

**604.** *The Properties of Freshly Formed Surfaces. Part XVII. The Measurement of Surface and Interfacial Tensions of Solutions, employing Stationary Waves on a Vertical Jet.*

By C. C. ADDISON and T. A. ELLIOTT.

The paper describes an experimental technique developed for the formation and measurement of the stationary waves produced when a vertical jet of water or aqueous solution strikes a barrier, and the method of calculating surface tension from wave lengths and jet diameters is discussed. The influence of surface tension on the formation and measurement of waves has been studied, and the technique has been extended to the measurement of waves on a jet of carbon tetrachloride flowing into water and aqueous solutions.

PARTS X (*J.*, 1949, 2789), XV, and XVI (preceding papers) have described methods whereby the surface and interfacial tensions of aqueous solutions of surface active compounds may be determined at small surface ages from the dimensions of a contracting jet of liquid flowing from a circular orifice. These measurements are restricted to the first 2 cm. of jet, since thereafter, when the jet approaches cylindrical form, its dimensions are little influenced by changes in surface tension. However, when the jet strikes a solid or a liquid barrier, stationary waves are set up on the jet over a distance of about 1 cm. from the barrier. It was considered that, if the surface tension of solutions could be determined from the length of these waves, such measurements (taken in conjunction with the tensions determined from jet dimensions) would permit the study of the surface films over the full jet length. The tensions determined from jet dimensions over the 0.2—2.0-cm. range are expanding-surface values; beyond this range, where the wave method is applicable, the rates of surface expansion gradually diminish, so that tensions may be determined from wave lengths at smaller rates of surface expansion than those available in the rapidly contracting portion of the jet. Further information can therefore be obtained on the influence of expansion rates on the properties of the films, and this information should ultimately be of use in determining rates of adsorption on to stationary surfaces. Again, the formation and measurement of waves is independent of orifice size, so that by variation in orifice radius a wide range of expansion rates can be obtained.

The method of stationary waves has been applied by Satterly and his co-workers (*Trans. Roy. Soc. Canada*, 1934, **28**, 177; 1935, **29**, 105; 1936, **30**, 129) to the measurement of the surface tension of pure water and mercury, with jets of these liquids in air. The present paper describes some preliminary experiments carried out to determine whether the method is applicable to aqueous solutions. The technique has also been extended to jets of carbon tetrachloride flowing into water and aqueous solutions.

The mathematical theory of the stability of jets was presented by Rayleigh (*Proc. Roy. Soc.*, 1879, **29**, 71) and a modified treatment of the theory is given by Lamb ("Hydrodynamics," Cambridge Univ. Press, 1932, p. 472). Satterly and Strachan (*loc. cit.*, 1935) applied this general treatment by considering a small symmetrical displacement of the surface of a cylindrical jet,

giving rise to stationary waves, and developed equation (1) relating flow rate, wave length ( $\lambda$ ), radius ( $r$ ), and surface tension ( $\gamma$ ). If  $\rho$  is the liquid density and  $v$  the linear velocity, then

$$\gamma = \frac{\rho v^2 \cdot 2\pi r^2}{\lambda} \cdot \frac{I_0(2\pi r/\lambda)}{I_1(2\pi r/\lambda)} \cdot \frac{1}{(2\pi r/\lambda)^2 - 1} \cdot \dots \cdot \dots \quad (1)$$

where  $I_0$  and  $I_1$  are Bessel's functions, the values of which are given by

$$I_0(z) = 1 + \frac{z^2}{2^2 \cdot (1!)^2} + \frac{z^4}{2^4 \cdot (2!)^2} + \frac{z^6}{2^6 \cdot (3!)^2} + \dots$$

$$I_1(z) = \frac{z}{2} + \frac{z^3}{2^3 \cdot 1! \cdot 2!} + \frac{z^5}{2^5 \cdot 2! \cdot 3!} + \dots$$

where  $z$  represents  $2\pi r/\lambda$ . Satterly and Levitt (*loc. cit.*, 1936) employed an equation which was identical with equation (1) except that the term  $2\pi r/\lambda$  was replaced by  $2r/\lambda$ . Since it is not clear how this equation was derived, it has not been considered further in this work. In the derivation of equation (1) the influence of gravity is neglected, and uniform liquid velocity in the direction of the jet axis is assumed.

