**143.** *The Properties of Freshly Formed Surfaces. Part I. The Application of the Vibrating-jet Technique to Surface-tension Measurements on Mobile Liquids.*

By C. C. ADDISON.

The application of the vibrating-jet technique to surface-tension measurement has hitherto been restricted owing to practical difficulties and to the complex mathematical treatment required. A practical technique and simple mathematical treatment are described which enable the method to be more readily applied to the measurement of the surface tension of pure mobile liquids and to the study of adsorption at freshly formed surfaces. The method is applicable to liquids of widely different density, surface tension, and chemical nature, and the constants as defined are independent of temperature.

THE forces determining the distribution of surface-active solute molecules between the surface and the bulk of a solution do not normally require more than several seconds to bring the surface to a condition of stable equilibrium. For any given liquid medium the properties of the equilibrium surface depend upon the concentration and the structure of the absorbent molecules, and have been investigated for long-chain carbon compounds (Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243 *et seq.*), dyes (Gibby and Addison, *J.*, 1936, 119), and small molecules (Addison, *Nature*, 1939, **144**, 250, 783). The time taken for the establishment of equilibrium also varies with the structure of the surface-active molecule concerned, and is partly dependent upon the type of measurement employed. For instance, the establishment of a true capillary rise in a clean capillary tube is almost instantaneous, whereas (Powney and Addison, *Trans. Faraday Soc.*, 1938, **34**, 356) in the drop-weight method at least 12 seconds must be allowed for the formation of each drop in order to obtain equilibrium conditions.

Little information is available on the properties of freshly formed surfaces, to which surface-active molecules are in the process of migrating and where surface orientation is not fully completed. A knowledge of the properties of such surfaces has practical as well as academic significance, since in many detergent processes the operative surfaces are never sufficiently old for equilibrium to be established. In such processes the operative surface energy lies between two limits, the " static " and the " dynamic " surface tension. The latter term is used here to denote the tension at any given surface age below that at which equilibrium is established. Therefore, although the term surface tension (which is widely accepted as an abbreviation for equilibrium or static surface tension) has a significance alone, the term dynamic surface tension has no significance unless related directly to surface age.

Adam (" Physics and Chemistry of Surfaces," Oxford Univ. Press, 1930, p. 324) considers that any method for studying the development of surface equilibrium should be capable of operating at surface ages of the order of $10^{-4}$ sec. The study of dynamic surface tensions has been handicapped by the lack of a method capable of measuring the surface tension of a liquid at very low surface ages, which at the same time utilised readily available apparatus and lent itself to simple mathematical interpretation. The vibrating-jet method is particularly suited to dynamic studies, since it provides stationary waves bounded by a continually renewed surface, but it has been little used because of the difficulty of standardising the conditions for wave-length measurement, and because the mathematical treatment necessary has rendered the method almost prohibitive where large numbers of measurements are contemplated. The work now described represents an attempt to adapt this method to routine laboratory work, and to simplify the mathematical relationship between measured wave-length, flow rate, and surface tension; it is a necessary precursor to experiments, to be described later, in which the vibrating-jet technique has been applied to the study of freshly formed surfaces less than 1 second old, in order to assess the rates at which surface-active molecules migrate to a surface and to determine the factors controlling their subsequent orientation.

The fact that the cross-sectional form of a jet of liquid issuing from an unsymmetrical orifice will oscillate between that of the orifice and the circular, thus giving rise to a series of waves, was first observed by Bidone (" Expériences sur la Forme et sur la Direction des Veines et des Courans d'Eau lancés par diverses Ouvertures," 1854) and Magnus (*Pogg. Ann.*, 1855, 95), who worked with large orifices of various shapes. Only a very few waves were obtained, and the experiments served only as illustrations of the phenomenon. Neither author offered an explanation of the recurrent return of the jet to the original cross-sectional shape, and the fact that it was due to surface tension (or "capillary force ") was first suggested by Buff (*ibid.*, 1857, Bd. C). Rayleigh (*Proc. Roy. Soc.*, 1879, **29**, 71) developed a mathematical relationship connecting the surface tension with the wave-length and the jet velocity, and reported a series of experiments designed rather to illustrate the theory than to prove that it could be applied to practical measurements. Piccard (*Arch. Sci. phys. nat.*, 1890, **26**, 561) and Meyer (*Wied. Ann.*, 1898, **66**, 523) used the method for comparative measurements only. The jet amplitudes used were large, and the measurements cannot be used for the direct determination of surface tension.

Pederson (*Phil. Trans.*, 1907, *A*, **207**, 341) first developed an accurate practical technique, but ignored the variations in wave-length which invariably occur at the beginning of a jet even when a pure liquid is employed, and an accurate treatment of the method from both practical and theoretical aspects was first made by Bohr (*ibid.*, 1909, *A*, **209**, 281), who related the dimensions of the jet of water flowing from an elliptical orifice with the surface tension by a formula which took into account the inertia of the atmosphere surrounding the jet, the viscosity of the liquid, and the correction for changing amplitude of oscillation in the jet. The practical measurements were limited to pure water, but the result obtained (72·23 dynes/cm. at 20°) would seem to indicate that for water at least no other complicating factors play a major part. Bohr's technique was applied by Stocker (*Z. physikal. Chem.*, 1920, **94**, 149) to a range of aqueous inorganic salt solutions.

