INTERFACIAL TENSION BY PENDANT DROPS

by

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Signature of Author ______________________

Department of Chemical Engineering, May 1, 1938

Signature of Professor
in Charge of Research ______________________

Signature of Chairman of Department
Committee on Graduate Students ______________________

The Graduate House, M. I. T.,
Cambridge, Massachusetts.
May 1, 1938.

Professor George W. Swett,
Secretary of the Faculty,
Massachusetts Institute of Technology,
Cambridge, Massachusetts.

Dear Sir:

In accordance with the requirements for the degree of Doctor of Science, I submit herewith a thesis entitled "INTERFACIAL TENSION BY PENDANT DROPS".

Respectfully,

John M. Andreas

ACKNOWLEDGMENT

The author wishes to thank Dr. Ernst A. Hauser for his unstinted cooperation throughout the course of the work. His buoyant enthusiasm and unfailing confidence in ultimate success were a guiding light at times when progress seemed barred by insurmountable obstacles.

CONTENTS

NOMENCLATURE FOR BOUNDARY TENSION EQUATIONS

The fluid drop is in all cases a solid of revolution about a vertical axis. In general, the shape of a drop will be studied from the shape of its profile curve. The positions of points in the liquid surface are referred to a system of rectangular coordinates where z is the vertical distance measured from the point where the liquid surface cuts the axis of rotation, and x is the horizontal coordinate measured outward from the axis.

b = radius of curvature at the origin

B_h = horizontal paper shrinkage

B_o = optical magnification of camera

B_v = vertical paper shrinkage

β = dimensionless group describing drop shape

c = numerical constant

C & C' = the principal centers of curvature

d_e = diameter at the plane of the equator

d_s = diameter at the selected plane

e = eccentricity of an ellipse

g = acceleration of gravity

γ = boundary tension

h = vertical distance between two planes

H = a dimensionless function of S

k = a numerical constant

K = a point

l = a linear dimension

L = a point

M = a point

N = a point

p = pressure discontinuity across the interface

p_0 = pressure discontinuity at the origin

ϕ = angle between the normal and the axis

r = internal radius of a tube

R & R' = the two principal radii of curvature

ρ = the density of a fluid

s = length of an arc measured from the origin

S = d_s/d_θ

σ = the effective density = $\rho_1 - \rho_2$

θ = an angle

V = volume of fluid cut off by some plane

x = horizontal distance from the axis

X = x/b

z = vertical distance from the origin

Z = z/b

INTRODUCTION

This thesis presents one of two investigations carried out with the pendant drop camera which was built and operated by J. M. Andreas and W. B. Tucker during 1937 - 1938.

The problem was to examine the possibilities of the method of pendant drops for the measurement of the boundary tension of liquids, to construct an apparatus with which the method could be tested, and to make measurements of both the surface tensions and of the interfacial tensions in typical fluid systems so that the capabilities of the method could be judged.

It is customary to divide fluid boundaries into two classes: those between a liquid and a gas, and those between two incompletely miscible liquids. The free energy of the surface between a liquid and its pure vapor or between a liquid and a gaseous mixture is called surface tension. The free energy of the interface between two incompletely miscible liquids is called interfacial tension.

It has been found convenient to present the results of the present program in two parts of which each is a complete whole. This thesis deals with the development of the method of pendant drops and its application to the determination of interfacial tension. That part of the investigation which deals with surface tension is presented in a companion volume.[*] In general, those aspects of the problem which apply to the measurement of either surface tension or interfacial tension are presented in both theses; those which apply to only one are presented in the thesis and with the data to which they apply.

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[*] TUCKER, W. B.; "Surface Tension by Pendant Drops," Sc. D. Thesis, M. I. T., Course X, (1938).

APPLICATIONS AND USES OF BOUNDARY TENSION

The value of a knowledge of surface energy has long been recognized by colloid and physical chemists, and only the lack of a precise and rapid method for determining boundary tension has retarded progress in its widespread application to a variety of problems.

In the field of colloid chemistry, the importance of boundary tension determinations is well established. From the correlation of comprehensive data, it is possible to deduce much about surface structure and the migration to or from the surface of those solutes which are said to be positively or negatively adsorbed. The energy of a surface gives a valuable criterion for judging the efficiency of grinding, spraying, and emulsifying operations, since it indicates the minimum amount of energy which must be expended to produce a given result. Solubility changes with particle size are recognized as manifestations of surface energy. A comprehensive knowledge of interfacial tensions would be of tremendous importance to technicians interested in the production, inversion, and destruction of emulsions.

To organic chemists, the rapid and accurate determination of surface tensions offers a tool of rapidly increasing importance. In the extensive literature developed since the introduction of parachors by Sugden, in 1924, the technique for deducing organic molecular structure from a knowledge of molecular weight, surface tension, and the difference between liquid and vapor density has been demonstrated.* The chemist is also interested in the use of boundary tension determinations in analytical work. While its use has been severely restricted by the unwieldiness of the existing methods for boundary tension measurement, this tool is of great potential value. Boundary tensions are sensitive to minute traces of impurities if these are surface active.

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* The parachor is an additive property of the constituents of molecules which is defined by the approximate equation, $P = (M \gamma^{+0.25})(D - d)^{-1}$, where M is the molecular weight, γ is the surface tension, and D and d are the liquid and vapor densities. The values of the parachors for members of a homologous series increase by 39 for each additional CH_2 group; similarly definite parachor increments result from the addition of other aromic or structural constituents. The parachor is particularly valuable for detecting the presence of double bonds. It is insensitive to isomerism.

A large portion of the literature on surface tension deals with its application to problems in medicine. Doctors have studied the surface tensions of blood serum, spinal fluid, and gastric juice in normal and abnormal individuals. Unfortunately, the problems are extremely complex and it is difficult to disentangle the factors producing the observed result. Surface tension measurements have been used in standardizing the concentration of some antiseptic solutions.

Biology also makes frequent use of surface tension measurements. Such interesting items as the surface tension of sea urchin eggs are to be found in the literature.

Surface tension measurements have been recommended for the control of filtration and acid treatment processes for the refining of lubricating oil.

A knowledge of the boundary tensions of solid surfaces has great potential value, though there are no generally satisfactory methods for obtaining these data. However, studies of the change of solubility with particle size and certain extrapolation methods permit the estimation of such boundary tensions. Important fields of application for solid-liquid boundary tensions are casting operations, lubrication, paint manufacture, and adhesives.

METHODS OF MEASURING BOUNDARY TENSION

Many methods have been proposed for the determination of boundary tension. Dorsey, in 1926, listed and discussed seventeen methods for boundary tension measurement. Since that time a great deal of literature has appeared describing proposed new methods and improvements in existing methods. However, only a few are of outstanding importance, and the present discussion will be limited to the more important methods and to some of their modifications.

I The Capillary Rise Method

The capillary rise method is the only primary method at present in use, and it is the one by which all secondary methods are calibrated.

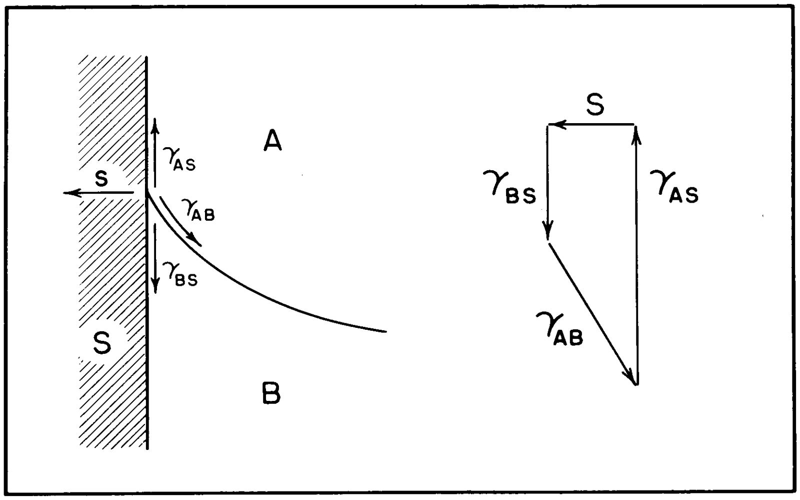

Figure 1.

If an interface between two fluids exists in a small vertical tube there will be a total of three interfaces in the system; the one between the two fluids, and an additional one between each fluid and the wall of the tube. The fluids may be two liquids, or one of the fluids may be a liquid and the other may be a gas. There is one and only one contact angle of the fluid interface with the wall of the capillary tube which satisfies the conditions for static equilibrium between the three boundary tensions. (Figure 1) The equilibrium curvature of the center of the liquid surface is completely determined by the radius of the tube, the angle of contact, and the physical constants of the system.

Associated with any given curvature of the liquid surface is a pressure which may be visualized by thinking of the surface as if it were a stretched membrane under tension. Accordingly, if it is to be in equilibrium, the liquid surface must satisfy two conditions: (1) the angle of contact with the wall must have a specified value, and (2) the pressure resulting from the curvature at any point in the liquid surface must be balanced by a corresponding fluid head.

The difference in elevation between the center of the interface in the capillary tube and the level of a horizontal free surface outside the tube is a function of the boundary tension of the interface, the contact angle between the interface and the wall of the tube, the radius of the tube, and the specific weights of the fluids.

In practice it is impossible to form a "free surface" of infinite extent and it is even difficult to approximate this condition satisfactorily, since the curvature of a liquid surface formed in a tube with a diameter of as much as three or four centimeters is still appreciable. It is therefore necessary to calculate the position of the free surface and this must be done from a knowledge of the dimensions of the reservoir.

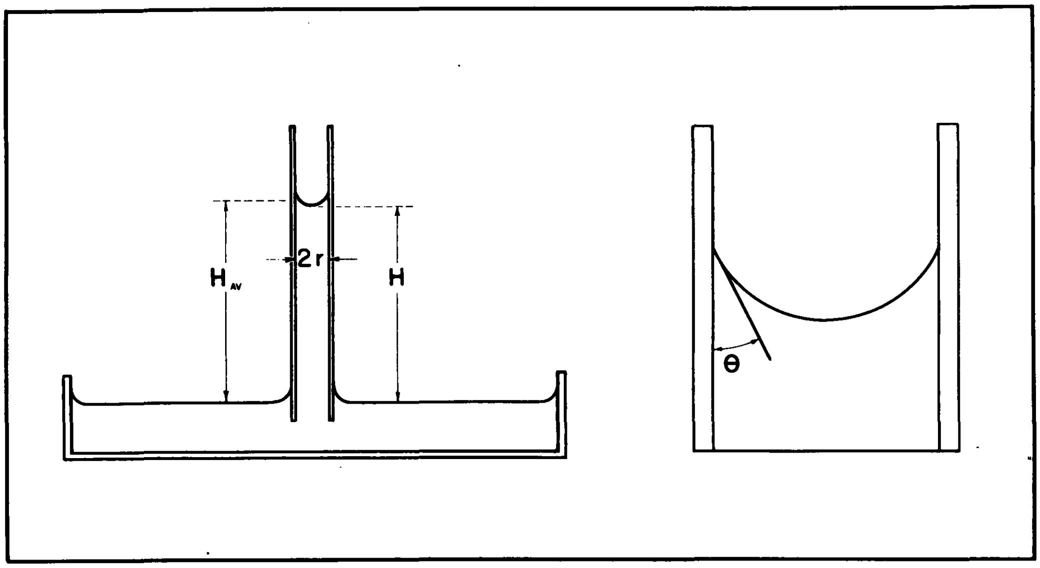

Figure 2.

Consider a vertical capillary tube standing in a dish of liquid which is so large that the surface of the liquid is level. (Figure 2.)

If the liquid meets the wall of the tube at an angle θ, the vertical pull at the plane of contact is $(2 \pi r \gamma \cos \theta)$.

If H_{av} is the average height of the liquid meniscus above the free surface of the liquid in the dish, $(\pi r^2 H_{av} (\rho_1 - \rho_2) g)$ is the weight of the liquid column.

At equilibrium, the vertical forces are balanced and:

$$2 \pi r \gamma \cos \theta = \pi r^2 H_{av} (\rho_1 - \rho_2) g$$

By solving for γ we obtain:

$$\gamma = \frac{r H_{av} (\rho_1 - \rho_2) g}{2 \cos \theta}$$

This formula is exact, but it is useless for the exact determination of boundary tension since the average height, H_{av}, can only be estimated with satisfactory precision when r is very small. It is not practical to use capillary tubes of extremely small diameters because of the difficulties of measuring such small internal diameters with adequate precision, cleaning them, and obtaining a sufficiently uniform, cylindrical bore.

The formula requires a knowledge of the contact angle, θ . Since this angle cannot be measured accurately, the practical usefulness of the capillary rise method is limited to cases where θ is either zero or 180°. Fortunately, a majority of the important pure liquids wet glass completely in air, and in this case θ is zero.

The various complicated formulas for the capillary rise method which appear in the literature arise from the experimental necessity of using H, the distance from the free surface to the center of the meniscus, in place of H_{av}.

The exact integrated equations of the capillary surface have never been derived, and therefore the exact relationship between H and H_{av} cannot be expressed analytically. However, approximate formulae of any required precision can be derived by the use of series expansions or from the correlation of empirical data.

The formulae of Raleigh, Sugden, Verschaffelt, and others result from the use of different series expansions and various assumptions which simplify the equations and limit the generality of the results.* Of special interest are euqations which assume: (1) Small tubes, (2) Large tubes, or (3) Contact angle not zero.

The capillary rise method is applicable to a wide variety of problems in boundary tension measurement, but it has some important limitations. It is particularly applicable to pure, non-viscous liquids which wet the tube wall completely. For such fluids it gives results of the highest precision. It has even been applied with success to the determination of the surface tension of very viscous liquids such as tar or bitumen, although in this case a very long time is required to obtain equilibrium.**

The capillary rise method is not suited to the determination of the change of boundary tensions of capillary active solutions with time because there may be a considerable lag between the change in the boundary tension of the interface and a complete adjustment in the vertical position of the liquid meniscus.

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* A critical discussion of the different formulae is given by DORSEY, N. E.; U. S. Bureau of Standards, Scientific Papers, 21, 563, (1936).

** LEAUTE, A.; Compt. Rend., 201, 41-43, (1935); reports that it required 360 hours to establish equilibrium with a certain sample of bitumen.

An experimental difficulty common to all methods, but particularly troublesome in the capillary rise method, is the problem of satisfactorily cleaning all parts of the apparatus which come in contact with the fluids being studied. Complicated procedures have been developed for cleaning glassware and particularly for cleaning capillary glass tubes. Most of these procedures involve acid cleaning solutions and prolonged steaming.

In its basic form, the capillary rise method requires the use of rather large samples. This disadvantage has been partially met by a number of microcapillary methods.

One of the requirements of the capillary rise method is that the diameter of a small capillary tube be known within very close limits. This is usually accomplished by indirect methods, such as by weighing a thread of mercury which fills the tube for a measured distance. It is difficult to obtain and calibrate tubing suitable for precise capillary rise work, since the bore of the tube must have a uniform, circular cross section. The literature is full of seemingly fantastic reports of testing hundreds of feet of capillary tubing in search of a single short piece of sufficient perfection. Many research workers have sought to circumvent this problem by using one or another of the null point capillary rise methods.

One variation depends upon the direct measurement of a pressure with a manometer. (Figure 3.) A capillary tube stands vertically in the liquid and a gas pressure is applied in such a way that the level of the interface in the capillary tube is the same as the level of the free surface outside the tube. Since the meniscus is always formed at the same point in the capillary tube, it is only necessary to have accurate information about the dimensions of the tube at a single point. Irregularities in other parts of the tube are totally irrelevant. The pressure measuring device is commonly some type of manometer. This

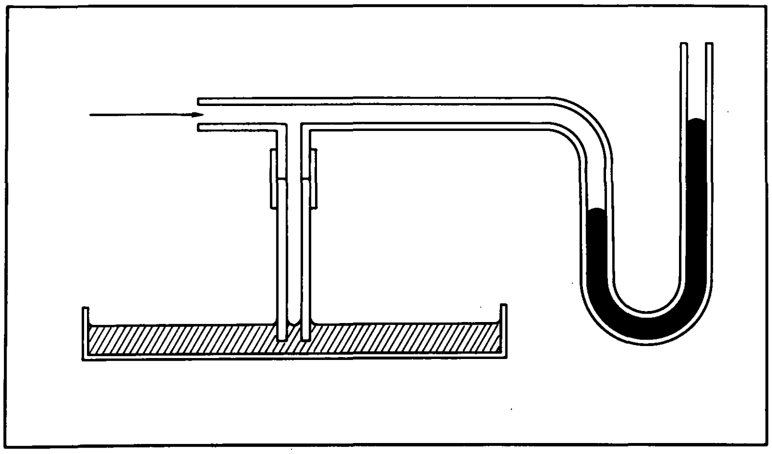
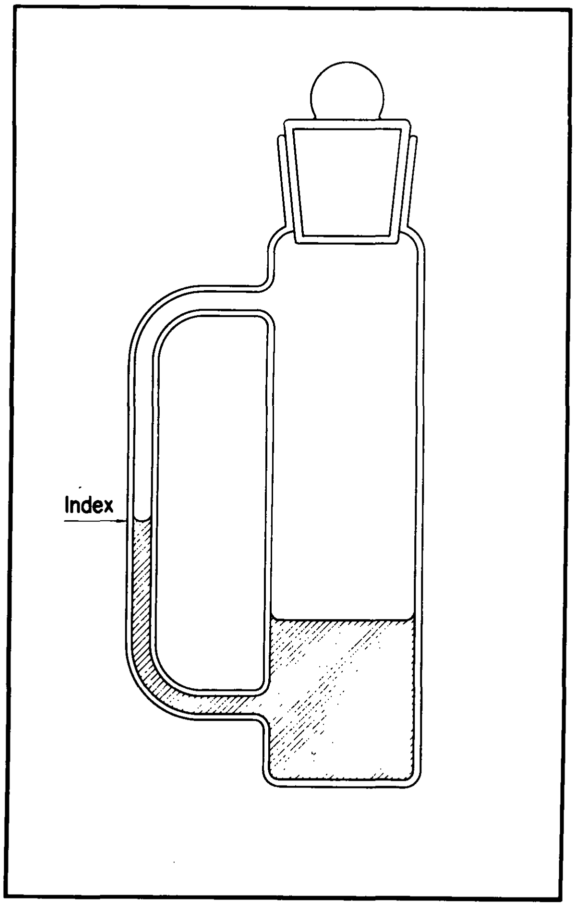


Figure 3.

introduces two additional capillary surfaces into the system which is being studied. There may also be complications due to the inequality in vapor density above the two legs of the manometer.

Recently, Jones and Ray have improved on the null point technique and have developed a secondary method of high precision which is especially valuable for determining the surface tension of dilute solutions relative to the known surface tension of the pure solvent. (Figure 4.)

Figure 4.



They avoid the measurement of linear dimensions by computing the surface tension from the weight of liquid which must be added to the U-tube to bring the meniscus to a standard position in the capillary. The method is standardized by observing the behavior of pure water and using the accepted value of its surface tension which was obtained by the standard capillary rise technique.*

Representative of the microcapillary methods is the so-called "conical capillary tube." (Figure 5.) A small capillary tube is welded to

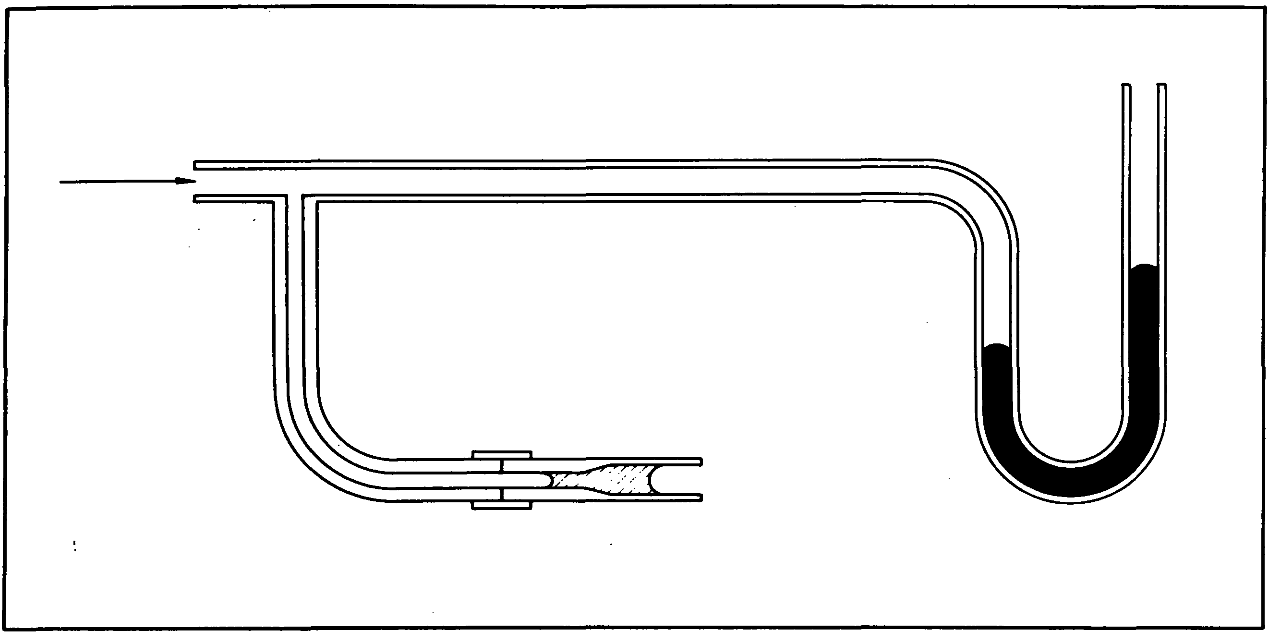


Figure 5.

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* JONES and RAY; Ph. D. Thesis, Harvard, (1936).
JONES and RAY; J.Am.Chem.Soc., 59, I, 187,(1937).

the end of a larger one. If such a tube is placed in a horizontal position and a slug of liquid which wets the walls is introduced, the fluid will tend to move into the smaller tube. This tendency of the fluid to move can be balanced by a gas pressure applied to the smaller end and measured with a manometer. The conical capillary may be used as either a primary or a secondary method, depending upon the method of calculation. It has the advantage that it uses very small samples, and it is claimed to give results which are as accurate as those obtained by other capillary rise methods.

If used to measure the boundary tension of substances to which it is suited, the capillary rise method is the most accurate known. It is possible to obtain results which are consistent to within ± 0.01 %, and the work of different investigators checks within less than a tenth of a dyne.

II The Drop Weight Method

The drop weight method shares with the method of Jones and Ray the distinction of being one of the most rapid of the precise, secondary methods for determining surface tension. If drops are formed slowly on a small drop-forming tip and are allowed to detach under the influence of gravity when they exceed the maximum stable size, the volume and weight of the drops will be functions of many variables of which the most important are tip size, effective weight of the fluid, and the boundary tension. The boundary tension can be computed from the weight of a specified number of drops or from the number of drops which are formed from a given volume of fluid.

There is no complete mathematical theory that will permit the direct calculation of boundary tension from drop weight measurements, and therefore the method cannot be used as a primary standard. In fact, to quote Dorsey, "The drop weight method stands by itself as one involving undetermined factors." Some idea of the complexity of the problem can be gained from high speed

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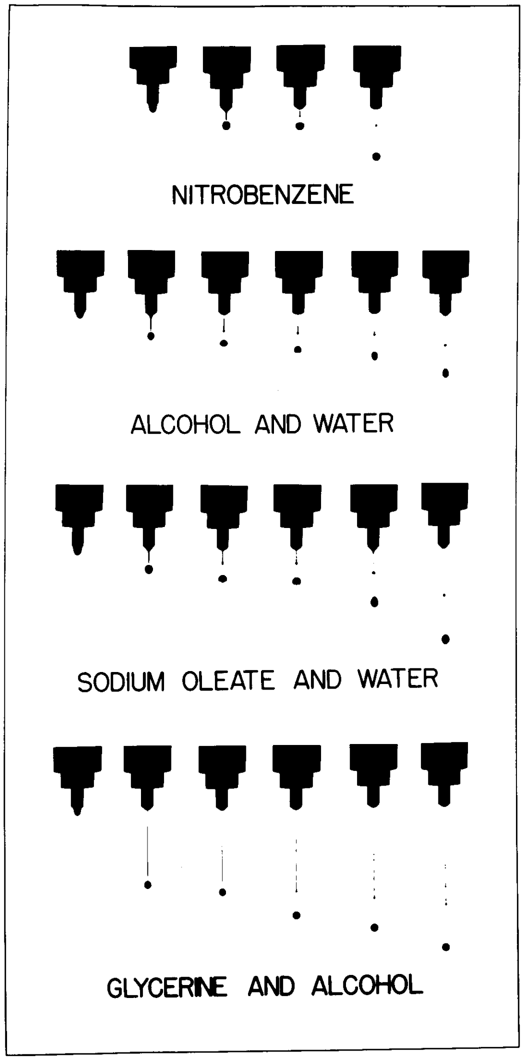
* EDGERTON, HAUSER, and TUCKER; J. Phys. Chem., 41, 1017 - 1028, (1937).

motion pictures showing the mechanism of drop detachment.[*] (Figures 6 and 7.)