Thus the theoretical requirements for the accurate determination of surface tension are: (a) the condition for stability ( $\lambda < 2\pi r$ ) must be maintained, (b) the rate of change of linear velocity along the jet should be negligible, (c) the wave amplitude must be small, and (d) the jet should be as nearly cylindrical in shape as possible, to permit the approximation  $v = f/\pi r^2$ .

#### EXPERIMENTAL.

*Apparatus.*—The apparatus used for the production of the liquid→air jets was identical with that described in Part X (*loc. cit.*), except that the orifice had external radius 0.419 cm. The interfacial jets were produced as described in Part XV (*J.*, 1950, 3090). Well-defined waves are not obtained at all flow rates; the clarity of the waves appears to be determined by the linear velocity of the liquid. This in turn is determined by the jet diameter, so that the position of the barrier must be adjusted, for any given flow rate, to the optimum position for distinct waves. Under the conditions employed (see results below) the orifice→barrier distance was about 3–4 cm.; the jet circumference was then at least four times the wave length, and the barrier was sufficiently far from the orifice that the change of linear velocity across a single wave was negligible.

*Illumination and Measurement.*—Jet diameters were measured by means of a travelling microscope. For this purpose the jet was illuminated directly from behind, through a diffuse screen, and it was possible to measure both crest and trough diameters with accuracy (see Fig. 1). For the measurement of wave length, the jet was illuminated solely by a point source of light suspended near, and at the same level as the microscope, so that only light reflected from the jet entered the objective. Under these conditions, the waves were clearly marked by sharp horizontal bars of light.

*Barrier.*—For the liquid→air jets, the spherical surface of a 50-ml. glass flask was used. The flask was so placed that the jet struck the flask symmetrically, and the glass surface was etched to ensure complete wetting. In the absence of external vibration, the solid barrier gave rise to steady waves capable of accurate measurement. Viewed by eye, the waves given by a liquid barrier (such as the surface of the same solution contained in a constant-level vessel) appeared to be more clearly defined, but when viewed by microscope the waves were seen to undergo constant movement. This is largely due to the fact that, in order to maintain the waves sufficiently stationary, the liquid barrier level should be constant within at least 0.005 cm., which is beyond the scope of normal constant-level devices. A photographic method may overcome this difficulty, but in addition it is found that at certain flow rates ripples are formed on the barrier surface; these ripples superimpose a secondary wave motion on the jet, and a plane section appears in the wave band.

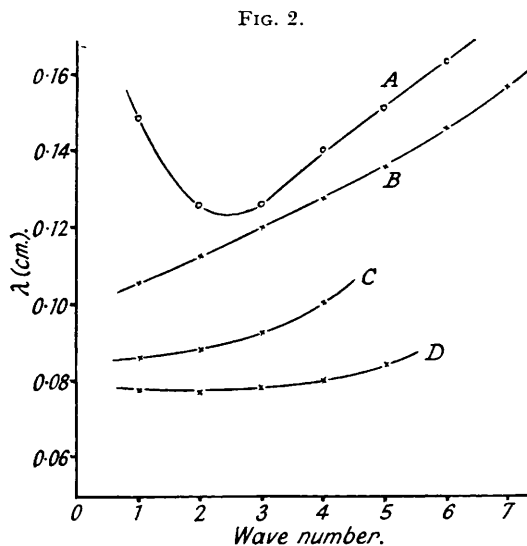
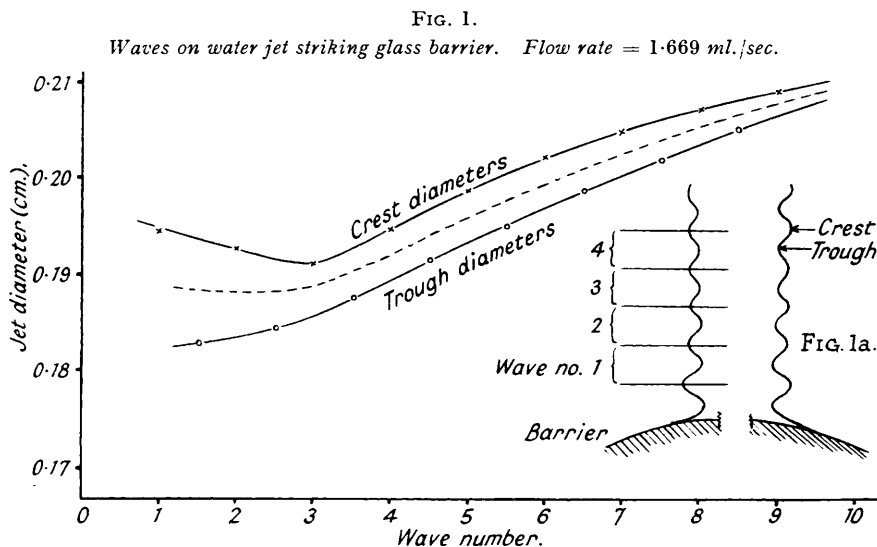
For the jets of carbon tetrachloride flowing into water or aqueous solutions, it was necessary to employ the liquid barrier and constant-level device shown in Part XV (*loc. cit.*). The barrier was then an interface submerged under several cm. of water. Surface rippling was not detectable, and variations in the flow of liquid through the constant-level device were so damped that the interface remained at a constant level. When a solid barrier was used, the point of impact of the jet moved continually over the surface, and no suitable solid could be obtained which was preferentially wetted by the carbon tetrachloride.

