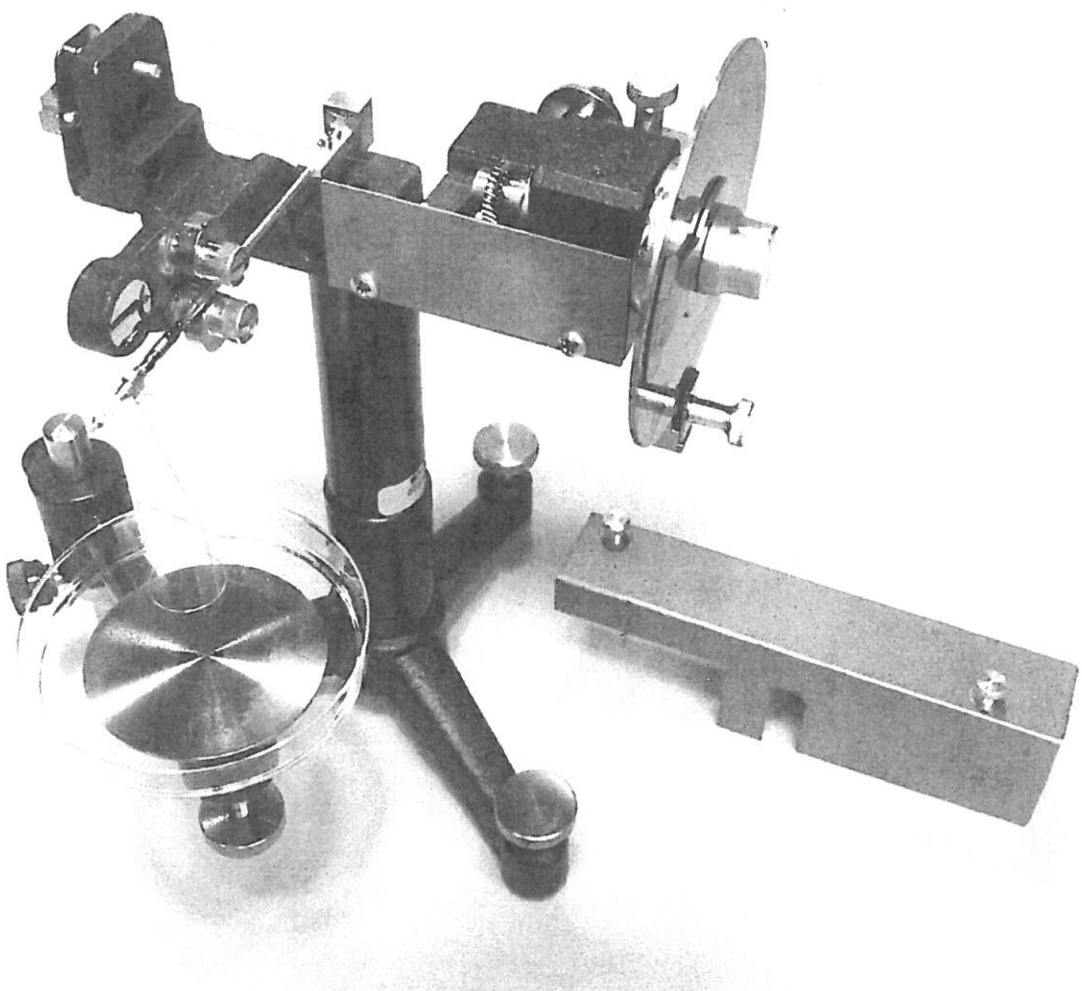
DuNouy Tensiometers



CSC SCIENTIFIC COMPANY, INC.

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CSC SCIENTIFIC DUNOUY TENSIOMETERS

PRECISION TENSIOMETER - 70535
INTERFACIAL TENSIOMETER - 70545

1. INTRODUCTION

The CSC-DuNouy Tensiometer is a precision instrument used for measuring both surface and interfacial tension of liquids, including serums, oils, and colloidal suspensions. Measurement values are reproducible to within +/- 0.05 dyne/cm and can be obtained by a direct scale reading.

The tensiometers employ the ring method of measurement, which allows measurements to be made in 15 to 30 seconds and is, therefore, the only method giving satisfactory results for colloidal suspensions, which exhibit rapid changes in surface tension. Other advantages of the ring method, in addition to speed of measurement, include elimination of mathematical calculations, and reduction in the quantity of test liquid required.

The CSC-DuNouy Tensiometer is available in two models. The Precision Tensiometer, CSC No. 70535, is used for measurements requiring only an upward pull on the ring; the Interfacial Tensiometer, CSC No. 70545, is used to measure both upward and downward forces on the ring. The Interfacial Tensiometer conforms to the specifications of ASTM Standard Method D971-50 for determining interfacial tension of oil against water by the ring method and the specification of ASTM Method D1331 for testing solutions of surface-active agents.

Both instruments can be quickly adjusted and calibrated. They are supplied completely assembled and are furnished with thee extra torsion wires and a 6 cm platinum-iridium ring.

2. DESCRIPTION

The CSC-DuNouy Tensiometers (Fig.1 and 2) use a fine torsion wire for applying the necessary force required to withdraw a platinum-iridium ring from the surface of the liquid under test. The torsion wire is secured in a tension clamp K at one end and a torsion head at the other end. Attached to the torsion head is a corrosion-resistant, graduated dial S with a vernier that permits reading the applied force directly to a 0.1 dyne and estimating it to 0.05 dyne. The graduated dial itself has a range of 0 to 90 divisions, each division corresponding to one dyne.