Figure 6.



An excellent empirical correlation has been developed by Harkins and Brown[*] which makes it possible to calculate surface tension from measurements of drop

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[*] HARKINS and BROWN; J.Am.Chem.Soc., 41, 499, (1919).

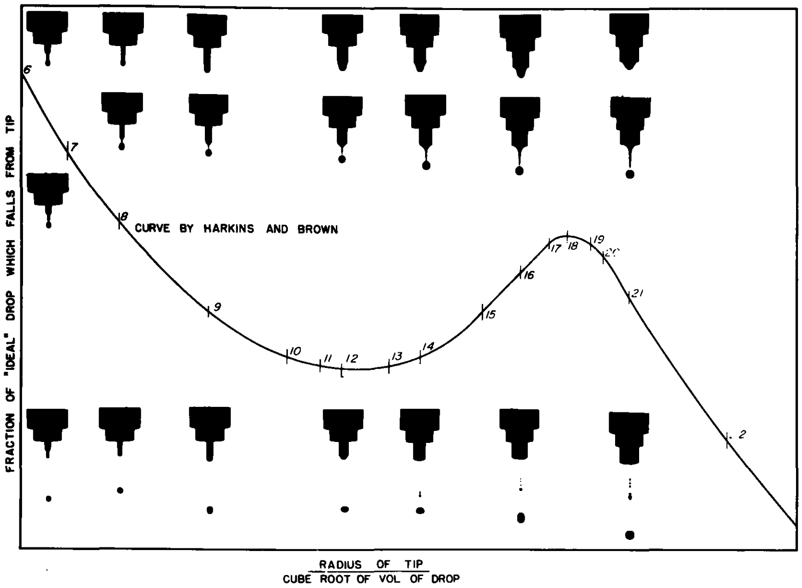

Figure 7.

weight, fluid density, and tip diameter. Their work is based on observations of water and benzene in the presence of air, and their empirical correlation was derived for use in determining the surface tension of pure, non-viscous liquids. Its application to the measurement of the surface tension of viscous liquids or to the determination of interfacial tension is open to question.

There is considerable doubt about the meaning of measurements made by drop weight method for the purpose of determining the effect of ageing surfaces. As the drop detaches, a certain amount of new surface is formed at the neck where the drop is pulling away from the tip. Thus, although the ageing of surfaces does have an effect on the results obtained by the drop weight method and serves to cloud the issue in all measurements, the method is unsuited for the direct measurement of this phenomenon.

If properly used, the drop weight method is rapid and will give consistent results which can be standardized to better than ± 0.1 %. The method requires the construction of an accurate set of drop forming tips, but does not offer any exceptional experimental difficulties. The tips are reasonably easy to clean, and the apparatus is subject to simple temperature control.

III The Maximum Bubble Pressure Method

The maximum bubble pressure method is a rapid, approximate method which is applicable under adverse conditions, such as are met in studying molten metals at high temperatures.*

If a small thin-edged tube is submerged in the liquid, there will be a well defined maximum pressure

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* SUGDEN, S.; J. Chem. Soc., 121, 858-866, (1922).

which is necessary to start the formation of a gas bubble on the end of the tube. This pressure may be used as a measure of the surface tension. (Figure 8.)

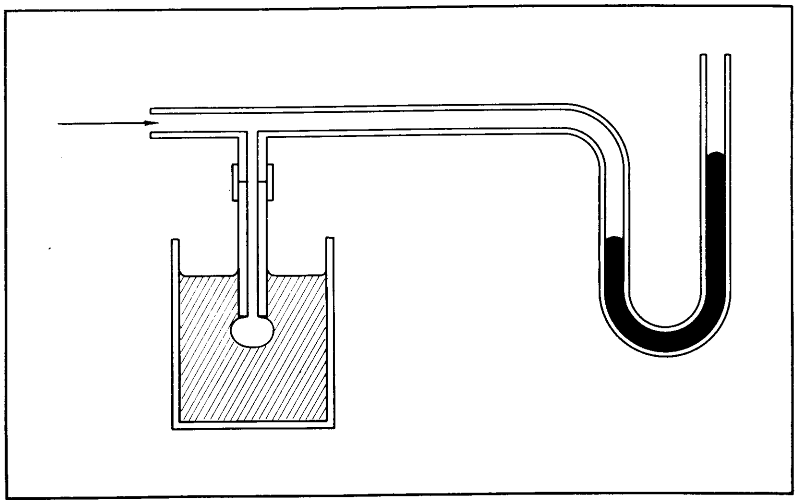

Figure 8.

There is no useable theory for the maximum bubble pressure method.* The method requires the calibration of each tube by measuring the surface tension of known liquids.

The method is currently popular and is in frequent use. It has been satisfactorily applied to measuring liquid metals and fluid glass.** The results appear to have an accuracy of from ± 2 to ± 5%.

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* This is also called Jaeger's Method.

** VICKERS, SUGDEN, and BELL; J. Soc. Glass Tech., 18, 224 - 254, (1935).

IV The Du Nüoy Ring Method

The Du Nüoy ring method is a rapid, approximate, secondary method for determining either surface tension or interfacial tension. It is notable for a remarkably simple theory, and for the obscure way in which practice deviates from the theoretical assumptions.

It has been conveniently assumed that, when a horizontal wire ring is lifted from an interface, it forms a thin cylindrical film of liquid whose length is equal to twice the circumference of the ring (since there is a surface inside the film as well as one on the outside). The pull on the ring at the time of rupture should therefore be, $p = 4 \pi r \gamma$. In practice it is found that the pull on the ring bears no simple mathematical relationship to the dimensions of the ring, and some sort of empirical correlation is necessary.

Harkins and his co-workers* have developed relationships with which it is possible to determine surface tension from a knowledge of the dimensions of the ring and of the physical properties of the fluids, but the direct calibration of each ring as suggested by Macy** is probably preferable.

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* HARKINS, YOUNG, and CHENG; Science, 64, 333, (1926).

** MACY; J. Chem. Ed., 12, 573, (1935).

It is possible to determine surface tensions by the ring method with an accuracy of from ± 1 % to ± 2 %, using the methods of either *Harkins* or *Macy*. The ring method is not subject to easy temperature control, but it is very rapid and the equipment is readily obtainable from dealers in scientific apparatus.

In Europe, the method of *Lenard* is more commonly used. This is a variation of the ring method in which a film is lifted from a U-shaped staple instead of from a horizontal ring. It is subject to the same advantages and limitations as *Du Nüoy's* method.

A clear idea of the complexity of the mechanism of the ring method and the reason why the simple theory fails may be had by studying the high speed motion pictures made by *Hauser, Edgerton, Holt, and Cox*.[*]

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[*] HAUSER, EDGERTON, HOLT, and COX; J. Phys. Chem., *40*, 973, (1936).

V The Method of Pendant Drops

In anticipation of material which will be presented in detail in a later section, it may be said now that the new method for calculating boundary tensions from photographs of pendant drops, which in this thesis is termed "The Method of the Selected Plane," is a versatile, rapid method of high precision. Early students of pendant drops used such unsatisfactory mathematical procedures that the method of pendant drops languished in undeserved disfavor for many years. The new method completely overcomes the difficulties and provides a means for obtaining a series of instantaneous measurements under conditions when other methods are completely incapacitated.

DERIVATION OF THE FUNDAMENTAL RELATIONSHIP

Between the Pressure Discontinuity, Boundary Tension, and Curvature of a Liquid Surface

The molecules of a liquid are subject to strong mutual attractions, which, for a molecule located in the interior, are balanced uniformly in all directions and give rise to the compressive stress known as its internal pressure. The importance of these forces can be emphasized by citing, as a typical example, benzene, which has an internal pressure at room temperature of about 4,000 atmospheres. That so great a pressure is normally overlooked can be explained by pointing out the fact that it is balanced in all directions and therefore is not apparent. In the same way, the atmospheric pressure is not easy to detect and its very existence was not suspected for thousands of years.

These cohesive forces exert a strong inward attraction on molecules located in the liquid surface so that the latter tend to move into the interior of the liquid. The net effect of the inward attraction on all of the surface molecules is a decrease in the area of the liquid surface which will continue until the surface has the smallest possible extent consistent with the volume of the fluid and the external constraints imposed on the system. (Figure 9.) This spontaneous behavior of the liquid surface is one of its most important properties.

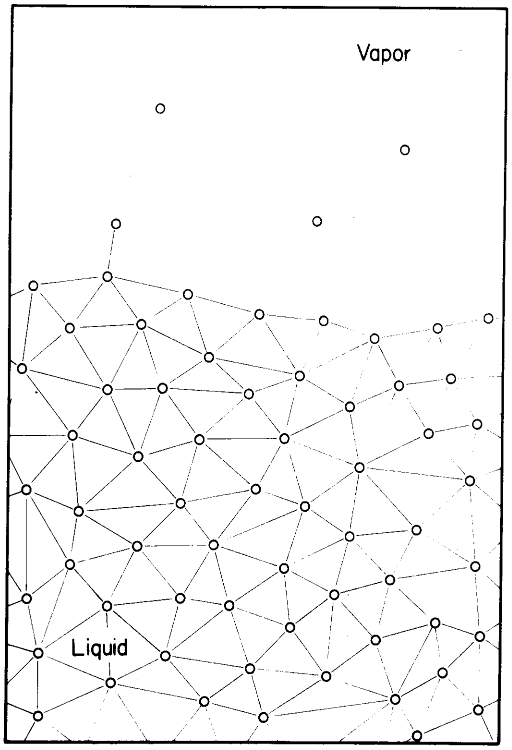

Figure 9.

Because of the presence of forces which tend to make the surface of the liquid contract, a definite amount of work must be done if the surface is to be increased by the action of an external agent. This work is done against intermolecular cohesion as additional molecules are brought from the interior to form the new surface. The isothermal, reversible work that is required to produce a unit area of new surface is its free energy and is denoted by γ; it has the dimensions of ergs per square centimeter.

In many problems, it is more convenient to look upon the free boundary energy as a tension acting equally in all directions in a homogeneous, isotropic surface.* Since boundary tension has the same numerical value and dimensions as boundary energy, it is possible to replace one by the other whenever a change in point of view will clarify the solution of a given problem. Thus, the work done in extending a surface which is pulling with a tension of 72 dynes per centimeter will be 72 ergs per square centimeter.

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* A homogeneous, anisotropic surface also has a definite free boundary energy; but it is a case which is excluded from the present discussion since the orientation of an anisotropic surface must be taken into consideration in determining the boundary tension acting in any particular direction. Certain of the surface films described by Langmuir appear to be homogeneous, anisotropic sheets. They may be regarded as "two-dimensional solids."

There is actually no net force in the liquid acting parallel to the surface among the surface molecules, and the concept of the surface as a stretched membrane is apt to be misleading. The tension in a membrane varies with the extent to which it has been stretched, but the tension in a liquid surface is independent of its shape or size. The boundary tension results from unbalanced forces acting in a direction perpendicular to the surface, but the tension in a membrane is the sum of real cohesive forces acting in the stretched sheet. Since the volume of a fluid is fixed, the inward attractions on the surface molecules cause the boundary to contract and give an effect which is qualitatively similar to what would be observed if the surface were replaced by a thin uniform membrane under tension.

The concept of boundary tension, in contrast to the more fundamental concept of free boundary energy, is a convenient mathematical device by which the net result of the forces between innumerable moving molecules is replaced by a fictitious static stress acting in a mathematical surface. This surface is itself an idealization of the actual interface. It is apparent from the nature of the assumptions which have been made that the concept of boundary tension can be valid only in systems which are large in comparison to the size of a molecule. Specifically, the idea of boundary tension developed here cannot be expected to apply to very thin liquid films or to colloidal liquid droplets.

The exact quantitative relationship between the boundary tension, the mean curvature, and the pressure difference between the inside and the outside of a curved liquid surface can now be derived in accordance with ideas originating with Young, Laplace, Adam, and others.*

The derivation given below requires that the small, rectangular element of area can be so chosen that pairs of adjacent normals will intersect. This requirement is satisfied whenever the liquid surface is a surface of revolution. It has been shown that a more elaborate derivation leads to the same differential equation regardless of the shape of the liquid surface, but a completely general derivation will not be given here since the simpler treatment is rigorous for the cases under consideration.

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* YOUNG, Thomas; Phil. Trans., 5, 65, (1805).

LAPLACE, Pierre Simon; "Méchanique Céleste," supplement to the tenth book, (1806).

ADAM, N. K.; "The Physics and Chemistry of Surfaces," Oxford, (1930). Page 12-13-14.

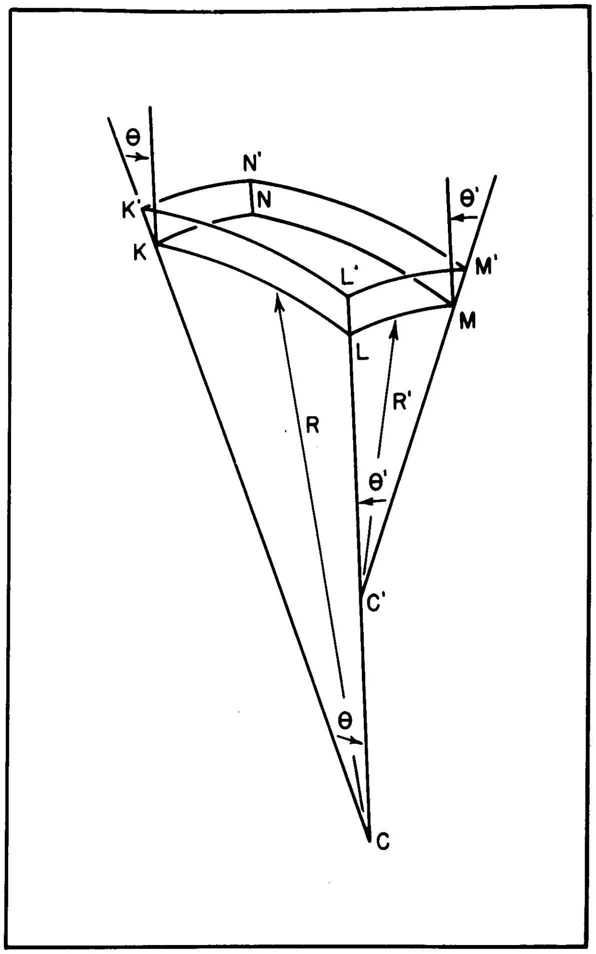

Figure 10.

Consider the work involved when each point of a small, rectangular element of the surface, KLMN, is displaced (normal to the original surface and away from the concave side) by a small distance, dR, equal to KK', etc. (Figure 10.)

The normals at K and L have been extended to meet at C, and those at L and M have been extended to meet at C'.

Let the radius of curvature of the arc KL be called R and that of the arc LM be called R'.

The angle KCL is now KL/R radians, and the angle LC'M is LM/R' radians.

The area of the element of surface after displacement is (KL +(KL/R) dR) (LM + (LM/R') dR) or, neglecting second order quantities, KLMN (1 + (dR/R) + (dR/R')).

The work done against the free boundary energy or boundary tension, γ, is (KLMN)(dR)(1/R + 1/R')(γ).

If the pressure difference between the two sides of the surface is p, the work done in moving KLMN a distance dR is, p (KLMN) dR.

The only force resisting the movement of the surface is the boundary tension, therefore:

$$p = \gamma \left(1/R + 1/R' \right) \qquad \text{-- (1)}$$

This is the required fundamental relationship. It applies to any free, homogeneous fluid interface, irrespective of whether the interface separates a liquid from a gas or from another liquid, provided only that the surface is in static equilibrium.

METHODS FOR COMPUTING BOUNDARY TENSION

From the Shape of Pendant Drops

For convenience, it is customary to divide all symmetrical liquid drops into two classes: sessile drops and pendant drops. (Figure 11.)

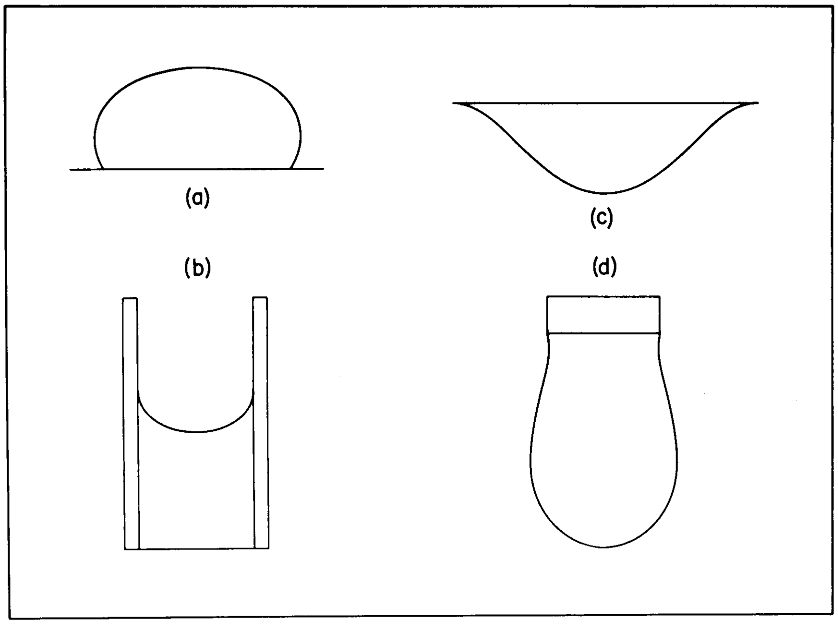

Figure 11.

Sessile drops correspond roughly to an oblate spheroid. They are formed when a drop of liquid rests upon a flat, horizontal plate (a). The liquid surface in a capillary tube also has the "sessile" shape (b).

Pendant drops correspond to a prolate spheroid; and, as their name implies, they result when the liquid drop is hanging from a flat, horizontal surface (c), or from a vertical cylindrical tip (d).

All methods for determining the boundary tension between two fluids from measurements of the equilibrium shape and size of their common boundary depend upon one or both of two basic equations.

The first was derived in the preceding section. It connects the pressure difference between the two sides of an interface with its boundary tension and with its mean curvature:

$$p = \gamma \left(1/R + 1/R' \right) \qquad \text{-- (1)}$$

The second is an application of statics to a liquid drop which, from considerations of symmetry, is known to be bounded by a surface of revolution about a vertical axis. It expresses the fact that, when the fluid is in equilibrium, the vertical forces acting across any horizontal plane are balanced.

$$2 \pi x \gamma \sin \phi = V \sigma g + \pi x^2 p \qquad \text{-- (2)}$$

The conditions of physical equilibrium for the drop are completely defined by these two laws, but the solution of the problem of finding the best way to determine the boundary tension from measurements of a given drop is only begun. It is obvious that many sets of measurements might be made and that the labor as well as the precision of the result will depend upon a judicious choice of both experimental and mathematical procedure.

During the course of the present investigation, six different mathematical procedures were considered:

I The Method of Ferguson,
II The Method of Worthington,
III The Method of Two Planes,
IV The Method of the Plane of Inflection,
V The Method of the Plane of the Equator, and
VI The Method of the Selected Plane.

It is convenient to develop first the mathematical equations which are used in each of these six methods and then to discuss in the next section certain experimental problems which are of the greatest importance in determining the selection of the method which best combines the desired qualities of speed, accuracy, and precision.

I The Method of Ferguson[*]

Ferguson considered that the profile curve of a pendant drop could be fitted, in the region close to the origin[**] by the parabola:

$$z = c\,x^2 \qquad \text{-- (3)}$$

Forming the first and second derivatives:

$$z' = 2\,c\,x, \text{ and}$$

$$z'' = 2c.$$

At the origin, $x = 0$, and the two radii of curvature are equal, therefore:

$$R = R' = (1/z'')\,(1 + (z')^2)^{3/2} = \frac{1}{2c}$$

Equation (1) can now be applied at the origin where it becomes:

$$\gamma = \frac{pR}{2} = \frac{h\,\sigma g\,R}{2} = \frac{h\,\sigma g}{4c} \qquad \text{-- (4)}$$

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[*] FERGUSON, A.; Phil. Mag., (6), 23, 417-430, (1912)

[**] The origin is the point at which the liquid surface cuts the axis of rotation.

The value of c was determined by fitting equation (3) by the method of least squares to the coordinates of a number of points measured on an enlarged photograph of the drop. The static head, h, between the origin and the free surface was measured from a second photograph showing the entire apparatus.

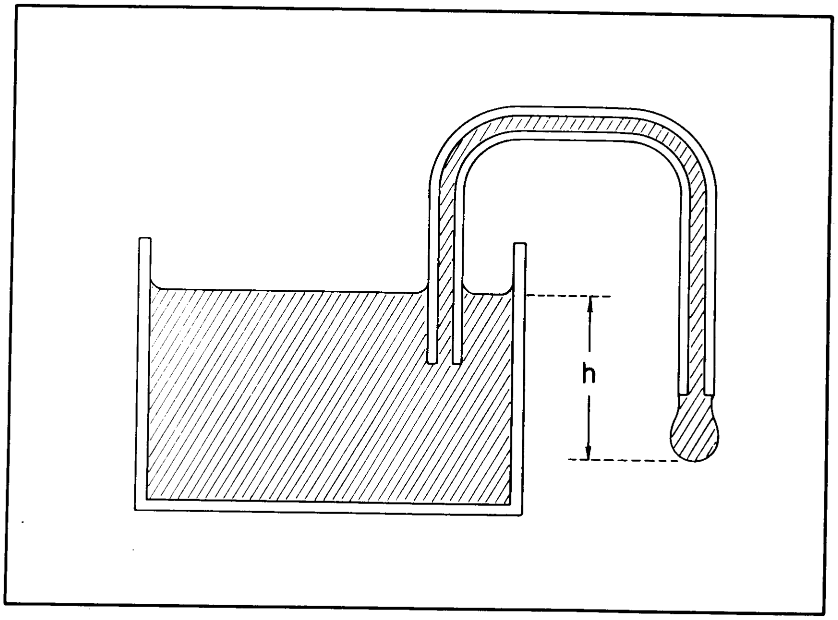

Figure 12.

The method of Ferguson can be regarded as a variation of the capillary rise method. (Figure 12.) Both methods require the direct measurement of a static head, but they differ in that the capillary meniscus is sessile whereas Ferguson uses a pendant drop. In the capillary rise method, the curvature at the center of the meniscus is usually inferred from the measured diameter of the tube.* Ferguson determined the curvature by fitting a parabola to the measured coordinates of a number of points on the liquid surface.

Ferguson's computed values for the surface tension of pure water were too low by 2 % and scattered rather badly. He attributed this to using too low a magnification and to the approximation introduced by fitting a parabolic curve to the drop. He suggested the use of the biquadratic, $z = cx^2 + kx^4$, to obtain a closer fit.

The use of a biquadratic greatly complicates the calculation and would probably not make the method practical because of its other disadvantages. The method requires two simultaneous photographs, a large number of very precise measurements, and curve fitting.

This method was not tested in the present program, since the direct measurement of the static head is impossible in equipment designed to give optimum results by the other pendant drop methods.

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* Special tables which are valid when the angle of contact is zero have been prepared for this purpose. SUGDEN; J. Chem. Soc. London, 119, 1483,(1921).

II The Method of Worthington *

Worthington noted that the excess pressure, p, at any level in a drop is the difference between the pressure at the origin, p_o, and the static head, $z\sigma g$, between the origin and the plane under consideration.

$$p = p_o - z\sigma g \qquad \text{-- (5)}$$

Thus, at any plane, all but two of the quantities appearing in equation (2) are either known or can be measured directly from a profile of a drop. These unknowns are γ and p_o .

Worthington passed four arbitrary planes through the drop and solved for γ and p_o between each of the possible pairs of equations. (Figure 13.)

$$2\pi x_1 \gamma \sin\phi_1 = V_1\sigma g + \pi x_1^2 (p_o - z_1\sigma g) \qquad \text{-- (2.1)}$$

$$2\pi x_2 \gamma \sin\phi_2 = V_2\sigma g + \pi x_2 (p_o - z_2\sigma g) \qquad \text{-- (2.2)}$$

$$2\pi x_3 \gamma \sin\phi_3 = V_3\sigma g + \pi x_3 (p_o - z_3\sigma g) \qquad \text{-- (2.3)}$$

$$2\pi x_4 \gamma \sin\phi_3 = V_4\sigma g + \pi x_4 (p_o - z_4\sigma g) \qquad \text{-- (2.4)}$$

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* WORTHINGTON, A.M.; Proc. Roy. Soc. London, 32, 362-377 (1881).
WORTHINGTON, A.M.; Phil. Mag., (5), 19, 46-48, (1885).

