

AN INTERFACIAL TENSIO METER FOR UNIVERSAL USE.

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PLATE 5.

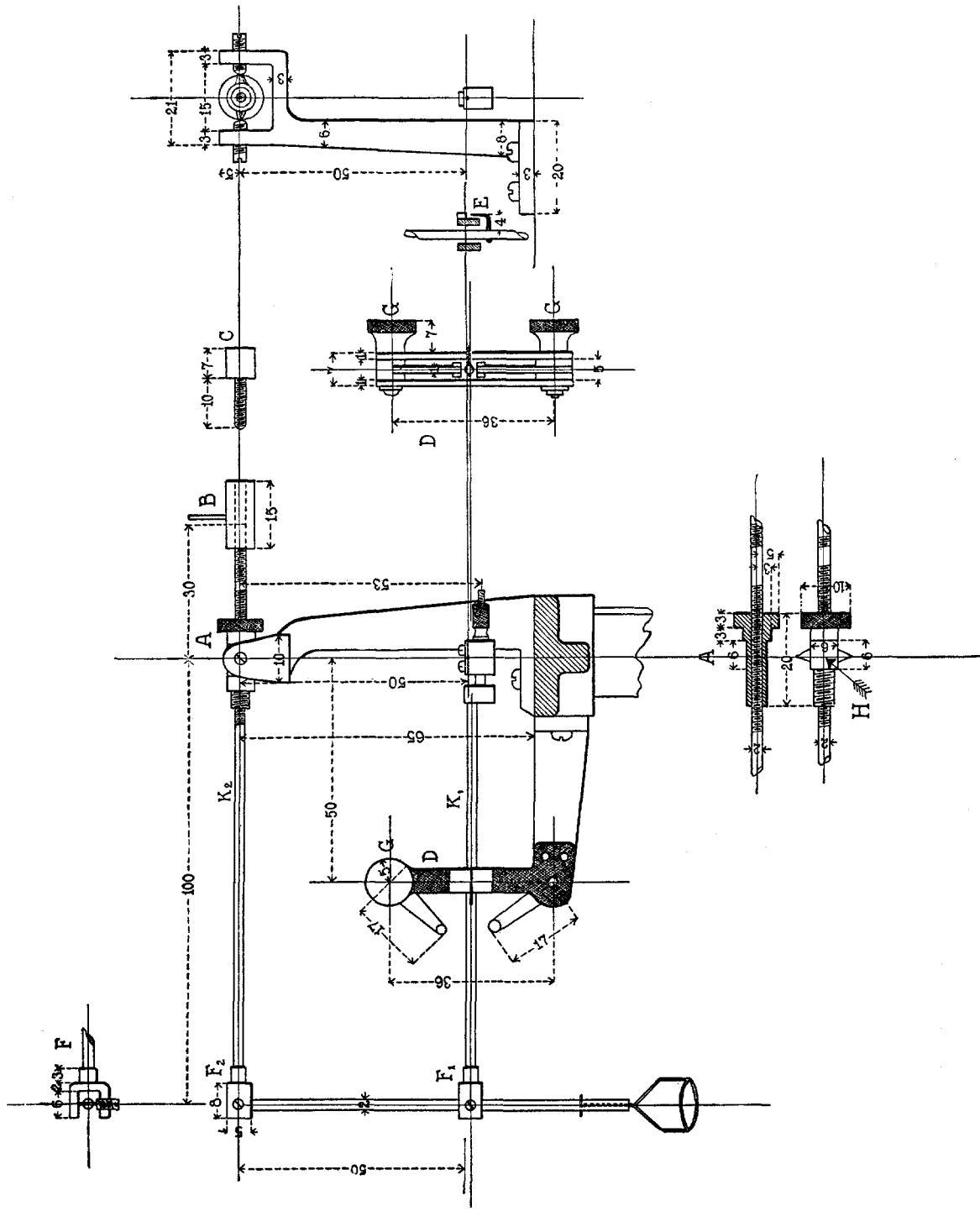
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The important and fundamental works of Quincke, Hardy, McC. Lewis, Morgan, and lately Harkins and his collaborators have thrown much light on the behavior of liquids at interfaces, and it may seem hardly necessary to develop a new method in order to study this phenomenon, as those existing have reached a high degree of accuracy. However, if the values of the interfacial tensions of pure liquids have been well established by these investigators and others, the changes of the interfacial tension due to adsorption in function of time—a phenomenon similar to that first studied in our laboratory¹—have not, to our knowledge, been studied so far, for lack of proper technique. Consequently, considering the number of new phenomena which were brought to light by the use of the tensiometer first described in this Journal 6 years ago² we thought it might be of interest to devise a similar instrument with which measurements of interfacial tension could be made in a few seconds, conveniently, in any laboratory, to 0.1 dyne.