A	Knurled Knob	J	Wire Retaining Screw
B	Sample Table Adjustment Screw	K	Rear Clamp Spring Support
C	Dial Clamp	L	Base Leveling Screw
D	Adjustable Stops	M	Torsion Arm
F	Fine Adjustment Screw	R	Cap
G	Adjustment Nut	S	Dial
H	Hook	T	Sample Table
I	Index	V	Vernier
		Y	Torsion Wire Cover

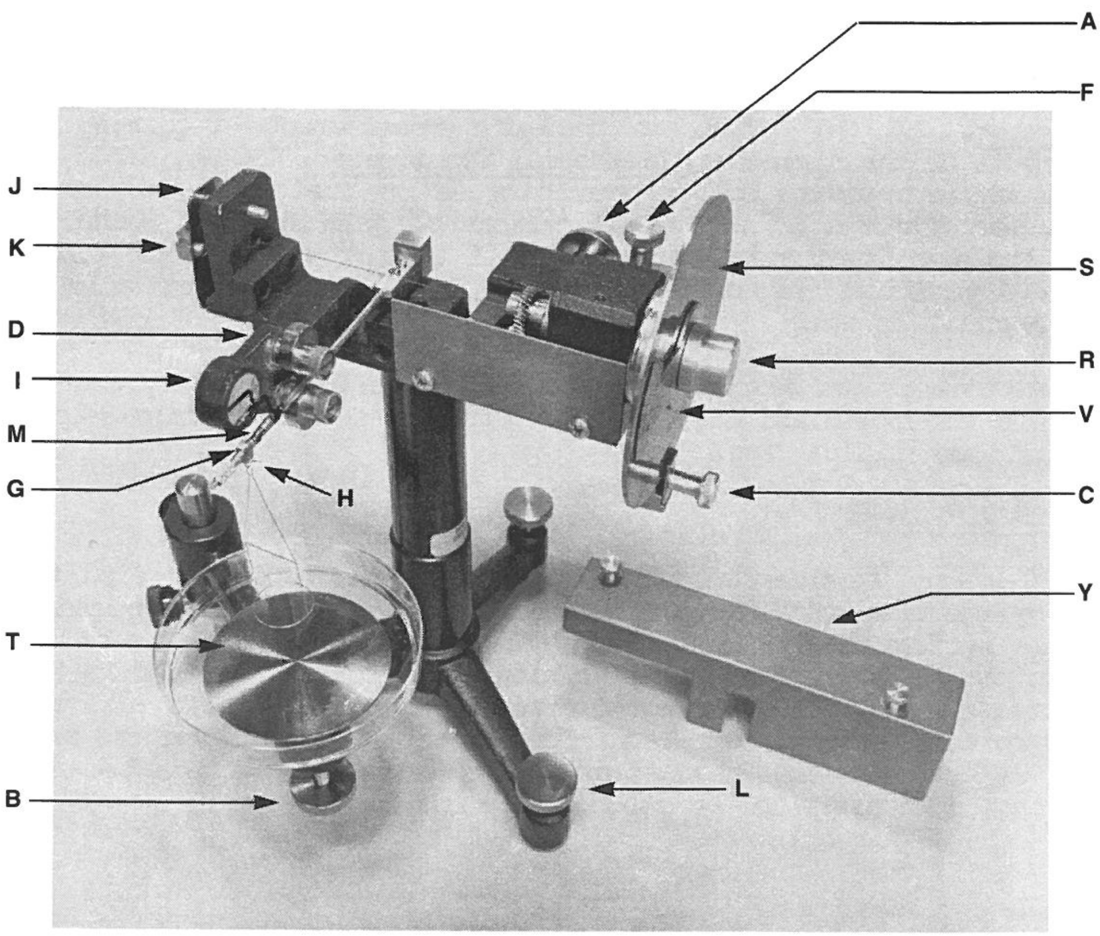

FIG. 1 - TENSIOMETER NO. 70535

A Knurled Knob
B Sample Table Adjustment Screw
C Dial Clamp
D Adjustable Stops
E Counter Weight
F Fine Adjustment Screw
G Adjustment Nuts
I Index
J Wire Retaining Screw
K Rear Clamp Spring Support
L Base Leveling Screw
M Torsion Arm
N Knurled Release
P Vertical Arm
R Cap
S Dial
T Sample Table
V Vernier
X Clamping Jaws
Y Torsion Wire Cover