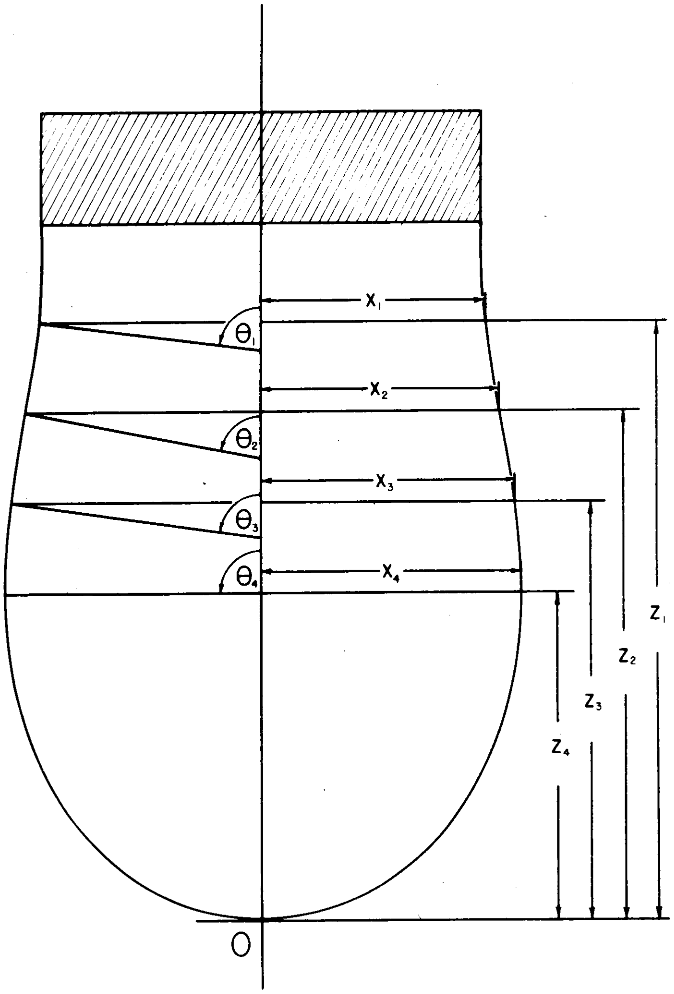

Figure 13.

The most probable values of γ and p_0 were then computed by the method of least squares.

The method of Worthington suffers from the disadvantage that values of low precision, resulting from solutions between planes which are close together, are averaged with more precise values obtained from solutions between more favorably located planes. The precision of the final result is thereby lowered. It is better to make only a single solution between the two most favorably located planes of a given drop, and to examine more drops.

Some of Worthington's results were in error by as much as three or four per cent due to the use of extremely crude apparatus. He attempted to trace the projected images of the drops by hand, had no thermostat, and did not use a telecentric lens system.

III The Method of Two Planes

If the value of the boundary tension is to be computed by applying equation (2) to a given drop at each of two favorably located planes, it is convenient to eliminate the pressure from the equations at once, since it is a quantity which cannot be conveniently measured and whose value is not required.

$$2\pi X_1 \gamma \sin\phi_1 = V_1 \sigma g + \pi (X_1)^2 P_1 \qquad \text{-- (2.1)}$$

$$2\pi X_2 \gamma \sin\phi_2 = V_2 \sigma g + \pi (X_2)^2 P_2 \qquad \text{-- (2.2)}$$

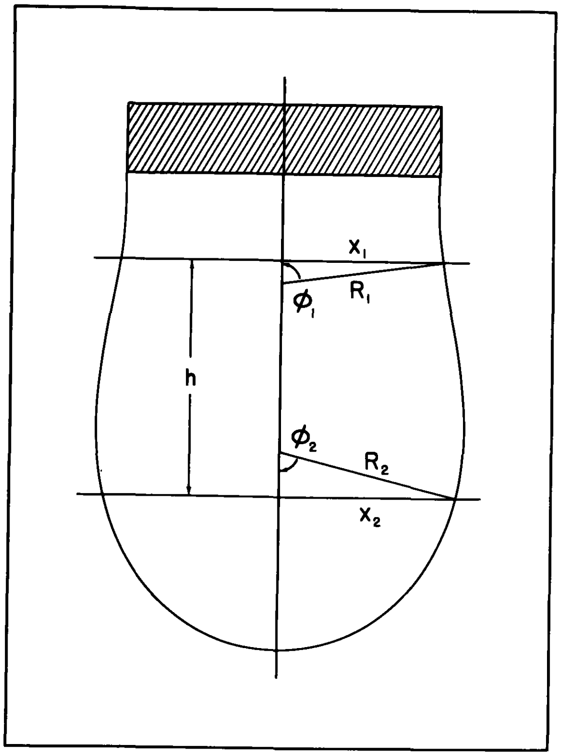

Figure 14.

Note that :

$\sin \phi_1 = x_1/R_1$,

$\sin \phi_2 = x_2/R_2$,

$p_2 = p_1 + h \sigma g$.

Combining these expressions with equations (2.1) and (2.2):

$$2\pi (x_1)^2 \gamma = [V_1 \sigma g + \pi (x_1)^2 p_1] R_1$$

$$2\pi (x_2)^2 \gamma = [V_2 \sigma g + \pi (x_2)^2 p_1 + \pi (x_2)^2 h \sigma g] R_2$$

Eliminate p_1 and get :

$$\frac{2\pi x_1^2\gamma - V_1\sigma g R_1}{x_1^2 R_1} = \frac{2\pi x_2^2\gamma - V_2\sigma g R_2 - \pi x_2^2 h\sigma g R_2}{x_2^2 R_2}$$

Solve for γ and obtain :

$$\gamma = \frac{\sigma g}{2\pi}\left[\frac{V_1 x_2^2 R_1 R_2 - V_2 x_1^2 R_1 R_2 - \pi x_1^2 x_2^2 R_1 R_2 h}{x_1^2 x_2^2 R_2 - x_1^2 x_2^2 R_1}\right]$$

Divide both numerator and denominator by R_1R_2/x_1x_2 :

$$\gamma = \frac{\sigma g}{2\pi}\left[\frac{V_1\left(\frac{x_2}{x_1}\right) - V_2\left(\frac{x_1}{x_2}\right) - \pi x_1 x_2 h}{x_2\left(\frac{x_1}{R_1}\right) - x_1\left(\frac{x_2}{R_2}\right)}\right] \text{-- (6)}$$

This is a general equation for computing the boundary tension from measurements made at any two arbitrarily selected, horizontal planes which pass through a static fluid drop.

If the second plane happens to be the plane of the equator, $x_2/R_2 = 1$, and, after multiplying through by x_1/x_2, a form which is more convenient for computations is obtained:

$$\gamma = \frac{\sigma g}{2\pi}\left[\frac{V_1\left(\frac{x_2}{x_1}\right)^2 - V_2 - \pi (x_2)^2 h}{x_2\left[\frac{x_2}{R_1} - 1\right]}\right] \text{-- (6.1)}$$

If the planes are close together, both numerator and denominator contain "small differences between large numbers" and the precision will then be very low.

Best results are obtained when the first plane is roughly half way between the end of the tip and the equator and when the drop has a pronounced "neck" obtained by forming a drop of maximum size from a tip whose diameter is about three-quarters of the diameter of the largest section of the drop.

Under the most favorable conditions, when both the shape of the drop and the locations of the two planes are well chosen, $(V_1 (x_2/x_1)^2)$ will be about twice $(V_2 + \pi (x_2)^2 h)$, and (x_2/R_1) will be roughly 1.25. If linear dimensions of a drop can be measured to within ± 0.2 %, the uncertainty in the resulting value of the boundary tension will be about ± 3 %.

IV The Method of the Plane of Inflection

The principal difficulty in the use of equation (1) is the practical impossibility of making a sufficiently precise determination of the mean curvature, $(1/R + 1/R')$. Since R is always equal to $x/\sin \phi$,* it can usually be estimated to about ± 0.2 %. However, R' is much more difficult to determine. The

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* This is a general property of solids of revolution.

value of this radius can be expressed in terms of first and second differentials:

$$R' = (1/z'')\,(1 + (z')^2)^{3/2}$$

Careful measurements by the best available methods may lead to an uncertainty of as much as two or three per cent in R'.

The only exception to this difficulty is the plane of inflection at which R' is infinite and 1/R' equals zero. (Figure 15.)

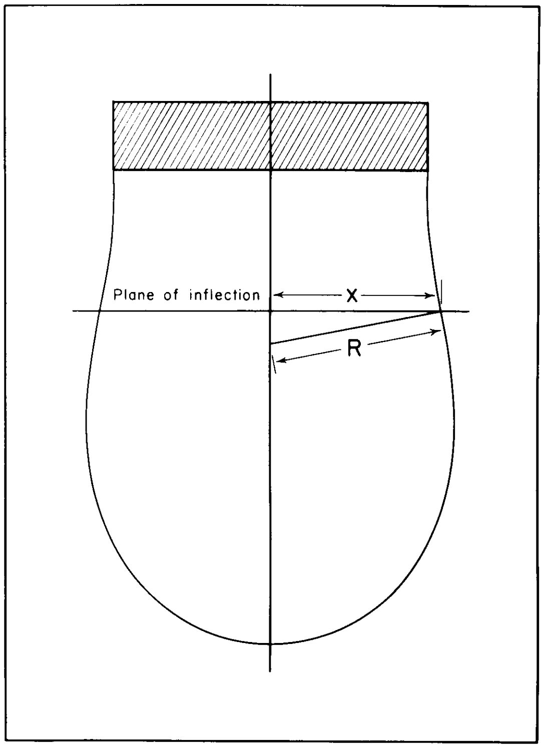

Figure 15.

By combining equations (1) and (2) we get:

$$\gamma = \frac{V \sigma g}{2\pi x \sin\phi - \pi x^2 \left(\frac{1}{R} - \frac{1}{R'}\right)} \quad \text{-- (7)}$$

At the plane of inflection this reduces to:

$$\gamma = \left(\frac{g}{\pi}\right) \frac{V \sigma R}{x^2} \quad \text{-- (8)}$$

This is a useful equation of high precision (since it involves a small number of easily measured quantities and no subtractions) provided that the location of the plane of inflection can be accurately found.*

In the case of pendant drops of the usual shapes, if the plane of inflection is estimated too high, V will be too large, R/x will be approximately unchanged, and x will be too small. The computed value of γ will therefore be too large because of an error in both V and x. These two errors will act in the same direction and augment each other. For drops hanging from a horizontal surface of infinite extent, the errors tend to cancel.

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* The pictures from which the surface tensions of the first 33 samples of the system water-methanol-glycerol were determined were computed in two different ways: the method of the plane of inflection and the method of the selected plane. These results are tabulated for comparison in the thesis of Tucker, TABLE VIII. Since the method was found slower and less precise than the method of the selected plane, it was not used at any other time.

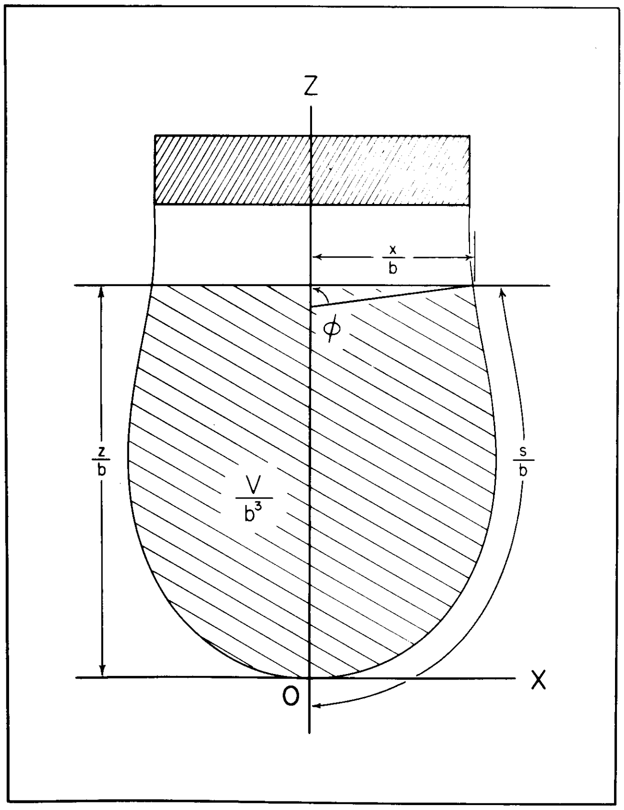
V The Method of the Plane of the Equator

Bashforth and Adams have shown that equation (1) can be rewritten as a relationship between dimensionless groups in the form:

$$Z'' + \left[1+(Z')^2\right]\frac{Z'}{X} = (2-\beta Z)\left[1+(Z')^2\right]^{3/2} \quad \text{-- (9)}$$

Where, $X = x/b$, $Z = z/b$, $Z' = dZ/dX$, $Z'' = d^2Z/dX^2$, b is the radius of curvature of the drop at the origin, and $\beta = \frac{g\sigma b^2}{\gamma}$. This quantity, beta, is a dimensionless group which determines the shape of the profile curve. It is negative for sessile drops and positive for pendant drops.

Figure 16.



Bashforth and Adams* have obtained a number of numerical solutions for equation (9) and published the values of ϕ, x/b, z/b, s/b, and V/b^3 for sets of points on curves of constant beta. The results which deal with the shapes of pendant drops have been plotted and are presented in Figure 17. These curves coincide with a circle of unit radius at the origin, pass through a point of inflection, and eventually approach a horizontal asymptote as X approaches infinity. When X is $dZ/dX = 0$, $d^2Z/dX^2 = 0$, and the distance from the asymptote to the origin is:

$$Z_{oo} = z/b = \frac{2}{\beta} = \frac{2\ \gamma}{g\ \ b^2} \qquad \text{-- (10)}$$

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* BASHFORTH and ADAMS; "An Attempt to Test the Theories of Capillary Action," Cambridge, (1883).

This book represents the combined work of three men: Bashforth, whose interest in capillarity was the motivating force behind the publication; Adams, whose knowledge of mathematics made the mathematical treatment possible; and Encke, who carried out the numerical computations.

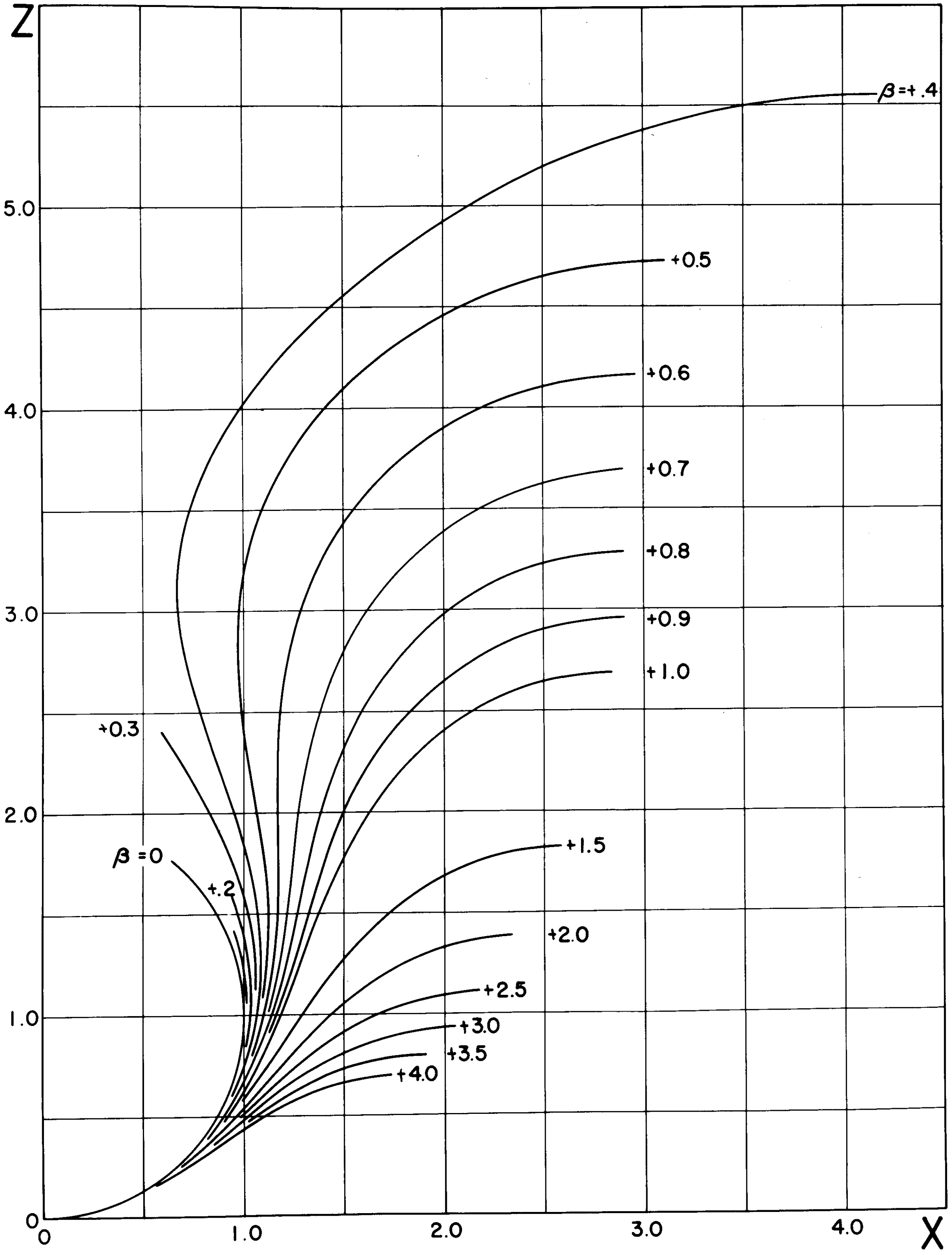
Z
5.0
4.0
3.0
2.0
1.0
0
0
1.0
2.0
3.0
4.0
X
β=+.4
+0.5
+0.6
+0.7
+0.8
+0.9
+1.0
+0.3
β =0
+.2
+1.5
+2.0
+2.5
+3.0
+3.5
+4.0

Figure 17

The fact that the curves computed by Bashforth and Adams do not approach the correct asymptotes indicates that cumulative errors crept into their calculations. These errors are negligible at points near the origin, but they become progressively greater as s/b increases. The curves were computed by a stepwise, algebraic procedure, commencing at the origin. The uncertainty in the result arises from the difficulty of the mathematical problem, rather than from any lack of labor or care on the part of the computer.

An alternative method was suggested by Lord Kelvin many years ago.* A guess is first made of the radius of curvature, R', at a neck of arbitrarily selected diameter. The profile curve is then extended toward the origin by a series of stepwise graphical constructions. If the curve is horizontal when it meets the axis of rotation, the true profile curve of a static drop has been found; if not, a new guess must be made and the laborious construction must be repeated. Typical of the results which can be obtained by this method are the curves which were

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* LORD KELVIN; "Popular Lectures and Addresses," Vol. I, p. 1-72, Macmillan, (1889).

constructed by Perry[*] and more recently by Porter[**]. The precision of the method is so low that the curves are of only qualitative interest.

Since actual drops are bounded by these curves, they may be determined experimentally, but it is impossible to reproduce the entire length of a desired curve with a pendant drop. The part of the curve near the origin can always be realized, but the arms will be cut off by the support from which the drop hangs.

If an attempt is made to increase the volume of the drop in order to form a greater area of the bounding surface, the drop becomes unstable and falls off.

Observations of the behavior of pendant drops indicate that the instability of large drops arises from their inability to recover from small deformations caused by vibrations in the room.

If the drop is small, its principal mode of vibration is a pendulum-like swaying and is characterized by a negligible vertical shift in the center of gravity of the fluid mass and a large restoring force resulting from the relatively great increase in surface

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[*] THOMSON, Sir Wm.; Nature, 34, 290-294, (1886).

[**] PORTER, Alfred W.; Phil.Mag.,(7),8,180-186,(1929).

energy which is required by even a small displacement. The drop is therefore quite stable toward this type of oscillation.

If the drop is allowed to grow to a large size, it will then have an additional mode of vibration, vertical bouncing. This type of motion is characterized by large changes in the potential energy of the fluid which are only barely overbalanced by corresponding changes in the surface energy. When a large drop starts to vibrate in this way in response to some sonic or mechanical disturbance with which it is in resonance, the amplitude of the motion increases rapidly until the limit of stability is passed, the neck contracts to a zero diameter, and large portion of the fluid will detach itself from the residual mass.

One of the purposes for which the tables of Bashforth and Adams were prepared was to assist in the measurement of boundary tension. They pointed out that it is sufficient to make a precise determination of x, z, and ϕ for a single point on the surface of a drop. In particular, if a point is chosen at the equator, $\phi = 90°$. and the boundary tension can be computed from precise measurements of x and z.

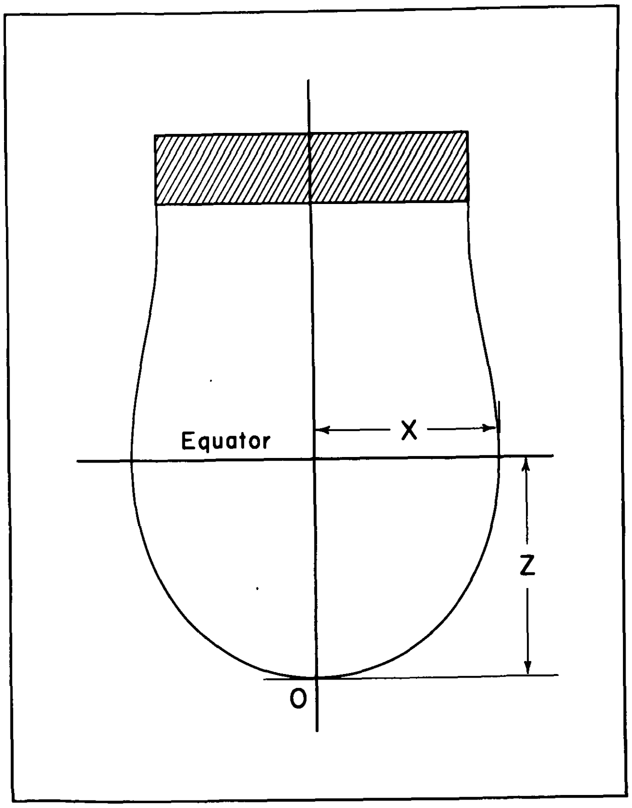
TABLE ONE

By Graphical Interpolation of the Data of Bashforth and Adams

$\phi = 90°$

Beta	x/z	x/b	z/b
0.0	1.000	1.0000	1.00
+ 0.1	0.984	1.0175	1.03
+ 0.2	0.958	1.0378	1.08
+ 0.3	0.918	1.0598	1.15
+ 0.4	0.872	1.0872	1.25
+ 0.5	0.814	1.1220	1.38
+ 0.6	0.690	1.1729	1.70

Figure 18.



With Table One available,* it is possible to rewrite the definition of beta and to solve for the value of the boundary tension:

$$\gamma = \frac{g\sigma b^2}{\beta} = \frac{g\sigma x^2}{\beta\left(\frac{x}{b}\right)^2} \qquad \text{-- (11)}$$

In using this method, one first locates the equator, measures x and z, computed x/z, finds beta and x/b from Table One, and then calculates the boundary tension from equation (11).

This method would be valuable if a sufficiently detailed tabulation of the value of $\beta\,(x/b)^2$ as a function of x/z were available and if there were a sufficiently rapid and precise method for determining the location of the equator. In practice, the equator cannot be located with satisfactory speed and precision.

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* The extensive tabulation of Bashforth and Adams which corresponds to Table One deals with sessile drops because of the importance of the shape of the liquid meniscus in capillary tubes. Nevertheless, their methods are equally applicable to pendant drops.

VI The Method of the Selected Plane

The published work of Bashforth and Adams on pendant drops is too incomplete to be valuable for experimental determinations of boundary tension. However, it is sufficient to suggest the general outlines which such tables would have if they were constructed. The greatest value of their work lay in their clear recognition of the fact that the surfaces of all possible symmetrical liquid drops form a two parameter family. In their work, it was convenient to use b, the radius of curvature at the origin, as a parameter descriptive of the SIZE of the drop and to use beta ($\beta = \frac{g\sigma b^2}{\gamma}$) as a parameter descriptive of its SHAPE. The selection of this pair of parameters was arbitrary. Any other pair of convenient parameters might have been used.

As an illustration of this fact, consider the set of all possible ellipses which is also a two parameter family. For some problem, it might be convenient to use the length of the major axis (2a) as the size parameter and the eccentricity ($e = \frac{\sqrt{a^2-b^2}}{a}$) as the shape parameter. It would be equally justifiable to use the area as a size parameter and to use the ratio of the area to the square of the minor axis as a shape parameter. (Figure 19.)

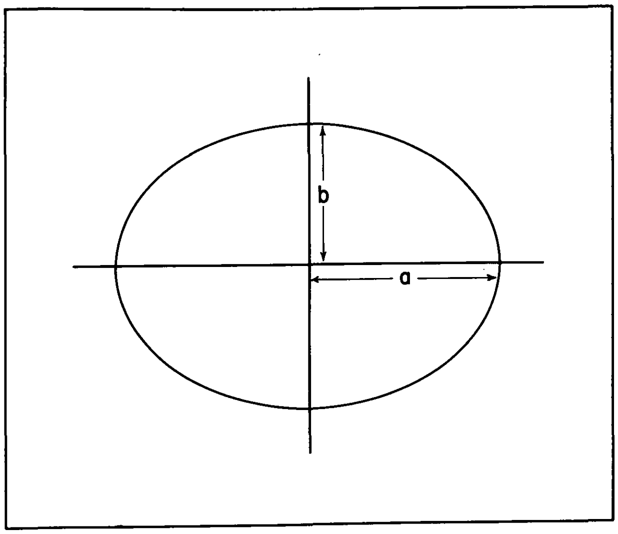

Figure 19.