Although in applying equation (1) it is necessary to use symmetrical vibrations, it is of interest that the waves produced by allowing the jet to impinge on an unsymmetrical object (such as a piece of wire or a glass plate held at an angle other than  $90^\circ$ ) are more pronounced and thus more readily observed.

*Vibration.*—The waves on a jet of liquid in air are extremely sensitive to external vibration. Any sound, even normal speech, caused the waves to fluctuate, and it was not possible to carry out wave measurements while any other person was moving about the laboratory. The measurements described below were carried out in an isolated building, and the supports for the apparatus were built into the walls. Even under these conditions, the shunting of a railway engine at a distance of half-a-mile was reflected by tremors in the jet. If still conditions were not available, it would be essential to employ a fast photographic plate to record the wave dimensions. The waves on a jet of carbon tetrachloride flowing into an aqueous solution were much less sensitive to vibration.

DISCUSSION AND RESULTS.

It follows from equation (1) that the surface-tension value varies with approximately the first power of the wave length, but with at least the fourth power of the jet diameter. Therefore small errors in the measurement of the diameter are of major significance. The diameter



Curve.	Nature of jet.	$\gamma$ (dynes/cm.).	$f$ (ml./sec.).
B	Water $\rightarrow$ air	73.3	1.669
C	0.155% isoAmyl alcohol solution $\rightarrow$ air	62.5	0.935
D	0.350% isoAmyl alcohol solution $\rightarrow$ air	53.9	1.053
A	Carbon tetrachloride $\rightarrow$ water	44.8	0.950

required is the mean value between crests and troughs (Fig. 1a). Crest and trough diameters for a typical jet are shown in Fig. 1. The amplitude of oscillation is one-quarter of the distance between the crest and trough diameter curves; over the major portion of the wave band the amplitude is approximately 0.5% of the diameter, and never rises above 1%. While this order of amplitude is sufficiently small to satisfy the theoretical requirements of equation (1), it is still sufficiently large to render the determination of the mean diameter necessary. The mean

diameter is represented in Fig. 1 by the broken curve; in all experiments both crest and trough diameters were measured, and, except where otherwise stated, surface tensions were calculated from the mean diameter. The shapes of the crest- and the trough-diameter curve are of interest. In all experiments on jets of liquid in air the trough diameters decreased in a regular manner as the barrier was approached. The trough directly in contact with the barrier has been ignored throughout; its diameter was difficult to measure, and was influenced by contact with the barrier. Crest diameters decreased similarly, but increased again slightly over the one or two waves adjacent to the barrier.

For jets of water in air, the wave length decreased regularly as the barrier was approached (curve *B*, Fig. 2). Curves *C* and *D* (Fig. 2) show corresponding curves for *isoamyl* alcohol solutions of lower surface tension. Although for these solutions of lower surface tension the shape of the crest- and the trough-diameter curve remain essentially as shown for water in Fig. 1, the decrease in surface tension appreciably modifies the form of the wave length-wave number curve, so that at a tension of 53.9 dynes/cm. (curve *D*, Fig. 2) the wave-length values pass through a minimum.

*Calculation of Surface Tensions.*—Table I shows a typical set of measurements carried out on a water jet at 20°. The barrier was 2.8 cm. from the orifice.

