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

A METHOD FOR THE DETERMINATION OF SURFACE AND INTERFACIAL TENSION FROM THE MAXIMUM PULL ON A RING

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1. Introduction

Although many thousands of measurements have been made to determine the pull necessary to detach a ring from the surface of a liquid, it is a surprising fact that *until three years ago there was no "ring method" for the measurement of surface tension.* Thus in "International Critical Tables," nine experimental methods for surface tension are listed but a ring method is not included, since the procedure which had been designated by this term did not supply even one single measured value of surface tension of these tables.

The failure of the ring procedure was due to the fact that the theory had not been sufficiently developed to permit its use as a method of measurement, although an incomplete theory had been developed by Cantor,[1] Lohnstein,[2] Lenard,[3] Tichanowsky[4] and MacDougall.[5]

In 1926 Harkins, Young and Cheng,[6] on the basis of the well-justified assumption that the capillary height method, properly applied, gives correct values for the surface tensions of suitable liquids, showed how the ring procedure could be used as a moderately accurate method for such measurements. In the present paper the method is given a still higher degree of accuracy (about 0.25%).

In a third paper from this Laboratory, Drs. B. B. Freud and Henrietta Zollman Freud convert this into an absolute method, since by the use of the fundamental differential equation of Laplace they have been able to calculate the shapes of the surfaces upheld by rings. It is of considerable interest that their theoretical and our experimental procedure agree within approximately the limits of accuracy of either, that is, to about 0.25%, where the two have been compared.

Symbols

γ = surface tension in dynes per centimeter
a = square root of the capillary constant

[1] Cantor, *Wied. Ann.*, **47**, 399 (1892).
[2] Lohnstein, *Ann. Physik*, **25**, 815 (1908).
[3] Lenard, *ibid.*, **74**, 395 (1924).
[4] Tichanowsky, *Physik. Z.*, **25**, 300 (1924); **26**, 523 (1925).
[5] MacDougall, *Science*, [N. S.] **62**, 290 (1925).
[6] Harkins, Young and Cheng, *ibid.*, **64**, 333 (1926).

M = weight of liquid raised above the free surface of the liquid; $\mathbf{M}$ = maximum value of M

P = total pull on the ring in dynes = Mg; $\mathbf{P} = \mathbf{M}g$

p = P divided by $4\pi R$; $\mathbf{p} = \mathbf{P}/4\pi R$

R = radius of the ring measured from the center of the ring to the center of the wire

r = radius of the wire

V = the volume of liquid raised above the free surface of the liquid, or $M/(D - d)$ $\mathbf{V}$ = maximum volume

D = density of the liquid

d = density of air saturated with vapor of the liquid

S = shape of the surface

h = the "pressure height" or the vertical distance from the point in the meniscus under the center of the ring to a point in the liquid where the pressure is equal to that in the vapor at the same level

In much of the earlier work the entirely false assumption was used that the maximum pull (p) per cm. on the ring is equal to the surface tension of the liquid or

$$\mathbf{P} = \mathbf{M}g = 4\pi R\mathbf{p} = 4\pi R\gamma \tag{1}$$

in which $\mathbf{P}$ is the total maximum pull on the ring as determined by the balance.

The results obtained by the use of this entirely incorrect equation vary from 30% too high to 30% too low, and even more. The high values are commonly obtained for surface, and the low for interfacial, tensions.

Harkins, Young and Cheng considered that the size of the surfaces outside and inside the ring is determined mostly by the size of the ring (R), and that its shape is determined by the surface tension and density of the liquid, the radius of the ring (R) and of the wire (r), and certain other variables. In order to determine the form of the functional relation they used the principle of similitude, which in this case indicates that the shape of each surface supported by the pull of the ring depends entirely, when at rest, upon a few simple dimensionless variables. These are (1) the ratio (R^3/V) of the cube of the radius of the ring to the volume of the liquid; (2) the ratio (R/r) of the radius of the circular ring to the radius of the circular wire of which it is made, and (3) the ratio (h^3/V) of the cube of the "pressure height" to the volume of liquid which the ring supports. Thus, the shape S is given by

$$S = f\,(R^3/V,\ R/r,\ h^3V),\ \text{or}$$
$$S = \varphi(R/a,\ R/r,\ h/a)$$

The surface tension is a function of the shape, and, therefore, of these same variables, and its value is given by the equation

$$\gamma = \frac{Mg}{4\pi R} \times f_1(R^3/V,\ R/r,\ h^3/V)$$

Since the volume upheld by the ring becomes a maximum at a certain definite shape for which the value of h^3/V is determined by the values of R^3/V and R/r

$$\gamma = \frac{\mathbf{M}g}{4\pi R} \times \alpha(R^3/V,\, R/r), \text{ or}$$

$$\gamma = \frac{\mathbf{M}g}{4\pi R} \times \frac{\gamma}{\mathbf{p}} = \frac{\mathbf{M}g}{4\pi R} \times F$$

The values of F may be determined experimentally by determining the true surface tensions of various liquids by the capillary height or drop weight methods, and comparing with the values of $\mathbf{p}$ as shown in the above equation.

A number of values of F were determined experimentally by Harkins, Young and Cheng, and it was shown that if R/r is held constant by regulating the dimensions of the rings, F varies with R^3/V along a smooth curve, regardless of the values of R. However, this work was not sufficiently extensive or precise for general use with accurate data.

2. Outline of Procedure

The present work is a thorough investigation of the technique of the ring method, and the accurate determination of the correction curves which were found in a preliminary way by Harkins, Young and Cheng.

The general method of procedure was to determine the surface tension of water, of benzene and of bromobenzene by the capillary height method, and the values of $\mathbf{p}$ for these liquids by the use of sixteen different rings, with values of R between 0.4 and 1.8 cm., of r between 0.009 and 0.05 cm. and of R/r between 13.9 and 78.3. The quantities $\gamma/\mathbf{p}$ and R^3/V were calculated and plotted against each other, and the curves so obtained for the various rings were corrected to even values of R/r. Thus curves for R/r equal to 30, 40, 50, 60 and 80 were obtained. Interpolated curves were also obtained for intermediate values of R/r.

The liquids water, benzene and bromobenzene were chosen for the standardization for the following reasons: first, because their contact angles against glass and against platinum also are zero, and their surface tensions may, therefore, be accurately determined by the capillary height method; and second, because they are easily purified and kept in the pure condition. While pure liquids were not required for the purposes of standardization as long as the same sample of liquid was used throughout and its true surface tension known, it was considered desirable to use pure liquids so that the surface tension values may be compared with those obtained by others.

3. Determination of the Surface Tension of Liquids by the Capillary Height Method

The surface tension of each liquid used in this investigation was determined by capillary height measurements made on very pure liquids. The method applied was similar to that of Richards and Coombs, Harkins and Brown and Young and Gross. The apparatus was exactly that of the last-named investigators, except that a special stopcock (S, Fig. 1) was inserted between the trap (T) and the large tube (L), to facilitate the drying of the capillary. The average radius of the capillary, a 3-cm. section of a tube selected by Harkins, and Brown, and Davies, was 0.02557 cm. and of the large tube 1.805 cm. The mean diameter of this tube had been determined by these investigators, but was recalibrated by us at 26 levels by a determination of the capillary height with pure water at 25°, at which temperature its surface tension is 71.97 dynes per cm.

