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Surface Tension by the Ring Method

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for retaining the gears in the position desired are shown in Fig. 3. The use of a four stage cone pulley adds further flexibility.

All the gears used, except wheel *B*, may be readily secured from nearly any machinery or model maker's supply house. Wheel *B* has 24 teeth at 24 pitch with  $\frac{1}{4}$  inch hole and  $1\frac{1}{2}$  inch face. This wheel was obtained from the Boston Gear Works.

#### SUMMARY

1. Herein has been described and illustrated a belt paper kymograph, electrically driven, and provided with a three speed gear shift.

2. By the use of this gear shift the operator may instantaneously change the speed of his paper from intermediate to high speed which is four times faster or to low speed which is four times slower.

3. By the arrangement of gears here shown no clutch or clutch lever is needed, and the operator may readily alter the speed by the use of either hand.

4. Although this gear box may appear somewhat complicated and difficult to construct it was built by junior and senior college students in mechanical engineering.

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## SPECIAL ARTICLES

### SURFACE TENSION BY THE RING METHOD

SINCE surface tension determinations are made frequently by chemists and physicists, and especially by biologists and in the industries, it is important that the quantity measured shall be the surface tension itself and not some other force. Of all the methods which are applied the determination of the pull on a ring is the most often used, as is evidenced by the fact that in one biological laboratory sixty thousand such determinations were made in a period of five years. The wide-spread popularity of this method is probably due to the ease with which a ring of platinum or platinum-iridium may be cleaned, and the resultant rapidity of the measurement, since all that apparently needs to be done is to put the ring in contact with the surface of a liquid, and to determine the force needed to pull it away from the surface.

Although what has been called the "ring method" has been so widely applied, it is a surprising fact that *until four years ago there was no ring method for the measurement of surface tension*, since all that was determined was the pull on the ring, which is related to the surface tension in a way that was before that time unknown. Thus in "International Critical Tables" nine experimental methods for such measurements 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 for these tables.

The failure of the ring procedure was due to the fact that the theory had not been developed with sufficient completeness, though an excellent beginning had been made by Cantor,<sup>1</sup> Lohnstein,<sup>2</sup> Lenard,<sup>3</sup>

Tichanowsky,<sup>4</sup> MacDougall<sup>5</sup> and others. Since, however, their equations are not extremely simple, and moreover apply only to rings of such dimensions as make them impractical for use, it was customary to neglect their theory, and to calculate the surface tension from the entirely incorrect equation

$$\gamma = \frac{P}{4\pi R} \quad (\text{incorrect}) \quad (1)$$

in which *P* is the maximum pull in dynes as determined by a balance, *R* is the mean radius of the circular ring and  $\gamma$  is the surface tension in dynes per centimeter.

In 1926 Harkins, Young and Cheng<sup>6</sup> demonstrated that a correct value of the surface tension is given by the expression

$$\gamma = \frac{P}{4\pi R} \times F \quad (2)$$

Since  $P = Mg$ , in which *M* is the mass in grams indicated by the balance, and *g* is the gravitational acceleration, this may be written

$$\gamma = \frac{Mg}{4\pi R} \times F \quad (3)$$

That the equation (1) generally used is entirely incorrect and does not give the surface tension at all is shown by the fact that in our experiments the value of the factor by which this must be multiplied to give the surface tension has varied from 0.72 to 1.45, or it exhibits a variation of 100 per cent. The most harmful and absurd fallacy in this connection is the statement which appears so often in connection with this incorrect equation: "It may be true that it does not give the proper absolute values, but of course it gives the correct relative magnitudes." This is entirely untrue,

<sup>4</sup> Tichanowsky, *Physik. Z.*, 25: 300, 1924; 26: 523, 1925.

<sup>5</sup> MacDougall, *SCIENCE*, 62: 333, 1926.

<sup>6</sup> Harkins, Young and Cheng, *SCIENCE*, 64: 333, 1926.

<sup>1</sup> Cantor, *Wied. Ann.*, 47: 399, 1892.

<sup>2</sup> Lohnstein, *Ann. Physik*, 25: 815, 1908.

<sup>3</sup> Lenard, *ibid.*, 74: 395, 1924.

since the factor ( $F$ ) is, as has been stated, highly variable.