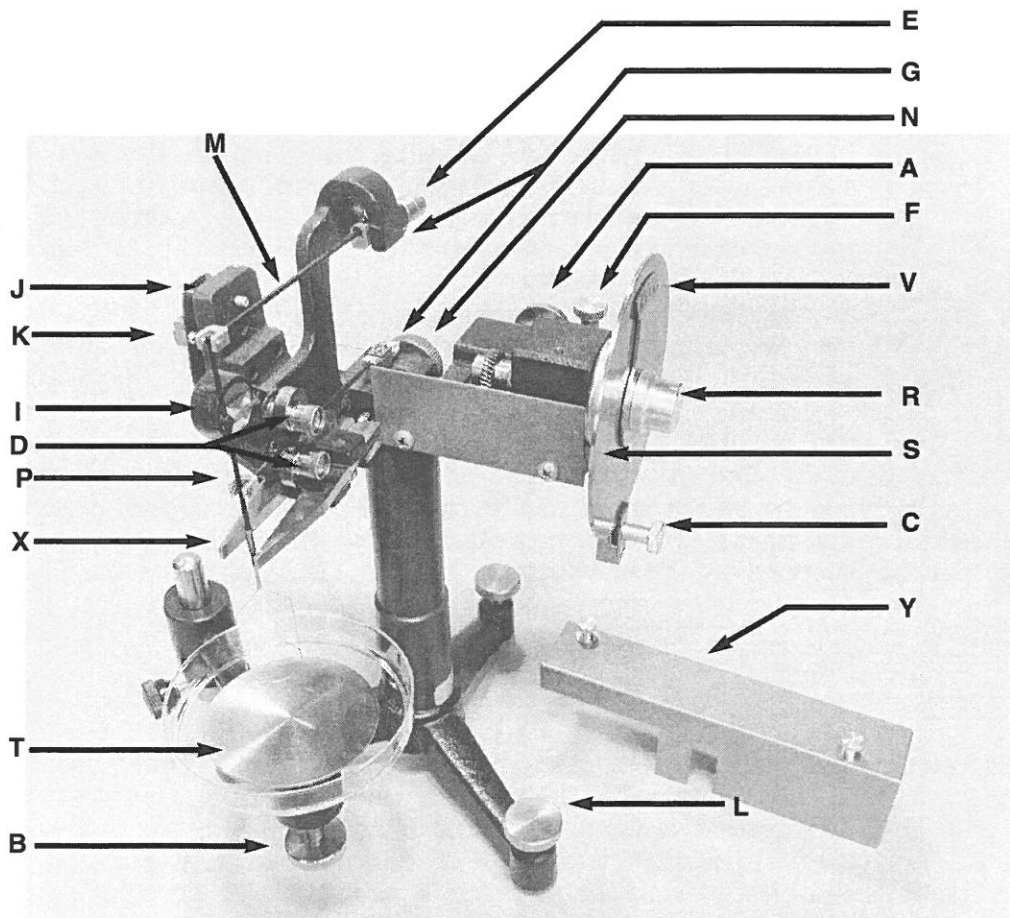

FIG. 2 - TENSIOMETER NO. 70545

A lever arm M is fastened at the midpoint of the torsion wire of the 70535 Tensiometer (Fig. 1). Any change in the torsion of the wire causes a change in the position of the lever arm. The length of the lever arm can be adjusted to make the tensiometer a direct reading instrument. The platinum-iridium ring is attached to a small hook on the end of the lever arm.

The lever arm system M of the 70545 Tensiometer (Fig. 2) is constructed in the form of an articulated parallelogram, having one vertical limb P and two horizontal limbs. This structure affords stability for keeping the ring aligned during a downward movement. One corner of the lever arm system is clamped to the torsion wire, and the other three corners are mounted in low-friction bearings so they can pivot freely. The length of the two horizontal limbs can be independently adjusted by means of finely threaded screws so that the instrument can be adapted for direct readings. A special clamping device, attached to the frame, permits the lever arm system to be clamped firmly when the ring is attached or removed. The ring can be attached to the lower end of the vertical limb of the lever arm system.

The graduated dial S reads in both directions from 0 to 90. A double vernier is provided for each scale. The two scales and corresponding verniers have graduations and figures of different colors, thus preventing confusion about the direction of the measured force. The double vernier permits a single zero setting for either scale. (Caution: do not increase torsion on wire beyond +/- 90 dynes/cm or wire may become damaged. If your unit was manufactured after January 1, 1988, the dial clamp C will stop the vernier V from inadvertently turning beyond a safe point. If it is necessary to go beyond that point, the clamp can be temporarily removed.)

In both the 70535 and 70545 Tensiometers, a pointed index line is attached to the lever arm system to indicate the zero-balance position of the arm in relation to a line engraved on a small plane mirror.

A platform, or sample table T, is provided to hold the vessel containing the liquid being tested. The platform can be raised or lowered quickly to an approximate setting by means of a clamp on a vertical rod and adjusted to a precise setting by means of a micrometer screw B. At a given height, the platform can be swung away from the ring by a collar on the rod.

3. SETTING UP THE INSTRUMENT

3.1 General

The tensiometer has been screwed to the bottom of its storage cabinet for protection during shipment. Remove the screw holding the instrument in place, and then unscrew the mounting board from the tripod base. Set the instrument on a level vibrationless surface. Remove the packing material that protects the lever arm system. Place a small level on the sample table and adjust the leveling screws L until the level indicates that the table is perfectly horizontal.

and adjust the leveling screws L until the level indicates that the table is perfectly horizontal.
Although each tensiometer was adjusted at the factory before shipment, a final and accurate calibration is required before the instrument can be operated

3.2 Calibration

3.2.1 Precision Tensiometer, CSC No 70535

Clamp the lever arm with the adjustable stops D. Carefully remove the ring from its container and clean it by heating it momentarily to a dull red in the oxidizing portion of a flame. Flame only that portion of the ring which will be immersed in liquid and do not overheat; otherwise the ring may become deformed or loosened from its stirrup. (For subsequent calibrations, it may be necessary to clean the ring as described in Section 4.1.) Hang the dry ring on the hook H.

Cut out a small strip of paper and place it on the ring as a platform. Release the lever arm and turn the knurled knob A until the index I and its mirror image are exactly in line with the reference line on the mirror. Loosen the dial clamp C and rotate the dial S until the vernier V indicates approximately zero. Tighten the dial clamp and rotate the dial by means of the fine adjustment F, until the vernier reads exactly zero. (The vernier and dial can be read more easily through a magnifying glass.)