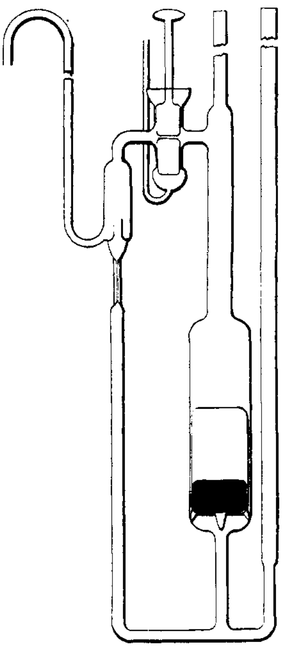

Fig. 1.—Capillary height apparatus.

The observed heights were corrected by adding $^1/_3\, r$ to correct for the volume of the small meniscus, and by adding 0.0018 cm. to correct for the rise in the larger tube when water was used. This latter correction was negligible with the other liquids.

Six values for the surface tension of benzene at 25° were obtained as follows: 28.19, 28.24, 28.23, 28.24, 28.24, 28.23, with a mean value of 28.22 dynes per cm. The density 25/4° was 0.8733, and $D - d = 0.8718_7$ was used.

For bromobenzene the values are: 35.75, 35.73, 35.75, 35.73, 35.75, 35.76, 35.77, 35.77, or a mean of 35.75, at 25°. The density was 1.4887 (25/4°), and $D - d$ was taken as 1.4875.

4. Apparatus for the Ring Method

The rings were made of platinum-iridium wire containing 10% iridium to give the wire stiffness, with the exception of rings 15 and 16. These contained no iridium, and proved to be unsatisfactory for practical purposes. It was found necessary to use wire of this alloy, as platinum wire bends too easily and rings made of it soon lose their shape through handling. The rings were constructed by bending the wire around a brass rod turned down to the exact inner diameter desired, and welding the ends of the wire together with a spot welder. This has to be done with extreme care or the wire will be flattened at the spot of the weld. The stirrups were then welded on to the top or side of the ring, and all protuberances and unevenness removed with a fine file and emery paper. In four of the rings, made with fine wire, silver solder was used instead of welding. The loop at the top of the stirrup was made in the form of an ellipse with the least possible radius of curvature at the uppermost part, so that the ring would always hang in the same position. All the rings with radii greater than 0.8 cm. were made with two stirrups whose planes were at right angles to each other.

It was found that the DuNoüy tensiometer is too inaccurate for measurements of the high precision desired in the present investigation. Therefore, a chainomatic balance, sensitive to 0.05 mg., was adapted for the work. The left pan was removed and a hole three-eighths of an inch in diameter was bored in the base of the balance directly under it, through which an aluminum rod connected the ring with the beam of the balance. The righ-hand pan was replaced by a very light aluminum pan, in order that the momentum of the beam and pan might be reduced to a minimum. The pan rest was disconnected, as it was found to be troublesome in making measurements.

In order to prevent ripples in the surface of the liquid, which might have been formed by lowering the level of the liquid or the containing vessel, a machine was devised to lower and raise the balance with great ease and smoothness. While such a machine is not essential to measurements by the ring method, it was deemed advisable to use it in this work in order to remove the source of error mentioned above. The machine is represented diagrammatically in Fig. 2. It consists essentially of four heavy upright steel rods, which are screwed into a heavy cast-iron base provided with leveling screws. Fitted onto these rods are two heavy bronze castings. The lower one is fastened to the rods, and supports the set of gears which raise and lower the upper movable casting. To the upper casting are attached the balance platform and its counterweight. Frictional effects were reduced to a minimum by a delicate counterbalancing of weights throughout. For example, the balance is counterbalanced by the movable weight W′. These and the casting which supports them are, in turn, counterbalanced by the weight W. This is connected to the upper casting by a steel piano wire which runs over a stationary pulley. The smoothness of operation was also increased by reducing the bearing surface of the movable casting to a minimum. The balance platform is provided with two large oval-shaped openings, through which the rod connecting the ring with the balance beam passes.

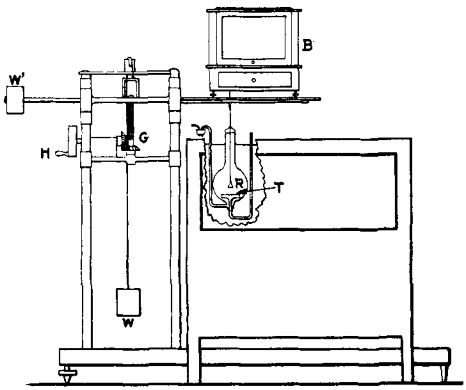

Fig. 2.—Apparatus for determination of surface tension by the ring method.

The flask used in the measurements is illustrated in Fig. 3. The principle involved in the design is to provide a means of overflowing the surface to prevent surface contamination. The flask was constructed by sealing a cup (C) 7.5 cm. in diameter and 2 cm. high near the bottom of a two-liter flask, and by replacing the neck with a longer and wider one. The liquid is introduced in the side-arm (A) and the excess withdrawn through (B).

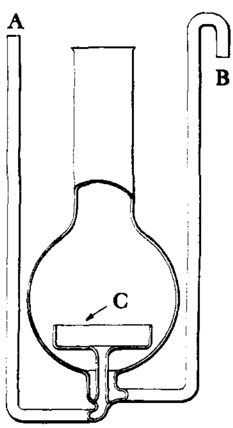

Fig. 3.—Flask for the ring method.

5. Measurement of Rings

Since the correction factor (γ/p or F) is a function of the variable R/r, it is necessary to have very accurate measurements of the radii of the wires of which the rings are made, as well as of the radii of the rings.

The diameters of the rings were measured by a screw micrometer carrying a microscope with a magnification of ten diameters. One division on the screw head corresponds to 0.0005 cm. The instrument had been originally calibrated by Dr. E. H. C. Davies, by comparison with a standardized invar scale by a series of 5000 measurements, and later checked by Mr. Frank Frese. In order to make precise measurements it is necessary to illuminate the ring from below, and the method was as follows. A reading glass about two and one-half inches in diameter was mounted in a hole in the top of a box, and within the box at the principal focus of the lens was placed a 100-watt lamp painted black with the exception of a spot about a centimeter in diameter. This provided for practical purposes a point source, with parallel light coming through the lens. Above the lens and about two inches away from it was placed the leveling table containing the ring. This was constructed as is shown in Fig. 4. It may be leveled with leveling screws, or, with the leveling screws removed, may be attached to a microscope by removing the microscope platform. In the top of the cylinder in the table was mounted a transparent celluloid disk (D), roughened with emery paper. The disk had two slits cut in it at right angles to each other (S) through which the stirrups were passed, and on it were scratched a series of concentric circles (C) to aid in centering the ring. Measurements on the rings were made across twelve evenly spaced diameters from the outer edge of the ring on one side to the inner edge on the other. Readings were taken at the point where the cross-hair, which had been previously made perpendicular to the direction of travel, became tangent to the edge of the ring.

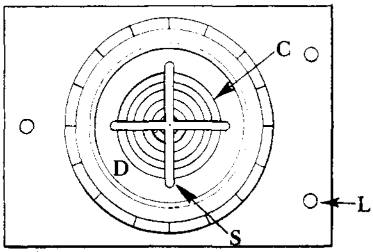

Fig. 4.—Apparatus for measurement of diameter of rings.