In determining the value of the boundary tension from the shape and size of pendant drops, b and beta are not convenient parameters since neither one of them can be readily determined by direct measurement.

The equatorial diameter, d_e, can be measured with greater accuracy than any other dimension of a drop, since it is the distance between two clearly defined parallel lines and its length is relatively unaffected by a small error in estimating the location of the plane of the equator.

If a second horizontal plane is selected at an arbitrary distance from the origin, its diameter can also be measured with a high degree of accuracy. (Figure 20.)

The manner in which this second plane is selected is determined by considerations of convenience. A careful examination of numerous pictures of pendant drops suggested that the diameter, d_s, of a plane for which $z = d_e$, would best combine the desired qualities of being susceptible to precise measurement and of being influenced rapidly and continuously by a progressive change in the shape of the drop.

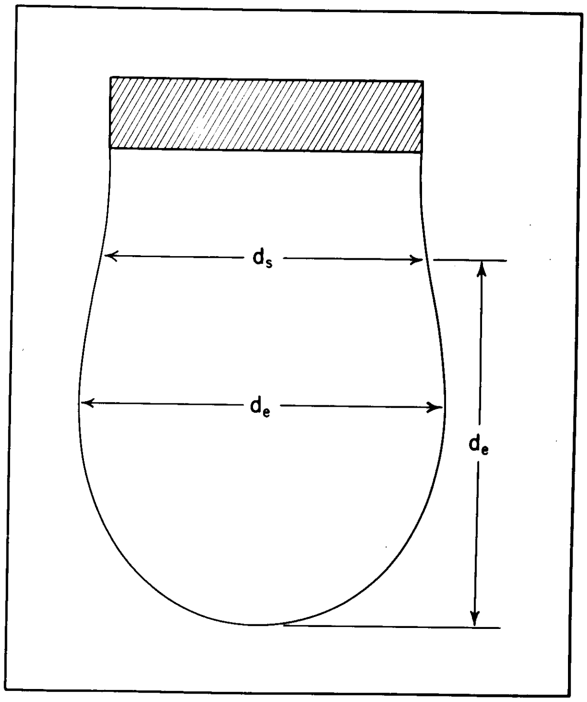

Figure 20.

It was therefore decided to use the diameter, d_e, as the SIZE parameter, and to use the ratio, d_s/d_e, as the SHAPE parameter. These parameters have the advantage that they can be measured readily, with high precision, from a picture of a drop. They have the disadvantage that no analytical functions are known with which they can be used to give the integrated equation of the profile of the drop or the value of its boundary tension. The required relationships must be determined empirically by the examination of drops of known surface tension or mathematically from the differential equation by a laborious combination of stepwise calculations, series expansions, and interpolations.

Both beta and d_e/b are functions of the shape parameter, $S = d_s/d_e$. Accordingly, by graphical interpolation of the data of Bashforth and Adams we can form Table Two.

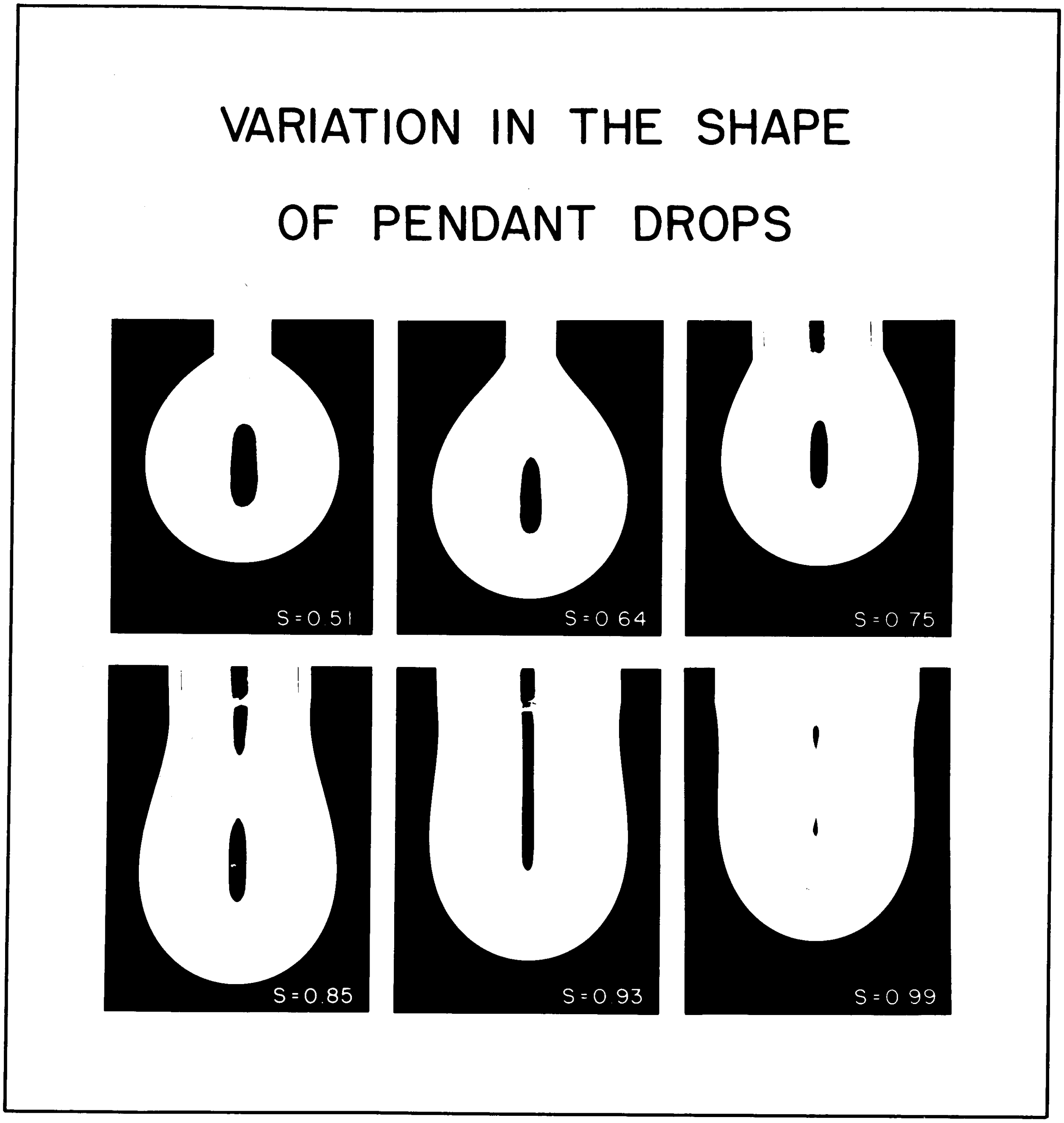
VARIATION IN THE SHAPE
OF PENDANT DROPS
S = 0.51
S = 0.64
S = 0.75
S = 0.85
S = 0.93
S = 0.99

Figure 21

TABLE TWO

Pendant Drops

Beta	d_e/b	d_s/b	$S = d_s/d_e$	$H = \beta(\frac{d_e}{b})^2$
- 0.1	Beta is negative for sessile drops.			
0.0	2.000	0.000	0.0000	0.0000
+ 0.1	2.035	-----	------	+0.4141
+ 0.2	2.076	-----	------	+0.8620
+ 0.3	2.120	1.531	0.7222	+1.3483
+ 0.4	2.174	1.786	0.8215	+1.8905
+ 0.5	2.244	2.049	0.9131	+2.5178
+ 0.6	2.346	2.352	1.0025	+3.3022
+ 0.7	There is no equator here or beyond.			

We can now convert the new parameters to the old ones and use the definition of beta:

$$\gamma = \frac{g\sigma b^2}{\beta} = \frac{g\sigma(d_e)^2}{\beta(\frac{d_e}{b})^2} \qquad \text{-- (12)}$$

It is convenient to define a new function,

$$H = \beta\left(\frac{d_e}{b}\right)^2 \qquad \text{-- (13)}$$

and to obtain its value directly as a tabulated function of the shape parameter, S.

Then* :

$$\gamma = \frac{g \sigma d_e^2}{H} \qquad \text{-- (14)}$$

This method is unquestionably the most promising of the six which have been considered: The only quantities which must be measured are three linear dimensions, and these dimensions have been deliberately selected for their ease of measurement. It is not necessary to determine angles, tangents, volumes, or points of inflection. No subtractions are involved. The function, H, can be determined with all necessary precision in either of two ways: The method is a primary standard if H is computed from the differential equation. The method is a secondary standard if H is determined by calibrating the method against drops of some pure liquid of known surface tension.

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* The signs of the terms in equation (14) have been determined by a convention at variance with that used by Bashforth and Adams as is shown by the form of equation (9): Gamma, g, and d_e are taken to be always positive. Beta is positive for pendant drops. Sigma is considered to be positive when the weight of the drop acts in a direction away from the supporting tip. Accordingly, H is positive for pendant drops.

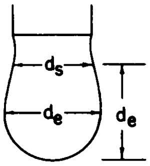
Precision is limited by the accuracy with which linear measurements can be made. If the linear measurements have an uncertainty of ± 0.1 %, the computed boundary tension will have an uncertainty of ± 0.5 %.

The accompanying tabulations of the relationship between H and S were prepared from a smoothed curve obtained by calculating backwards from measurements of the surface tension of a carefully prepared sample of conductivity water in air at 25° C. (γ = 72.00 dynes per centimeter) It is believed that these tables are correct to within about ± 0.1 % which is all that is required by the present camera. If a more precise pendant drop camera is built at some time in the future, it will be necessary to prepare more detailed and more accurate tables. A check on the accuracy of the tables is given by the excellent agreement between the measured values of the surface tension of a number of pure liquids and corresponding values reported in the literature. A table showing these values is given in the section in which surface tension measurements are reported.

TABLE THREE

ARITHMETIC TABULATION OF H-S FUNCTION FOR PENDANT DROPS

S vs. 1/H



$$S = \frac{d_s}{d_e}$$

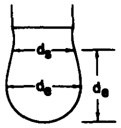
$$\gamma = \frac{(\rho_1 - \rho_2) g d_e^2}{H}$$

Interpolation is unwarranted

S	0	1	2	3	4	5	6	7	8	9
0.70	0.797	.795	.792	.790	.787	.785	.782	.780	.777	.775
.71	.772	.770	.767	.765	.762	.759	.757	.754	.752	.749
.72	.747	.744	.742	.739	.737	.735	.732	.730	.727	.725
.73	.722	.720	.718	.715	.713	.711	.709	.706	.704	.702
.74	.699	.697	.695	.692	.690	.688	.685	.683	.681	.679
.75	.676	.674	.672	.670	.668	.665	.663	.661	.659	.657
.76	.655	.652	.650	.648	.646	.644	.642	.640	.637	.635
.77	.633	.631	.629	.627	.625	.623	.621	.619	.617	.615
.78	.613	.611	.609	.607	.605	.603	.601	.599	.597	.595
.79	.593	.591	.589	.587	.585	.583	.581	.579	.577	.575
0.80	.573	.571	.570	.568	.566	.564	.562	.561	.559	.557
.81	.555	.553	.551	.550	.548	.546	.544	.542	.540	.539
.82	.537	.535	.533	.532	.530	.528	.526	.524	.523	.521
.83	.519	.518	.516	.515	.513	.511	.509	.507	.506	.504
.84	.502	.501	.499	.498	.496	.494	.493	.491	.490	.488
.85	.486	.485	.483	.482	.480	.479	.477	.476	.474	.473
.86	.471	.470	.468	.467	.465	.464	.462	.461	.459	.458
.87	.457	.455	.454	.452	.451	.450	.448	.447	.446	.444
.88	.443	.441	.440	.439	.437	.436	.434	.433	.431	.430
.89	.429	.428	.426	.425	.423	.422	.420	.419	.418	.417
0.90	.415	.414	.413	.411	.410	.409	.408	.406	.405	.404
.91	.403	.401	.400	.399	.398	.396	.395	.394	.393	.391
.92	.390	.389	.388	.386	.385	.384	.383	.382	.381	.379
.93	.378	.377	.376	.375	.373	.372	.371	.370	.369	.368
.94	.366	.365	.364	.363	.362	.361	.359	.358	.357	.356
.95	.355	.354	.353	.352	.351	.350	.349	.348	.346	.345
.96	.344	.343	.342	.341	.340	.339	.338	.337	.335	.334
.97	.333	.332	.331	.330	.329	.328	.327	.326	.325	.324
.98	.323	.322	.321	.320	.319	.318	.317	.316	.315	.314
.99	.313	.312	.311	.310	.309	.308	.307	.306	.305	.304
1.00	.303									

TABLE FOUR

LOGARITHMIC TABULATION OF H-S FUNCTION FOR PENDANT DROPS



$S = \frac{d_s}{d_e}$

$10 + \text{Log}_{10}\ S$ vs. $10 + \text{Log}_{10}\ 1/H$

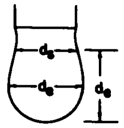
Interpolation is unwarranted

$\gamma = \frac{(\rho_1 - \rho_2) g d_e^2}{H}$

S	0	2	4	6	8	S	0	2	4	6	8
9.700	10.18 68	65	62	58	55	9.750	10.09 92	88	84	80	77
.701	52	48	45	42	38	.751	73	69	65	62	58
.702	35	32	28	25	22	.752	54	50	47	43	39
.703	18	15	12	08	05	.753	35	32	28	24	20
.704	02	*98	*95	*92	*88	.754	17	13	09	05	02
.705	.17 85	82	78	75	72	.755	.08 98	94	90	87	83
.706	68	65	62	58	55	.756	79	75	72	68	64
.707	52	48	45	42	38	.757	60	57	53	49	45
.708	35	32	28	25	21	.758	41	38	34	30	26
.709	18	14	11	07	04	.759	22	19	15	11	07
9.710	00	*97	*94	*90	*87	9.760	04	00	*96	*92	*89
.711	.16 84	80	77	74	70	.761	.07 85	81	77	73	69
.712	67	64	60	57	54	.762	65	61	58	54	50
.713	50	47	43	40	36	.763	46	42	39	35	31
.714	33	30	26	23	20	.764	27	23	20	16	12
.715	16	13	10	06	03	.765	08	04	01	*97	*93
.716	.15 99	96	92	89	85	.766	.06 89	85	82	78	74
.717	82	78	75	71	68	.767	70	66	62	58	54
.718	64	61	58	54	51	.768	51	47	43	39	35
.719	47	44	40	37	33	.769	31	27	23	19	15
9.720	30	26	23	19	16	9.770	12	08	04	00	*96
.721	12	09	05	02	*98	.771	.05 92	88	85	81	77
.722	.14 95	91	88	84	81	.772	73	69	65	61	57
.723	77	74	70	67	63	.773	53	49	45	42	38
.724	60	56	53	49	46	.774	34	30	26	22	18
.725	42	39	35	32	28	.775	14	10	06	02	*98
.726	25	21	18	14	10	.776	.04 94	90	86	82	79
.727	07	04	00	*97	*93	.777	75	71	67	63	59
.728	.13 90	86	83	79	76	.778	55	51	48	44	40
.729	72	69	65	62	58	.779	36	32	28	24	20
9.730	55	51	48	43	40	9.780	16	12	08	04	00
.731	36	33	29	26	22	.781	.03 96	92	88	84	80
.732	19	15	12	08	05	.782	76	72	68	64	60
.733	01	*98	*94	*90	*87	.783	56	52	48	44	40
.734	.12 83	80	76	73	69	.784	36	32	28	24	20
.735	66	62	59	55	52	.785	16	12	08	04	00
.736	48	44	41	37	33	.786	.02 96	92	88	84	80
.737	30	26	22	19	15	.787	76	71	67	63	59
.738	11	08	04	00	*97	.788	55	51	47	43	39
.739	.11 93	90	86	83	79	.789	35	31	27	23	18
9.740	76	72	68	64	61	9.790	14	10	06	02	*98
.741	57	53	50	46	42	.791	.01 94	90	85	81	77
.742	39	35	31	28	24	.792	73	69	65	61	57
.743	20	17	13	09	05	.793	53	49	45	41	37
.744	02	*98	*94	*91	*87	.794	32	28	24	20	16
.745	.10 83	80	76	72	69	.795	12	08	04	00	*95
.746	65	61	58	54	50	.796	.00 91	87	83	79	75
.747	47	43	39	36	32	.797	71	66	62	58	54
.748	28	25	21	17	14	.798	50	46	42	37	33
.749	10	06	02	*99	*95	.799	29	25	21	17	13
9.750	.09 92	88	84	80	77	9.800	08	04	00	*96	*92

TABLE FIVE

LOGARITHMIC TABULATION OF H-S FUNCTION FOR PENDANT DROPS



$S = \frac{d_s}{d_e}$

$10 + \log_{10} S$ vs. $10 + \log_{10} 1/H$

Interpolation is unwarranted

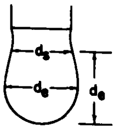
$\gamma = \frac{(\rho_1 - \rho_2) g d_e^2}{H}$

S		0	2	4	6	8	S		0	2	4	6	8
9.800	10.00	08	04	00	*96	*92	9.850		04	*99	*95	*90	*86
.801	9.99	88	83	79	75	71	.851	9.88	81	77	72	67	63
.802		67	63	58	54	50	.852		58	53	49	44	39
.803		46	42	38	33	29	.853		35	30	25	21	16
.804		25	21	17	13	08	.854		11	07	02	*97	*92
.805		04	00	*96	*92	*87	.855	.87	88	83	78	74	69
.806	.98	83	79	75	70	66	.856		64	59	55	50	45
.807		62	58	53	49	45	.857		40	36	31	26	21
.808		40	36	32	27	23	.858		17	12	07	02	*98
.809		19	15	10	06	02	.859	.86	93	88	83	79	74
9.810	.97	98	93	89	85	81	9.860		69	64	60	55	50
.811		76	72	68	64	59	.861		45	41	36	31	26
.812		55	51	47	42	38	.862		21	16	11	05	01
.813		34	29	25	21	16	.863	.85	97	92	87	82	77
.814		12	08	03	*99	*95	.864		73	68	63	58	53
.815	.96	90	86	82	77	73	.865		48	43	38	33	29
.816		69	64	60	56	51	.866		24	19	14	10	05
.817		47	43	38	34	30	.867		00	*95	*90	*86	*81
.818		25	21	17	12	08	.868	.84	76	71	66	61	56
.819		04	*99	*95	*91	*86	.869		52	47	42	37	32
9.820	.95	82	78	73	69	65	9.870		27	22	17	13	08
.821		60	56	52	47	43	.871		03	*98	*93	*88	*83
.822		39	34	30	25	21	.872	.83	78	73	68	63	58
.823		16	12	08	03	*99	.873		53	48	44	39	34
.824	.94	95	90	86	81	77	.874		29	24	19	14	09
.825		73	68	64	59	55	.875		04	00	*95	*90	*85
.826		50	46	42	37	33	.876	.82	80	75	70	65	60
.827		28	24	19	15	10	.877		55	50	45	40	35
.828		06	02	*97	*93	*88	.878		30	25	20	15	10
.829	.93	84	79	75	70	66	.879		05	00	*95	*90	*85
9.830		61	57	53	48	44	9.880	.81	80	75	70	65	60
.831		39	35	30	26	21	.881		55	50	45	40	35
.832		17	12	08	03	*98	.882		30	25	20	15	10
.833	.92	94	89	85	80	76	.883		05	00	*95	*90	*85
.834		71	67	62	58	53	.884	.80	79	74	69	64	59
.835		49	44	40	35	31	.885		54	49	44	39	33
.836		26	22	17	13	08	.886		28	23	18	13	08
.837		04	*99	*95	*90	*86	.887		03	*97	*92	*87	*82
.838	.91	81	77	72	68	63	.888	.79	77	72	67	61	56
.839		59	54	50	45	41	.889		51	46	41	36	31
9.840		36	32	27	23	18	9.890		26	21	16	11	06
.841		14	09	04	00	*95	.891		01	*96	*90	*85	*80
.842	.90	90	86	81	76	72	.892	.78	75	70	65	59	54
.843		67	63	58	53	49	.893		49	44	39	33	28
.844		44	39	35	30	26	.894		23	18	13	07	02
.845		21	17	12	07	03	.895	.77	97	92	87	81	76
.846	.89	98	93	89	84	79	.896		71	66	61	55	50
.847		75	70	66	61	56	.897		45	40	35	29	24
.848		52	47	42	38	33	.898		19	14	09	04	*98
.849		29	24	19	15	10	.899	.76	93	88	83	78	72
9.850		04	*99	*95	*90	*86	9.900		67	62	57	52	46

TABLE SIX

LOGARITHMIC TABULATION OF H-S FUNCTION FOR PENDANT DROPS

$10 + \log_{10} S$ vs. $10 + \log_{10} 1/H$



$$S = \frac{d_s}{d_e}$$

Interpolation is unwarranted

$$\gamma = \frac{(\rho_1 - \rho_2) g d_e^2}{H}$$

S		0	2	4	6	8	S		0	2	4	6	8
9.900	9.76	67	62	57	52	46	9.950		05	00	*94	*88	*83
.901		41	36	31	25	20	.951	9.62	77	71	66	60	54
.902		15	10	04	*99	*94	.952		49	43	37	32	26
.903	.75	89	83	78	73	68	.953		20	15	09	03	*98
.904		62	57	52	46	41	.954	.61	92	86	81	75	69
.905		36	30	25	20	14	.955		64	58	52	47	41
.906		09	04	*98	*93	*88	.956		35	30	24	18	13
.907	.74	82	77	72	66	61	.957		07	01	*96	*90	*84
.908		56	50	45	40	34	.958	.60	79	73	67	62	56
.909		29	24	18	13	08	.959		50	45	39	33	28
9.910		02	*97	*92	*86	*81	9.960		22	16	11	05	*99
.911	.73	76	70	65	60	54	.961	.59	94	88	82	76	71
.912		49	43	38	32	27	.962		65	59	54	48	42
.913		22	16	11	05	00	.963		36	30	25	19	13
.914	.72	94	89	84	78	73	.964		07	01	*95	*90	*84
.915		67	62	56	51	45	.965	.58	78	72	66	60	54
.916		40	35	29	24	18	.966		48	43	37	31	25
.917		13	07	02	*96	*91	.967		19	13	07	01	*96
.918	.71	86	80	75	69	64	.968	.57	90	84	78	72	66
.919		58	53	47	42	36	.969		60	54	49	43	37
9.920		31	25	19	14	08	9.970		31	25	19	13	07
.921		03	*97	*92	*86	*81	.971		02	*96	*90	*84	*78
.922	.70	75	70	64	59	53	.972	.56	72	66	61	55	49
.923		48	42	37	31	26	.973		43	37	31	25	19
.924		20	15	09	04	*98	.974		13	07	01	*95	*89
.925	.69	93	87	82	76	71	.975	.55	83	77	72	66	60
.926		65	60	54	49	43	.976		54	48	42	36	30
.927		38	32	26	21	15	.977		24	18	12	06	00
.928		09	04	*98	*92	*87	.978	.54	94	88	82	76	70
.929	.68	81	75	70	64	58	.979		64	58	52	46	40
9.930		53	47	42	36	31	9.980		34	28	22	16	10
.931		26	20	15	10	04	.981		04	*98	*92	*86	*80
.932	.67	99	94	88	83	78	.982	.53	74	68	62	56	50
.933		72	67	62	56	51	.983		44	38	32	26	20
.934		46	40	35	30	24	.984		14	08	02	*96	*90
.935		19	14	08	03	*97	.985	.52	84	78	72	66	60
.936	.66	92	86	81	75	70	.986		54	48	42	36	28
.937		64	59	53	48	42	.987		22	16	10	04	*98
.938		37	31	26	20	15	.988	.51	92	86	80	74	68
.939		09	04	*98	*93	*87	.989		62	56	50	44	38
9.940	.65	82	76	71	66	60	9.990		32	26	20	14	08
.941		55	49	44	38	33	.991		01	*95	*89	*83	*77
.942		27	22	17	11	06	.992	.50	71	64	58	52	46
.943		00	*95	*89	*84	*78	.993		40	33	27	21	15
.944	.64	73	67	62	56	51	.994		09	02	*96	*90	*84
.945		45	39	34	28	23	.995	.49	78	71	65	59	53
.946		17	12	06	01	*95	.996		46	40	34	28	21
.947	.63	90	84	79	73	68	.997		15	09	02	*96	*90
.948		62	56	51	45	39	.998	.48	83	77	71	64	58
.949		34	28	22	17	11	.999		52	45	39	33	26
9.950		05	00	*94	*88	*83	10.000		20	14	07	01	*95

MATHEMATICAL PROCEDURES USED IN THE COMPUTATIONS

I Means of Computing the Volume of the Drop

Of the six methods which have been considered for computing the boundary tension from pictures of pendant drops, three require the calculation of the volume of fluid hanging pendant below some arbitrary plane.

