of sodium, the compound NaHg which is formed appears to be identical with that formed in the reduction of ordinary salts of mercury under corresponding conditions.

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THE DETERMINATION OF SURFACE TENSION FROM THE RISE IN CAPILLARY TUBES

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Richards, Speyers and Carver[1] in a recent paper describing a method of measuring surface tension by observations of capillary rise in two connected tubes refer to the equations of Rayleigh[2] for very narrow and very wide tubes and then state that "the problem presented by the intervening region has not as yet been solved mathematically." It is the object of this short paper to point out that a solution of this problem for all sizes of tube commonly used was given by the author three years ago.[3] Richards, Speyers and Carver refer to this paper as giving "a somewhat similar empirical method;" since however, it contains the corrections referred to below derived from a mathematical discussion of the equation to the meniscus and gives new absolute determinations of the surface tension of benzene and water at 20° it seems necessary to reaffirm the soundness of the theoretical methods employed by the author.

The chief feature of the 1921 paper is a new method of correcting the simple equation

$$\frac{2\gamma}{g(D-d)} = a^2 = rh \tag{1}$$

which is strictly true only for infinitely small tubes. Here γ is the surface tension, g the gravitational constant, D the density of the liquid, d the density of air + vapor, r the radius of the capillary tube and h the capillary rise measured from a plane surface of the liquid. Of the numerous formulas which have been devised to correct this equation for larger values of r, the most precise is that of Rayleigh[2] which may be put in the form

$$a^2 = rh\left(1 + \frac{1}{3}r/h - 0.1288\frac{r^2}{h^2} + 0.1312\frac{r^3}{h^3}\right) \tag{2}$$

Inspection of this formula shows from its mathematical form that it can only be used for a limited range and it is pointed out below that when r/h is greater than 0.4 the error introduced by the use of this formula in-

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[1] Richards, Speyers and Carver, This Journal, **46**, 1196 (1924).

[2] Rayleigh, *Proc. Roy. Soc.*, **92A**, 184 (1915).

[3] Sugden, *J. Chem. Soc.*, **119**, 1483 (1921).

creases rapidly. It is possible however, by a slight modification of Equation 1 to obtain an equation which is strictly true for all values of r, namely,

$$a^2 = bh \tag{3}$$

where b is the radius of curvature at the lowest point of the meniscus in a vertical tube. The quantity b cannot be measured directly (except for large bubbles or drops) but it is readily seen that for a very small tube $b = r$, and for a very large tube $b = \infty$,—that is, the surface is plane. Hence the problem resolves itself into that of determining how r/b varies with r and a^2 between the limits $r/b = 1$ for infinitely small tubes and $r/b = 0$ for infinitely large ones. This has been done by the present writer by using the tables of Bashforth and Adams.[4]

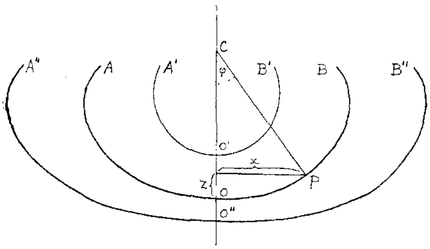

Fig. 1.

The very important contribution to the mathematical theory of capillarity which we owe to these eminent mathematicians is frequently mentioned by later workers but it does not seem to be realized that this monograph (now, unfortunately, out of print) contains a very complete numerical solution of one of the most important equations involved in several of the methods used for measuring surface tension. This is the equation to a surface of revolution about a vertical axis for a liquid in equilibrium under the forces of capillarity and gravity. Let A O B represent the meridional section of such a surface of which O C is the axis of revolution, and let any point P on this section be defined by coördinates x and z with the tangent and normal at O as axes. Let the normal at P make an angle φ with the axis O C. The equation to A O B may then be written

$$\frac{d^2z}{dx^2} + \left\{1 + \left(\frac{dz}{dx}\right)^2\right\}\frac{dz}{x\,dx} = (2 + \beta z)\left\{1 + \left(\frac{dz}{dx}\right)^2\right\}^{3/2} \tag{4}$$