Our first idea was to utilize the tensiometer as it actually exists on the market, with perhaps a slight modification of the platinum ring. However, as the ring can only be pulled upwards, it limits the measurements for water interfaces, to liquids floating on water; *i.e.*, having a specific gravity < 1. In order to render the instrument universal, it was decided to fix the ring to a rigid support, so that it could be pressed down by means of the torsion wire, as well as pulled

¹ du Noüy, P. L., Papers I-X and XII, *J. Exp. Med.*, 1922-25, xxxv-xli; Paper XI, *J. Gen. Physiol.*, 1923-24, vi, 625.

² du Noüy, P. L., *J. Gen. Physiol.*, 1918-19, i, 521.



TEXT-FIG. 1.

up. This rigid support is kept in its perpendicular position by means of an articulated parallelogram, $K_1F_1K_2F_2$ as seen in Text-fig. 1. The length of both horizontal arms can be adjusted so as to change the moment of the force applied to the ring, and to make the instrument direct reading.

The balance of the whole moving system is grossly obtained by a counterweight, B , and the finer adjustment of the zero is realized, as in the ordinary tensiometer, by twisting more or less the end of the torsion wire.

The instrument is standardized with weights, in the usual way by considering that the formula

$$\gamma = \frac{M \cdot g}{2L}$$

in which M = mass in gm. (arbitrary) placed on the ring, $g = 981$, L = mean length of circumference of ring (6 cm., for instance), gives a value γ which must be the figure read on the dial, when the equilibrium is attained. In case the figures do not coincide, the length of both arms, the upper one, K_2 , and the lower one, K_1 is slightly increased or shortened, according to the difference. The weights are then removed and the vernier is brought back to zero by means of the knob. If, in this position, the needle E on the lower arm, does not coincide with the index line on the post D , it is set by means of the torsion wire, and the operation must be repeated with weights. It takes usually less than 10 minutes to standardize the instrument perfectly. When this is done, it is, of course, standardized not only for upward pull (vernier on upper part of the scale) but also for downward push (vernier on lower part of the scale) and the readings are identical in both ways. The scale is graduated throughout the circumference of the dial.

A few measurements were taken with substances studied by Harkins, Brown, and Davies (drop method).³ No attempt was made to secure pure liquids, our only aim being to check the soundness of the method. As Harkins and his collaborators took special pains in order to secure absolutely pure materials the discrepancies found

³ Harkins, W. D., Brown, F. E., and Davies, E. C. H., *J. Am. Chem. Soc.*, 1917, xxxix, 356.

between their values and the tensiometric values may be accounted for in this way for the substances spreading on water (Table I). However, the values disagree entirely for the liquids which do *not* spread on water, namely those having an interfacial tension greater

TABLE I.
Surface Tension and Interfacial Tension against Water.