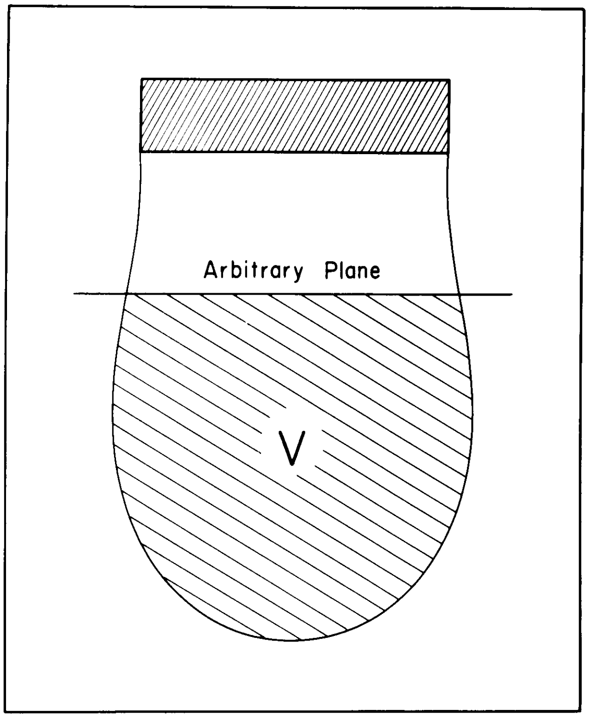


Figure 22.

(a) Graphical Integration

Let the solid be divided into thin slices by a large number of equally spaced horizontal planes. Then each slice may be considered as a cylinder having the average radius and the total volume will be the sum of the volumes of the parts.*

$$V = \pi \Sigma_1^n \left(\frac{x_{n-1} + x_n}{2} \right)^2 dz \qquad \text{-- (15)}$$

The labor of squaring the radii can be avoided by reading the square of the average radius directly with the aid of an accurately ruled glass plate laid over the photograph. (Figure 23.)

Even with a device of this sort and with an adding machine, the labor of summing a sufficiently large number of finite increments is so great that the method would only be used as a last resort.

---

* An alternative method was used by Worthington who found it convenient to fit a zone of a sphere near the origin and to fit frustrums of cones between the other planes.

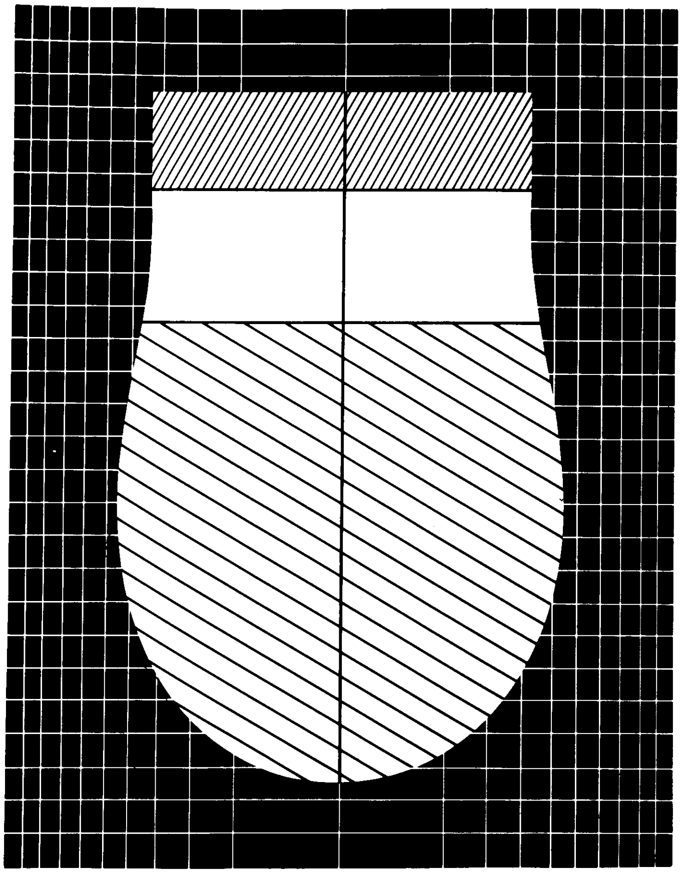


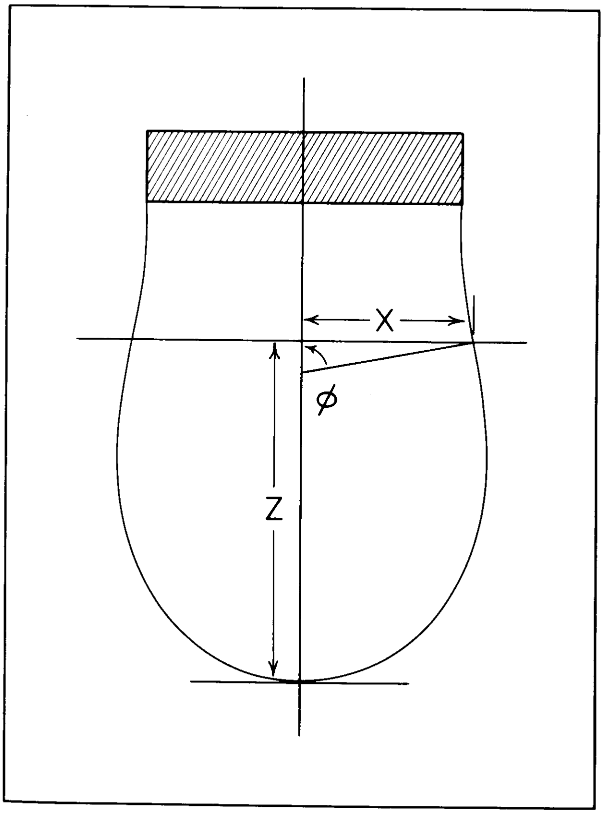
Figure 23.

The grid in the background consists of equally spaced horizontal lines and vertical lines which are placed at equal increments of x^2. This is sometimes called a "parabolic ruling."

(b) Calculation from the Equation of the Surface

Bashforth and *Adams* have shown that it is possible to compute the volume of the solid from the differential equation of its surface. They have done this and give the results for a few selected drops. These scattered data serve to indicate a possible method of procedure. If additional values were computed, the data could be rearranged to produce a two parameter table giving the value of V/x^3 for any combination of values of x/z and ϕ.

Figure 24.



Given a picture of a drop (Figure 24.) one would measure x, z, and ∅ at the plane below which the volume is required. The tabulation is entered with the value of x/z and of ∅. Knowing both V/x^3 and x, V can be readily calculated.

The Bashforth and Adams tables are too incomplete and the labor of enlarging them is too great to make this method available for the present problem.

(c) Mechanical Integration

Integration of the volume of the drop requires the evaluation of the integral,

$$V = \pi \int_0^z x^2 \, dz \qquad \text{-- (16)}$$

around one half of the cross section of the drop.

A special type of planimeter, known as the "Amsler Three-wheel Integrator,"* is able to obtain the line integral,

$$M = 40m = \frac{1}{2} \int_0 x^2 dz \qquad \text{-- (17)}$$

---

* For the theory of this planimeter see: LIPKA; "Graphical and Mechanical Computation," p.250, Wiley, (1918).

where M is the moment of the area traced, with reference to the axis of moments, and m is the reading of the moment dial of the instrument.

By comparison of these two integrals, it can be seen that if the pointer of the instrument travels in a figure-eight around the two halves of the cross section of the drop, (Figure 25.) the moment dial will read $1/40\pi$ times the apparent volume in cubic inches, if the planimeter is

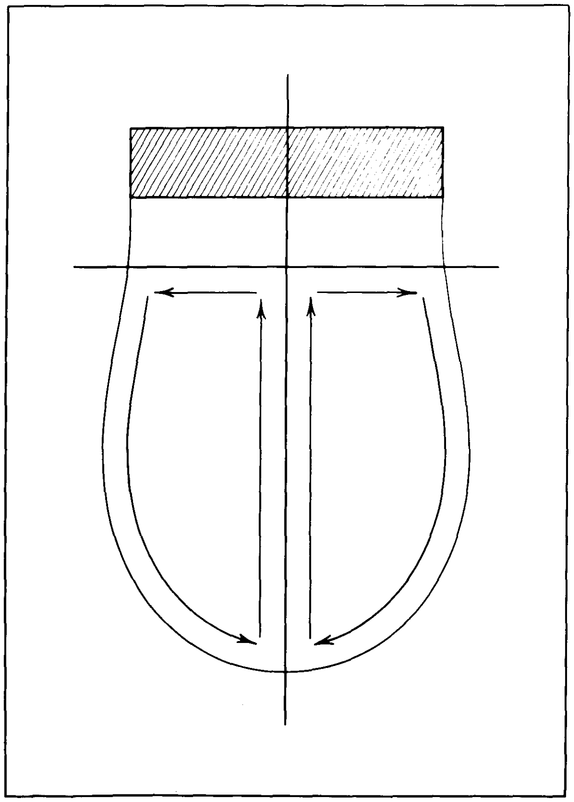


Figure 25.

designed to give results in English units.

$$V = 40 \pi m \qquad \text{-- (18)}$$

This method is much faster than the method of finite increments. A skilled operator can measure and check the volume of a drop in about five minutes with a probable error of less than ± 0.1 %.

II Means of Finding the Normal to a Curve

The present importance of the problem of finding the normal to the profile curve of a drop is a consequence of the geometry of solids of revolution.

If x is the radius of the section, R' is the radius of curvature in the profile plane, R is the other principal radius of curvature, C' and C are the corresponding centers of curvature, and ϕ is the angle between the normal and the axis of rotation; then, $\sin \phi = x/R$, both centers of curvature lie on the normal, and R is the distance from the surface to the axis of rotation measured along the normal. (Figure 26.)

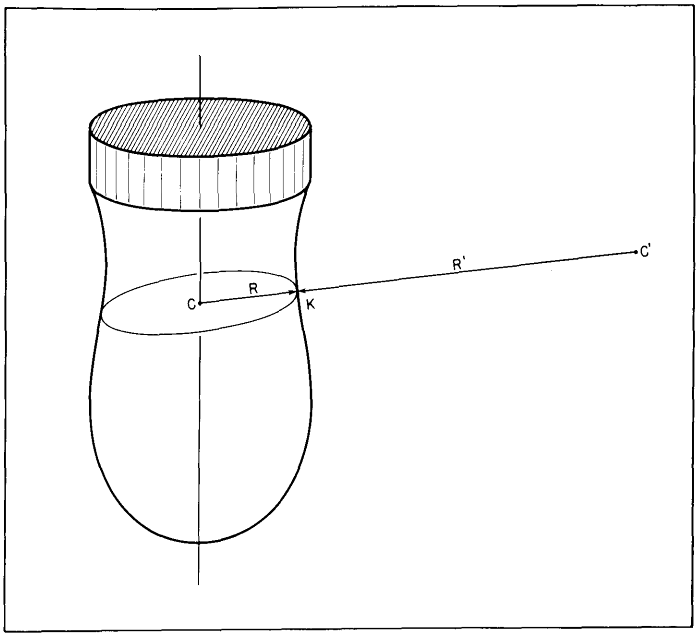


Figure 26.

(a) The Logarithmic Spiral

The logarithmic spiral is the locus of its own center of curvature, consequently it may be used to find the normal and radius of curvature at a point on a curve.

The spiral is allowed to slide through some chosen point, K, until it coincides with the given curve in both direction and curvature. Then, the normal may be drawn tangent to the spiral at C' and extended to cut the axis of rotation at C. Both radii of curvature of the surface at the point, K, have now been found since, R = KC, and R' = KC'. (Figure 27.)

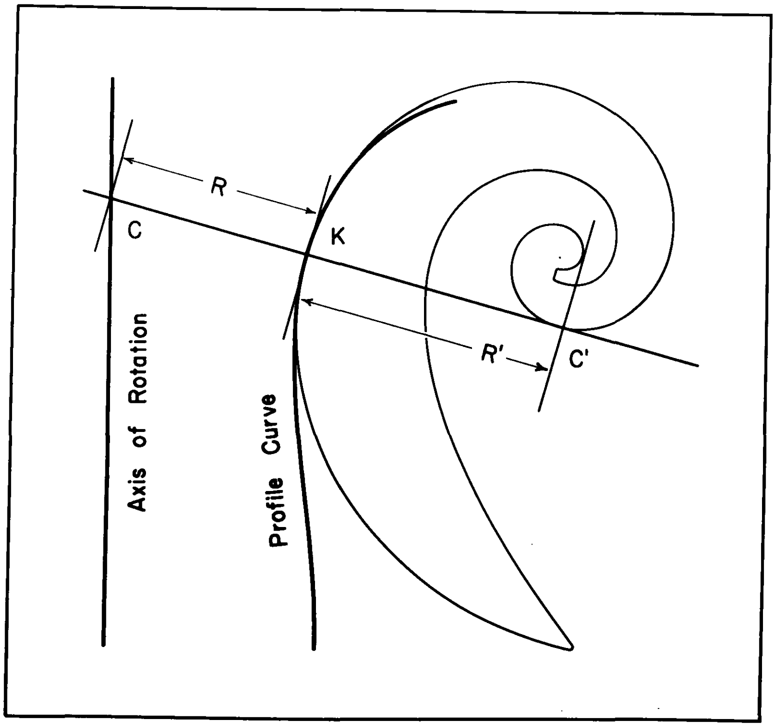


Figure 27.

This method is theoretically exact, but it involves errors due to imperfections in the shape of the celluloid spiral and to the experimental difficulty of deciding when the spiral is in the right place.

Commercially available spirals* can only be used when the radius of curvature, KC', is between 1.5 and 5.5 inches. An experienced operator can expect to find the direction of the normal within ± 1° and the length of the radius, R', within about ± 3 %.

(b) Analytical Curve Fitting

If the equation of the curve were known, the first derivative, dz/dx, could be formed and evaluated at any point and would be equal to the cotangent of ϕ. The known second order, second degree, differential equation of the curve has not been integrated. Accordingly, neither the exact first derivative equation nor the exact integrated equation is available.

It would be possible to fit an empirical equation to a portion of any particular curve under consideration. This equation could then be differentiated, and the slope of the normal at any desired point could be computed. When enough points are

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* "The Logarithmic Spiral Curve, No. 1861," Keuffel & Esser Co., instructions by Wm. Cox, no date.

measured with sufficient precision and when the coefficients are accurately determined by the method of least squares, this is undoubtedly the most accurate and precise method for determining the normal. The labor and time required are so great that the method is impractical for problems where the operation must be carried out many times.

(c) The Mirror Method

If the curve is not too irregular, the normal can be found by drawing a line along the edge of a plane, front-silvered, vertical mirror held in such a position that the uncovered half of the curve is continuous with its own image. This method is very rapid. It works best on curves which are nearly straight and gives results accurate to within about ± 1°. (Figure 28.)

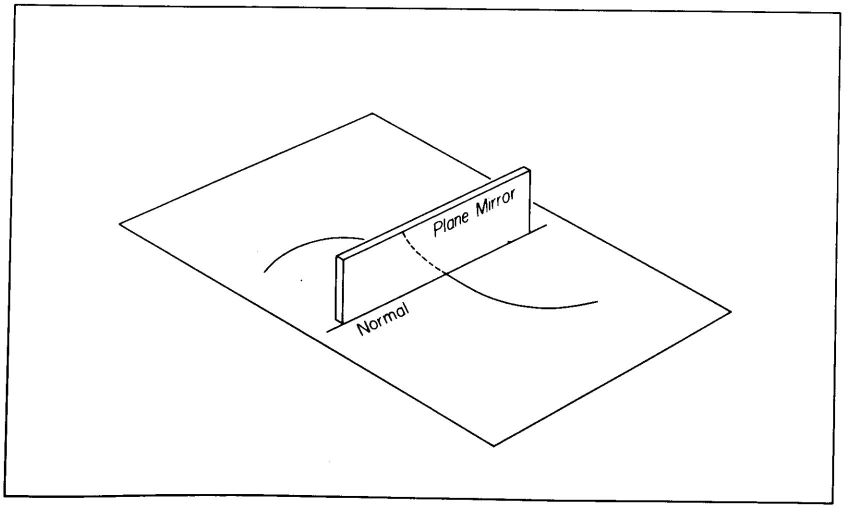

Figure 28.

(d) Use of a Protractor

Experience shows that the most satisfactory method is to construct a perpendicular to the apparent tangent to the curve with the aid of a transparent protractor of convenient size. The probable accuracy which can be expected with curves of the type under consideration is ± 0.5°, and the method is extremely rapid.

III Means of Finding the Point of Inflection

(a) Analytical Curve Fitting

Special methods have been developed* for fitting curves to the coordinates of a number of points whose positions are spaced in a predtermined way. It is found possible to fit a fourth degree equation to seven points on a given curve.

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* AVAKIAN, A. S.; M. I. T., Course XVIII, Math. Thesis, (1933). The expressions for the coefficients of the quartic in terms of the ordinates have been rearranged in a more convenient form by Professor R. D. Douglass.

If the fourth degree equation is to be written in the form, $y = a + bx + cx^2 + dx^3 + ex^4$, and if the ordinates of seven points whose abscissas differ by h are measured and found to be, y_{-3}, y_{-2}, y_{-1}, y_0, y_1, y_2, and y_3, the coefficients of the quartic which best fits the data are found by the method of least squares to be:

$$a = y_0$$

$$b = \frac{58(y_1-y_{-1}) + 67(y_2-y_{-2}) - 22(y_3-y_{-3})}{252\ h}$$

$$c = \frac{-70y_0 - 19(y_1+y_{-1}) + 67(y_2+y_{-2}) - 13(y_3+y_{-3})}{264\ h^2}$$

$$d = \frac{(y_3-y_{-3}) - (y_2-y_{-2}) - (y_1-y_{-1})}{36h^3}$$

$$e = \frac{6y_0 + (y_1+y_{-1}) - 7(y_2+y_{-2}) + 3(y_3+y_{-3})}{264\ h^4}$$

At a point of inflection, the second derivative of the equation of the curve is,

$$\frac{d^2y}{d\ x^2} = 2c + 6\ dx + 12\ ex^2$$

whence

$$x = \frac{-3d \pm \sqrt{9d^2 - 24ce}}{12e}$$

unless $e = 0$, in which case,

$$x = \frac{-c}{3\ d}$$

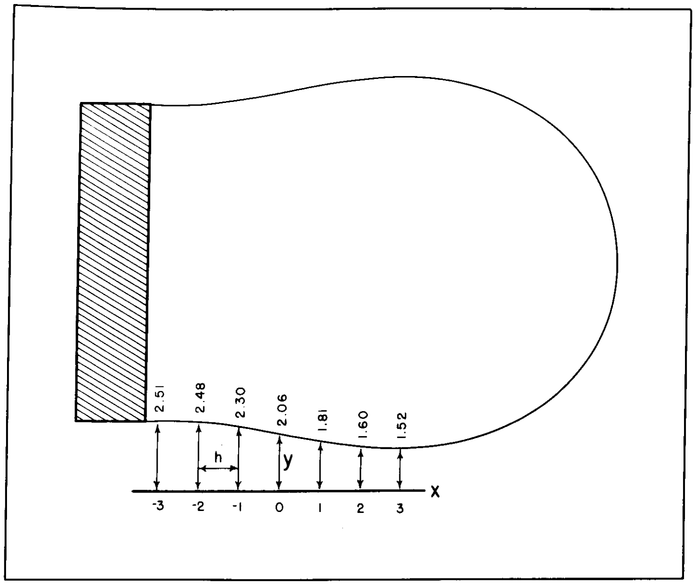

Figure 29.

As an example, consider the problem of finding the point of inflection in the profile of a pendant drop.

The seven ordinates were spaced 1.5 centimeters apart and were measured upward from an arbitrarily selected base line. (Figure 29.) Using these experimental values, the coefficients were computed and found to be:

$$c = \frac{274.68 - 273.36}{594} = 0.00222$$

$$d = \frac{1.37 - 0.99}{121.5} = 0.00315$$

$$e = \frac{28.56 - 28.56}{1136.5} = 0.00000$$

As might have been foreseen, e turns out to be zero since it is the coefficient of an even term which is a power series expansion of an odd function.

The unfavorable nature of the subtractions is apparent at once and makes the precision of the final result very low.

$$x = (-0.00222)/(0.00945) = -0.23 \text{ cm.}$$

When linear measurements can only be made with a precision of ± 0.1 %, this method is probably inferior to a good guess. It is certainly less satisfactory than the prism instrument described below. The numerical calculation requires about thirty minutes.

(b) Use of a Prism

A device which is of value in the examination of experimental curves consists of a 90° prism securely mounted in a suitable framework. (Figure 30.)

In all cases, the instrument indicates the perpendicular bisector, MN, of a chord, KL, of the curve. For many curves, this bisector does not differ appreciably from a normal, and the device can be used to determine the approximate normal, tangent, or slope at a point on a given curve.*

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* RICHARDS and ROOPE; Science, new series, 71, 290-291, (1930).

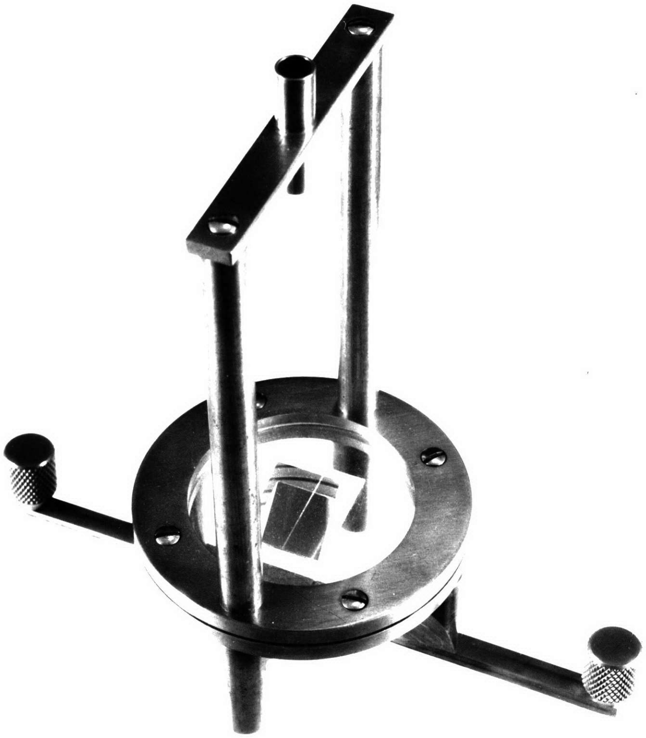

Figure 30

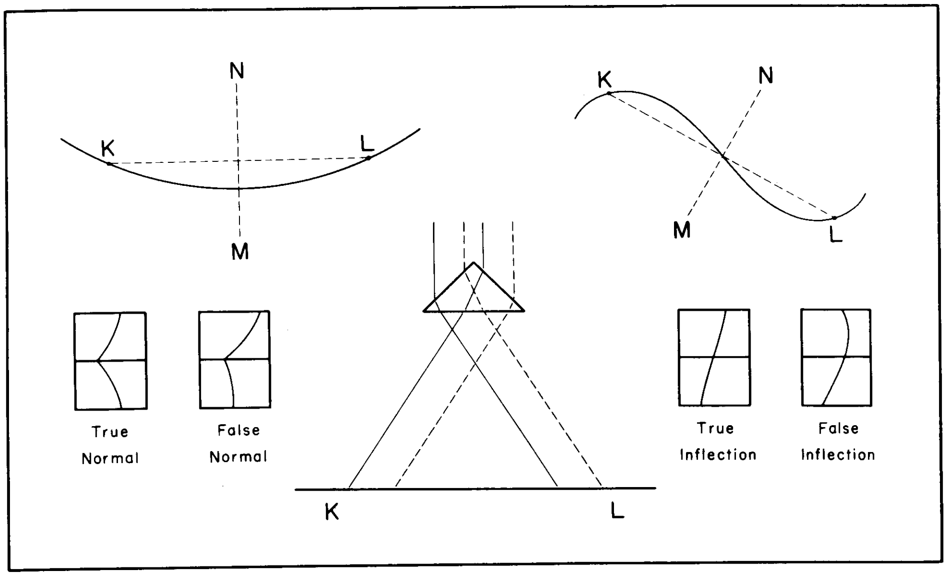

Figure 31.

If the curve is a symmetrical odd function, the perpendicular bisector of a chord joining two points where the curve has the same slope will pass through the point of inflection. For irregular, S-shaped curves, the instrument will indicate a point too near the straighter arm, but the error will usually be negligible, provided that the curve is not too unbalanced in the region examined. To find a point of inflection with the instrument, the axis of the prism is turned perpendicular to the curve in such a way that the two arcs seen by looking vertically down through the prism meet in a point. (Figure 31.) If the prism is at one side of the point of inflection, the matched arcs will show a change in direction at their junction, but if the prism is directly above the point of inflection the cusp will have disappeared. The instrument is placed above a convenient point on the curve and moved along until the cusp disappears. Its position is then marked, and a second reading is obtained by approaching the point of inflection from the other side. The two readings will seldom differ by more than 1 or 2 millimeters and their midpoint can be taken as the point of inflection.