where

$$\beta = \frac{g(D - d)b^2}{\gamma} \tag{5}$$

b as before being the radius of curvature at O. This equation corresponds to two families of curves; when β is positive we obtain the outline of a bubble of air under a horizontal plate, a drop of mercury on a plane surface, or the meniscus in a vertical tube, while negative values of β correspond to the case of a pendent drop or of a bubble of air emerging upwards from a submerged tube. In the first case, the shape of the curve depends upon the magnitude of β. When β is small the surface approximates to a sphere as at A′ O′ B′ while large values of β give the outline of a large drop or bubble

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[4] "An Attempt to Test the Theories of Capillary Action," Cambridge University Press, 1883.

as at A″ O″ B″ with a large radius of curvature at O″. Equation 4 has not been integrated in the usual sense of the term, that is, a general relation between x and z in terms of elementary functions which satisfies this differential equation has not been found. It is possible, however, to obtain a numerical solution with any desired degree of accuracy. Bashforth and Adams devised special methods for dealing with this equation and have computed and recorded in a series of tables the values of x/b and z/b for every 5° variation in φ for each of a large range of values of β. These ratios are given to five significant figures so that over a wide range from $\beta = 0.125$, which corresponds to water in a capillary tube of less than 1 mm. radius to $\beta = 100$ which corresponds to water in a tube nearly 9 mm. in radius, the outline of the meniscus is defined with a high degree of precision.

It should be emphasized that the numerical solutions of Equation 4 are obtained by rigid mathematical reasoning which does not involve any simplifying assumption as to the form of the whole or part of the curve. The mathematical argument is too lengthy to be restated here; it is summarized by Bashforth and Adams[5] as follows.

> "We may however, as in all cases where the differential equation to a curve is given, develop the increments of the coördinates in series proceeding according to ascending powers of the increments of the quantity chosen as the independent variable. Thus we can trace a small portion of the curve starting from a known point, and then we may make the point which terminates this portion a new starting point for tracing another small portion and so on successively until any desired portion of the curve has been traced."

The process is therefore one of analytical extension; the general theory of such methods is discussed elsewhere.[6] The method is limited in accuracy only by the number of terms of the infinite series of ascending powers of the increment of the dependent variable which are taken into account in the numerical calculations; it is, however, very laborious. Bashforth and Adams give full details of the methods of computation with numerical examples; as stated above they have worked out and tabulated a large number of solutions accurate to five significant figures.

The present author's contribution has been to use Bashforth and Adams'

TABLE I

r/h	r/a	r/b Sugden	r/b Rayleigh	r in mm. for water at 20°
0.1	0.3113	0.9689	0.9688	1.2
.2	.4338	.9414	.9411	1.7
.4	.5974	.8944	.8920	2.3
.5	.6592	.8743	.8689	2.5
.6	.7125	.8562	.8460	2.8
..	2.29	.3030	...	8.9

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[5] Ref. 4, p. 15.

[6] Goursat's, "Mathematical Analysis," translated by E. R. Hedrick and O. Dunkel, Ginn and Co., Boston, 1916, Vol. II, Part I. Functions of a Complex Variable, Chap. 4.

figures for $\varphi = 90°$ (which corresponds to a liquid with zero contact angle in a vertical tube) to calculate the values of r/b required in Equation 3. It is readily shown that this quantity is a function only of r/a, and in the author's 1921 paper r/b is tabulated to four figures for the range from $r/a = 0$ to $r/a = 2.29$. Table I shows clearly that this enables a much larger range of tubes to be used for the measurement of surface tension.

