 33, 349 (1911).

Description of the Apparatus.

The fundamental requirements of a first-class drop-weight apparatus are that the glass or metal tip from which the drop is suspended must be as nearly as is possible a perfect circle, and that the edges of the tip must be sharp.[1] Above the tip the glass capillary is ground to fit into a monel metal stopper, which in turn fits into the weighing bottle into which the

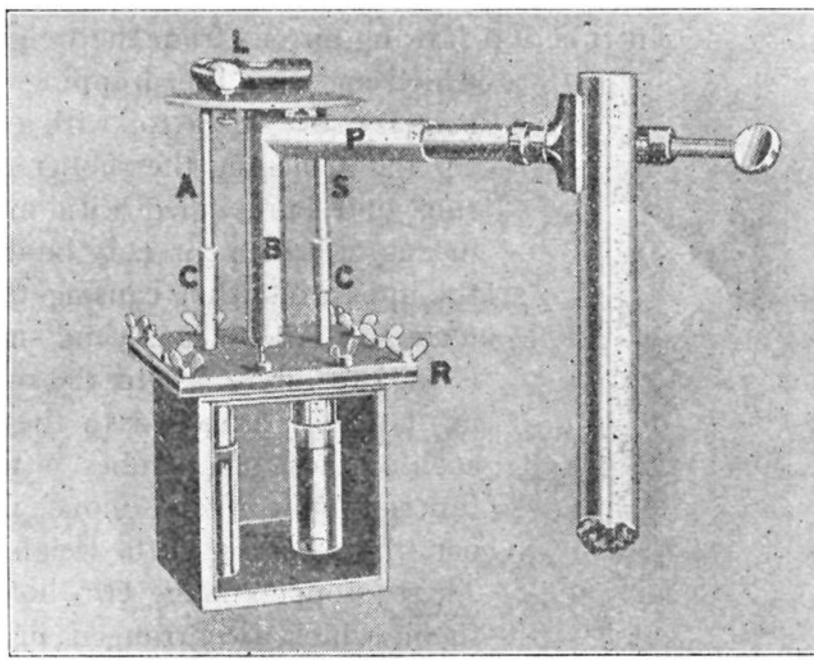

Fig. 1.

drops are caused to fill. This glass capillary tube is bent in the shape of an inverted U, and the other limb of this tube is inserted through a second monel metal stopper and passes down into a second weighing bottle which contains the liquid whose surface tension is to be determined.

The two weighing bottles with their two monel metal stoppers and the dropping tube and tip are supported inside of a rectangular metal box about 10 × 12 cm. of nickel plated brass, with two large glass windows on opposite sides so that the interior may be easily observed. The apparatus is kept supported in a water filled thermostat during a measurement, and this outer box is necessary to keep the weighing bottles dry. The apparatus is supported by an arm, P, which is a part of the column B. The arm is hollow and slides on the rod of the suitable laboratory support which should have a tripod base with 3 leveling screws. The vertical rod of this support should be at least 30 mm. in diameter.

The top part of the column B terminates in a circular platform with two leveling screws and a resting point on which the cross level L is placed.

[1] The glass tips ground by the instrument maker of this laboratory, Captain A. de Khotinsky, are much more perfect than the writers had been able to obtain from any other source.

The level, by means of the two leveling screws, can be easily set parallel to the drop surface of the surface tension tip D, thus insuring a correct position of the tip whenever the instrument is leveled by means of the screws in the base of the support. Two tubes, C, C′, are placed in the cover and these are made of sufficient length to prevent leakage of water from the constant temperature bath into the apparatus when this is submerged 5 cm. below the water line. Through these tubes are fitted two smaller tubes, one, S, a suction tube for drawing air out from the weighing bottle which contains the dropping tip. This tube is fitted at the top with a corrugated tip for attaching the rubber tube which runs to a buret filled with mercury, by means of which air may be drawn from the apparatus, thus causing the drop to form and fall. The second small tube A is used to admit air to the other weighing bottle. Attached to the bottom of each of these small tubes is the slightly tapering noncorrosive monel metal stopper which fits one of the weighing bottles. These stoppers have two holes through them, which are arranged in the same way as in a two-hole rubber stopper as sold commercially, except that the hole which carries the tip is as close to the center as is possible. One of these holes is attached to the small metal tube just described, and into the other is fitted the glass capillary tube which carries the tip.