Place on the paper platform a mass whose weight, in the 500 to 800 mg range, is accurately known. Turn knob A until the index I is again opposite the reference line on the mirror. Record the dial reading to the nearest 0.10 division. Determine what the dial readings should be according to the equation.

$$P = Mg/2L \qquad (1)$$

where

M = weight placed on ring, expressed in grams
g[1] = value of gravity, expressed on cm/sec^2
L = mean circumference (the average of the inside and the outside circumference) of the ring
P = dial reading = apparent surface tension in dynes per cm

As an example, suppose that a weight of 600 milligrams is used, and the mean circumference of the ring, which is given on the container, is 6.00 cm,

M = 0.600 gram
L = 6.00 cm
g = 980.3 cm/sec^2 (at Chicago)

then

$$p = Mg/2L = 0.6 \times 980.3/\ 2 \times 6 = 49.015 \text{ dynes/cm}$$

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[1] The exact value of g for the particular locality in which the tensiometer is to be used can be found in a suitable handbook, or by contacting the National Geophysical Data Center, Bolder, Colorado.

If the recorded dial reading is greater than the calculated value by 0.5 dyne/cm adjust nut G to shorten the lever arm; if the dial reading is less than the calculated value by 0.5 dyne/cm, adjust nut G to lengthen the arm.

Repeat the calibration procedure, readjusting the zero position with the paper on the ring after each adjustment of nut G until the dial reading agrees with the calculated value. If the tensiometer has been correctly calibrated, each unit on the dial represents a surface or interfacial tension of exactly 1 dyne/cm.

After the calibration has been completed, remove the paper from the ring and readjust the zero position: turn knob A until the index I and its mirror image are exactly in line with the reference line on the mirror; loosen the dial clamp C and rotate the dial until the zero on the vernier is nearly opposite the zero on the dial; tighten the clamp and, using the fine adjustment screw F, rotate the dial until the zeros coincide exactly. The tensiometer is now ready for use.

3.2.2 Interfacial Tensiometer, CSC No. 70545

Unpack the tensiometer and level it according to Section 3.1. Lock the vertical arm P by means of the clamping screw N. Remove the ring from its container and clean it by heating it momentarily to a dull red in the oxidizing portion of a flame. Flame only that portion of the ring which will be immersed in liquid and do not overhear it; otherwise the ring may become loosened from its stirrup. (For subsequent calibrations, it may be necessary to clean the ring as described in Section 4.1.) Insert the shaft of the platinum ring into the lower end or the arm. If the shaft fits too loosely, pinch the lower end of the lever arm slightly with a pair of tweezers. If the shaft fits too tightly, open up the lower end of the lever arm slightly with an awl or similar tool. Release screw N and open the adjustable stops D so that the arm moves freely up and down between the clamping jaws X.

Place a small strip of paper on the ring to serve as a platform. With knob A, bring the index I and its mirror image exactly in line with the reference line on the mirror. Loosen the dial clamp C and rotate the dial until the zero on the vernier is nearly opposite the zero on the dial. Tighten the clamp and, using the fine adjustment screw F, rotate the dial until the zeros coincide exactly.

On the strip of paper place an accurately known mass weighing between 500 and 800 milligrams. Turn knob A until the index I is exactly opposite the reference line on the mirror. Record the scale reading to 0.10 division.

As an example, assume that a weight of 800 milligrams is used, and the circumference of the ring, which is given on the container, is 6 cm.

Substitute in Eq.(1) and determine what the dial reading, and hence the surface tension, should be.

$M = 0.800$ gram

$L = 6.00$ cm

$g = 980.3\ cm/sec^2$ (at Chicago)

and

$p = Mg/2L = 0.8 \times 980.3/ 2 \times 6.00 = 65.353$ dynes/cm

If the recorded dial reading is greater than the calculated value by 0.25 dyne/cm or more, the lever arm must be shortened. If the recorded dial reading is less than the calculated value by 0.25 dyne/cm or more, the lever arms must be lengthened. To change the length of the arms, remove the torsion wire cover Y and adjust the nuts G. Turn nuts G clockwise to shorten the lever arms and counterclockwise to lengthen them. One complete turn of the nuts (360°) is equivalent to a change of about 3 dynes/cm. Lengthen or shorten the two arms simultaneously and equally to keep the vertical arm of the moving system exactly vertical. Repeat the calibration procedure; remove the weight and readjust the zero setting (with the paper in place) each time the length of the arms is changed, until the dial reading agrees with the calculated value. If the tensiometer has been correctly calibrated, each unit on the dial represents a surface of interfacial tension of exactly 1 dyne/cm in either direction from zero.

After the calibration has been completed, remove the paper from the ring and readjust the zero position: turn knob A until the index I and its mirror image are exactly in line with the reference line on the mirror; loosen the dial clamp C and rotate the dial until the zero on the vernier is nearly opposite the zero on the dial; tighten the clamp and, using the fine adjustment screw F, rotate the dial until the zeros coincide exactly. Replace the torsion wire cover, and the tensiometer is ready for use.

4 OPERATION

4.1 General

In both surface and interfacial tension measurements, cleanliness of the ring and vessels is of utmost importance. The cleaning procedure recommended after insulating oils have been tested is as follows: clean the glassware by removing any residual oil with petroleum naphtha or benzene followed by several washes with methyl ethyl ketone and water and immersion in a hot cleaning solution of chromic acid; rinse thoroughly with tap water and then with distilled water; clean the platinum ring by rinsing it in petroleum naphtha or benzene followed by rinsing in methyl ethyl ketone. Then heat in the oxidizing portion of a gas flame. Flame only the portion of the ring which will be immersed in the liquid under test and do not overheat. To duplicate measurement values, clean the ring between each measurement. When measurements are made of liquids other than insulating oils, other cleaning methods or, perhaps, even a less elaborate procedure, may suffice.