Thus Rayleigh's formula gives values which are too low by one part in four hundred parts when $r = 2.4$ mm. for water, while the author's tables give the corrections for tubes up to 18 mm. in diameter with an accuracy of one part in three thousand parts or more. There is still a gap left between $r/b = 0.3030$ which corresponds to the highest value of β used by Bashforth and Adams and $r/b = 0.05$ at which Rayleigh's formula for wide tubes[2] may be used. Since the capillary rise in the wide tube comes into the calculation as a correction term, approximate values for this region were found by a graphical interpolation between the Bashforth and Adams curve and that for values calculated by the Rayleigh formula.[7]

In view of the generality of the mathematical treatment adopted by Bashforth and Adams it appears probable that the solutions to Equation 4 obtained by them will be of great value in dealing with many of the problems of capillary measurement. Up to the present time the only workers who have used these tables appear to be Stöckle[8] for the measurement of the surface tension of mercury and the present writer in discussing the theory of the method of capillary rise and that of the method of maximum bubble pressure.[9]

Summary

The mathematical work of Bashforth and Adams on the solution of the equation to a liquid surface of revolution about a vertical axis in equilibrium under the action of gravity and surface tension forces is described, and its significance in connection with methods of measuring surface ten-

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[7] The error introduced by the use of approximate corrections in this intermediate region is very small. Bashforth and Adams' tables end at $\beta = 100$, which corresponds to $r/a = 2.29$, $r/b = 0.303$. Rayleigh gives a formula for wide tubes which he does not regard as valid when r/a is less than 5; when, however, we use it for $r/a = 2.29$ we find $r/b = 0.288$, about 5% lower than the true value. On the other hand the simple empirical formula, $r/b = 3.0e^{-r/a}$, coincides with Rayleigh's formula when r/a is greater than 4.5 and gives $r/b = 0.304$ when $r/a = 2.29$. The prolongation of the curve obtained by plotting r/b against r/a must lie at its lower extremity between these two converging curves and can be obtained by graphical methods with an error which is probably less than 1%. Since in most instruments the capillary rise in the wide tube is small compared with that in the narrow tube the resultant error in the surface tension is very small. For water at 20° in Coombs' apparatus V [THIS JOURNAL, **43,** 834 (1921)] for which $r_1 = 0.3798$ mm. and $r_2 = 9.32$ mm., an error of 1% in calculating r/b for the wide tube introduces an uncertainty of 1 part in 8500 parts in the calculated surface tension.

[8] Stöckle, *Wied. Ann.*, **66,** 499 (1898).

[9] *J. Chem. Soc.*, **121,** 860 (1922).

sion discussed with special reference to the author's modification of the method of capillary rise.

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[Contribution from the Chemical Laboratory of the University of Colorado]

THE DETERMINATION OF CHLORIDES BY MEANS OF A CALORIMETRIC TITRATION AND SOME EXPERIMENTS ON THE TITRATION OF MIXTURES OF CYANIDE AND HALIDES[1]

By Paul M. Dean and Evelyn Newcomer

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The experiments described in this article were undertaken with a view to determine the applicability of a calorimetric titration to the analysis of chlorides and mixtures of cyanide and halides. The apparatus used and the methods of procedure were similar in most respects to those employed by Dean and Watts[2] in the calorimetric determination of sulfur, except for the following modification: tap water at approximately 12.5° was made to flow through the glass jacket surrounding the buret. The solutions to be titrated were cooled to a temperature slightly below that of the standard solution. When this procedure was followed, more uniform results were obtained than when the titrations were carried out at room temperature without the water-jacketed buret.

Standardization of Silver Nitrate Solution

An approximately 0.5 *N* solution of silver nitrate was titrated calorimetrically against weighed portions of carefully purified samples of potassium chloride.

Determination of Chlorine in Soluble Chlorides

Six samples of mixtures containing soluble chlorides were titrated using the standard silver nitrate solution. The results of these titrations are given in Table I.

Table I

Determination of Chloride with Standard Silver Nitrate Solution

Sample	Calorimetrically			Gravimetrically
1	20.36	20.07	20.34	20.31
2	34.51	34.32	34.42	34.74
3	22.97	22.76		23.04
4	25.13	25.35	24.97	25.30
5	20.24	20.40	20.13	20.31
6	39.95	40.36	40.30	39.95

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[1] Adapted from a thesis submitted by Evelyn Newcomer in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Colorado.

[2] Dean and Watts, This Journal, **46,** 854 (1924).