The values of  $F$  are given in Fig. 1. It may be seen that the value depends on the ratio of the radius

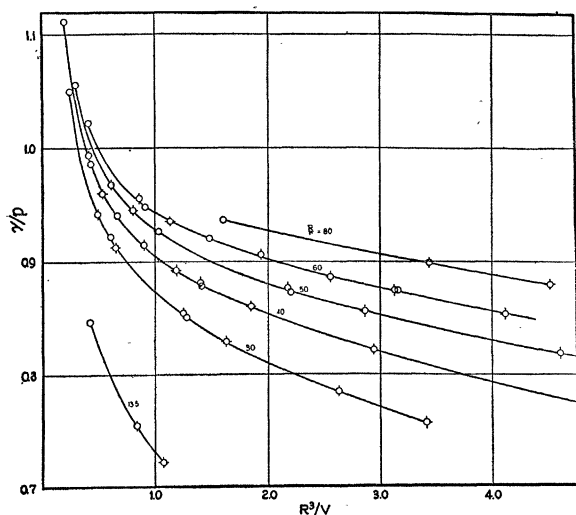


FIG. 1. Correction Factors ( $F$ ) or  $\frac{\gamma}{p}$  for the Ring Method for Surface Tension.

( $R$ ) of the ring to that of the circular wire ( $r$ ) from which it is made, and also on the ratio of the cube of the radius of the ring to the volume of liquid upheld by the ring ( $R^3/V$ ). This volume is equal to the maximum pull ( $M$ ) on the ring in grams, divided by the density ( $D$ ) of the liquid phase, or more exactly to  $(M/D-d)$ , in which  $D$  is the density of the liquid of higher density, and  $d$  that of the fluid (liquid or gas) of lower density. The number on the curve gives the value of  $R/r$ , and the abscissas the values of  $R^3/V$ . Both of these are known in any determination, and the unknown value of  $F$  is the proper ordinate. An extensive table of the values is given in the May, 1930, number of the *Journal of the American Chemical Society*, pages 1759 to 1770.

Dorsey<sup>7</sup> has recently suggested that many workers, particularly those who use the du Noüy tensiometer, may be unknowingly measuring the pull of a film of liquid on the ring, rather than the maximum pull ( $P$ ). The pull on the ring varies with the height ( $H$ ) of the ring above the plane portion of the surface. For example, ring 10 as used by us has a radius  $R$  of 0.6366 cm, while its wire has a radius ( $r$ ) of 0.01570, so the value of  $R/r$  is 40.55. Fig. 2 shows that the maximum pull of 0.5912 grams is attained when the height ( $H$ ) is 0.302 cm, and that the pull is smaller for either greater or smaller heights. However, it is difficult to increase the height above that for the maximum pull, so what is measured with the ordinary technique is the

<sup>7</sup> Dorsey, *SCIENCE*, 69: 187, 1929.

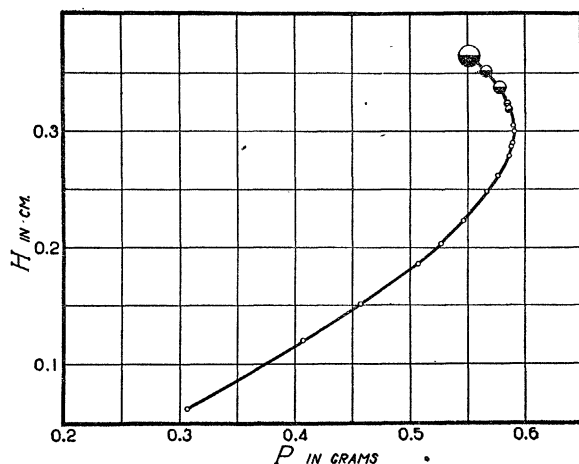


FIG. 2. Variation of the Pull on a Ring with its Height above the Surface of a Liquid.

maximum pull, at least if a chainomatic balance is used for the measurement.

Fig. 3 shows the flask used to contain the liquid whose surface tension is to be measured. The surface

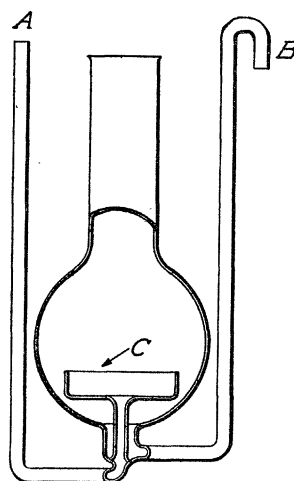


FIG. 3. Flask for the Liquid used in Determining Surface Tension by the Ring Method.

of the liquid is held at C, and the diameter of the surface should be in general 7.5 cm or larger. The use of such small quantities of liquid as to give a much smaller surface invalidates the measurement. Thus the ordinary custom of using small evaporating dishes for this purpose should be discontinued. In order to give a clean surface, the surface is caused to overflow at C before the surface tension is measured. This is particularly important with water.

Fig. 4 gives the apparatus as a whole. The ring is lifted away from the surface by raising the balance by a mechanism which operates so smoothly that it transmits almost no vibration to the beam of the balance. This obviates lowering the vessel that contains the

liquid, which sets up vibrations in the surface, and as a result the ring detaches at a pull less than the maximum.