Calibrate the tensiometer periodically, especially each time the instrument is used after a period of idleness.

4.2 Surface Tension Measurements

To measure surface tension, attach the clean ring to the lever arm. Place the liquid whose surface tension is to be measured in a clean container, such as an evaporating dish, watch glass, or beaker, at least 4.5 cm in diameter. Place the container on the sample table. With screw B in its uppermost position, raise the entire sample table assembly until the ring is immersed approximately 5 mm into the liquid. Lower the assembly until the ring is just below the surface of the liquid and is approximately centered with respect to the container. Lower the liquid further by means of screw B until the ring is just in the surface of the liquid and the index is approximately on zero.

Increase the torsion of the wire by rotating knob A and, at the same time, lower the sample table by means of screw B to keep the index on zero. The index is to be kept on zero even though the surface of the liquid is distended. Continue adjusting the knob and the screw simultaneously until the film breaks.

The scale, reading at the breaking point of the film is the force of the pull exerted on the ring, or the apparent surface tension p.

4.3 Interfacial Tension Measurements

Interfacial measurements that require only an upward pull on the ring can be made with either of these CSC tensiometers. The accepted practice is to move the ring from water and into the other liquid.

Ordinary adjustments are the same as for surface tension measurements. In raising or lowering the liquid, make approximate adjustments in height by moving the entire table assembly and make fine adjustments by means of screw B.

To make a measurement on the interface between water and a liquid less dense than water, pull the ring upward according to the following procedure. Set a clean dish containing water only on the sample table. Raise the sample table until the ring is immersed from 5 to 7 mm in the water. Carefully pour the second liquid on the surface of the water to a depth (usually 5 to 10mm, depending upon the liquid used) sufficient to prevent the ring from entering the upper surface before the film breaks. Adjust the position of the dish until the ring is in the interface and the lever arm is in the neutral position. Next, increase the torsion of the wire and lower the dish, keeping the index of the lever arm at zero. The reading when the film at the interface breaks is the apparent interfacial tension p.

To make an interfacial measurement between water and a liquid denser than water, and instrument is required that will exert a downward force on the ring. CSC No. 70545 Tensiometer meets this requirement.

The measuring procedure is as follows: Pour the liquid of greater density in the vessel to a depth of 10 mm or more, then pour water to a depth of 5mm on the surface of the denser liquid. Raise the vessel until the ring is immersed in the water and is in the interface of the liquids with the lever arm index at zero. Increase the torsion on the wire to force the ring downward and, simultaneously raise the vessel, keeping the lever arm index at zero. The scale reading when the film breaks is the apparent interfacial tension.

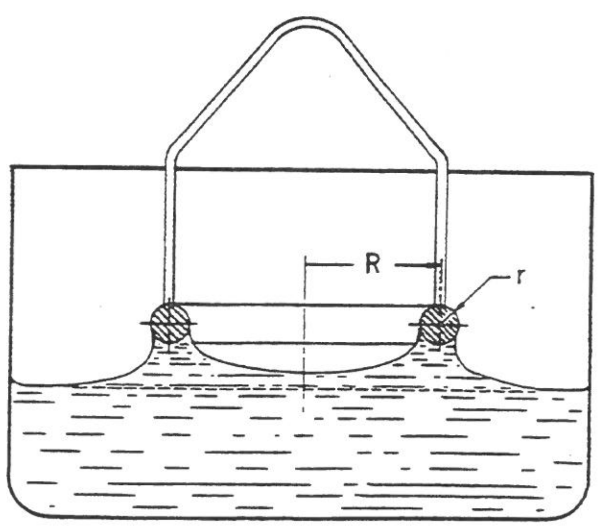

FIG. 3 - DISTENTION OF SURFACE FILM DURING SURFACE TENSION MEASUREMENT

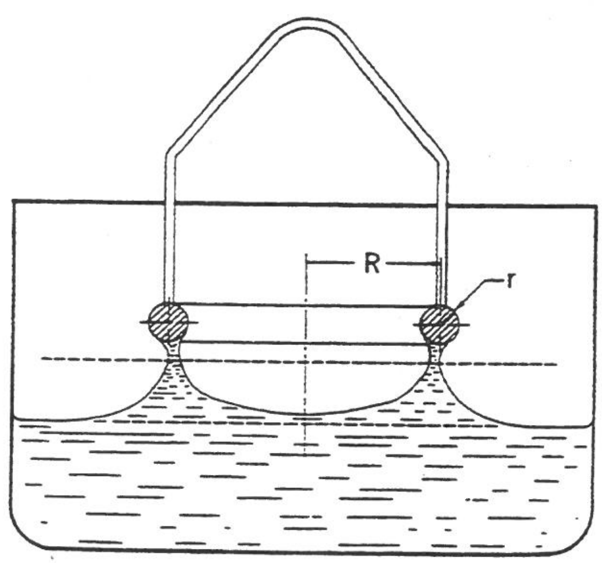

FIG. 4 - CONDITION OF SURFACE FILM AT BREAKING POINT

4.4 Correction Factor

The value of the surface or interfacial tension given by the scale reading of a tensiometer, or the apparent surface or interfacial tension, may differ from the true value by as much as 30 percent, although for most measurements the difference is probably less than 5 percent. To obtain the true surface tension, it is necessary to correct the apparent surface tension p. The reason for the correction and the method of obtaining the correction factor are discussed in the remainder of this section.