TABLE I.

*Jet of water → air. Flow rate, 1.558 ml./sec.*

Wave no.	$\lambda$ , cm. (crest-crest).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).	$\lambda$ (cm.) (trough-trough).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).
1	0.1173	0.1853	73.1	0.1133	0.1844	71.3
2	0.1225	0.1880	72.4	0.1195	0.1864	64.5
3	0.1288	0.1920	70.5	0.1256	0.1900	71.3
4	0.1370	0.1960	69.7	0.1334	0.1938	70.7
5	0.1490	0.2018	68.2	0.1460	0.1984	71.7
6	0.1700	0.2047	71.1	0.1670	0.2014	79.9
		Mean $\gamma = 70.9$			Mean $\gamma = 71.5$	

By appropriate adjustment of the illumination it was possible to obtain points or bars of light at both the crests and the troughs of the waves. The crest-crest distances given in Table I (column 2) correspond with the wave numbers shown in Fig. 1*a*. The trough-trough distance shown in Table I (column 5) as corresponding to wave number 1 is actually the distance between the troughs of waves 1 and 2 (Fig. 1*a*), and the other recorded trough-trough distances are similarly to be regarded as displaced by half a wave (in a direction away from the barrier) from the corresponding crest-crest distances. The distilled water employed in these experiments had a surface tension of 71.8 dynes/cm. when measured by the drop-weight method. Since the mean values recorded in Table I are within 1 dyne/cm. of this value, the experimental method and equation (1) were considered to be applicable to the study of aqueous solutions. Although most of the calculated tensions are close to the mean value, it has been found in this work that occasional discrepancies occur (as with the trough-trough measurements for waves 2 and 6). This arises from the sensitive nature of the measurements, and individual results are not sufficiently accurate to permit the study of tension changes across the wave band, unless such changes are large. However, this does not diminish the significance of the results since under suitable experimental conditions the surface age of the jet in the neighbourhood of the barrier will be about 0.2—0.3 second. The six waves recorded in Table I represent a jet length of 0.82 cm., so that the wave band is equivalent to a time range of only 0.015 second. It follows that, in the case of aqueous solutions, changes in tension will in general be small, and that in the study of dynamic tensions the values calculated from different waves are to be combined to give a single tension value on the tension-time curve.

Measurements carried out on jets of aqueous solutions have shown that, when the surface tension is decreased, the waves are much less pronounced, and are fewer in number, than in the case of the water jet at a comparable flow rate. Table II gives measurements carried out on two solutions of *isoamyl* alcohol at 20°.

Beyond the wave numbers shown in Table II, the waves were not sufficiently well defined to be measured with the necessary accuracy. With these solutions it has been found in general that the surface tensions calculated by equation (1) from the crest-crest wave lengths are somewhat higher than those derived from the trough-trough values, but it is clear from Table II that the mean of all results for a particular solution lies within 0.1 dyne/cm. of the drop-weight

tension. It has not been found possible, with the present technique, to measure surface tensions below about 50 dynes/cm. Decrease in surface tension results in a decrease in the mean diameter and in the wave length (Fig. 2). In consequence, the experimental errors involved at tensions below about 50 dynes/cm. are considerable. Also, below this tension value the waves were scarcely distinguishable at practicable flow rates.

TABLE II.

*Jets of isoamyl alcohol solution*→*air*.

Experiment .....		A		B	
isoAmyl alcohol concn. (%) .....		0.140		0.350	
Flow rate (ml./sec.) .....		1.233		1.053	
$\gamma$ , by drop-weight method (dynes/cm.) .....		63.3		53.9	
$\gamma$ , by wave-method (mean of all determinations) (dynes/cm.) .....		63.2		54.0	

Expt.	Wave no.	$\lambda$ (cm.) (crest-crest).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).	$\lambda$ (cm.) (trough-trough).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).	
A	1	0.0905	0.1563	66.5	0.0790	0.1566	57.5	
	2	0.0897	0.1564	64.1	0.0805	0.1560	60.1	
	3	—	—	—	0.0845	0.1569	62.1	
	4	—	—	—	0.0870	0.1588	61.1	
				Mean $\gamma = 65.3$				
B	1	0.0775	0.1451	56.7	0.0720	0.1449	52.5	
	2	0.0770	0.1449	56.6	0.0690	0.1457	48.8	
	3	0.0780	0.1465	55.0	0.0788	0.1468	55.0	
	4	0.0795	0.1468	55.6	—	—	—	
				Mean $\gamma = 56.0$				
					Mean $\gamma = 61.1$			
					Mean $\gamma = 52.1$			

TABLE III.