The method has thus been developed to give accurate results for single liquids where a constant wave-length obtains over a major part of the jet. The mathematical relationships involved have been deduced by pre-determining the probable complicating factors, and introducing the appropriate correction. As with all dynamic methods, there can be no guarantee that a relationship deduced by this means and found to be correct for one liquid will be universally applicable. The drop-weight method, for instance, has received similar mathematical treatment, but in order to make the method universally applicable, Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499) found it necessary to connect drop size and surface tension by purely empirical tables of figures deduced from many actual measurements over the full range of surface tension. From a study of the relationship between jet dimensions and known values of surface tension (giving due consideration to the mechanism by which any particular complicating factor influences the measurements), it has now been possible to formulate a simple relationship which enables the vibrating-jet technique to be applied to the measurement of a wide range of surface tensions and is capable of rapid and simple mathematical treatment. Although suitable for determinations on single pure liquids, the method also finds very ready application where changes in tension are more important than high accuracy in the values themselves.

Surface tensions calculated by the method given below deviate from the true value if the test liquid has a high viscosity, and the method is only applicable to liquids or solutions of such viscosity that the energy dissipation due to the damping of the vibrations is negligible over the length of the jet. True results are obtained at all viscosities below 0·02 c.g.s. unit, but deviations occur at higher viscosities. As all the dilute aqueous solutions used, and the majority of common organic liquids, fall inside this range, the viscosity limit imposes no undue restriction on the applicability of the method.

<p style="text-align:center;">EXPERIMENTAL.</p>

*Apparatus.*—The apparatus used is shown in Fig. 1. A 2-l. aspirator $A$ was fitted with water manometer $M$ and a fine capillary tube $BB_1$. This tube was coated with a film of vaselin where it passed through the rubber bung, so that it could be readily adjusted to any required position. The liquid under test was led from the tubulure down a glass tube $C$, and both $A$ and $C$ were fixed rigidly in position. The lower end of tube $C$ was connected to the jet tube $D$ by a small piece of rubber tubing so that $C$ and $D$ made glass-to-glass contact. The jet tube, which was about 10 cm. long, was clamped at about 10° to the horizontal, and a millimetre scale $E$ was fixed immediately behind the jet so that the tip of tube $D$ lay on the zero of the scale. By this means the part of the jet of liquid to be measured flowed horizontally in front of the scale, and could be measured directly. The liquid was received in vessel $F$, which carried a 50-ml. calibration mark on the narrow neck immediately above the bulb. The jet was illuminated by a striplight $G$ (at least equal in length to the jet of liquid) placed horizontally over the jet.

*Arrangement for constant flow of liquid.* It was necessary to maintain a steady and constant flow of liquid over a period of several minutes for each determination. The jet is very sensitive to disturbances in the reservoir, and most of the standard types of constant-head equipment are unsuitable owing to a pulsing action which is reflected in the jet. Both Pederson (*loc. cit.*) and Bohr (*loc. cit.*) described arrangements based on the distribution of test liquid between several reservoirs, but these are applicable only when an unlimited supply of test liquid is available, and when only small amounts of liquid were available, Pederson had to determine wave-lengths under a falling head of pressure. In view of the almost direct proportionality between wave-length and flow rate, a perfectly constant flow rate is essential, as emphasised by the fact that true oscillation takes place over only part of the jet length and the selection of the appropriate section of the jet involves measurement over the full length : this is only possible under a constant head of pressure.

In the apparatus shown, the head of pressure ($h$) is equal to the vertical distance from $D$ to the lower tip of $B$ (*i.e.*, $B_1$) irrespective of the level of the liquid above $B_1$. If $B$ has a large internal diameter, the bubbling of air from $B_1$ to replace liquid flowing from the aspirator gives rise to a regular pulsing of the jet stream, which prevents measurement of wave-lengths. Under these conditions the operative head of pressure fluctuates over a range equal to the diameter of each air bubble. As the internal diameter of $B$ is reduced, the pulsing action diminishes ; when the bore of $B$ is sufficiently fine the air issues as a continuous stream of small bubbles and a steady jet stream is obtained. If the reservoir $A$ is rigidly fixed so that it cannot transmit mechanical vibration to $D$, the jet stream is not influenced by disturbances on the surface of the liquid in $A$. The appropriate internal diameter of $B$ depends on the order of flow rates used, and therefore on the cross-sectional area of orifice $D$ ; the tube used had an internal diameter of 0·06 cm.