The measurements of the radii of the wires were made with a microscope, with a magnification of ten diameters and provided with a micrometer eyepiece. This was calibrated by comparison with an invar scale standardized by the Bureau of Standards. One division on the micrometer screw head corresponds to 0.0001 cm. at this magnification. In these measurements the leveling table was attached to the microscope in place of the microscope platform by means of a special adapter, and the illumination from below was used as in the previous measurements. In place of the celluloid disk a piece of bond paper was stretched over the top of the cylinder. In order to make the ring appear very black and the edges sharp, a narrow strip of thin cardboard with a slit very slightly wider than the diameter of the wire was slipped under the wire to cut down the extra light. This method gives excellent illumination, and precise measurements of the wire can be made in this manner. Measurements at twelve different, evenly spaced points on the ring were made and the average of these was used. The values for the radii of the rings and the radii of the wires are given in Table I.

Table I

Radii of Rings

No. of ring	R	r	R/r	No. of ring	R	r	R/r
1	0.4143	0.01070	38.72	9	0.4678	0.01607	29.11
2	.6065	.00903	67.17	10[a]	0.6366	.01570	40.55
3	.5103	.00973	52.45	11	1.5245	.02946	51.75
4	.8078	.01877	43.04	12	1.8277	.02986	61.21
5	1.0142	.02001	50.69	13	1.1806	.04009	29.45
6	1.2185	.02008	60.68	14	0.7759	.02578	30.80
7	1.2144	.02913	41.69	15	0.9421	.01585	59.44
8	0.6767	.04875	13.88	16	1.2603	.01610	78.28

[a] Ring number 10 was the ring furnished with a DuNoüy Tensiometer.

6. Measurement of Surface Tension by the Ring Method

The difficulties involved in making precise measurements by the ring method are far more numerous than most investigators have assumed. Any rigorous theory of the ring method would require: (1) that the wire of the ring lie in one plane; (2) that the plane of the ring be horizontal; (3) that the vessel containing the liquid under investigation be large enough so that any curvature of the free surface of the liquid would not be great enough to affect the shape of the liquid raised by the ring; (4) that the surface of the liquid be free from wave motion; (5) that there be no motion of the ring except an infinitesimally slow upward motion; (6) that there be no evaporation and consequent cooling of the surface; and (7) that the ring be round. These are requirements that are inherent in the proper technique of the ring method, and must be approximated as nearly as possible. Of these sources of error, the last is probably the least important.

The most important source of error arises from the ring not being horizontal. This was investigated in a quantitative way by measuring the pull on the ring when tipped by various amounts. The stirrup was bent so that the plane of the ring was not horizontal, and the difference in height between the two sides was measured with a cathetometer. From this the angle made between the plane of the ring and the horizontal was calculated. Ring Number 12 was used, and the data, which are given in the table below, are illustrated in Fig. 5.

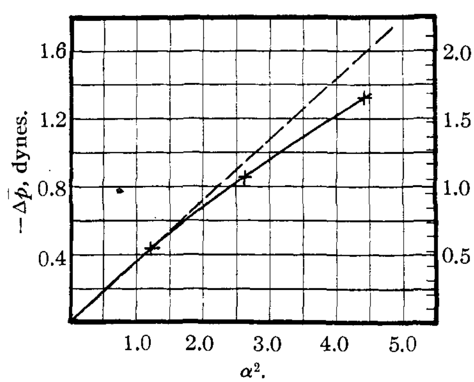

Fig. 5.—Error due to tipping of ring.

TABLE II

DATA WITH RING 12

Angle, α	α^2	p	Δp	Error, %
0.00	0.00	84.05	0.00	0.00
1.10	1.21	83.61	0.44	0.52
1.62	2.62	83.20	0.85	1.01
2.10	4.42	82.73	1.32	1.67

It is seen from the graph of the above data that for small angles such as are liable to be encountered in practice, the error introduced is proportional to the square of the angle. Δp is, therefore, expressed by the equation

$$-\Delta p = k\alpha^2$$

In the present case the equation holds for angles not greater than 1.5 degrees, and k has the value 0.36. From the graph it may be seen that for the error due to this source to be less than 0.1% the angle of tip must be less than 0.47 degree, and for an angle of 1 degree the error introduced is 0.43%.

The effect of the curvature of the meniscus and the size of the vessel was studied by making measurements of water contained in crystallizing dishes of various sizes. The crystallizing dish was placed on a glass desiccator triangle in a 2-liter beaker, and overflowed from the top, thus insuring uniformly clean surfaces. To prevent evaporation the top of the beaker was covered with a plate of glass in which a hole was bored. Measurements could not be made when the diameter of the dish was less than 7 cm., as the curvature of the meniscus was so great as to cause the ring to cling to the side of the dish. Ring Number 12 was used. The data are given in Table III.

TABLE III

OBSERVATIONS ON MENISCUS CURVATURE

Diam. of dish, cm.	7	8	9	10	12
p	83.96	84.03	84.08	84.05	84.06

While this effect is not great for dishes more than 7 cm. in diameter in the measurement of surface tension, it becomes of much greater importance in the measurement of interfacial tension.

The error caused by not having the wire all in the same plane cannot be measured quantitatively with any accuracy, but it was observed that this was an important source of error. This results in a consistently lower pull on the ring, and is one of the troublesome factors in measurements with the larger rings made of fine wire. In straightening the wire a small brass plate was used in which a groove was cut. The ring was set on the plate with the portion of the ring to be straightened across the groove, and then tapped gently with a small brass rod rounded at the end. While this method is not entirely satisfactory, it was the best of a number that were tried.

7. Method of Measurement of Surface Tension

The method of measurement was as follows. The flask was cleaned with hot cleaning solution (10 cc. of saturated potassium dichromate solution and 990 cc. of concd. sulfuric acid) and the solution was allowed to stand in the flask for fifteen minutes. The flask was then rinsed thoroughly with conductivity water. In the case of measurements on liquids other than water it was also dried by circulation of air, previously dried over sulfuric acid, and by gentle heating on the outside with a steam jet. The flask was then filled with the liquid (already at the temperature of the thermostat) to be measured and allowed to stand in the thermostat for three-quarters of an hour before measurements were made.

The ring was leveled as follows. It was suspended over a small gold plated brass table, fitted with leveling screws and polished to a mirror finish on top. The table was made level by a small right angle level, and the ring was lowered to within a half millimeter of the top of the table. By sighting between the top of the table and the ring in two mutually perpendicular directions, and by looking at the ring and its mirror image at the same time, considerably less then 30′ of tilt could be determined. The stirrup of the ring was bent until the plane of the ring appeared to be perfectly horizontal. It was then cleaned by heating to red heat in a flame. In the case of three or four of the rings in which the stirrups were silver soldered to the ring, the ring was cleaned by dipping into warm cleaning solution, rinsing thoroughly in conductivity water, and drying at some distance above a gas flame.

The flask was then put in position under the balance so that the plane of the inner cup was as nearly horizontal as possible. The ring was then connected with the fine aluminum rod from the left-hand stirrup of the balance beam by a jointed aluminum rod composed of links about two inches in length. On its end was a hook, the inner circumference of which was beveled to a knife edge to allow free motion of the stirrup loop over it. An inverted Erlenmeyer flask with a hole about 1 cm. in diameter blown in the bottom was placed in the top of the measuring flask to prevent evaporation.