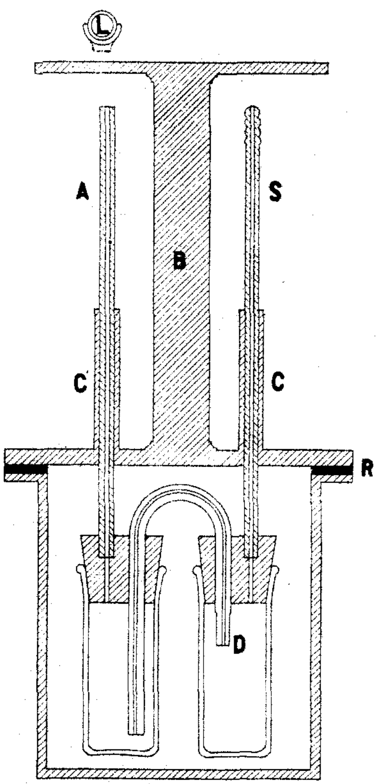

Fig. 2.—Drop-weight apparatus.

To set up the apparatus and make a surface tension measurement the box is removed from its cover. This is easily done by loosening the thumb screws (Fig. 1) at the top which hold it tight against a rubber gasket. The ground tip of the U tube is then inserted in the stopper to which the suction tube is attached. The joint is air-tight. The top of the suction rod S is then pushed up through the tube C until the top bend of the surface tension tube nearly touches the cover of the apparatus. The atmospheric tube A with its attached monel metal stopper, is inserted in the tube C′ in such a way that the other arm of the surface tension tube passes through the second hole of the stopper. The eccentric arrangement of the supporting tube and the second hole in the stopper makes it easy to accommodate any inaccuracies in the bending of the surface tension tube.

To level the surface tension tip, a square cover glass is moistened with glycerine and placed on the ground tip. Then the apparatus is adjusted so that when the cover slip is viewed from one corner through the cathetometer telescope, the three visible corners are in a straight line. Now the leveling screws are so manipulated that both bubbles of the cross level rest at zero, and then they are clamped in this position.

A weighing bottle, which fits the stopper provided with the atmospheric tube, is filled about two-thirds full of the liquid whose surface tension is to be measured and set on the stopper. Friction alone will easily hold it if it is properly ground,[1] and this is very easily done, since the sides of the stoppers are made at a very slight angle in order to give a long line of contact. One advantage of the monel metal stoppers is that they are so hard that a large number of weighing bottles may be ground on one stopper without any appreciable effect upon the stopper. Another weighing bottle is weighed with its glass stopper, and is then fitted on the monel metal stopper which carries the surface tension tip. A rubber tube is attached to the suction tube, and is connected with the special buret used for reducing the pressure.

The modification in the design of the stoppers when they are made from glass, is shown in Fig. 3.

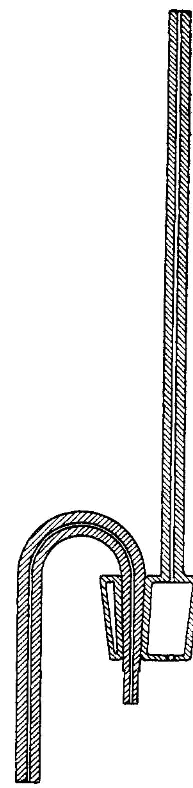

Fig. 3.—Glass stopper, tip tube, and suction tube for drop-weight apparatus.

The Control of the Drop.—In the determination of surface tension by the drop-weight method it is very important that the detachment of the drop from the tip shall be as slow as is possible, since in no other way is it possible to obtain a considerable degree of constancy in the weight of the drop, and furthermore, the simple theory developed by Lohnstein for the correction of drop-weight results, is based upon the detachment of the drop while it is increasing in size at only an infinitesimal rate.