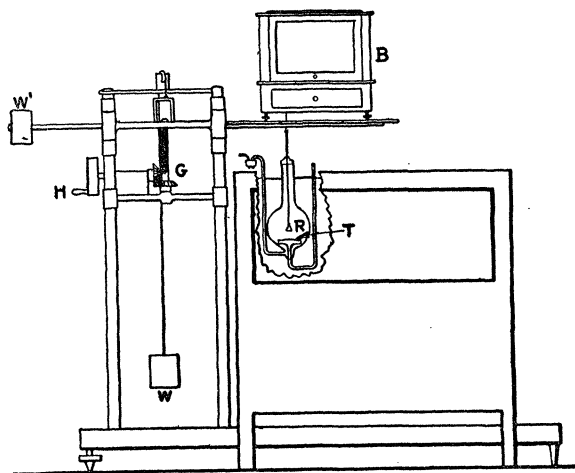


FIG. 4. Apparatus for Determining Surface Tension by the Ring Method.

For accurate work it is important that the ring be kept level. Fig. 5 illustrates the error due to tipping

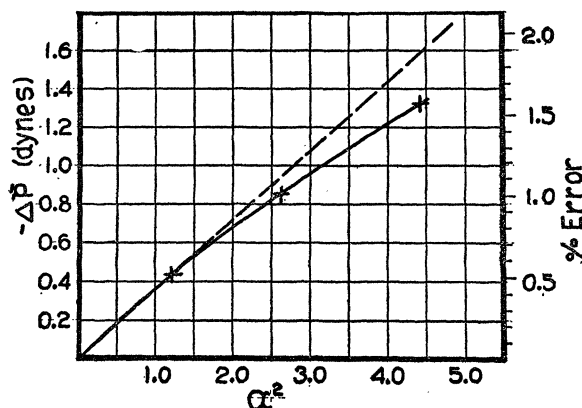


FIG. 5. Error in the Ring Method caused by Tipping the Ring.  $\alpha^2$  is the square of the angle of deviation from the horizontal.

the ring. Here  $\alpha^2$  is the square of the angle of deviation from the horizontal. With an angle of 1 degree the error is approximately half a per cent. This is in marked contrast with the drop weight method for which an angle of 1 degree has no measurable effect, and even an angle of 5 degrees produces an error of only 0.04 per cent.

It should be kept in mind that while the drop weight method is independent of the angle of contact between the liquid and the solid of the tip, provided proper tips are used, the ring method is highly dependent on the angle, and should be used only when it is zero.

The four most widely used methods for the determination of surface tension are: (1) capillary height, (2) drop weight, (3) ring and (4) bubble pressure.

Of these the capillary height and drop weight methods are the most accurate, and the bubble pressure method is the least accurate. With pure liquids the methods are accurate under the best condition to the following extent: capillary height,  $\pm 0.05$  per cent.; drop weight,  $\pm 0.1$  per cent.; ring,  $\pm 0.25$  per cent., and bubble pressure,  $\pm 1.5$  per cent. However, with certain solutions, especially biological liquids, the drop weight method is much more accurate than the determination of the capillary height.

The large error of the bubble pressure method is due to the fact that those who use it most do not determine the maximum pressure, which the theory demands, but only a mean pressure, which is related in an unknown way to the surface tension. Dr. T. F. Young is now engaged in a critical study of the method, and it seems probable that its accuracy will be greatly increased.

Of the four methods only that of the capillary height has been an absolute method. However, Drs. B. B. and H. Z. Freud have recently published a communication<sup>8</sup> in which they present a satisfactory theory, which gives the same results as our experiments. Thus the ring procedure becomes an absolute method for the determination of surface tension. The determination of the bubble pressure would give a third absolute method if the procedure were carried out in a way demanded by the theory, but, unfortunately, most of those who use it do not meet the conditions of the theory.

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#### THE REVIVAL OF COMATOSE ADRENALECTOMIZED CATS WITH AN EXTRACT OF THE SUPRARENAL CORTEX

IN previous brief reports published in this journal<sup>1</sup> the writers described the preparation of an active extract of the suprarenal cortex of beef and its effect upon the life-span of bilaterally adrenalectomized cats. It was demonstrated that extract-treated animals survive in normal health indefinitely and when the extract treatment is discontinued death from adrenal insufficiency results within a short time. To date we have not had an adrenalectomized animal present any symptoms of adrenal insufficiency while receiving treatment. At the end of one hundred days of treatment (an arbitrarily selected period, after which the extract is discontinued) the animals can not be distinguished from normal cats. Mention was also made in the earlier publications of the fact that non-treated adrenalectomized cats showing early

<sup>8</sup> SCIENCE, 71: 345, 1930.

<sup>1</sup> SCIENCE, 71: 321, and 71: 489, 1930.