The weight of the ring suspended in air was determined and taken as the zero weight. The cup in the flask was overflowed with plenty of liquid to insure a clean surface, and enough liquid withdrawn through the side-arm (A) (Fig. 3) to cause the liquid in the cup to become *level* instead of concave upward. With large rings the initial surface was made slightly convex upward, to such an extent that the outer part of the surface becomes plane when the ring is lifted to the height of detachment. The balance was lowered until the ring met the liquid, and then slowly raised while weights were added to determine the approximate maximum pull. In this procedure the addition of weights to the pan was made with the beam rest supporting the beam as in ordinary weighing, and during the addition of weight by the chain the rest was lowered only enough to allow the pointer to swing three divisions in either direction. The final addition of weight and the raising of the balance were so regulated as to keep the pointer always at the scale zero. In check determinations the beam of the balance was raised and lowered again when the pull was about 10 mg. less than the maximum to insure its proper position, and the additional weight was added very slowly. When the maximum weight is reached, the balance pointer suddenly swings to the left and the liquid may or may not become detached from the ring, but any attempt to raise the balance—to bring the pointer back to zero—causes detachment of the liquid. The maximum weight was taken as the weight required to make the pointer suddenly move to the left, and which cannot be compensated by raising the balance without detachment of the liquid from the ring.

8. Experimental Results

The experimental results obtained by the ring method for water, benzene and bromobenzene are given in Tables IV, V and VI.

TABLE IV

WATER

Ring no.	M	p	V	R^3/V	γ/p
1	0.3446	64.89	0.3461	0.2055	1.1091
2	.5446	70.05	.5469	.4079	1.0274
3	.4451	68.04	.4470	.2973	1.0578
4	.7866	75.96	.7899	.6673	0.9475
5	1.0080	77.53	1.0123	1.0305	.9283
6	1.2196	78.08	1.2248	1.4771	.9218
7	1.2689	81.51	1.2743	1.4055	.8830
8	0.7374	85.00	0.7405	0.4185	.8467

TABLE IV (*Concluded*)

Ring no.	M	p	V	R^3/V	γ/p
9	0.4123	68.75	0.4140	0.2474	1.0468
10	.5950	72.91	.5975	.4318	0.9871
11	1.6040	82.08	1.6108	2.1996	.8768
12	1.9239	82.11	1.9320	3.1601	.8765
13	1.2853	84.92	1.2907	1.2749	.8475
14	0.7741	77.84	0.7774	0.6009	.9246
15	.9178	75.99	.9217	.9072	.9471
16	1.2435	76.97	1.2488	1.6030	.9350

TABLE V

BENZENE

Ring no.	M	p	V	R^3/V	γ/p
1	0.1514	28.51	0.1736	0.4096	0.9902
2	.2273	29.24	.2606	.8561	.9655
3	.1900	29.05	.2179	.6099	.9718
4	.3283	31.70	.3765	1.4000	.8905
5	.4180	32.15	.4793	2.1765	.8781
6	.5037	32.25	.5776	3.1320	.8754
7	.5306	34.09	.6084	2.9437	.8281
8	.3243	37.39	.3719	0.8333	.7550
9	.1804	30.09	.2069	.4949	.9392
10	.2515	30.82	.2884	.8946	.9160
11	.6699	34.28	.7682	4.6122	.8235
12	.8029	34.27	.9207	6.6312	.8238
13	.5465	36.11	.6267	2.6256	.7818
14	.3271	32.89	.3751	1.2452	.8538
15	.3768	31.20	.4321	1.9352	.9048
16	.5085	31.48	.5831	3.4332	.8968

TABLE VI

BROMOBENZENE

Ring no.	M	p	V	R^3/V	γ/p
1	0.1984	37.36	0.1333	0.5334	0.9569
2	.2939	37.80	.1976	1.1290	.9456
3	.2462	37.63	.1655	0.8030	.9500
4	.4255	41.09	.2861	1.8423	.8700
5	.5419	41.68	.3643	2.8635	.8577
6	.6534	41.83	.4393	4.1181	.8547
7	.6924	44.48	.4655	3.8474	.8037
8	.4291	49.47	.2885	1.0741	.7227
9	.2358	39.32	.1585	0.6461	.9092
10	.3265	40.01	.2195	1.1753	.8935
11	.8729	44.67	.5868	6.0380	.8003
12	1.0450	44.60	.7025	8.6909	.8016
13	0.7179	47.44	.4826	3.4096	.7536
14	.4269	42.93	.2870	1.6275	.8238
15	.4874	40.36	.3277	2.5517	.8858
16	.6583	40.75	.4426	4.5230	.8773

In the treatment of the results above the first problem was to find the variation of $\gamma/\mathbf{p}$ with R/r when R^3/V is kept constant at various values, so that the values of $\gamma/\mathbf{p}$ found experimentally could be converted into those of the closest even value of R/r. While the values could have been

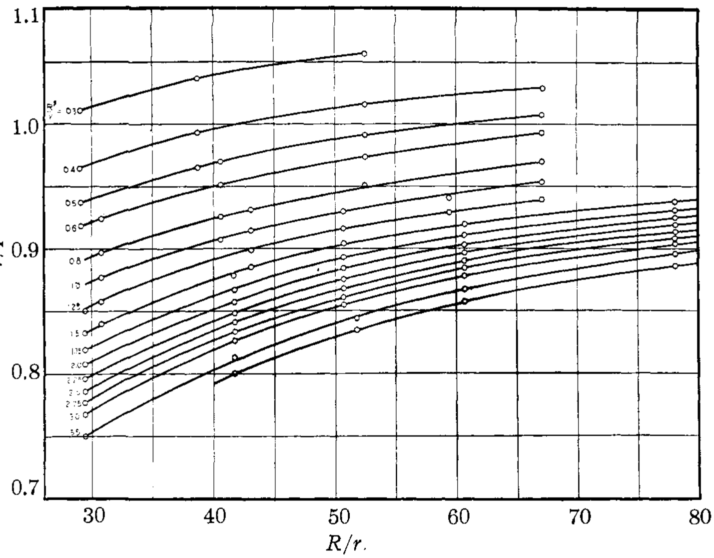

Fig. 6.—Correction curves for ring method.

read from the $\gamma/\mathbf{p} - R^3/V$ plots of the values above, it was found that in the case of the smaller rings the curvature of the plot was so great that this could not be done accurately. Other functions were then resorted to

Table VII

Experimental Values

Ring no.	Water R^3/V	Water $\gamma/\mathbf{p}$	Bromobenzene R^3/V	Bromobenzene $\gamma/\mathbf{p}$	Benzene R^3/V	Benzene $\gamma/\mathbf{p}$	R/r
1	0.2055	1.1116	0.5334	0.9569	0.4096	0.9932	40
2	.4079	1.0222	1.1290	.9356	.8561	.9555	60
3	.2973	1.0556	0.8030	.9459	.6099	.9680	50
4	.6673	0.9408	1.8423	.8600	1.4000	.8810	40
5	1.0305	.9268	2.8635	.8557	2.1765	.8764	50
6	1.4771	.9208	4.1181	.8532	3.1320	.8742	60
7	1.4055	.8785	3.8474	.7967	2.9437	.8217	40
9	0.2474	1.0496	0.6461	.9122	0.4949	.9412	30
10	.4318	0.9859	1.1753	.8920	.8946	.9145	40
11	2.1996	.8725	6.0380	.7953	4.6122	.8185	50
12	3.1601	.8744	8.6909	.7989	6.6312	.8211	60
13	1.2749	.8504	3.4096	.7570	2.6256	.7848	30
14	0.6009	.9216	1.6275	.8288	1.2452	.8541	30
15	.9072	.9481	2.5517	.8869	1.9352	.9058	60
16	1.6030	.9368	4.523	.8773	3.4332	.8989	80

in order to reduce this inaccuracy. The values for rings with R^3/V between 0 and 1.0 were determined by plotting V/R^3 against $\gamma/\mathbf{p}$, and the values for rings with R^3/V values above 1.0 were determined by plotting log R^3/V against log $\gamma/\mathbf{p}$. In this way the curvature of the graphs was decreased to a minimum, and the accuracy greatly increased. When the resulting values of $\gamma/\mathbf{p}$ are plotted against R/r, the series of curves shown in Fig. 6 is obtained. The values of $\gamma/\mathbf{p}$ were then corrected to those of the closest value of R/r. These values are 30, 40, 50, 60 and 80. The corrected experimental values are given in Table VII.