The apparatus which has been developed for the control of the drop is extremely simple, and consists of a dropping tube (Fig. 4) fitted with three stopcocks. The tube is filled with mercury by means of the funnel C, and is attached to the suction tube of the drop-weight apparatus by a rubber tube connected at A. When it is desired that a drop be formed, the stopcocks B and E are opened and D is closed. The mercury then

[1] Thus an experiment showed that a weight of 1100 g. was held up in this way when the weighing bottle was set on only moderately tight, so that it could be taken off with a fair degree of ease. There is therefore no need of any other support.

runs in a stream from the very fine tip of the tube at F. When enough mercury has been run out to cause the drop to form rather rapidly, the stopcock E is closed. The correct amount to run out depends upon the size of the drop. When the drop is fully formed and ready to fall, which condition is readily recognized by an experienced worker, the stopcock D is opened to bring the apparatus to atmospheric pressure, and then it is closed. The speed of formation of the drop is thus reduced to practically zero in a very short time. Then the stopcock E is rotated half way round rather rapidly, thus allowing a very small amount of mercury to escape through the fine opening F. The extremely slight reduction of pressure which results, is sufficient under these circumstances, to cause the drop to detach itself from the tip as slowly as is possible.

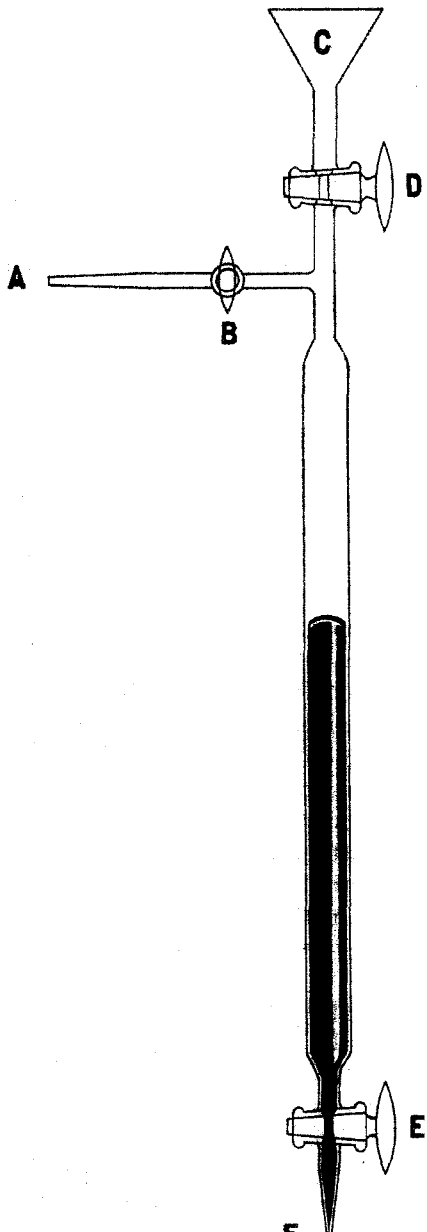

Fig. 4.—Apparatus to control the formation of drops.

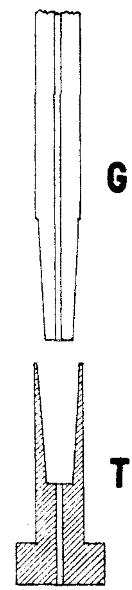

Fig. 5.—Interchangeable metal tips for drop-weight apparatus.

Interchangeable Monel Metal Tips.—Fig. 5 shows a monel metal tip, T, and the method of holding it on the glass tip-holding tube G. The glass tube is ground exactly to fit the monel metal tip, and with such a slight angle that friction holds on the tip very firmly. Any number of tips of different sizes may be turned to fit the one glass tube. The tip depicted in the figure is 2 cm. in diameter, and is for use in the apparatus designed by Harkins and Humphery for the determination of the surfacet ension at the interface between two liquids. When used with the apparatus described in this paper the tip is made shorter. These shorter tips may be used in either form of the apparatus.

When such large tips are used the liquid will not completely wet the tip unless the bottom is made with a fine grain. If the grain is coarse the diameter of the tip is affected but with large tips it should not be made too fine, or the liquid will not spread over it. To prevent spreading the vertical sides of the tip are always made with a high polish.

The Thermoregulator.—In some surface tension work it is desirable to have a thermostat whose temperature may be varied as rapidly as possible, and with a thermoregulator which is accurate, and which can also be set at once to regulate to any temperature within the range for which it was designed.