For surface tension measurements, the wire ring is placed in the surface of the liquid. During the measurement, the withdrawal of the ring causes a film of liquid to be pulled up, as shown in Fig. 3. Observe that there are two surfaces to this film. As the upward movement of the ring continues, the deformation of the liquid surface increases, as shown in Fig. 4, until the film ruptures along the ''breaking line.''

The force required to pull the ring out of the surface is equal to the weight of the ring W plus the downward pull due to surface tension. Taking account of both the inner and outer surfaces of the liquid film, we can see that the total downward force F due to surface tension is given by the equation

$$F = 2LT \qquad (2)$$

Where L is the mean (average of inside and outside) circumference of the wire ring, and T is the surface tension. Solving this equation for T gives

$$T = f/2L \qquad (3)$$

For calibration of the tensiometer, the acceleration of gravity g acting upon a known weight M is substituted for the total downward force f, so that Eq. (3) becomes

$$T = Mg/2L \qquad (4)$$

Up to this point, certain facts have been ignored which may lead to serious error. Fig. 4 shows that the pull of the liquid on the ring is not quite vertically downward. Since only the vertical component of the downward force is measured, the true value of F is less than that given by Eq. (2).

There is, however, another factor which tends to produce an error of the opposite sign. The pressure on the top of the ring is atmospheric, whereas the pressure on the bottom of the ring is atmospheric minus hDg, where h is surface of the liquid, D is the density of the liquid, and g is the acceleration due to gravity. Obviously, this factor tends to make F larger than the value given by Eq. (2).

Although these errors are opposite in sign they do not, in general, compensate each other and Eq. (3) must be changed to read
Where the correction factor F depends upon the circumference of the ring, the size of the wire in the ring, and total downward pull on the ring, and the density of the liquid. $T = (f/2L)F$

Zuidema and Waters[4] have published a formula which accounts for these factors. Also, curves have been plotted using different numerical values for these factors to facilitate determining the correction factor F (see Fig. 5).

To use these curves, it is necessary to know the ratio R/r, the value of p, the value of D, and the value of d where

R = radius of the ring

r = radius of the wire

D = density of liquid used in surface tension measurement or density of lower liquid used in an interfacial tension measurement.

d = density of saturated air in surface tension measurement or density of upper liquid used in interfacial tension measurement.

In the case of surface tension, the density of air d is so small in comparison to the density of most liquids that it may be ignored. Therefore, to determine the correction factor F, mark the value of p divided by the different D-d on the abscissa of the curve. Then refer this reading on the curve to the ordinate on the left, which indicates the correction factor.

4.5 Correction Factor for the Downward Method

As mentioned in Section 4.4, the apparent surface or interfacial tension may differ from the true value by an appreciable percentage. Thus, a correction factor must be applied. The correction factor F is given by

$$F=S/P$$

where

S is the reading by the capillary method[5], and
P is the measurement of the downward push.

The correction factor results from two effects. First of all, the drag of the liquid on the tensiometer ring is not quite vertical. The effect on the reading obtained is the same in both the upward and downward methods. If this were the only factor involved, the two correction curves would be similar.