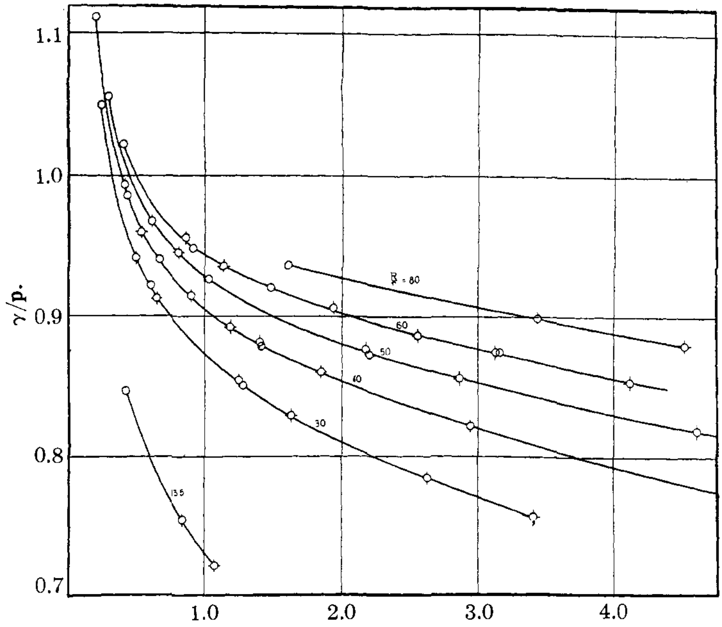

Fig. 7.—Correction curves for ring method.

The curves obtained by plotting the values above are shown in Fig. 7. Those obtained by plotting the values logarithmically are shown in Fig. 8. It is seen that the curvature is greatly reduced by plotting the values in the latter way. By use of the $\gamma/\mathbf{p} - R/r$ graphs, curves were also obtained for intermediate values of R/r, from which were read the values that compose the table mentioned in the following section.

9. Ring Method Correction (F) for the Shapes of the Surfaces

In order to avoid the necessity of plotting the corrected experimental values for use in actual work, a table was constructed for a number of intermediate values of R/r as well as the even values. The values of $\gamma/\mathbf{p}$ given in the tables for R/r (except for too low values of R^3/V) equal to 30, 40, 50, 60 and 80 are considered accurate to 0.3% with a probable error of less than 0.2%, while those for the intermediate values of R/r are con-

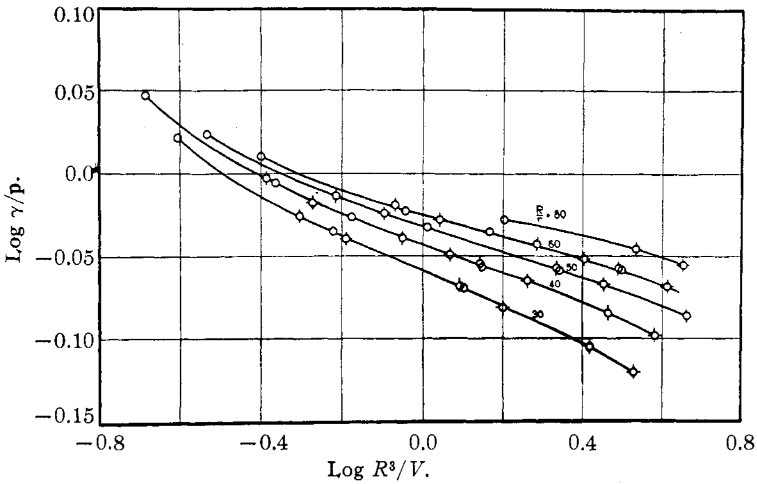

Fig. 8.—Correction curves for ring method.

sidered accurate to 0.4% with a probable error of less than 0.3%. The values are given in Table VIII.

10. Weights of the Residual Drops on the Rings

There has been a discussion concerning the importance of the drops of liquid which adhere to the ring after it has been pulled out of the liquid. Klopsteg[7] suggested that the zero weight should be taken at the weight of the ring plus the weight of the drops of liquid which adhere to it, while MacDougall[8] considers that such a correction is not justified. As a result manufacturers have printed instructions that in the use of their apparatus the intial reading be taken at the weight of the ring in air plus the weight of the adhering drops, and suggest that additional accuracy is acquired. Since, as may be seen from the experimental data presented in this paper, most of the values for surface tension (p) obtained by the

TABLE VIIIA

CORRECTION FACTORS FOR EVEN VALUES OF R/r

R^3/V	γ/p or F R/r = 30	γ/p or F R/r = 40	R^3V	γ/p or F R/r = 30	γ/p or F R/r = 40
0.20	...	1.119	0.26	1.048	1.070
.21	...	1.108	.26	1.039	1.063
.22	...	1.097	.27	1.031	1.056
.23	...	1.087	.281	1.025	1.050
.24	1.056	1.078	.29	1.018	1.043

[7] Klopsteg, *Science*, **60**, 319 (1924).

[8] MacDougall, *ibid.*, [N. S.] **62**, 290 (1925).

TABLE VIIIB

CORRECTION FACTORS (F) FOR THE RING METHOD

R^3/V	$R/4$ = 30	32	34	36	38	40	42	44	46	48	50	R/r = 52	54	56	58	60
0.30	1.012	1.018	1.024	1.029	1.034	1.038	1.042	1.046	1.049	1.052	1.054					
.31	1.006	1.013	1.018	1.024	1.028	1.033	1.039	1.041	1.044	1.046	1.049					
.32	1.001	1.008	1.012	1.019	1.023	1.028	1.033	1.035	1.039	1.041	1.045					
.33	0.9959	1.003	1.008	1.014	1.018	1.024	1.028	1.030	1.035	1.036	1.040					
.34	.9913	0.998	1.003	1.010	1.014	1.019	1.023	1.026	1.031	1.032	1.036					
.35	.9865	.993	0.999	1.006	1.008	1.015	1.019	1.022	1.026	1.027	1.031					
.36	.9824	.989	.995	1.002	1.005	1.010	1.015	1.018	1.022	1.024	1.027					
.37	.9781	.985	.991	0.998	1.001	1.006	1.011	1.014	1.018	1.020	1.024					
.38	.9743	.981	.987	.995	0.998	1.003	1.007	1.010	1.015	1.017	1.020					
.39	.9707	.977	.983	.991	.994	0.9988	1.004	1.007	1.011	1.013	1.017					
.40	.9672	.974	.980	.986	.991	.9959	1.000	1.004	1.008	1.010	1.013	1.016	1.018	1.020	1.021	1.022
.41	.9636	.970	.976	.983	.987	.9922	0.997	1.001	1.005	1.007	1.010	1.013	1.015	1.017	1.019	1.019
.42	.9605	.968	.973	.980	.984	.9892	.994	0.998	1.002	1.004	1.007	1.010	1.013	1.014	1.016	1.017
.43	.9577	.964	.970	.977	.981	.9863	.991	.995	.999	1.001	1.005	1.007	1.010	1.011	1.014	1.014
.44	.9546	.961	.967	.974	.979	.9833	.988	.992	.997	0.998	1.002	1.005	1.007	1.009	1.011	1.011
.45	.9521	.959	.965	.971	.976	.9809	.986	.990	.993	.996	0.9993	1.002	1.004	1.006	1.009	1.009
.46	.9491	.956	.962	.969	.973	.9779	.983	.987	.991	.994	.9968	1.000	1.002	1.004	1.006	1.007
.47	.9467	.954	.960	.966	.971	.9757	.980	.985	.988	.992	.9945	0.998	1.000	1.002	1.004	1.005
.48	.9443	.951	.957	.963	.968	.9732	.978	.983	.986	.989	.9922	.995	0.997	0.999	1.002	1.003
.49	.9419	.949	.955	.961	.966	.9710	.976	.981	.984	.987	.9899	.993	.995	.997	1.000	1.001