Experiment No	Liquid.	Temperature. °C.	Dynes cm. γ	Interfacial tension against water. γ_{wp}	Difference. $\gamma - \gamma_{wp}$	Sp. gr.	
1	Chloroform.....	25.0	27.5	27.9	+0.4	1.526	
2	Isoamyl alcohol.....	23.5	24.2	4.4	-19.8	0.825	
3	Octyl alcohol.....	25.0	28.6	10.8	-17.8	0.837	
4	Benzyl alcohol.....	25.0	43.3	4.8	-38.5	1.023	
5	Ethyl iodide.....	25.0	32.3	36.6	+4.3	1.944	
6	Ethyl ether.....	23.0	18.0	10.9	-7.1	0.718	
7	Ethyl phthalate.....	25.0	40.8	16.4	-24.4	1.126	
8	Ethyl carbonate.....	25.0	29.0	11.9	-18.1	0.978	
9	Oleic acid.....	25.0	34.2	12.8	-21.4	0.708	
10	Benzene.....	25.0	29.0	32.3	+1.3	0.880	
11	Toluene.....	25.0	28.0	32.5	+4.5	0.882	
12	<i>m</i> -xylene.....	23.0	30.0	35.0	+5.0	0.878	
13	Castor oil.....	23.0	36.4	15.4	-21.0	0.950	
14	Olive oil.....	23.0	33.0	17.0	-16.0		
15	Dimethyl aniline.....	26.0	38.4	21.0	-18.9	0.955	
16	Diethyl aniline.....	25.0	35.4	21.3	-14.1		
17	Turpentine.....	25.0	29.2	13.7	-15.5		
18	"Non-spreading liquids," according to Harkins.	Carbon bisulfide.....	20.0	34.0	33.8	-0.2	1.259
19		Paraffin oil.....	25.0	32.0	47.0	+15.0	0.850
20		Carbon tetrachloride.....	23.0	28.0	40.0	+12.0	1.608
21		Bromoform.....	25.0	39.5	27.5	-12.0	
22		Liquid petrolatum Squibbs....	24.0	33.0	49.0	+16.0	

than the difference between the surface tension of water and that of the liquid. In this case, no tension is greater than the sum of the other two, and a triangle of forces is possible and real.

Nevertheless, and without questioning the accuracy of Harkins' values for the interfacial tension between water and this special class

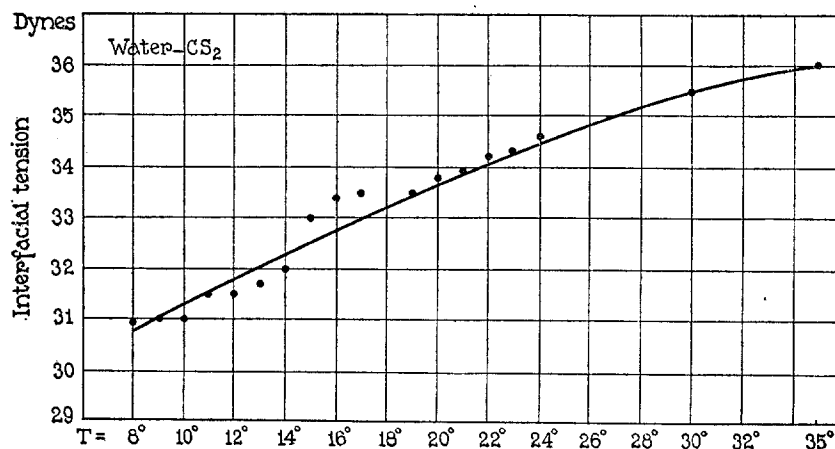
TABLE II.
Comparison between Interfacial Values.

No.....	"Non-spreading."																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	18	19	20	21	22
Tensiometer (du Noüy).....	27.9	4.4	10.8	4.8	36.6	10.9	16.4	11.9	12.8	32.3	32.5	35.0	15.4	17.0	21.0	33.8	47.0	37.2	27.5	49.0
Drop method (Harkins).....	27.7	4.42	8.52	4.75	40.02	10.7	16.27	12.86	15.5	34.97	36.10	37.6	22.63	25.78	54.09	52.63	40.85	55.32		
Cathetometer (Quincke).....													18.2	37.4						

TABLE III.
Interfacial Tension as a Function of Temperature.

Temperature, °C.....	8	9	10	11	12	13	14	15	16	17	19	20	21	22	23	24	30	35	40	45
Interfacial tension, water-CS ₂	30.9	31.0	31.0	31.5	31.5	31.7	32.0	33.0	33.4	33.5	33.5	33.8	33.9	34.2	34.3	34.6	35.5	36.0		
" " water-ethyl ether.....	9.5	9.5			9.7		10.0	10.3		10.4	10.6		10.9		11.2	11.7	11.9	12.2	12.9	

of substances, it might be pointed out that Quincke,⁴ using a cathetometric method, gave, for the interfacial tension water-CS₂, the value 42.6 dynes. As he finds 82.5 for the surface tension of water, while we find 72.8, one might think that it is permissible to reduce this value 42.6 in the ratio $\frac{82.5}{72.8}$ and one obtains 37.4. Our value for water-CS₂ is 33.8, and that of Harkins, 54.09. Quincke's method seems quite reliable, and his figures are in good agreement with Harkins' and ours for water-chloroform (26.5 corrected as above) and water-olive oil (18.2). The difference between the values of Harkins' and those of Quincke and ourselves is probably due to the fact that Harkins