The regulator used in this laboratory for this purpose (Fig. 6) was designed by Captain de Khotinsky, and possesses a number of advantages over the usual thermoregulator. In order to reduce the lag, and make it respond quickly to changes of temperature, it is made from nickel plated steel and is filled with mercury. The great advantage of the steel tube is that steel has about 66 times the thermal conductivity of glass. While ordinary steel has a higher coefficient of expansion than glass, steels high in nickel have a lower coefficient, and steels have been made even with a negative coefficient. Toluene, which is often used to fill thermoregulators, is about sixty times as poor a conductor of heat as mercury.

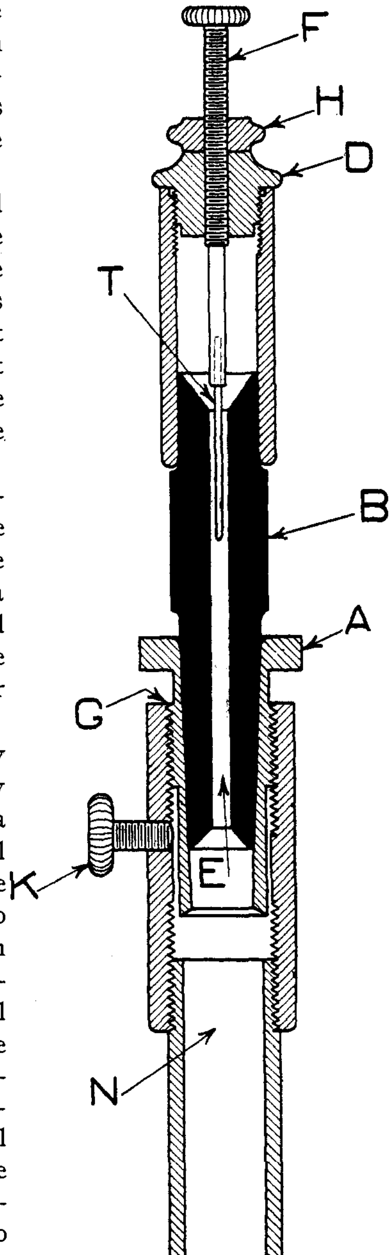

Fig. 6.—Metal thermoregulator.

Its supposed advantage comes from the fact that it has about twice as great a coefficient of expansion, but this is not an advantage after all, since the heat is conducted through the toluene so slowly that only a thin film of the toluene next to the material of the regulator, changes its temperature, so the effective expansion is usually less than that of mercury. The following approximate data make it easy to compare these different materials.

	Linear coefficient of expanson.	Thermal conductivity.
Liquids:		
Toluene	0.000366	0.000307
Mercury	0.000182	0.0177
Solids:		
Soft glass	0.0000094	0.0015
Jena hard glass	0.0000073	....
Iron	0.00000118	....
Nickel steel, high in Ni	0.0000050	0.100

At the suggestion of one of the writers Captain de Khotinsky has provided this thermoregulator with a glass capillary tube, B, which makes visible the contact between the platinum point and the small mercury meniscus. This capillary is ground to fit exactly the metal parts, and this gives the advantage that the platinum contact point is exactly centered, which is very important.

This regulator can be set very quickly at any temperature from 1° to 97° by turning the regulating screw A. For the more delicate adjustment the screw F is turned and the check nut H is set. The apparatus may be filled by releasing the set screw K, unscrewing the thermoregulating head-screw A, and adding mercury up to within 10 mm. from the top G. The regulating head-screw is then replaced and turned until the milled head A comes to within 1 mm. of the shoulder G. Next the cap D is unscrewed and all the mercury above the capillary glass tube B is removed. The meniscus is brought into the proper position in the capillary by turning the head-screw A. The capillary may be cleaned by unscrewing the head-screw, and pushing a small ball of absorbent cotton through the capillary. It is important that the hollow cones at E and T be cut into the top and bottom of the capillary tube.

At N is screwed on the steel tube containing the greater part of the mercury. When a very delicate regulation of the temperature is desired, several tubes joined together at the top are substituted for this one tube.

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