TABLE VIIIC

CORRECTION FACTORS (F) FOR THE RING METHOD

R^3/V	R/r = 30	32	34	36	38	40	42	44	46	48	50	52	54	56	58	60
0.50	0.9402	0.946	0.952	0.959	0.964	0.9687	0.973	0.978	0.981	0.985	0.9876	0.991	0.993	0.995	0.997	0.9984
.51	.9378	.944	.950	.956	.961	.9665	.971	.976	.979	.983	.9856	.989	.991	.993	.995	.9965
.52	.9354	.942	.948	.954	.959	.9645	.969	.974	.977	.981	.9836	.987	.989	.991	.994	.9945
.53	.9337	.940	.946	.952	.957	.9625	.967	.972	.975	.979	.9815	.985	.987	.990	.992	.9929
.54	.9315	.938	.944	.950	.955	.9603	.965	.970	.974	.977	.9797	.983	.986	.988	.990	.9909
.55	.9298	.936	.942	.948	.953	.9585	.964	.968	.972	.975	.9779	.981	.984	.986	.988	.9892
.56	.9281	.934	.940	.946	.951	.9567	.962	.966	.970	.974	.9763	.980	.982	.984	.986	.9879
.57	.9262	.932	.939	.944	.949	.9550	.960	.964	.968	.972	.9745	.978	.980	.983	.984	.9861
.58	.9247	.930	.938	.942	.947	.9532	.958	.963	.966	.970	.9730	.976	.979	.981	.982	.9842
.59	.9230	.929	.935	.940	.946	.9515	.956	.961	.965	.968	.9714	.975	.977	.979	.981	.9827
.60	.9215	.927	.933	.939	.944	.9497	.954	.959	.963	.967	.9701	.973	.976	.978	.979	.9813
.62	.9184	.924	.930	.936	.041	.9467	.951	.956	.960	.964	.9669	.970	.973	.975	.976	.9784
.64	.9150	.921	.927	.932	.938	.9439	.948	.953	.957	.961	.9643	.968	.970	.972	.973	.9754
.66	.9121	.918	.925	.930	.935	.9408	.946	.950	.954	.959	.9614	.965	.967	.969	.971	.9728
.68	.9093	.915	.921	.927	.932	.9382	.943	.948	.951	.956	.9590	.963	.965	.967	.968	.9703
.70	.9064	.912	.919	.924	.929	.9352	.940	.945	.949	.953	.9563	.960	.962	.964	.966	.9678
.72	.9037	.910	.916	.921	.927	.9328	.937	.943	.946	.951	.9542	.957	.960	.962	.964	.9656
.74	.9012	.907	.913	.919	.924	.9303	.935	.940	.944	.949	.9519	.955	.958	.960	.962	.9636
.76	.8987	.905	.911	.916	.922	.9277	.933	.938	.942	.947	.9459	.953	.956	.958	.860	.9616
.78	.8964	.902	.908	.914	.920	.9258	.930	.936	.939	.944	.9475	.951	.954	.956	.958	.9598

TABLE VIIID

CORRECTION FACTORS (F) FOR THE RING METHOD

R^3/V	R/r = 30	32	34	36	38	40	42	44	46	48	50	52	54	56	58	60
0.80	0.8937	0.900	0.906	0.912	0.918	0.9230	0.928	0.933	0.937	0.942	0.9454	0.949	0.952	0.954	0.956	0.9581
.82	.8917	.898	.904	.909	.915	.9211	.926	.931	.935	.940	.9436	.947	.950	.952	.954	.9563
.84	.8894	.895	.902	.907	.913	.9190	.924	.929	.933	.938	.9419	.946	.949	.951	.953	.9548
.86	.8874	.893	.900	.905	.911	.9171	.922	.927	.932	.936	.9402	.944	.947	.949	.951	.9534
.88	.8853	.891	.898	.903	.909	.9152	.921	.926	.930	.934	.9384	.942	.945	.947	.950	.9517
.90	.8831	.889	.896	.902	.907	.9131	.919	.924	.928	.933	.9367	.940	.943	.946	.948	.9504
.92	.8809	.887	.894	.900	.905	.9114	.917	.922	.926	.931	.9350	.939	.942	.945	.947	.9489
.94	.8791	.885	.892	.898	.904	.9097	.915	.920	.925	.929	.9333	.937	.940	.943	.945	.9476
.96	.8770	.883	.890	.896	.902	.9074	.914	.919	.923	.928	.9320	.936	.939	.942	.944	.9462
.98	.8754	.882	.888	.894	.900	.9064	.912	.917	.922	.926	.9305	.934	.937	.940	.943	.9452
1.00	.8734	.880	.886	.892	.899	.9047	.910	.916	.920	.925	.9290	.933	.936	.939	.941	.9438
1.05	.8688	.875	.882	.888	.895	.9007	.906	.912	.916	.921	.9253	.929	.932	.936	.938	.9408
1.10	.8644	.871	.878	.885	.891	.8970	.903	.908	.913	.917	.9217	.925	.929	.933	.935	.9378
1.15	.8602	.867	.875	.881	.888	.8937	.900	.905	.910	.914	.9183	.922	.926	.930	.933	.9352
1.20	.8561	.864	.871	.878	.885	.8904	.897	.902	.907	.911	.9154	.920	.923	.927	.930	.9324
1.25	.8521	.860	.868	.875	.882	.8874	.893	.899	.904	.908	.9125	.916	.920	.924	.927	.9300
1.30	.8484	.856	.864	.871	.879	.8845	.891	.896	.901	.905	.9097	.914	.917	.921	.925	.9277
1.35	.8451	.853	.861	.869	.876	.8819	.888	.893	.898	.903	.9068	.911	.915	.919	.922	.9253
1.40	.8420	.850	.858	.866	.873	.8794	.885	.891	.896	.900	.9043	.909	.913	.916	.920	.9232
1.45	.8387	.847	.855	.863	.871	.8764	.883	.888	.893	.898	.9014	.906	.910	.914	.918	.9207