FIG. 5

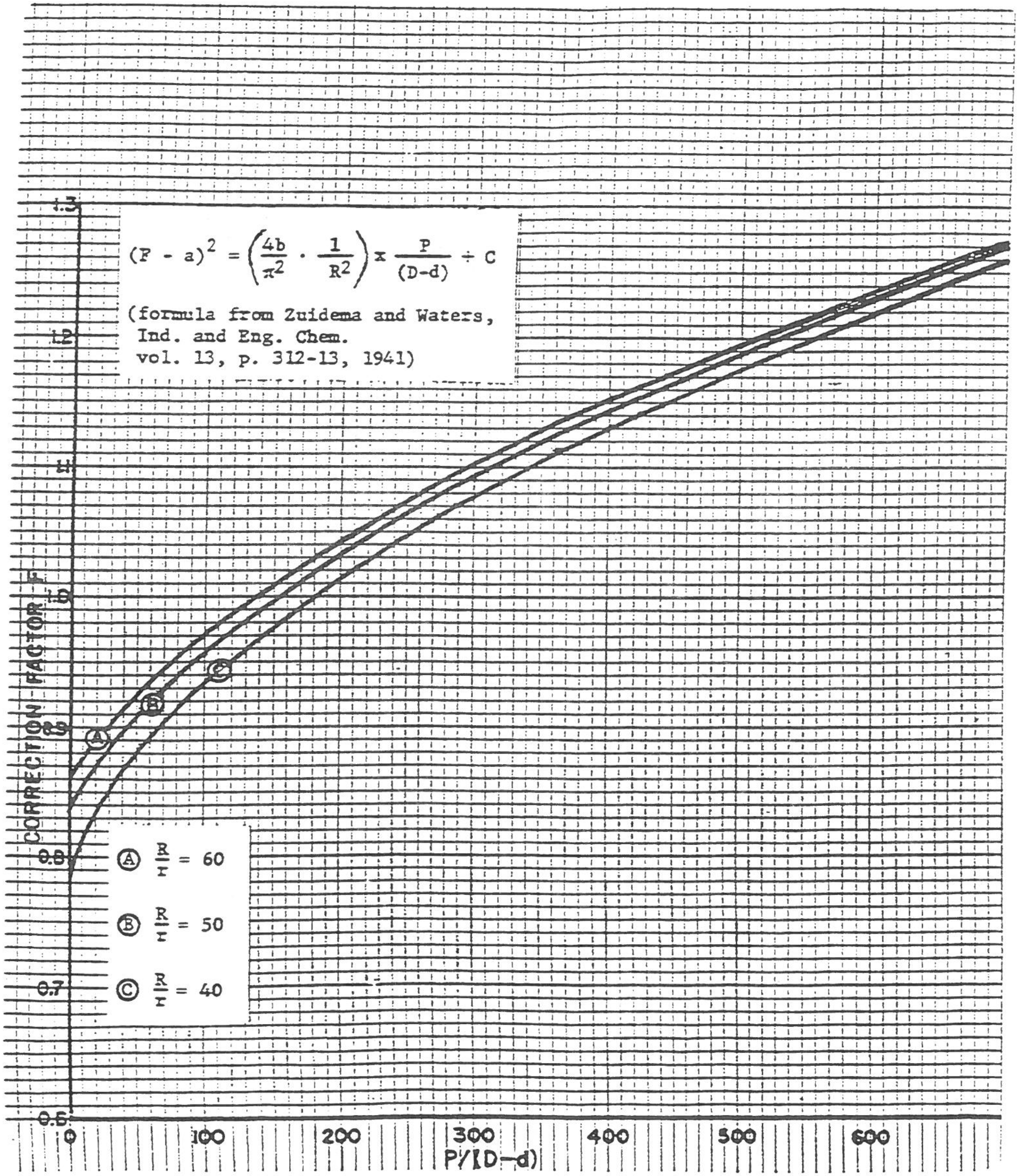

FIG. 5 CORRECTION FACTOR FOR SURFACE AND INTERFACIAL TENSION

FIG. 6

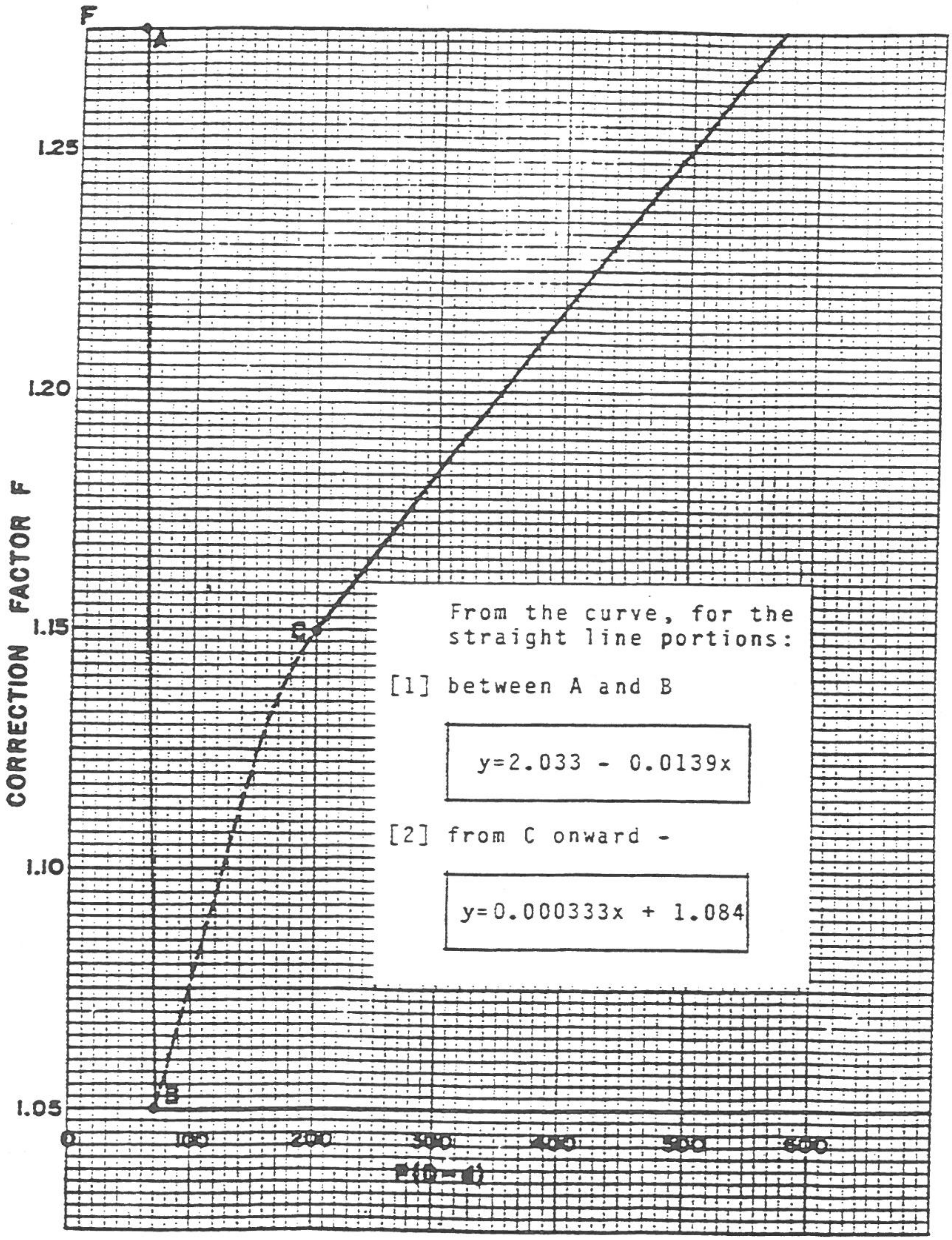

FIG. 6 CORRECTION FACTOR FOR SURFACE AND INTERFACIAL TENSION BY METHOD USING A RING OF A 6 CM CIRCUMFERENCE (DOWNWARD PUSH ONLY)

Secondly, an unbalanced force arises because the pressure on the top of the tensiometer ring is atmospheric while that on the bottom of the ring is atmospheric plus hDg, where h is the depth of the bottom of the ring below the surface level of the liquid, D the density of the liquid, and g the acceleration of gravity. The unbalanced force tends to make P smaller than S.