TEXT-FIG. 2.

measures the dynamic tension, while we measure the static value. Since Professor Harkins states that his "method is undoubtedly the most accurate of all those which have been devised, but [that] it has given the most inaccurate results because the corrections which have been used by workers other than ourselves are incorrect," we feel quite certain that his values are standard, and we do not pretend to compete with such a definite statement. Our aim was to devise a method which, although far from claiming to be the most accurate, would nevertheless not require corrections so important as to render it inaccurate in the hands of others. In other words, a simple, rapid,

⁴ Quincke, M. G., *Phil. Mag.*, 1871, xli, series 4, 245.

convenient technique which would make it possible to study the adsorption at interfaces and give the static value of interfacial tension, just as the tensiometer gives the static value of surface tension. The action of temperature will be very easy to investigate. From a first series of experiments with water-CS₂, we have gathered evidence that, contrary to what happens at the air-liquid surface the interfacial tension increases with increasing temperature. The same holds true for ethyl ether and octyl alcohol. Harkins observed the same phenomenon for octyl alcohol also and for heptaldehyde and heptin, but did not report the temperature coefficient of ethyl ether nor that of carbon disulfide.⁵ See Table III and Text-fig. 2.

These measurements were repeated four times with two different sized rings (circumference, No. 1 = 6 cm.; No. 2 = 12 cm.) in order to increase the sensitivity. In the four cases the values checked within a few tenths of a dyne, the four cases showing the same bump in the curve between 14 and 19 degrees. Around 35°C. the measurements became very difficult owing to the bubbles forming permanently at the interface.

⁵ Harkins, W. D., and Cheng, Y. C., *J. Am. Chem. Soc.*, 1921, xliii, 35.

EXPLANATION OF PLATE 5.

FIG. 1. Interfacial tensiometer, with 6 cm. ring.

FIG. 2. Appearance of the interface between water (top) and carbon tetrachloride (below) when the ring is pressed down. Picture taken just before breaking, in the state of equilibrium.

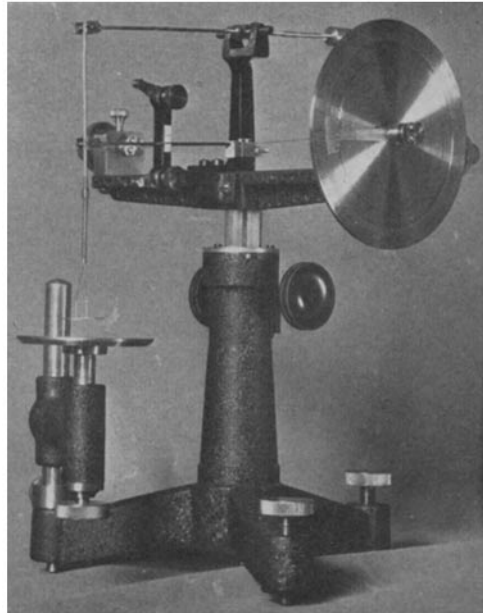


FIG. 1.

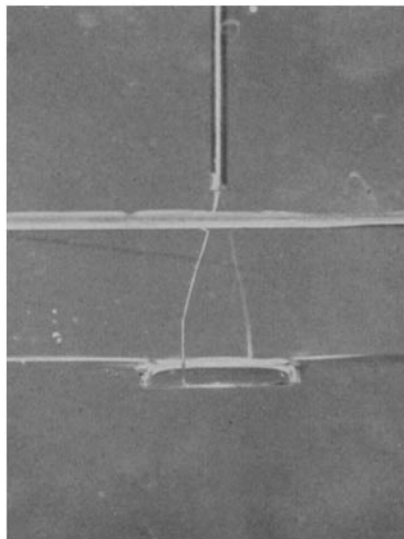


FIG. 2.

(du Noüy: Interfacial tensiometer.)