*Jets of 0.023% sec.-octyl alcohol solution*→*air*.  $\gamma$ , by drop weight method = 53.5 dynes/cm.

Flow rate (ml./sec.).	Wave no.	$\lambda$ (cm.) (crest-crest).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).	$\lambda$ (cm.) (trough-trough).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).
0.990	1	0.0790	0.1399	60.0	0.0697	0.1406	50.1
	2	0.0757	0.1404	56.0	0.0693	0.1400	51.0
	3	0.0795	0.1416	61.0	0.0713	0.1418	50.0
	4	0.0855	0.1420	61.5	0.0765	0.1422	53.5
			Mean $\gamma = 59.6$				
1.001	1	0.0722	0.1402	54.5	0.0675	0.1397	51.0
	2	0.0760	0.1406	57.1	0.0703	0.1402	52.7
	3	0.0805	0.1416	59.1	0.0735	0.1410	54.3
	4	0.0847	0.1434	59.8	0.0775	0.1424	55.3
			Mean $\gamma = 57.6$				
				Mean $\gamma = 53.3$			

Table III shows measurements carried out on an aqueous solution of *sec.*-octyl alcohol.

The tensions calculated from crest wave lengths are again greater than those calculated from trough wave lengths. The two sets of results given in Table III indicate that this tension difference may vary from experiment to experiment, but the mean value remains constant (55.35 dynes/cm. in the first, and 55.45 dynes/cm. in the second experiment).

The mean of the crest and the trough diameter is the appropriate value for substitution into equation (1); from a consideration of this equation, it will be seen that the high tensions calculated from the crest wave lengths may arise from the use of wave-length values which are too high, or jet-diameter values which are too small. Since the wave-length values used are measured directly, it appeared that the high values of tensions may arise from the fact that the mean crest-trough diameters are too small for the correct operation of equation (1). Conversely, the low values of tensions calculated from the trough wave lengths would indicate that the mean diameter is too large, when substituted into equation (1) together with the trough wave lengths. As an empirical approach to this problem, the surface-tension values given in the first experiment in Table III have been recalculated by using the mean of the crest diameters, and the mean of the trough diameters, respectively, in place of the mean between crest and trough diameters, and the results are given in Table IV.

Table IV shows that when this method of calculation is used, the differences between the two mean values is reduced from 8.5 dynes/cm. (Table III) to 3.5 dynes/cm., without any appreci-

able alteration in the mean of all results (54.85 dynes/cm., compared with 55.35 dynes/cm. in Table III). This method of calculation, though somewhat empirical, therefore appears to be preferable.

TABLE IV.

Wave no.	Mean of crest diameters (cm.).	$\gamma$ (dynes/cm.).	Mean of trough diameters (cm.).	$\gamma$ (dynes/cm.).
1	0.1412	57.9	0.1392	52.8
2	0.1417	54.3	0.1394	52.1
3	0.1426	55.5	0.1400	52.9
4	0.1436	58.5	0.1416	54.7
		Mean $\gamma$ = 56.6	Mean $\gamma$ = 53.1	

Although the tension calculated for the *isoamyl*-alcoholic solution by the wave method agreed closely with the drop-weight value, the wave method gives a tension value about 2 dynes/cm. above the drop-weight value for *sec.*-octyl-alcoholic solutions of the same surface tension. This is consistent with experiments reported in Part X (*loc. cit.*). The high rate of expansion of the jet surface was shown to be without influence on the surface activity of *isoamyl* alcohol. Because of the slower rate of adsorption of *sec.*-octyl alcohol, the tensions calculated from jet dimensions over the contracting portion of the jet were found to be 4.4 dynes/cm. higher than the drop-weight value for a similar solution. The rate of surface expansion is known to decrease at greater distances from the orifice, but as the tension at the wave band is 2 dynes/cm. higher than the drop-weight value, the rate of expansion at the wave band may be regarded as still in excess of the rate of adsorption.