TABLE VIIIE

CORRECTION FACTORS (F) FOR THE RING METHOD

R^3/V	R/r = 30	32	34	36	38	40	42	44	46	48
1.50	0.8356	0.844	0.853	0.861	0.868	0.8744	0.881	0.886	0.891	0.895
1.55	.8327	.841	.850	.858	.866	.8722	.878	.883	.888	.893
1.60	.8297	.839	.848	.856	.863	.8700	.876	.881	.886	.891
1.65	.8272	.836	.845	.853	.861	.8678	.874	.879	.884	.889
1.70	.8245	.834	.843	.851	.859	.8658	.872	.877	.882	.886
1.75	.8217	.831	.840	.849	.857	.8638	.870	.875	.880	.884
1.80	.8194	.829	.838	.847	.855	.8618	.868	.873	.878	.882
1.85	.8168	.827	.836	.845	.853	.8596	.866	.871	.876	.881
1.90	.8143	.824	.834	.943	.851	.8578	.864	.869	.874	.879
1.95	.8119	.822	.832	.841	.849	.8559	.862	.867	.872	.877
2.00	.8098	.820	.830	.839	.847	.8539	.860	.865	.870	.875
2.10	.8056	.816	.826	.835	.843	.8502	.856	.862	.867	.872
2.20	.8015	.812	.822	.831	.839	.8464	.853	.858	.864	.869
2.30	.7976	.808	.818	.828	.835	.8428	.849	.855	.861	.866
2.40	.7936	.804	.814	.824	.832	.8393	.846	.852	.857	.863
2.50	.7898	.800	.811	.820	.828	.8360	.843	.849	.854	.860
2.60	.7861	.797	.807	.817	.825	.8325	.840	.846	.851	.857
2.70	.7824	.793	.803	.813	.822	.8291	.836	.843	.848	.854
2.80	.7788	.790	.800	.810	.818	.8260	.834	.840	.846	.852
2.90	.7752	.786	.796	.806	.815	.8230	.831	.837	.843	.849
3.00	.7716	.783	.793	.803	.812	.8200	.828	.834	.841	.846
3.10	.7677	.779	.790	.800	.809	.8170	.825	.832	.838	.844
3.20	.7644	.776	.787	.797	.806	.8140	.822	.829	.835	.842
3.30	.7610	.772	.783	.793	.803	.8113	.820	.827	.833	.840
3.40	.7572	.769	.780	.790	.800	.8083	.817	.824	.831	.837
3.50	.7542	.766	.777	.788	.798	.8057	.814	.822	.829	.835

R^3/V	50	52	54	56	58	60	65	70	75	80
1.50	0.8995	0.904	0.908	0.912	0.916	0.9190	...	...	...	...
1.55	.8970	.901	.906	.910	.914	.9171	...	...	...	0.9382
1.60	.8947	.899	.904	.908	.912	.9152	0.922	0.928	0.933	.9365
1.65	.8927	.897	.902	.906	.910	.9133	.921	.927	.931	.9354
1.70	.8906	.895	.900	.904	.909	.9116	.919	.925	.930	.9341
1.75	.8886	.893	.898	.902	.907	.9097	.918	.924	.929	.9328
1.80	.8867	.891	.896	.900	.905	.9080	.916	.922	.927	.9317
1.85	.8849	.889	.895	.899	.903	.9066	.915	.921	.926	.9305
1.90	.8831	.888	.893	.897	.902	.9047	.913	.919	.925	.9291
1.95	.8815	.886	.891	.895	.900	.9034	.912	.918	.923	9281
2.00	.8798	.884	.890	.893	.899	.9016	.910	.917	.922	.9270
2.10	.8768	.881	.886	.890	.895	.8991	.908	.914	.920	.9247
2.20	.8738	.879	.883	.887	.892	.8962	.905	.911	.917	.9226
2.30	.8710	.876	.880	.884	.890	.8935	.903	.909	.915	.9206
2.40	.8680	.873	.878	.882	.887	.8910	.900	.907	.913	.9185
2.50	.8651	.870	.875	.879	.884	.8884	.898	.904	.910	.9166
2.60	.8624	.868	.872	.877	.882	.8859	.895	.902	.908	.9145
2.70	.8598	.865	.870	.874	.880	.8837	.893	.900	.906	.9126
2.80	.8570	.862	.867	.872	.877	.8813	.891	.898	.904	.9107
2.90	.8545	.860	.865	.870	.875	.8790	.889	.896	.902	.9089
3.00	.8521	.858	.863	.868	.873	.8770	.887	.894	.900	.9068

TABLE VIIIE (*Concluded*)

R^3/V	50	52	54	56	58	60	65	70	75	80
3.10	0.8494	0.855	0.860	0.866	0.871	0.8750	0.885	0.892	0.899	0.9049
3.20	.8472	.853	.858	.864	.869	.8730	.883	.890	.897	.9030
3.30	.8449	.851	.856	.862	.866	.8710	.881	.888	.895	.9012
3.40	.8424	.849	.854	.860	.864	.8688	.879	.886	.893	.8993
3.50	.8404	.847	.852	.858	.862	.8668	.877	.884	.892	.8974

pseudo-ring method are too high, the values seem to be improved, but this is done only by introducing a second error. The theory indicates that the zero point should be taken at the weight of the dry ring in air. The weight of liquid which adheres to one of our rings is constant if the air is saturated with vapor, and values of the weights of liquid which adhere to some of the rings are given in Table IX.

TABLE IX

WEIGHT OF RESIDUAL DROPS

Ring no.	Water	Benzene	Ring no.	Water	Benzene
2	0.0013	......	8	....	0.0033
3	.0015	......	9	0.0018	.0009
5	.0033	......	10	.0167	.0019
6	.0044	......	11	....	.0044
7	.0081	......	14	.0155	.0029

11. The Variation of the Pull on the Ring with the Height of the Ring above the Free Liquid Surface

Dorsey[9] has recently suggested that many workers, particularly those using the DuNoüy tensiometer, might be measuring the pull of a film of liquid upon the ring rather than the maximum pull of the liquid. It was therefore considered important to study the variation of the pull on the ring with the distance it is raised above the free surface of the liquid. The values, which are shown graphically in Fig. 9, are given in Table X. Ring 10 was used.

TABLE X

RESULTS

Pull in grams	Height in cm.	Pull in grams	Height in cm.
0.3064	0.062	0.5894	0.290
.4064	.120	.5909	.300
.4564	.151	Maximum = 0.5912	...
.5064	.186	0.5898 to 0.5899	.305
.5264	.203	.5836 to .5895	.319
.5464	.223	.5823 to .5875	.324
.5664	.248	.5730 to .5839	.338
.5764	.262	.5616 to .5712	.352
.5864	.279	.5425 to .5606	.365
.5884	.287	.5066 to ...	.380, height at detachment

[9] Dorsey, *Science*, 69, 187 (1929).

It is evident that as the ring is pulled out of the liquid the pull on it increases to a maximum and then decreases.

It is at once evident that there is no danger of measuring any other than the maximum pull with the balance with the technique used, since great difficulty was experienced in measuring points beyond the maximum. After the maximum pull had been reached, the balance pointer swung to the left and could be made to return only by decreasing the weight by fifteen or twenty milligrams, when it would swing quickly to the right and remain there. During this time its motion was restricted by the beam rest to one division in either direction from the scale zero. In

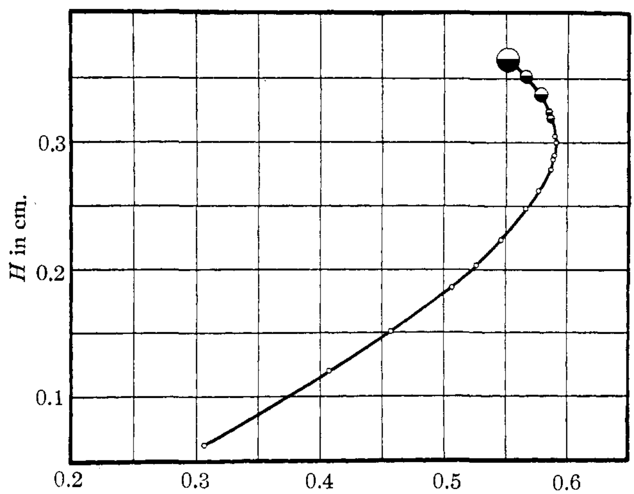

Fig. 9.—Variation of pressure with height of ring.

order to make any measurements of even low precision beyond the maximum it was necessary to attach a stop which would allow the pointer to swing from zero to a point one-half scale division away in one direction at a time. The weight that would just suffice to make the pointer leave zero in one direction and then the weight to make it leave in the other direction were determined. In this way the limits of the pull on the ring were determined for the heights above the height of maximum pull.