In the case of an upward pull, this difference reduces the force required. The result is that this effect offsets the first effect, and the correction factor decreases.

In the case of a downward push, however, this difference increases the force required, and the correction factor increases. Furthermore, because the effect increases with increasing density, the correction factor also increases with density as shown in the curve of F versus P/(D-d). For values of P/(D-d) in the range 70 to 200, the effects are nearly balanced, and the correction factor drops to unity.

In the region of P/(D-d) > 200, a curve of correction factor versus P/(D-d) attached shows it can be approximated by a straight line. The defining relation is:

$$F = 1.084 + 0.000333 \quad [P/(D-d)]$$

5. <u>MAINTENANCE</u>

5.1 <u>General</u>

If operated according to instructions, the CSC-DuNouy Tensiometer will give years of satisfactory service. When the instrument is not to be used for an extended time, it should be stored in its cabinet.

If the instrument is to be transported an appreciable distance, it should be securely fastened in its storage cabinet.

If difficulties arise that cannot be corrected, contact CSC SCIENTIFIC CO. and await further instructions. Do not return equipment without written authorization from CSC.

5.2 <u>Torsion Wire Replacement</u>

Occasionally it may become necessary to replace the torsion wire. Extra torsion wires are supplied with each instrument. When handling the replacement wire, do not let it kink. These wires, somewhat larger than necessary, are not calibrated because experience has shown that <u>it is necessary to calibrate each wire in the instrument in which it is used</u>. To replace the wire, the following procedure is recommended.

(1) Remove the torsion wire cover Y which is held in place by two screws.

(2) Tighten screw J until the rear clamp spring support touches the post. This action releases tension in the wire.

(3) Remove the cap R and loosen the clamps at each end of the wire.

(4) Loosen the clamp securing the lever arm to the wire and then remove the old wire.

(5) Feed the new wire through the openings in the clamps and tighten it in the front clamp.

(6) Pull the wire fairly taut and secure it in the rear clamp. The wire must not be clamped in a twisted condition.

(7) Release the screw J. The wire should now be held properly under a tension of 15 to 18 pounds.

(8) Secure the lever arm horizontally to the wire; the vernier should be in the lower left quarter of the dial (in a position corresponding to about seven o'clock).

(9) After replacing the wire, check the calibration of the instrument with weights, as described in Section 3.2. Generally, the dial reading will be found to be less than the calculated value. To correct this condition, the wire must be rubbed lightly with the fine polishing paper so its diameter is reduced. Rub carefully over the entire length of the wire and check the calibration frequently to avoid excessive rubbing.

(10) After the dial reading agrees closely with the calculated value, adjust the length of the torsion arms, if necessary, as described in Section 3.2.

References

[1]American Society for Testing Materials Standard Method D971-50.

[2]Harkins and Jordan, Journal American Chemical Society, Vol. 52, p. 1751-72 (1930)

[3]Freud and Freud, Journal American Chemical Society, Vol. 52, p. 1772-82

[4]Zuidema and Waters, Industrial and Engineering Chemistry, Vol. 13, p. 312

[5]Bartell and Miller, Journal American Chemical Society, Vol. 50, p. 1961 - 1967 (1928)

For those persons who are interested in a more complete treatment of surface tension, the following treatises, each of which contains an extensive bibliography, are recommended:

N.K. Adam, The Physics and Chemistry of Surfaces, Oxford University Press, 1938.

N.E. Dorsey, The Investigation of Surface Tension and Associated Phenomenon, Bulletin of the National Research Council, No. 69, 1929.

6. REPLACEMENT PARTS AND ACCESSORIES

Description

6 cm Platinum-Iridium Ring - 70537

For replacement on No. 70535 Tensiometer. The stirrup has parallel sides 25 mm high which permit the ring to be used in upward interfacial as well as surface tension measurements. The ring, packed in a protective container, has a mean circumference of approximately 6 cm, indicated to three significant figures, and is marked with the ration of the radii of the ring and cross section of the wire.

6 cm Platinum-Iridium Ring - 70542

For replacement on No. 70545 Tensiometer for upward and downward measurements of interfacial tension. The stirrup has parallel sides 25 mm high. The stem fits into the vertical limb of the tensiometer. The ring, packed in a protective container, has a mean circumference of approximately 6 cm, indicated to three significant figures, and is marked with the ratio of the radii of the ring and cross section of the wire.

Adjustable Ring Alignment Joint - 70543

For easy and rapid leveling of No. 70542 Ring when used with No. 70545 Tensiometer for interfacial measurements. This joint was suggested by Mr. R.G. Call of the American Gas and Electric Service Corp., Power, W. Va. First the joint is slipped into the socket of the vertical limb of the tensiometer and then the ring is inserted into the joint. The swivel-type joint allows the plane of the ring to be adjusted parallel to the surface of the liquid.

Torsion Wires

For use with No. 70535 Tensiometer - 70531
For use with No. 70545 Tensiometer - 70541