With a device of this type in which the chord is 4.5 centimeters long, the point of inflection can be estimated on pictures of pendant drops to within ± 1.5 millimeters.*

IV Means of Finding the Equator

(a) Curve Fitting

Since the slope of the tangent is given by the first derivative of the equation of the curve, the

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* This refers to a typical drop profile for which $S = 0.8$, and $d_e = 10$ centimeters.

equator could be found by fitting an empirical equation to a number of measured points, setting the derivative equal to infinity, and solving for the coordinates of the point where the tangent line is vertical.

The precision of this method depends upon the precision with which the coordinates of the points can be measured. It is doubtful if sufficient accuracy can be obtained to make the method of the plane of the equator practical. A single calculation requires about one hour.

(b) Use of a T-square

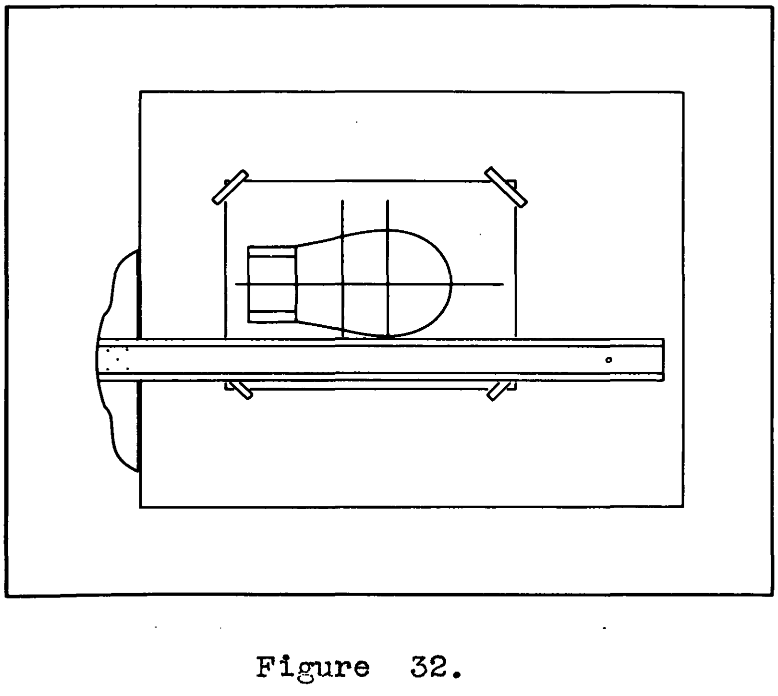

Figure 32.

Sufficient precision for the method of the selected plane can be obtained by finding the equator by eye with the aid of a T-square and triangle. (Figure 32.) On the present series of drop photographs the probable error in Z is about $\pm$ 0.1 centimeter, and the corresponding error in x is less than 0.001 cm.

V Means of Allowing for Magnification and Shrinkage

If the optical system of the camera is properly designed and in correct adjustment, all linear dimensions of the image will be some constant multiple of the corresponding dimensions of the drop itself. Let the optical magnification be B_0 diameters.

Since photographic paper is made on a Fourdrinier machine, it is a homogeneous, anisotropic sheet. Accordingly, some small area which was square when the image was projected on the paper in the camera will be subject to a uniform change in shape and size during the course of the processes of development, washing, and drying. Any such small area which was initially square will, in general, be a rectangle by the time the finished print is examined.

Let the final length of a unit horizontal distance on the new paper be designated by B_h, and let the final length of a unit vertical distance be B_v.

This distortion resulting from the use of photographic paper can be completely avoided by the use of glass plates. The distortion introduces an error into determinations of the normal, but it does not introduce error into the determination of the plane of inflection or of the plane of the equator.

We can now rewrite the working formulae for the various methods of measuring boundary tension and insert the necessary factors to convert "apparent" distances measured on the photographs to "actual" dimensions of the real drop.

WORKING FORMULAE USING THE "APPARENT" DIMENSIONS OF AN IMAGE

I The Method of Two Planes *

$$\gamma = \frac{\sigma g}{2\pi}\left[\frac{V_1\left(\frac{X_2}{X_1}\right)^2 - V_2 - \pi X_2^2 h}{X_2\left[\frac{X_2}{R_1} - 1\right]}\right]\frac{1}{B_0^2 B_h B_v} \quad \text{--(6.2)}$$

* (see next page)

II The Method of the Plane of Inflection[*]

$$\gamma = \frac{g}{\pi} \quad \frac{V \sigma R}{x^2} \quad \frac{1}{B_o^2 B_h B_v} \qquad \text{-- (8.1)}$$

III The Method of the Plane of the Equator[**]

Enter the table with $\left(\frac{x}{z} \right) \left(\frac{B_v}{B_h} \right)$

$$\gamma = \frac{g \sigma x^2}{\beta \left(\frac{x}{b}\right)^2} \left(\frac{1}{B_o B_h} \right)^2 \qquad \text{-- (11.1)}$$

IV The Method of the Selected Plane[**]

Find d_s from $d_e \left(\frac{B_v}{B_h} \right)$

Enter the table with $\left({}^{d_s}/_{d_e} \right)$

$$\gamma = \frac{g \sigma d_e^2}{H} \quad \left(\frac{1}{B_o B_h} \right)^2 \qquad \text{-- (14.1)}$$

---

[*] Approximations are introduced in assuming that B_h is the proper factor to be used to correct R and that the normal found after shrinkage is not appreciably different from the one which would have been found if there were no change in the shape of the photographic paper.

[**] Assumes only "uniformity" of the paper.

COMPARISON OF FIVE OF THE METHODS

For Computing Boundary Tension from Pictures of Pendant Drops

Assumptions on which the comparison is made:*

The optical magnification is 50 diameters.
Linear measurements can be made to ± 0.02 cm.
The equator can be found to ± 0.1 cm.
The plane of inflection can be found to ± 0.2 cm.
The volume is found with a planimeter to ± 0.1 %
The drops are pure water in air at 25° C.
There is no paper shrinkage.

	Method of Worthington	Method of Two Planes	Method of Plane of Inflection	Method of Plane of Equator	Method of Selected Plane
Time Required	6 hrs.	45 min.	15 min.	5 min.	5 min.
Precision ± %	4.0	3.0	2.0	1.0	0.5
Volumes Measured	4	2	1	0	0
Distances Measured	12	6	2	2	3
Other Measurements	four normals	two normals	locate inflection	locate equator	none

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* Based upon the performance of the present pendant drop camera. The ultimate precision possible with the method of the selected plane and superior apparatus could be about ± 0.05 %.

APPARATUS FOR PHOTOGRAPHING PENDANT DROPS

The determination of boundary tension by a study of the shape and size of pendant drops requires the development of special equipment. In fact, it has been the lack of such equipment that has retarded the development of pendant drop methods.

The essential features of pendant drop equipment are, (1) a camera capable of producing an enlarged, undistorted, photographic image of the profile of a pendant drop, and (2) an enclosed chamber where the drop can be formed and maintained at a desired constant temperature and in physical equilibrium with its surroundings. (Figure 33.)

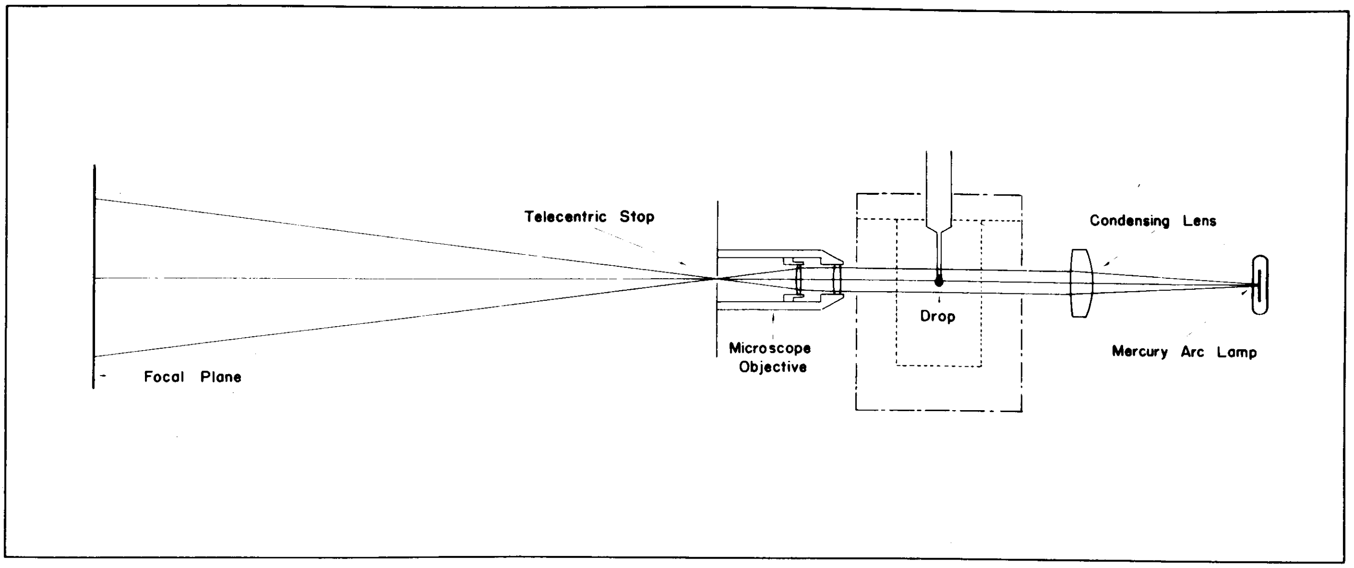

Figure 33.

The Camera

An optical system of this type requires the use of a light source of high intrinsic brilliancy and of low heat output. For this reason, a G.E., type H-3, 85 watt, high pressure, capillary mercury arc lamp was used. Since better definition is obtained by the use of monochromatic light, the lamp was equipped with a Wratten filter, number 77-A, to produce a beam of nearly pure light having a wave-length of about 5460 Å.

In order to avoid distortion resulting from false perspective, it is imperative that the drop be photographed in parallel light. No collimating lens system of satisfactory aperture will produce a beam

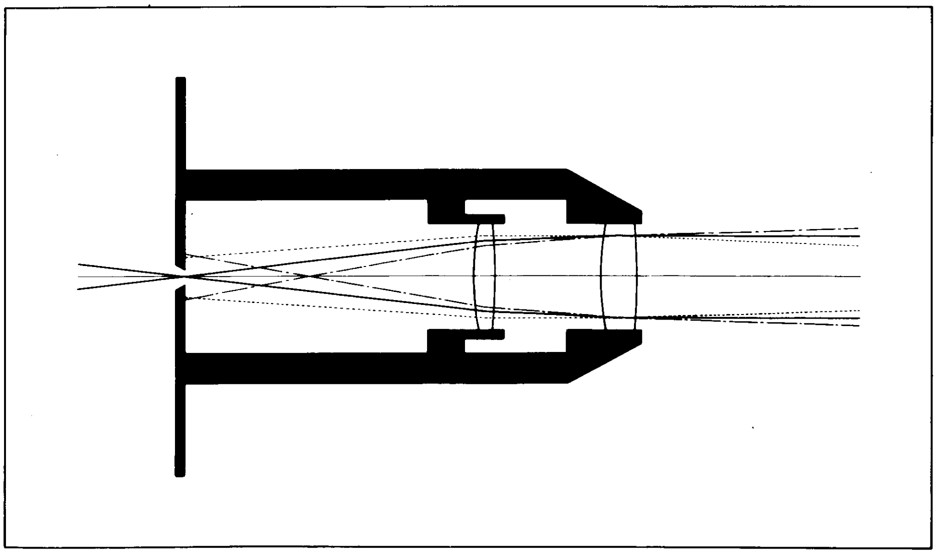

Figure 34. Microscope objective with telecentric stop.

of parallel light from the light source adopted, but the introduction of a small telecentric stop at the back focus of the objective lens gives the desired effect by passing the rays which were parallel to the optical axis and excluding all others. (Figure 34). A stop having a diameter equal to 5 % of the effective focal length has proven satisfactory.

A highly corrected objective of short focal length is necessary if sufficient magnification is to be obtained. For all surface tension measurements, a 48 millimeter standard microscope objective was used and found to be satisfactory. Additional lenses are desirable for interfacial tension measurements because of the greater variation in drop size. Since drops with low boundary tension and high effective density are necessarily formed from small tips, higher magnifications are occasionally necessary. A 24 millimeter objective is suitable for such conditions. If, on the other hand, the interfacial tension is high and the effective density is low, it is desirable to form large drops from big tips. Since a lens with a telecentric stop cannot form an image of an object which is larger than the front element of the lens, a larger lens than the standard 48 millimeter microscope lens may be required occasionally. The use of a 10 centimeter telescope objective has been suggested for use under these conditions.

The desirable size of the photographic image is dictated by the type of equipment which will be used to make the necessary measurements. Since, at the time the present apparatus was constructed, it seemed necessary to use a planimeter which required a large picture, an 11 by 14 inch picture area was adopted. This required an optical magnification of 50 diameters. The subsequent development of the method of the selected plane has demonstrated that 5 by 7 inch plates are sufficient if measurements are to be made with ordinary scales, and 2 by 2 inch plates would give adequate precision if measurements are made with a traveling microscope.

Three types of sensitized photographic material are available: paper, film, and plates. Of these, glass plates are the best and the most expensive. Processing and drying operations induce shrinkage and distortion in both film and paper and only shrinkage can be allowed for in the calculations. Because of the large size of the image which was used in the present camera, it was necessary to use Photostat paper, the cost of plates being prohibitive. Distortion of this paper is the largest source of error entering into the use of the present equipment.

The most difficult problem in the design of the optical system was the provision of a focussing device. An instrument which is only intended for surface tension measurements can be built with a fixed object distance as well as a fixed image distance. If the drop is formed in a tank of liquid for interfacial tension determinations, provision must be made to adjust the location of the object as the index of refraction of the external phase is changed.

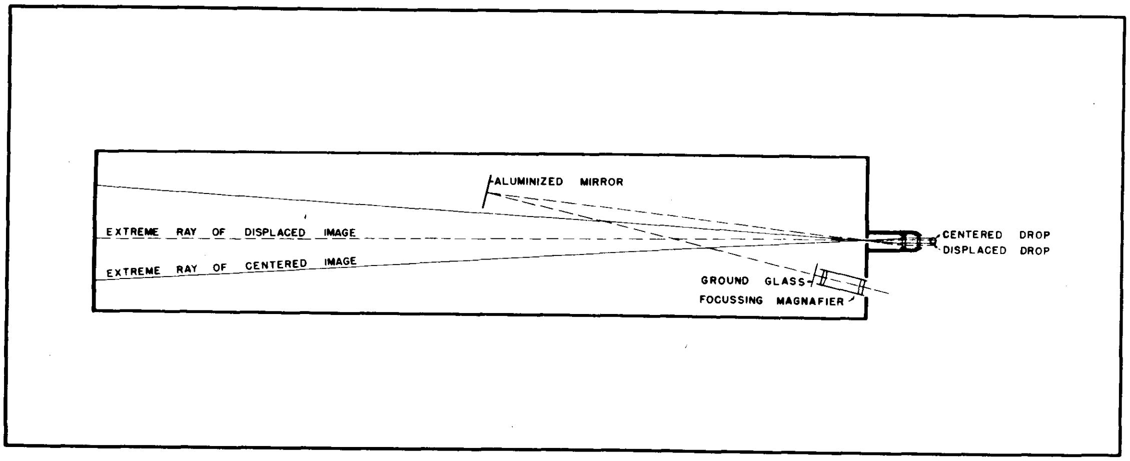

Figure 35.

The device which was adopted is shown in Figure 35. The camera was built with a fixed image distance (insuring a constant optical magnification), and the drop was suspended from a movable stage which could be shifted in rectangular coordinates parallel or at right angles to the optical axis. A mirror which had been aluminized on its front surface was placed just outside the normal optical path, half way from the lens to the focal plane. By moving the drop slightly to one side, the edge of the image of the drop could be sent along the dotted line to the mirror and back to a ground glass where it was viewed through a magnifier. The focussing was then accomplished by moving the drop parallel to the optical axis until the image on the ground glass was sharp. Following this, the drop was returned to its position on the optical axis.

The 48 millimeter lens required a 1/10 second exposure with white light or a one second exposure with mercury green. The 24 millimeter lens required three times as long an exposure.

The Thermostat System

Temperature control is absolutely essential to the accurate determination of boundary tension. This is true for two reasons: boundary tension is a function of temperature which approaches zero as a critical point is reached: phase composition is also a function of temperature. If the fluids are not held at a constant temperature, there will be a transfer of material and of heat across the surface which is being studied. This action will tend to disrupt any surface structure which might normally exist and may cause local abnormalities in composition and temperature.

The present apparatus was designed to operate at temperatures between 0° and 80° C. A two unit thermostat

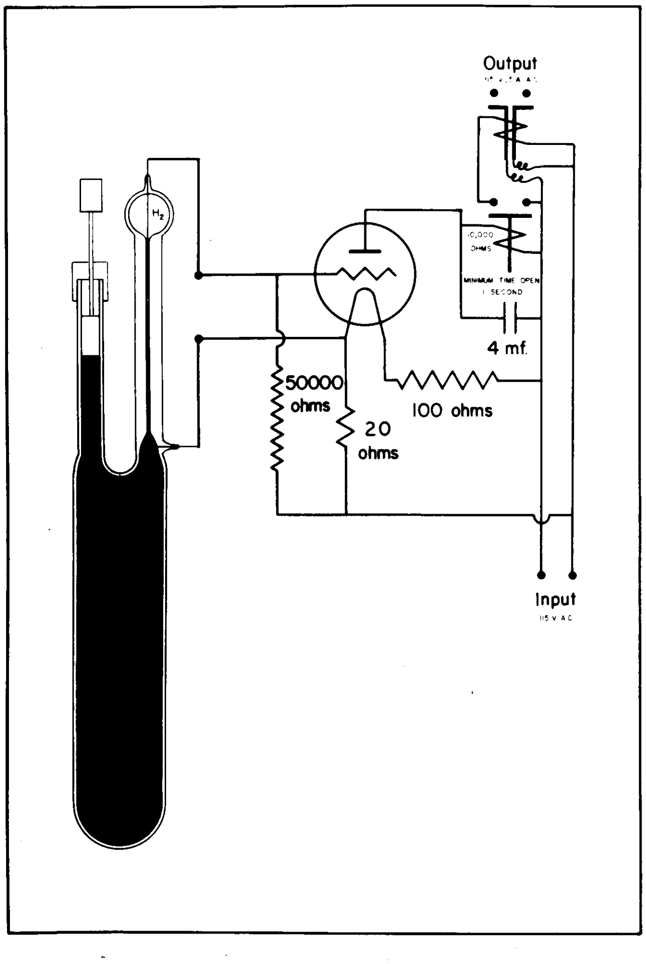

Figure 36.

system was adopted because it permits the influence of vibrations due to stirring to be minimized. The water in a five gallon thermostat tank was maintained to within ± 0.02°C. of a selected temperature by means of the control equipment shown in the figure on the preceding page. This consisted of a large, mercury filled, sensitive element which controlled a 500 watt blade heater through a vacuum tube and two mechanical relays arranged in cascade. (Figure 36) Small changes in the volume of mercury in the bulb of the sensitive element caused variations in the height of the mercury thread in a centrally located capillary tube. This thread made or broke contact with a tungsten electrode in an atmosphere of hydrogen. The regulator operated on only 0.4 milliamperes at 35 volts. A coil of copper tubing was also placed in the large thermostat tank, and cold water was circulated through the coil when it was necessary to work at or below room temperature.

Racks were placed in the large thermostat tank, and each specimen was stored in the tank for several hours before any measurements were made. The pycnometers with which densities were measured were also brought to temperature in this thermostat.

Water was siphoned from the large thermostat, circulated through a small thermostat which surrounded the drop chamber, and then pumped back again into the large tank. The circulation rate was about five gallons per minute.

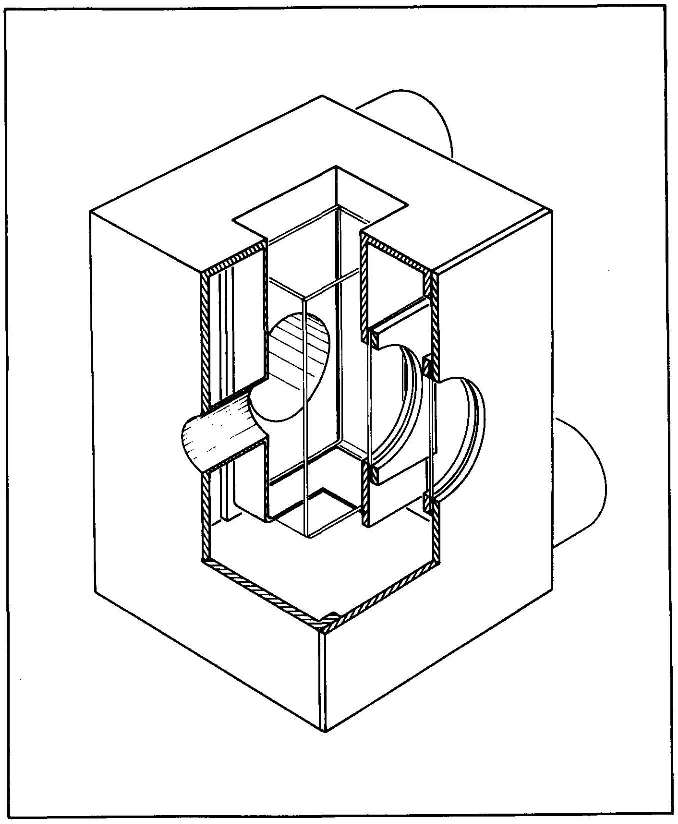

Figure 37.

This small thermostat consisted of a double walled brass tank of special construction. (Figure 37.) It was finished on the outside with chromium plating to reduce heat transfer, contained a rectangular chamber which accommodated the glass cuvette, and was provided with windows for admitting light from the mercury arc, for the objective lens, and viewing the drop. The cover of this tank was provided with dovetail slides which permitted lateral and longitudinal movement of the drop-forming syringes. The light from the mercury arc lamp was passed through a water cell formed by the jacket of the small thermostat tank to remove radiant heat from the beam before it reached the pendant drop.

Cuvettes and Drop-forming Syringes

One of the most important requirements for any apparatus for determining boundary tension is that all the parts of the equipment which come in contact with the fluids shall be readily removable and easily cleaned. The most suitable material of construction for such parts is resistance glass, but Pyrex is nearly as satisfactory, is more readily obtained and blown, and is more resistant to thermal shock. For high temperature work, quartz may be substituted for glass. It is not necessary for the tip to be made from a material which is "wet" by the liquid in the drop.

The cuvettes used were of the type shown in the accompanying photograph.* (Figure 38). They are

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* These are commercially available from the RESEARCH AND DEVELOPMENT CO., 8 West 40th Street, N.Y.C.

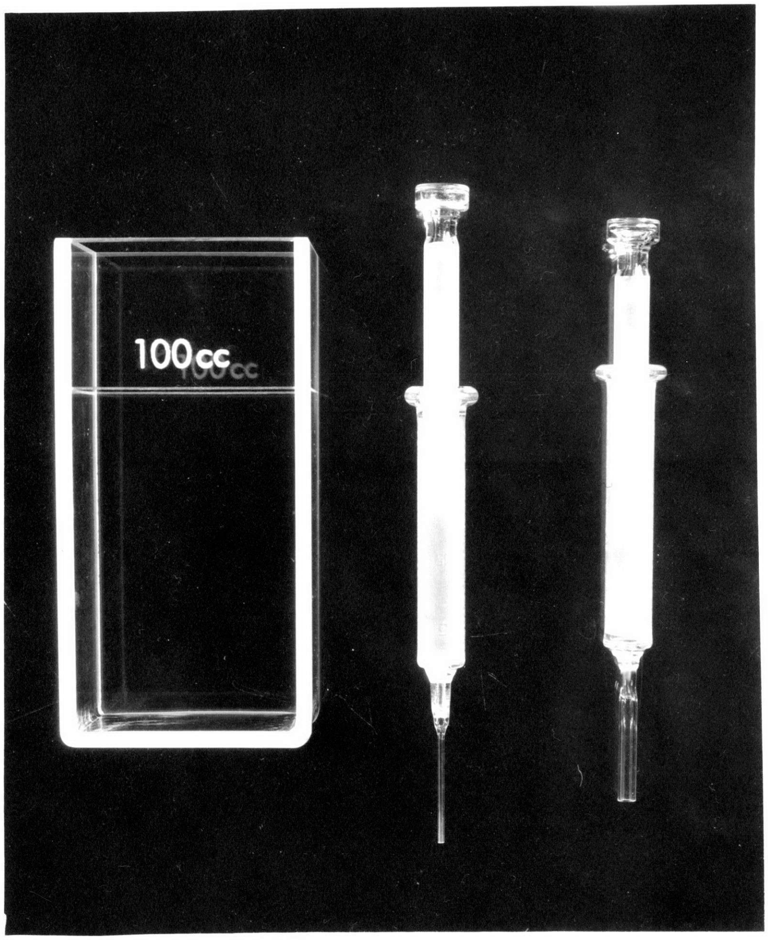

Figure 38

made of two optically flat sheets which are cemented to a U-shaped strip with an acid proof cement. They will withstand repeated cleaning in chromic acid and drying in an oven at 110° C. Their approximate outside dimensions are 1.8 x 2.3 x 4 inches.