It was noticed, particularly in the case of the smaller rings, that the liquid column had a tendency to adhere to the ring and be pulled out into a film after the pointer had swung to the left, signifying that the maximum pull had been reached. If, however, the beam rest is further released from under the balance beam the liquid breaks. Until the maximum pull is reached the edge of the liquid meniscus appears to be attached to the ring.

12. Preliminary Application of the Ring Method to Interfacial Tension

Measurements of the interfacial tension between water and benzene were also made in order to see whether the ring method is a practical one for such measurements.

The general method of measurement was the same as for surface tension with only slight modifications. The measurements were carried out in a 2-liter Erlenmeyer flask provided with a special long neck. The ring was connected with the aluminum rod running up to the balance beam by means of a length of platinum wire 0.1 mm. in diameter. This was quite fine, in order to reduce the effect of surface forces and the effect of buoyancy. The layer of benzene was several centimeters deep, so that the ring and its stirrups were completely immersed throughout the measurements. The initial weight was the weight of the ring completely immersed in benzene. The results obtained with Rings 7 and 5 are given in Table XI. The interfacial tension is calculated by use of the correction factors (F).

Table XI

Results

Ring	M	p	V	R^3/V	γ/p	γ
7	0.5345	34.33	4.335	0.4132	0.995	34.16
5	.4190	32.23	3.398	.3070	1.051	33.91

t, 25°; $(D - d) = 0.1233$; γ by the drop weight–volume method, 34.71.

On account of the steepness of the correction curves in this region, better results could probably be obtained with larger rings (of as small or smaller wire).

In the ring method the angle of contact between the interface and the ring must be zero, a condition which is more difficult to meet, in general, with interfacial than with surface tension.

There are probably a number of additional factors to be considered in the measurement of interfacial tension by the ring method, but the deviations from the standard value are not greater than is to be expected from the first preliminary determinations.

Measurements were also made with smaller rings and the values of γ/**p**

Table XII

Data

Ring	M	p	V	R^3/V	γ/p
1	0.1272	23.95	1.032	0.0689	1.449
2	.2103	27.05	1.706	.1308	1.283
3	.1680	25.68	1.363	.0997	1.352
4	.3120	30.13	2.530	.2083	1.134
9	.1513	25.23	1.227	.0835	1.376
10	.2281	27.95	1.850	.1395	1.242

γ, 34.71; $(D - d) = 0.1233$.

were calculated by assuming that the interfacial tension measured had the standard value. The purpose of this was to show the magnitude of the error that may be introduced by neglect of the correction factors. The data are given in Table XII.

It is seen that as high as 45% error may be incurred by this neglect in the measurement by the use of a moderately small ring, since R^3/V is very small, and the curvature in this region of the curve is very great. The neglect of the correction with the ring furnished with the Cenco Tensiometer gives results which are 20% too low, which accounts for the extremely inaccurate results which have been obtained in the measurement of interfacial tension by the "ring method."

Summary

1. Until three years ago there was no *ring method* for the *measurement* of surface tension, since, in general, all that was determined was the pull on a ring, and this pull was incorrectly assumed to be equal to the surface tension multiplied by twice the mean circumference of the ring. Even in cases in which attempts were made to use the incomplete theory of the ring method, it was found that rings of the dimensions required by the theory were incapable of use. Three years ago Harkins, Young and Cheng applied the principle of similitude to this problem, and determined the values of the function F in the correct equation

$$\gamma = \frac{\mathbf{M}g}{4\pi R} \times f(R^3/V,\ R/r) = \frac{\mathbf{M}g}{4R}\ F$$

In this paper a larger number of values of F, determined to a higher degree of accuracy, are given. These were obtained by determining the values of the maximum pull ($\mathbf{P} = \mathbf{M}g$) for sixteen rings with radii from 0.4 to 0.8 cm. made from wire with radii between 0.009 and 0.05 cm. and with values of R/r between 13.9 and 78.3.

2. The values of the maximum pull were determined for three liquids: water, benzene and bromobenzene. Accurate determinations of the surface tension by the capillary height method gave for the liquids used 28.23 dynes per cm. for benzene and 35.75 for bromobenzene at 25°.

3. Various sources of error in the experimental methods were investigated. (a) The error introduced when the plane of the ring is not horizontal is proportional to the square of the angle of tip when the angle is small. An angle of 0.4 degree causes an error of 0.1% and 1.0 degree of 0.45%. (b) The diameter of the vessel which confines the surface of the liquid should be not less than 8 cm. (c) An error is introduced if the ring does not lie in a plane.

4. An apparatus for the accurate determination of surface tension by the ring method is described. This consists of a chainomatic balance, supported by a machine which raises or lowers it with a minimum amount

of vibration, and a special flask, designed to give a clean liquid surface, buried under the water of a thermostat.

5. It was found that the accuracy of measurement of the dimensions of the rings depends greatly upon the method of illumination employed, and apparatus for these measurements was developed.

6. It was shown that at a certain height above the surface of the liquid the pull on the ring reaches a maximum. This maximum pull is what was determined in the measurements reported.

7. A necessary condition of the ring method is that the angle of contact between the ring and the liquid be zero.

8. Preliminary measurements indicate that the ring method may be used for the determination of interfacial tension.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND FROM ARMOUR INSTITUTE OF TECHNOLOGY]

A THEORY OF THE RING METHOD FOR THE DETERMINATION OF SURFACE TENSION

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The most convenient method for the determination of surface tension is perhaps what is known as the ring method. It has been used extensively, for example, by DuNoüy[1] in the case of numerous biological liquids. It is convenient because the experimental procedure necessary to obtain a fair degree of accuracy can be made very simple, although of course it becomes much more complicated when a higher degree of accuracy is sought. The essentials of the procedure are a ring, capable of being wetted by the liquid whose surface tension is to be measured, suspended horizontally in the flat surface of that liquid, and some device to measure the force necessary to separate ring and liquid. That the applied force may be changed gradually, a torsion balance is often used but a beam balance of the chainomatic type is also satisfactory. From this measured force, expressed as a weight, a quantity which many assume to be the value of the surface tension is often obtained from the relationship

$$W = 4\pi R\gamma \tag{1}$$

where R is the radius of the ring, γ the surface tension and W the maximum weight of liquid held up or the pull on the ring at the instant of rupture. Modifications have been introduced into this equation, such as the substitution of $(R_1 + R_2)/2$ for r, where R_1 and R_2 are the inner and outer radii of the ring. But the validity of this relationship is not at all obvious. An experimental study of it by Harkins, Young and Cheng[2] and

[1] DuNoüy, *J. Gen. Physiol.*, **1**, 521 (1918–1919), etc.

[2] Harkins, Young and Cheng, *Science*, **64**, 93 (1926).