*Calculation of Interfacial Tensions.*—The amplitude of the waves formed on a jet of carbon tetrachloride flowing into water was much less pronounced than with the liquid→air jets. It was still possible to obtain crest and trough diameters by employing diffuse illumination placed directly behind the jet, but the illumination of the waves was more difficult, and only the crest-crest distances could be obtained with accuracy. With liquid→air jets the use of a liquid barrier may often give rise to smooth sections within the wave band, caused by interference from the ripples on the barrier surface, but in the liquid→liquid system these barrier ripples are damped out to such an extent that smooth sections were not observed at comparable flow rates. The variations in wave lengths and diameter differ somewhat in the two cases. Curve *A* (Fig. 2) is a typical wave length-wave number curve; in form it resembles the liquid→air curve *D* (Fig. 2) obtained at low surface tension, but the minimum in the curve is more pronounced. The diameter-wave number curves are similar in shape to those for liquid→air jets given in Fig. 1, except that the increase in crest diameters near the barrier is more pronounced.

The interfacial tension between carbon tetrachloride and water has been calculated (Table V), equation (1) being employed. Since the density factor occurs in the kinetic energy term of equation (1), the density value employed was that of the jet liquid (1.602 g./ml. at 20°).

TABLE V.

*Jet of carbon tetrachloride*→*water.* Flow rate = 0.950 ml./sec.  $\gamma$ , by drop-volume method = 44.8 dynes/cm.

Wave no.	$\lambda$ (cm.) (crest-crest).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).	Wave no.	$\lambda$ (cm.) (crest-crest).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).
1	0.149	0.188	(55.1)	4	0.140	0.195	43.5
2	0.126	0.186	46.7	5	0.151	0.199	44.0
3	0.126	0.190	42.6	6	0.163	0.202	45.4
Mean $\gamma$ = 44.4 dynes/cm.							

Comparison of the dimensions in Table V, with those given in Table II (experiment *B*) for the lowest liquid→air tension studied, shows that both the wave lengths and the diameters of the liquid→liquid jet are considerably greater than the liquid→air values, and the contrast would have been even greater if it had been possible to study the liquid→air jets at a tension of 44.8 dynes/cm. This would be expected to lead to greater accuracy in the tension values at liquid-liquid interfaces, but this is somewhat offset by the greater difficulty experienced in making accurate measurements. Nevertheless, the mean calculated tension agrees closely with the drop-volume value. In contrast to the liquid→air jets, the tension value calculated from the first wave is not a true value, and is ignored in calculating the mean tension. In liquid→liquid jets the first crest is perceptibly larger than the others, and it would appear that at this point the oscillations are not pure.

In order to test the applicability of this technique to aqueous solutions, wave measurements have been carried out on a jet of carbon tetrachloride flowing into an aqueous solution of sodium dodecyl sulphate. The results are shown in Table VI.

TABLE VI.

*Sodium dodecyl sulphate concentration 0.00075M. Flow rate = 1.876 ml./sec. Orifice-barrier distance = 3.3 cm.  $\gamma$ , by drop-volume method = 33.5 dynes/cm.*

Wave no.	$\lambda$ (cm.) (crest-crest).	Mean $d$ (cm.).	$\gamma$ (dynes/cm.).
2	0.078	0.249	31.9
3	0.089	0.254	33.2

At this low interfacial tension and relatively high flow rate it was not possible to measure more than three waves, and the first wave has been ignored. The jet on which these wave measurements were made was one of the jets used for the determination of tensions from jet dimensions. The tension values nearer the orifice are therefore given in Part XVI (preceding paper), Fig. 5, curve *G*, and the results by the two methods are complementary. Over the 0.2—1.4-cm. distance from the orifice, the tension rises (as a result of surface expansion) from 35 dynes/cm. to a level value of 44 dynes/cm. The shape of the tension curve indicates that beyond 1.4 cm. the tension will fall again as the rate of surface expansion decreases, but tension measurement from jet dimensions is not accurate beyond this point. The above wave measurements indicate that the tension falls again to a value close to the drop-volume value and therefore that the rate of surface expansion has decreased, at a distance of 3.3 cm. from the orifice, to a rate comparable with that occurring in an expanding drop.

It is therefore considered that the method of wave measurement may be employed at interfaces, as well as at surfaces, in conjunction with the method of jet dimensions, for the study of dynamic tensions at small surface ages.

THE UNIVERSITY, NOTTINGHAM.

[Received, July 20th, 1950.]