The drop-forming syringes were made by welding drawn tubing to standard Pyrex hypodermic syringes of 1.5 cc. capacity. Tip diameters (outside) of 1, 2, and 4 millimeters are easily made in this way. The 2 mm. size is standard for surface tension work. Tips for drops "pendant up" are made in the same way, but a longer length of tubing is required and its end is bent around like the letter J. Very small tips can be made from standard, stainless steel hypodermic needles. The ends of all tips must be carefully ground perpendicular to the axis of the tube.

THE SIZE OF LIQUID DROPS

If the definition of beta is solved for b, we obtain:

$$b = \sqrt{\frac{\beta \gamma}{g \sigma}}$$

In other words, WHEN A COMPARISON IS MADE BETWEEN TWO STATIC FLUID SURFACES OF THE SAME SHAPE BUT OF DIFFERENT BOUNDARY TENSIONS AND OF DIFFERENT EFFECTIVE DENSITIES, THE RATIO OF ANY PAIR OF CORRESPONDING LINEAR DIMENSIONS WILL BE DIRECTLY AS THE SQUARE ROOT OF THE RATIO OF THEIR BOUNDARY TENSIONS AND INVERSELY AS THE SQUARE ROOT OF THE RATIO OF THEIR EFFECTIVE DENSITIES.

$$\frac{l_1}{l_2} = \sqrt{\frac{\gamma_1 \ \sigma_2}{\gamma_2 \ \sigma_1}}$$

This relationship can be made more clear by applying it to the solution of some typical problem.

I Suppose that a pendant drop of water in air has a convenient shape when the glass tip has a diameter of 2.5 millimeters. It is required to calculate the size of a tip from which a drop of mercury of the same shape can be hung.

$$\frac{2.5}{l_{\sim}} = \sqrt{\frac{72.0}{430.}\;\frac{13.6}{1.00}} = 1.51$$

$$l_{\sim} = 1.61 \text{ mm.}$$

Remembering that water drops hang from the OUTSIDE of glass tips and that mercury hangs from the INSIDE, the required tip should be built of tubing having an inside diameter of 1.61 millimeters. *

II Assume that the effective density, σ, equals 0.01 grams per cubic centimeter. Find the maximum surface tension which can be measured with an instrument limited to the use of tips whose outside diameter is less than 6.0 millimeters. Assume that the drops are to have the same shape as those of Problem I.

$$\frac{2.5}{6.0} = \sqrt{\frac{72.0}{\gamma_{\max}}\;\frac{0.01}{1.00}}$$

$$\gamma_{\max} = (\ 0.72\ )\ (\ 5.75\ ) = 4.14\ \frac{\text{dynes}}{\text{cm.}}$$

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* This calculation refers to the normal case of drops hanging from the rim of the tip. Differences in the angle of contact between the interface and the wall are irrelevant. In the case of drops hanging from the vertical wall of a tip, differences in the angle of contact, if present, can not be ignored in computing tip size.

PRECISION

The discussion in this section deals with a possible future instrument rather than with the one at present in use.* It seems more important to discuss the limitations of the best instrument which can be built on the basis of present experience than to restrict consideration to a crude, exploratory apparatus.

Factors which Cause Error in the Shape of the Drop

The attainment of physical and chemical equilibrium is of primary importance. The surface tension of water changes at the rate of about 0.2 % per Centigrade degree. Accordingly, if error from this source is to be less than ± 0.01 %, the temperature of the drop must be held within ± 0.05 Centigrade degree of the desired temperature. Not only must the average temperature of the drop be correct, but also fluctuations in temperature should be reduced to a minimum.

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* The present instrument gives checks to about ± 0.5 %. This is better than the ring method or the maximum bubble pressure method, but it is less precise than the drop weight method or the more elaborate variations of the capillary rise method.

If a steady state is not maintained, there will be an appreciable transfer of material through the interface which is being studied. This will tend to disturb whatever surface structure would normally exist in the boundary layer, and it may produce anamolous changes in the boundary tension. Furthermore, any evaporation from or condensation on the drop will cause a change in the composition of the surface.[*] Such distillation effects will be accompanied by the transfer of latent heat. It is therefore necessary to provide accurate temperature control, to form the drop in a sealed chamber, and to allow ample time for equilibrium to be attained. Fortunately, this is not difficult, and a thermostat can be held to better than ± 0.001 C°. if suitable precautions are taken in its construction.

Imperfections of tip design can cause errors in two ways: The end of the tip may be irregular in shape, and the piston may be so loose that the fluid drains down from the syringe while the drop is being observed. One of the outstanding advantages of the method of pendant drops is the fact that the measurements are made at points on the liquid surface which

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[*] Except in the case of a pure liquid in its own pure vapor.

are remote from the end of the tip. The method is insensitive to minor irregularities in the shape of the end of the tip because all non-uniformities are either bridged by the liquid surface or they are smoothed out very rapidly a short distance below the point of attachment. Thus, quite perfect drops can be formed from relatively imperfect tips. Major faults in tip shape are readily detected and corrected, minor faults produce negligible error.* It will probably be necessary to build special grinding equipment to make the tips for a precision camera, since handmade tips are not interchangeable. When the drops consist of a heavy liquid which does not wet the tip (mercury in glass) there may be trouble due to a tendency of the liquid to drain out of the syringe. This difficulty can be corrected by sealing the piston with a drop of some neutral liquid (mineral oil). Care must be taken to avoid contaminating the tip, but no unusual precautions

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* GANS and HARKINS, J. Am.Chem.Soc., 52, 2287, (1930). It is stated that inclinations of the tip as great as 3° cause negligible error in drop weight measurements. If the selected plane is reasonably remote from the end of the tip, this limit may also be considered applicable to the method of pendant drops.

appear to be necessary. Cleanliness is very important. Boundary tension is a surface phenomenon, and is profoundly affected by slight traces of contaminating substances. However, since the liquid in the drop has a very short time of contact with the drop forming syringe and since the drop is readily discarded and replaced by a new drop freshly formed from clean fluid, there is little probability of contamination of the drop surface by the transfer of surface active material from a reasonably clean tip.* The major effect of tip contamination is to cause non-uniform wetting or local abnormalities in the angle of contact. If this effect is present, it is readily detected and eliminated by washing the tip in the liquid and forming a new drop.

Precision work on boundary tensions should be conducted in the cleanest possible environment. Air conditioning may not be essential, but it is certainly very desirable.

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* Many procedures for cleaning glass are given in the literature, but there is no unanimity about which steps are necessary and which are traditional. The usual procedure involves boiling chromic acid, organic solvents, steaming with conductivity water, and drying with filtered air. Bashforth and Adams used "the pith of the stalk of the artichoke"? (B. & A., p. 73-74)

Vibration is objectionable in any apparatus used for the measurement of boundary tensions. It is particularly important in those methods which require the formation of pendant drops, irrespective of whether these drops are static or detached during the measurements. Vibration is also a source of error in the ring method, in jet formation, in the bubble pressure method, and in the capillary rise method. Drops have resonant frequencies which cannot be changed, it is therefore essential to eliminate those sources of vibration which have objectionable frequencies. Mechanical vibration can be reduced by building an instrument with a large inertia, free from moving parts, and mounted on shock absorbing pads. Sonic vibrations must be eliminated at their source or by insulating the room.

Physical Limitations of a "Perfect" Instrument

Assuming that measurements are to be made of the surface tension of drops of water having the usual shape ($S = 0.85$) and that the camera has an optical magnification of ten diameters, the permissible error in linear measurements is $\pm$ 0.002 % if the resulting error in the surface tension is to be less than 0.01 %. This means that the traveling microscope with which the photographs of the drops are determined must be capable of measuring distances to the nearest micron, an accuracy which is just within the reach of high precision equipment.

This tolerance amounts to ± 0.1 micron, or 1000 Ångstrom units, on the drop itself. The wave length of the shortest useable light for a glass optical system is about 4000 Å. It is commonly said that the resolving power of a perfect lens system is about one half of the wave length of the light used. This statement requires expansion if misunderstanding is to be avoided.

Resolving power is defined as the minimum distance between two points of the object for which the lens will form separate diffraction patterns. If, as in the present case, diffraction patterns are not in themselves objectionable, the limit of the accuracy of linear measurements is not set by the resolving power. In fact, it is found desirable to use monochromatic light in order to obtain a more distinct diffraction pattern. The image of a drop is then a clear area on the negative and is bordered by a succession of thin white lines on a black background. The first bright line of the diffraction pattern makes a very satisfactory outline to which measurements can be made. By a suitable application of this technique, it would be possible to make linear measurements with the required precision.

Standard photographic emulsions are capable of resolving a pattern of as many as 500 lines per centimeter. That is, the resolving power is limited by the grain of the emulsion to about 20 microns. However, as with optical resolving power, this difficulty is not of critical importance. If it is found that standard emulsions are too coarse, it is easy to greatly improve the photographic resolution by the use of fine grain emulsions and developers.

Physical limitations are seen to place some restrictions on the ultimate precision of the method of pendant drops, but the attainable precision is equal or superior to that obtained with competitive methods.

Limitations Imposed by Precision of Construction

Certain sources of error are traceable to precision of construction. In general, such inaccuracies can be reduced or eliminated by improvements in design or by more careful workmanship.

The problem of grinding a set of glass tips has already been mentioned. It will be necessary to build special jigs and polishing equipment, but no unusual or insurmountable difficulties are to be expected.

Modern high grade microscope lenses are very fully corrected to give an undistorted plane image. It seems probable that proper choice of standard optical equipment will make it possible to reduce errors due to image distortion below the limits set by the precision of the other parts of the apparatus.

It will be necessary to make linear measurements on glass plates with a traveling microscope capable of determining distances to the nearest micron. A similar problem has been met and solved in connection with spectroscopic work.

One of the most difficult problems is that of determining the optical magnification of the camera. Since the optical magnification enters the formula for the boundary tension to the second power, it must be measured with an accuracy twice as great as that required of the other measurements. It seems probable that the best method is to photograph a small cylinder whose diameter has been measured with an interferometer and to measure its image with the traveling microscope.

The precision of the boundary tension measurements is directly influenced by the precision to which the quantity, H, is known as a function of S. This precision is limited only by the labor and patience of the computer.

MEASUREMENTS OF INTERFACIAL TENSION

Determinations of interfacial tension by the method of pendant drops are subject to a number of special problems which are not encountered when surface tension is measured.

The Appearance of Interfacial Drops

Depending upon whether the tip is more readily wet by the internal or the external phase, the drop will hang from the outside or the inside rim of the drop-forming tip. If the index of refraction of the tip is nearly the same as that of the external phase, the tip becomes quite transparent and the position of an opaque fluid inside the tip can be clearly seen. An example of this is furnished by a mercury drop hanging from a glass tip in mineral oil. On the other hand, if the optical densities of the two fluids are similar, the drop becomes invisible with the exception of a thin, sharp outline. This condition is shown by a picture of a drop of water hanging from a stainless steel tip in ethyl ether. (Figure 51.)

VARIATIONS IN THE APPEARANCE OF PENDANT DROPS

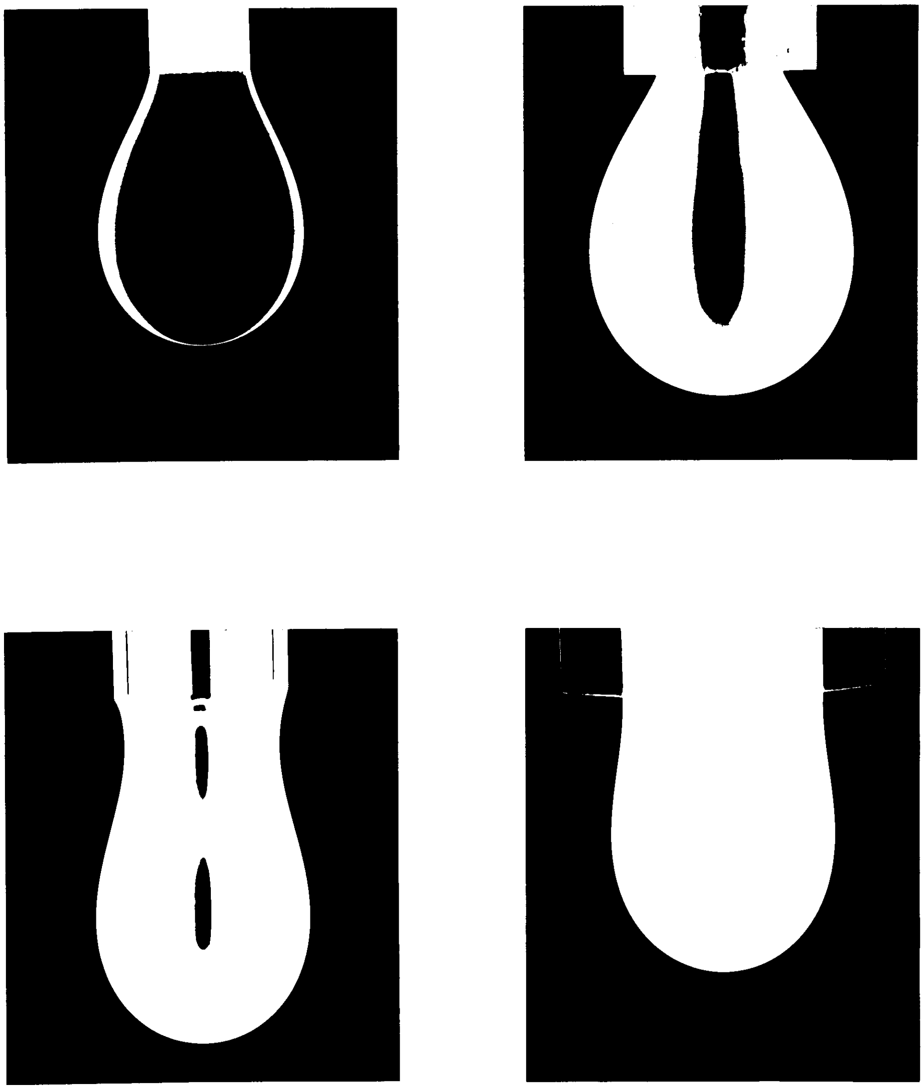

Figure 51

Pendant "Up" versus Pendant "Down"

Since the drop-forming tips are easier to build, are more rugged, and are more convenient to use when they are designed to support the drop from above, pendant drops are normally formed with the denser fluid hanging from the tip. There are three situations in which this is impossible and the drops must be formed with the lighter fluid hanging pendant up. If the lighter fluid is opaque but the denser fluid is not, the drops can be observed only when the opaque, lighter liquid is hanging pendant up in the transparent, heavier liquid. If one fluid is much more scarce or expensive than the other, it may be necessary to form the drops from the rare chemical since less than one cubic centimeter is required to form a number of drops but fifty or one hundred are needed for the continuous phase. In measuring the surface tension of a liquid mixture of which one component is much more volatile than the other, it may be preferable to use bubbles of vapor pendant up rather than drops of liquid pendant down since there is then less chance for the concentration of the volatile material in the liquid to be depleted by evaporation into the vapor space.

Invisible Drops

If the optical properties of the two fluids are identical, the pendant drop cannot be seen, and any method which requires an observation of the shape and size of the interface is inapplicable.* This is an extremely rare experimental problem which is almost unknown in practice. It is approximately found when studying certain mixtures of water, glycerol, and carbon tetrachloride; but even then, it never happens that the indices of refraction of the two phases are identical for all colors of light at the same time. If such an invisible interface must be measured, it will usually be possible to choose a convenient color of monochromatic light with which a photograph can be made. It is probably unwise to attempt to make one of the fluids visible by the addition of a trace of a selectively soluble dye since the influence of this dye on the interfacial tension will in general be unpredictable.

If both fluids are opaque or turbid, the method of pendant drops cannot be used.

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* CLAYTON, "Theory of Emulsions," 3rd ed., p. 121, transparent emulsions, Blakiston, (1935).

Weightless Drops

If the specific gravities of the two fluids are very nearly the same, the effective density (σ) cannot be determined with satisfactory precision and a corresponding uncertainty is introduced into the computed interfacial tension. In practice, this difficulty arises in two different situations: (1) As a critical point is approached, both the interfacial tension and the effective density approach zero since the two phases become indistinguishable. All that is possible is to measure the interfacial tension at a series of points approaching the critical and then to plot the results, extrapolating to a zero value at the critical point. (2) Certain pairs of incompletely miscible fluids have identical specific gravities but a large interfacial tension.*

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* This case seems to have been first studied by J. A. F. Plateau, "Statique Experimental et Theoretique des Liquides," (1873), but his interest was in the shape of the interface between weightless fluids and not in the magnitude of the interfacial tension. Equal density emulsions are discussed by Clayton, "Theory of Emulsions," p. 120-121, Blakiston, (1935).

A two component example of this is the system, water - orthotoluidine, at a temperature of 24° C. For such a system, the effective weight of a drop is zero, the liquid interface is truly spherical, and the capillary rise is infinite. The interfacial tension is best obtained by making a series of measurements at different temperatures, bridging the point where the densities are equal, and then determining the missing value by interpolation. If there are more than two components, it is possible to use a stepwise variation of the gross composition and to make all the measurements at the same temperature.* Satisfactory measurements can be made close to a point of equal density provided that the densities can be measured with high precision and if the size of the drop does not exceed the capacity of the camera.

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* The two-phase, three-component system, water-methanol-xylene, exhibits this case to a surprising degree. "Weightless," spherical drops having a diameter of as much as 3 inches are easily obtained.

Meaning of the "Age" of Drops

During the first few minutes after a drop is formed from a surface active solution, the value of its boundary tension changes continuously, and any measurement is meaningless unless the length of time which has elapsed between the formation of the surface and the measurement of its boundary tension is specified.

It is admittedly difficult to give a precise meaning to the term "age of surface" since a liquid surface is never formed "de novo" but is always produced by stretching a small, pre-existing surface. In the case of pendant drops, all that can be done is to form an discard a number of drops in quick succession until substantially all of the residual fluid on the end of the tip is "new." Another drop is now formed rapidly and its age is measured with a stop watch which was started at the instant when the drop first hung motionless. Such a procedure is arbitrary and subject to the influence of human factors, but it has been found workable and satisfactory in the case of surfaces which do not age too rapidly. The study of very rapidly ageing surfaces will necessitate the construction of some sort of automatic timing device which will accurately make pictures at predetermined time intervals after the drop is formed.

The rate at which a surface ages is controlled by the speed of diffusional processes. Accordingly, it may be expected that small drops will age more rapidly than large ones, since the distance from the most remote part of the fluid to the surface is greater in one case than in the other. Complicating effects of this sort may be impossible to eliminate. They cannot be ignored, but they do not invalidate the usefulness of comparative measurements as long as the nature of the measuring process is not forgotten when the interpretation of the results is sought.

Tremendous differences are observed in the behavior of liquid drops. Some pure substances exhibit their ultimate interfacial tension at the earliest instant at which a measurement can be made. On the other hand, the interfacial tension of certain solutions will slowly decrease during a period of minutes from a large initial value to a final, equilibrium value which is less than half as great.

Measurements of Typical Interfacial Tensions

As a check on the method of pendant drops, the interfacial tensions in six typical "water - organic liquid" systems were measured at 25° C.

The samples were prepared from C. P. grade chemicals and "conductivity" grade distilled water. They were thoroughly agitated in glass stoppered bottles and allowed to come to equilibrium in a thermostat kept at 25° C.

In general, six measurements were made of each interface. Each measurement represents a photograph of a different interfacial drop.

As a further check on the method, three sets of interfacial tension measurements were made on drops "pendant up." These are compared with measurements which were made on another day on drops of the same liquids "pendant down."

	INTERFACIAL TENSION AT 25° C.	
	Pendant Up	Pendant Down
Benzene - Water	30.1	30.1
CCl_4 - Water	43.9	43.8
Diethyl Ether - Water	11.0	11.2

The agreement is excellent and supports the belief that changes in the boundary tension with the curvature of the interface are negligible unless the curvature is very great. (colloidal droplets)

TABLE TWELVE

BOUNDARY TENSIONS FOR THREE-PHASE SYSTEMS

Surface 10 seconds old in saturated air at 25° C.

							AVERAGE
BENZENE - WATER - AIR							
W in B	30.1	29.9	29.9	29.7	30.6	30.6	30.1
B in W	29.7	28.8	30.4	30.6	30.5	29.5	30.1
B in A	28.8	28.7	28.5	28.9	28.6	----	28.7
W in A	67.4	67.9	66.9	67.2	66.6	----	67.2
CARBON TETRACHLORIDE - WATER - AIR							
W in C	43.4	43.7	43.0	44.0	44.5	44.7	43.9
C in W	43.8	44.0	44.1	43.9	43.3	43.8	43.8
C in A	26.9	27.0	26.9	26.8	27.0	26.8	26.0
W in A	70.6	70.6	70.1	70.1	70.1	72.0	70.7
CHLOROFORM - WATER - AIR							
C in W	31.7	31.8	32.4	31.7	30.9	31.5	31.7
C in A	26.7	26.7	27.0	27.0	26.9	27.0	26.8
W in A	65.8	65.6	66.7	66.7	66.8	66.5	66.5
DIETHYL ETHER - WATER - AIR							
W in E	11.3	11.3	11.3	11.1	11.2	----	11.2
E in W	11.4	10.7	11.1	10.7	10.9	10.9	11.0
E in A	17.1	17.3	17.1	17.3	17.2	17.2	17.2
W in A	32.8	32.9	33.2	32.6	33.0	33.1	32.9

MINERAL OIL* - WATER - AIR

W in O	44.1	45.5	45.3	45.3	45.7	----	45.2
O in A	30.0	30.3	30.0	30.8	30.3	29.6	30.2
W in A	72.5	72.6	72.1	71.8	73.2	72.3	72.9

TOLUENE - WATER - AIR

W in T	32.8	33.2	33.0	32.5	32.9	33.1	32.9
T in A	27.5	27.6	26.8	27.3	27.0	27.4	27.4
W in A	65.6	66.5	66.5	67.4	67.2	65.7	66.5

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* This system was prepared from "CENCO White Paraffin Oil" and distilled water.

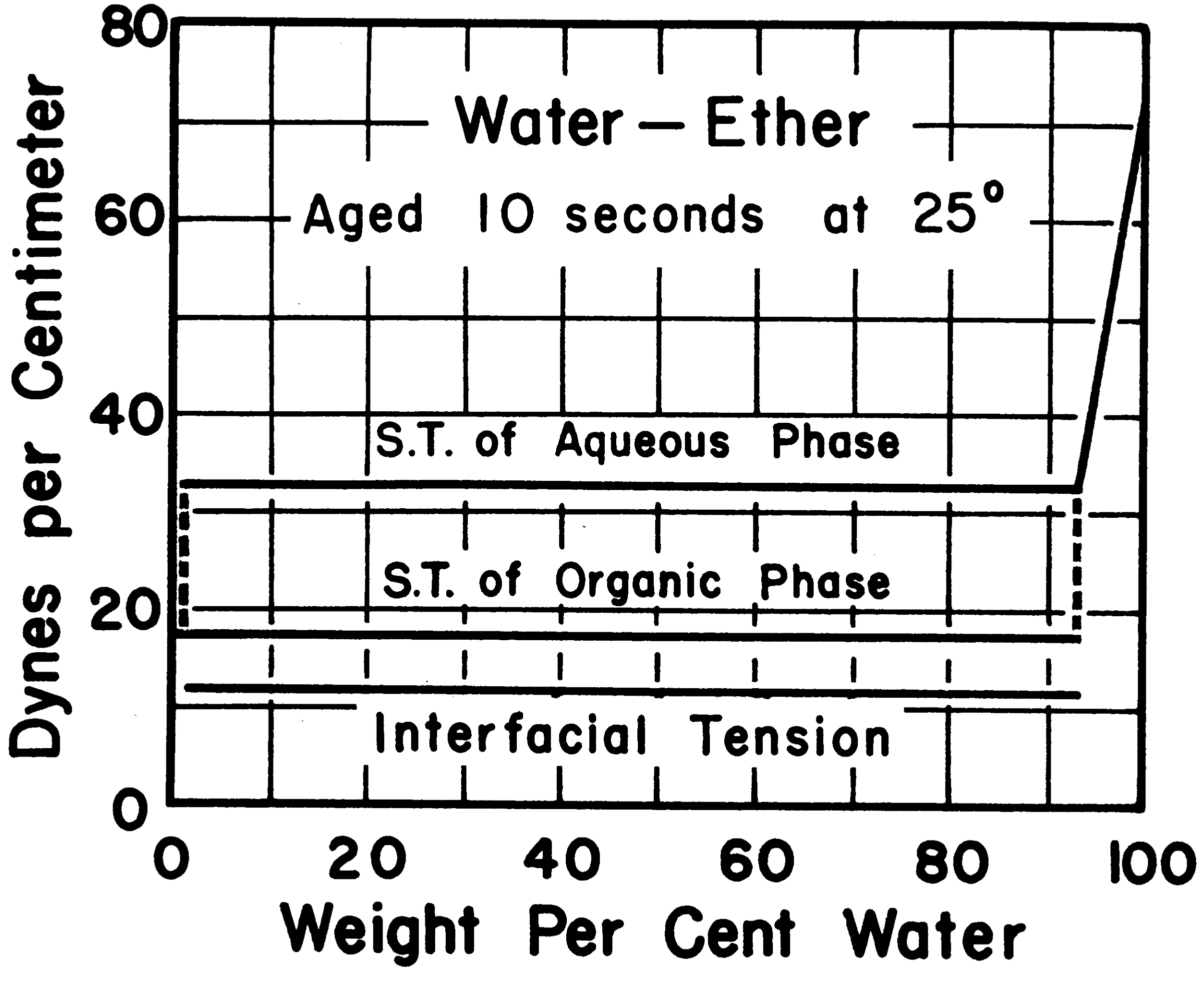
Water — Ether
Aged 10 seconds at 25°
S.T. of Aqueous Phase
S.T. of Organic Phase
Interfacial Tension
Dynes per Centimeter
0
20
40
60
80
0
20
40
60
80
100
Weight Per Cent Water

Figure 52

For comparison, the results of some measurements which are reported in the literature are summarized below:

TABLE THIRTEEN

	°C.	Interfacial Tension
BENZENE - WATER		
Speakman (1933)	23	34.1
Mack & Bartell (1932)	25.13	34.71
I. C. T. (1928)	25.00	34.71 ± 0.05
Reynolds (1921)	19	34.4
CCl_4 - WATER		
Lange (1937)	20	45
Mack & Bartell (1932)	25.07	43.44
I. C. T. (1928)	25.00	44.51 ± 1.0
Reynolds (1921)	17	43.8
$CHCl_3$ - WATER		
Speakman (1933)	20	32.8
I. C. T. (1928)	20	32.80 ± 0.2
Reynolds (1921)	18	33.4
DIETHYL ETHER - WATER		
Speakman (1933)	20	10.7
I. C. T. (1928)	20	10.70 ± 0.2
Reynolds (1921)	18	10.6
TOLUENE - WATER		
Mack & Bartell (1932)	30.12	35.90
I. C. T. (1928)	25	36.1

The scattering of the literature values and their relatively poor agreement with the pendant drop results can be traced to one or more of the following causes which are responsible for the unreliability of the results published in the literature:

(1) Interfacial tension varies more rapidly with temperature than does surface tension. Accurate temperature control is absolutely essential.

(2) The effective density, σ , is more difficult to measure with precision in interfacial work than in surface tension work, since it is the difference between two densities which may be nearly equal.

(3) Interfacial tension is more influenced by the presence of impurities. A one hundred fold decrease is possible with the former, and a five fold decrease is unusual in the latter instance.

(4) The capillary rise methods become very unreliable as soon as the angle of contact differs from 0°. This is a common case in interfacial tension work.

(5) The drop volume method assumes a zero angle of contact and no effects due to high liquid viscosities.

(6) The results given in the literature do not report the age of the surface at the time the interfacial tensions were measured.

Boundary Tension between Mercury and Various Fluids

A second series of measurements were made of the interface between C. P. redistilled mercury and thirteen different pure liquids. As before, each measurement was made from a photograph of a new drop which had been aged for 10 seconds at 25° C.

The surface tension of this same sample of mercury is also given for the sake of comparison.

TABLE FOURTEEN

INTERFACIAL TENSION DATA FOR MERCURY IN CONTACT WITH VARIOUS OTHER FLUIDS

	25° C.			10 Seconds			Average
Air	436	438	436	435	436	435	436
Acetone	379	382	383	382	385	383	382
Benzene	367	357	365	362	361	---	362
n-Butanol	379	383	383	381	387	381	382
CCl_4	359	356	358	361	357	357	358
Ethanol	392	392	392	391	394	389	392
Ethyl Ether	376	379	381	380	377	375	378
Glycerol	368	362	366	367	363	352	363
Glycol	378	377	377	382	377	376	378
Methanol	386	383	384	384	386	385	385
Mineral Oil	362	362	364	363	366	357	362
i-Pentanol	373	376	376	372	---	---	374
Toluene	352	353	359	358	359	---	356
Water	370	369	368	368	370	369	369

For comparison, the results of measurements which are reported in the literature are summarized below:

SURFACE TENSION

Mercury in Air The surface ages rapidly because of the formation of an oxide film. The results scatter widely because of variations in the purity of the metal, the age of the surface, and the method of measurement. The I. C. T., (1928), give 487 at 15° C. Lemarchands and Convers, (1935), give 494 at 10 seconds and 17° C. and 445 at 28 minutes and 17° C.

TABLE FIFTEEN

INTERFACIAL TENSION

Fluids	Authority	° C.	I.T.
BENZENE - MERCURY	I. C. T. (1928)	25	355.4
	Mack & Bartell (1932)	25.13	355.5
ETHANOL - MERCURY	I. C. T. (1928)	20	364
ETHYL ETHER-MERCURY	I. C. T. (1928)	20	379
TOLUENE - MERCURY	I. C. T. (1928)	20	359
WATER - MERCURY	I. C. T. (1928)	20	375
	Mack & Bartell (1932)	25.08	374.2

BOUNDARY TENSIONS IN THE FOUR-PHASE SYSTEM
AIR - XYLENE - METHANOL - SATURATED AQUEOUS K_2CO_3

In a system containing four fluid phases, there are six boundary tensions, and each of them is subject to measurement by the method of pendant drops.

As a typical example of a system of this type, methanol, xylene, and a saturated solution of potassium carbonate were mixed together and allowed to come to equilibrium at 25° C. Excess solid salt was removed by filtration. The chemicals were of the C.P. grade with the exception of the xylene. This was of CENCO'S "technical" grade and presumably consisted of a mixture of ortho, meta, and para xylene.

TABLE SIXTEEN

							AVERAGE
SURFACE TENSIONS, dynes per centimeter at 10 seconds:							
"Methanol" - "Air"	28.7	30.3	28.5	29.7	28.5	28.4	29.0
"Xylene" -"Air"	26.0	25.9	25.7	25.6	25.5	25.9	25.8
"Water" - "Air"	33.9	33.7	33.5	33.8	33.3	---	33.6
INTERFACIAL TENSIONS, dynes per centimeter at 30 seconds:							
"Methanol" - "Xylene"	2.8	2.4	2.4	3.0	2.9	2.9	2.7
" Xylene" - "Water"	8.0	7.9	8.1	7.9	8.0	8.0	8.0
"Water" - "Methanol"	2.8	2.8	2.8	2.8	2.8	2.8	2.8

INTERFACIAL TENSION FOR THE TWO-PHASE SYSTEM WATER, ACETIC ACID, METHYL ISOBUTYL KETONE

Six samples were prepared from commercial chemicals.* The gross compositions are given in weight per cent.

Sample	Water	Acid	Ketone
1	29.70	0.00	70.3
2	29.49	0.61	69.9
3	29.29	1.21	69.5
4	29.00	2.40	68.6
5	28.33	4.67	67.0
6	27.13	8.87	64.0

The interfacial tensions of drops aged 10 seconds at 25° C. are given in dynes per centimeter.

TABLE SEVENTEEN

Sample	Interfacial Tension						Average
1	8.9	8.7	8.9	8.8	8.8	8.7	8.8
2	8.6	8.7	8.7	8.8	8.5		8.7
3	8.5	8.4	8.3	8.3	8.3	8.4	8.4
4	7.8	7.8	8.0	7.9	7.8	7.8	7.9
5	6.5	6.7	6.6	6.6	6.0	6.7	6.5
6	5.3	5.3	5.1	5.2	5.2	5.3	5.2

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* These samples were of the same quality studied in the thesis of J. E. Evans, "A Study of Capacity Coefficients in Countercurrent Packed Extraction Columns," M.I.T.,(1938).

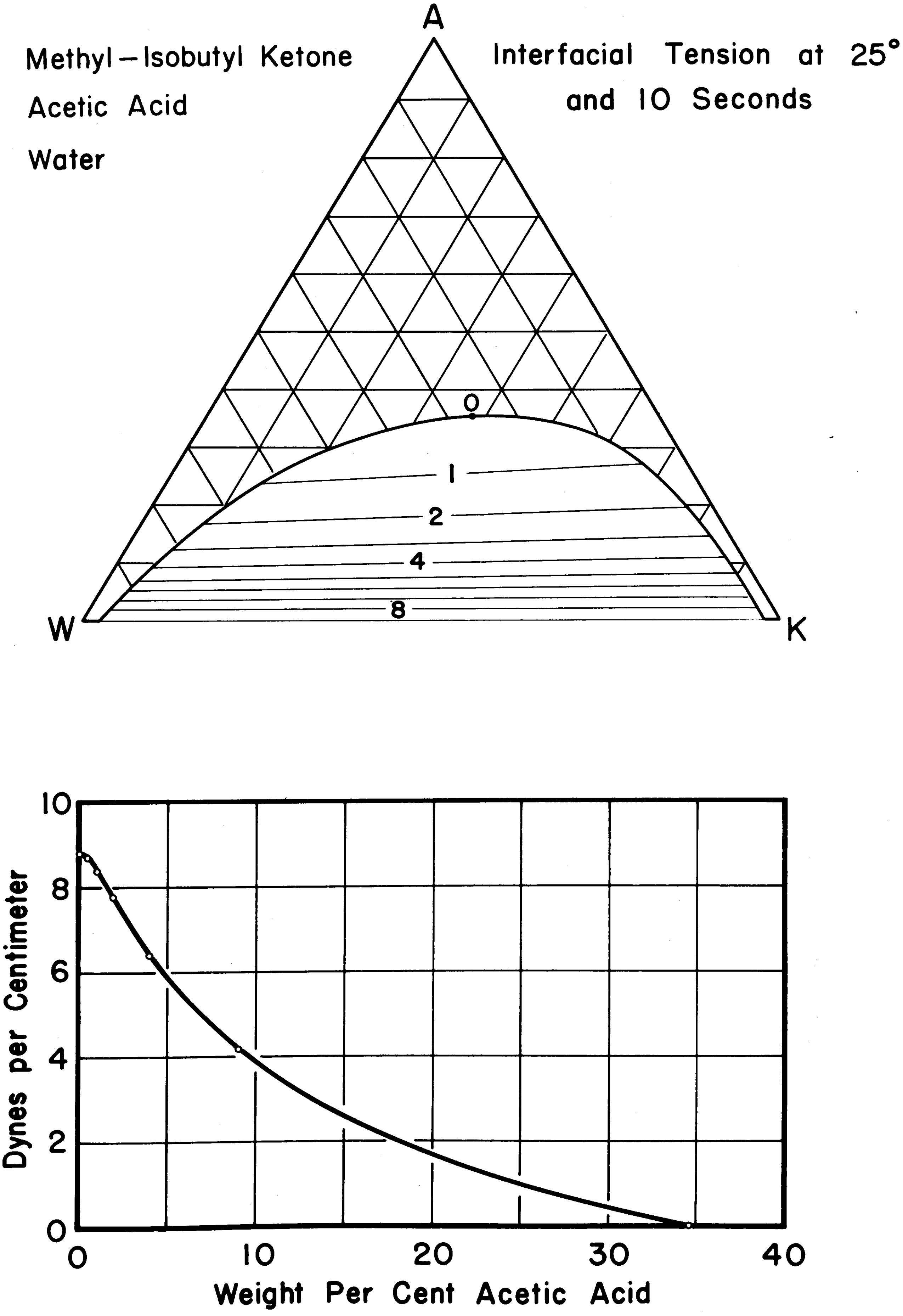
Methyl-Isobutyl Ketone
Acetic Acid
Water
Interfacial Tension at 25°
and 10 Seconds
A
W
K
0
1
2
4
8
Dyes per Centimeter
10
8
6
4
2
0
0
10
20
30
40
Weight Per Cent Acetic Acid

Figure 53

Application to Emulsions

One method by which technical emulsions are stabilized is the addition of a small amount of a material which greatly reduces the interfacial tension. Such an agent is very strongly adsorbed at the surfaces of the liquid droplets and prevents the emulsion from breaking. It is often necessary to compare the emulsifying power of several different agents and to determine the optimum concentration for producing the most stable result. In discovering this optimum, a knowledge of the interfacial tension resulting from the addition of each material is essential.

The measurement of interfacial tensions in liquid systems containing emulsifying agents is extremely difficult because of the great ease with which emulsions and scums are formed. These scums clog the apparatus, obscure the visability, and totally incapacitate nearly all the standard methods of measurement. Fortunately, the method of pendant drops will still operate. The scum can be wiped off the tip and a new, clean drop can be formed and photographed. Measurements can now be made in the usual way and reliable results can be obtained.

As an example of a system of this type, data are presented for mixtures of amyl chlorides and water.

THE EFFECT OF STABILIZING AGENTS ON INTERFACIAL TENSION

Four samples were prepared from water and a technical grade of mixed amyl chlorides. Two stabilizing agents were used which are called the "amide" and the "ester." Compositions are given in weight per cent.

Sample	Chlorides	Water	"Amide"	"Ester"
1	24 %	76 %	0 %	0 %
2	22	75	3	0
3	22	75	0	3
4	22	75	1.5	1.5

Ageing curves were obtained at 25° C. The age of the drops is given in seconds and the interfacial tensions are expressed in dynes per centimeter.

SAMPLE ONE

Age	10	20	30	45	60	120
I. T.	24.6	23.6	23.4	22.4	22.3	22.2

SAMPLE TWO

Age	10	20	30	45	60	120
I. T.	0.70	0.69	0.69	0.66	0.65	0.64

Age	10	10	20	30	45	60
I. T.	0.66	0.65	0.67	0.61	0.60	0.60

SAMPLE THREE

Age	10	15	20	20	25	30
I. T.	6.3	5.4	4.7	5.2	4.8	4.4

Age	40	10	15	20	25	30
I. T.	4.1	6.2	5.7	5.4	5.1	4.9

SAMPLE FOUR

This sample aged with such extreme rapidity and had such a low ultimate interfacial tension that no ageing curve could be obtained. The drops were aged for 3 ± 0.2 seconds. The scattering is due to the rapid ageing combined with small errors in timing the exposures. Six drops were measured giving: 0.50, 0.39, 0.42, 0.51, 0.39, and 0.43; average 0.44.

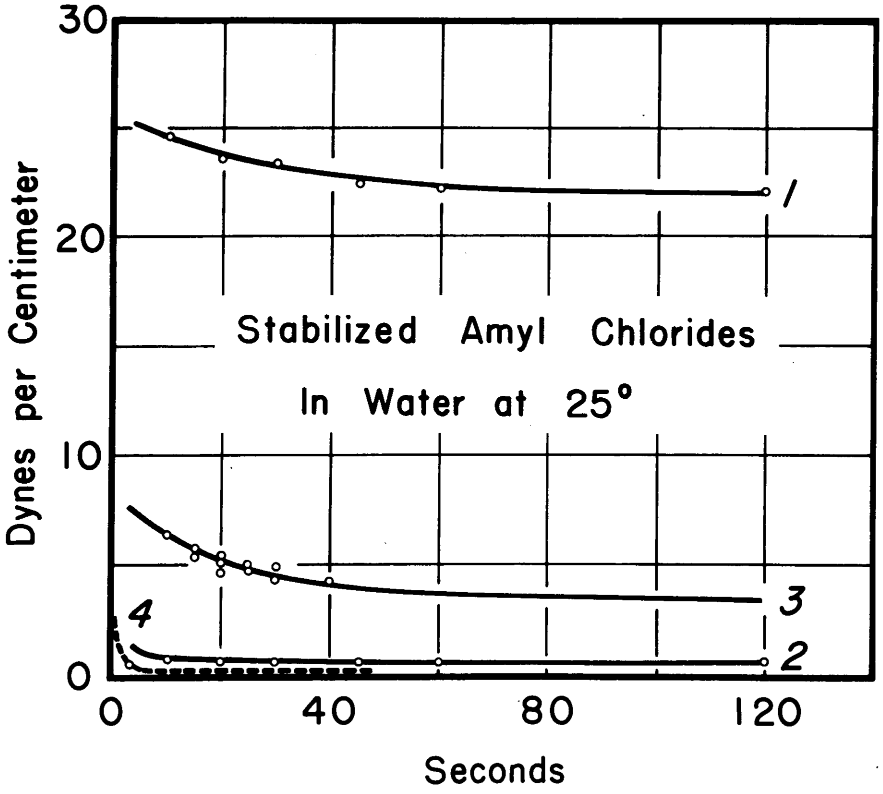

Figure 54.

Sample One was a typical "oil-water" system which did not form a stable emulsion when shaken by hand.

Sample Two shows that 3 % of the "amide" reduced the interfacial tension thirty-five fold.

Sample Three shows that 3 % of the "ester" reduced the interfacial tension to one fifth of its original value.

Sample Four shows that a mixture of these two emulsifying agents is superior to either one taken separately, 1.5 % of each reducing the interfacial tension to 2 % of that between the "pure" liquids.

Samples Two, Three, and Four all showed a pronounced tendency to form extremely stable emulsions. The slightest agitation of the samples tended to produce a persistent, creamy emulsion.

On the basis of these results, it seems probable that Sample Four will produce a more stable emulsion than either One, Two, or Three.

Soap Solutions and Mineral Oil

The interfacial tensions between solutions of sodium oleate in water and purified mineral oil* behave in a manner quite similar to the surface tensions of these same solutions in air.**

The surface shows pronounced "ageing" effects resulting from changes in surface energy which accompany the formation of the equilibrium surface structure.

Data and curves are presented which describe the behavior of nine samples of different concentrations. (Figure 55.)

The minimum in the 0.00025 % curve at 15 seconds is similar to a number of discontinuities of the same sort which were observed in the surface tension curves for sodium oleate solutions.** It is unfortunate that it was impossible to make enough measurements in this region to reveal the cause of this curious effect which appears to be occasionally associated with the formation of surface structure.

The fact that certain of the curves (0.0025 and 0.025) continue to fall as time increases while the

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* CENCO "Pure White Paraffin Oil."

** TUCKER, W. B., "Surface Tension by Pendant Drops," (1938).

AQUEOUS SOLUTIONS OF SODIUM OLEATE IN MINERAL OIL
25°C AGEING CURVES

Nine samples were prepared from Merk's Neutral Sodium Oleate and conductivity grade distilled water. The compositions are given in weight per cent, and the interfacial tensions in dynes per centimeter. The age of the surface, in seconds, is given by the column heading. The mineral oil was Cenco C. P. grade.

TABLE EIGHTEEN

AGE	5	10	15	20	30	45	60	120	240	480	960	1800	3600
0.00025%	46.7	46.5	46.1		46.8		46.4	45.2	49.0	46.5	46.3	44.6	46.4
		46.6	45.5		45.4		45.3	44.4	44.1	44.9	44.9	45.0	46.4
0.0025%	41.7		40.8		39.6		40.6	40.4	40.3	40.3	40.6	40.0	40.4
	42.5	42.0	41.0		40.2		41.9	41.3	41.3	41.3	41.6	40.8	40.4
0.025%	35.2	35.1	35.4		34.8		34.8	34.3	34.0	32.4	32.4		31.2
	34.9	35.5	34.3		34.7		34.3	33.9	33.3	32.3	31.6	31.6	30.9
0.25%	3.33	3.19	2.98	2.98	2.85								
	3.37	3.11	2.99	2.93	2.79	2.64	2.59						
					2.96	2.81	2.62	2.28	2.04	1.94	2.20	2.57	2.81
					2.95	2.79	2.65	2.47	2.46	2.22	2.49	2.60	2.99
0.50%	4.28	3.83	3.53										
	3.71	3.55	3.33	3.04	2.49	2.22	2.05						
			3.25	2.84	2.49		2.16						
					2.57	2.34	2.27	1.86	1.89	1.77	2.02	2.59	3.25
					3.12	3.03	2.93	2.64	2.27	2.15	2.29	2.58	3.15
1.00%	3.20	3.02	2.87	2.78	2.78	2.38	2.10	1.02	1.44				
	3.79	3.24	2.90	2.70	2.33	2.10	1.94						
					2.35	2.04	1.89	1.49					
					2.40	2.04	1.87	1.50	1.21				
2.00%	2.13	1.76	1.49	1.31									
	2.20	1.75	1.47	1.31									
				1.50	0.98	1.00	0.94	0.78					
				1.47	1.24	1.02	0.95	0.80					
								0.85	0.52				
4.00%	0.91	0.88	0.87	0.86	0.83	0.85	0.82	0.85	0.92	0.92	1.06		
		0.86	0.83	0.81	0.78								
					0.85	0.84	0.82	0.82	0.95	1.03	1.12		
8.00%	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.50	0.54	0.62			
	0.41	0.42	0.42	0.42	0.44	0.45	0.46	0.48	0.54	0.64			

others pass through a minimum and then slowly rise, points to the existence of more than one kind of stable surface structure. The kind of structure which will be formed depends upon the composition of the solution with which it is in equilibrium. Further work can be expected to reveal interesting results in this field.

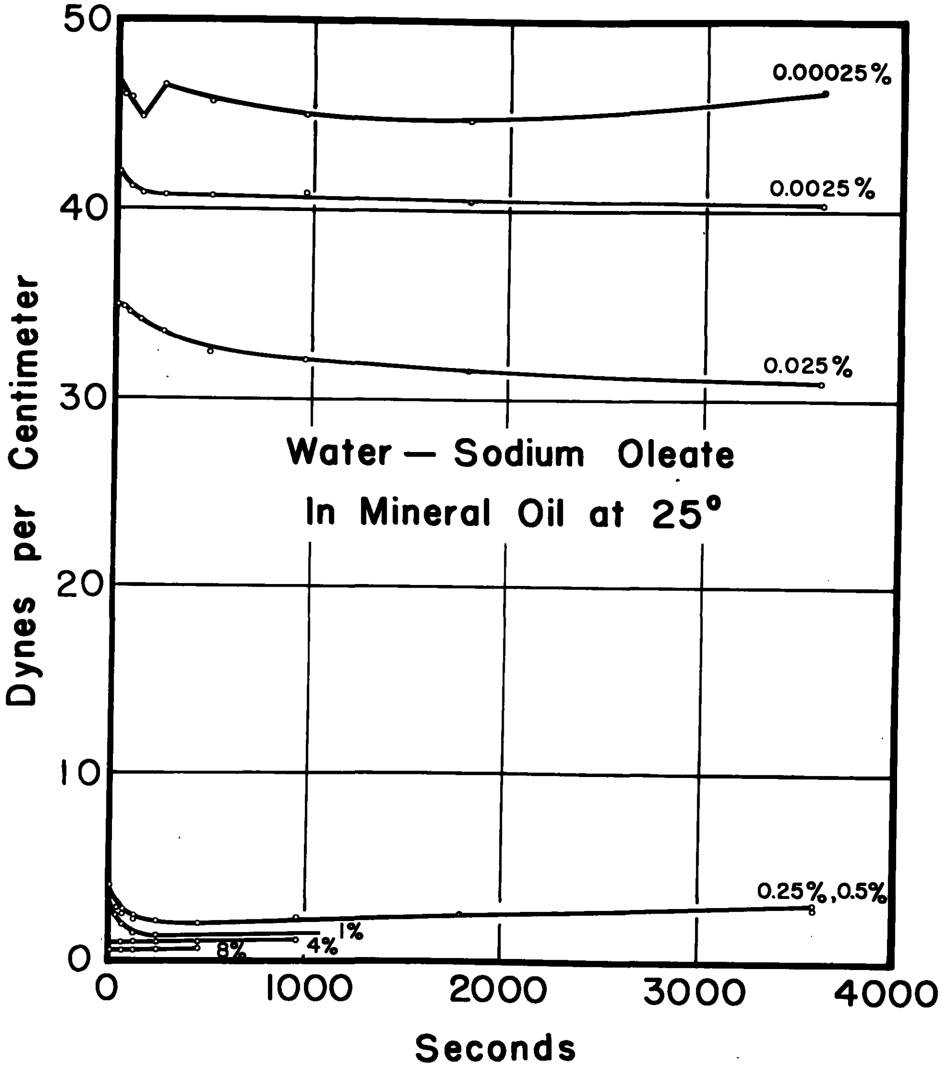

Figure 55.

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His undergraduate years were spent at Princeton as a member of the Class of 1935 where he graduated, with honors, and the degree of Bachelor of Science in Chemical Engineering. He was a member of the staff of The Daily Princetonian, of The Arbor Inn Club, and of the Phi Beta Kappa Society.

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