The length of tube $C$ was adjusted (for liquids of various densities) to give appropriate flow rates. As the resistance of the system is thereby altered, the jet velocity does not vary in proportion to $\sqrt{2gh}$ and the flow rate was measured directly in every case. The vessel $F$ was used for this purpose, and the flow rate (ml./sec.) was measurable to an accuracy of approx. 0·2% by taking the time required for the liquid to rise to the 50 ml. mark on the neck. (A similar instrument, with unbent neck was used in conjunction with the vertical jet.) The flow rate was confirmed by measurements taken before and after the readings on the jet.

*Dimensions of orifice tube.* In order to obtain the maximum length of unbroken jet, it is necessary that the jet should perform a single vibration only and that turbulent flow should be minimised. Any orifice formed by drawing down a tube of larger cross-sectional area than the final orifice gives rise to exaggerated jet amplitude, with consequent shortening of the unbroken stream. The longest unbroken jet was obtained from an orifice formed by slight lateral compression of a piece of capillary tubing. By this means the liquid stream issues from an orifice whose cross-sectional area is the same as that throughout the body of the tube, and optimum conditions for stream-lined flow are obtained. The sharp-

ness of the orifice edge also has a pronounced effect on the stability of the jet. Any form of grinding damages this edge and the jet used in these experiments was prepared by first softening and slightly flattening the end of a piece of capillary tubing (approximately 0·20 cm. internal diameter) and then breaking off the end of this tube at such a position that the major/minor axis ratio of the orifice so formed was as small as possible consistently with the formation of visible waves. The ratio used was 1·25.

*Measurement of Wave-lengths.*—A section of the jet is shown diagrammatically in Fig. 2. The jet formed by an elliptical orifice can be regarded for present purposes as composed of interlocking lenses in alternate vertical and horizontal planes. The true " nodes " are at $A$, $B$, $C$, and $D$, where the cross-section passes through the circular form. However, the jet must pass from $A$ to $C$ before the cross-section completes one full oscillation, and this distance represents the wave-length $\lambda$. This can be measured directly by two methods.
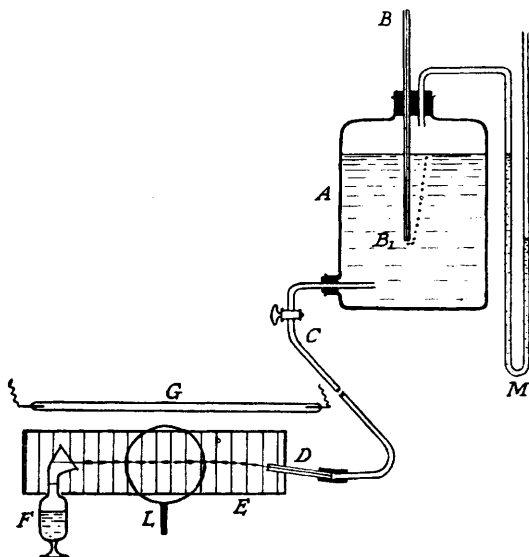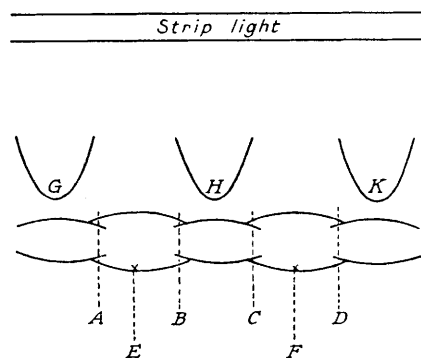
Fig. 1.



Fig. 2.



(a) *Large amplitudes.* When a striplight is placed vertically above the jet, and the jet is viewed in a horizontal plane, no reflection is seen in the horizontal lenses, but the lower boundary of the vertical lenses is outlined by a band of reflected light. As the light source is raised away from the jet, this strip of light is shortened, till eventually only a short narrow band remains on each vertical lens. The limits of this band are clearly defined, so the mean values (*i.e.*, points $E$ and $F$) can be accurately determined. The distance $EF$ is equal to $AC$, *i.e.*, the distance between successive bands of light represents one wave-length. By viewing the jet through a fixed lens $L$ against a millimetre scale, the individual wave-lengths could be measured with an accuracy of 0·01 cm. The accuracy increases beyond this as the number of uniform waves available for measurement increases.

(b) *Small amplitudes.* As the amplitude of the jet decreases for any given wave-length, the accuracy of measurement by method (a) decreases because the length of the bright band of reflected light along the bottom edge of the vertical lenses cannot be sufficiently clarified and reduced. In certain positions of the light source, the rays of light are reflected and doubly refracted by the jet, and a wave image of exaggerated amplitude is thrown on the background scale. Pederson (*loc. cit.*) utilised this effect to throw images on to a photographic plate. The position of the image with respect to the jet is shown at $G$, $H$, and $K$ in Fig. 2. The lowest point of each parabola of light corresponds exactly with the centre of a horizontal lens, and the distance between these points again represents the wave-length. As the amplitude of the wave image is many times greater than that of the jet itself, the accuracy is increased accordingly.
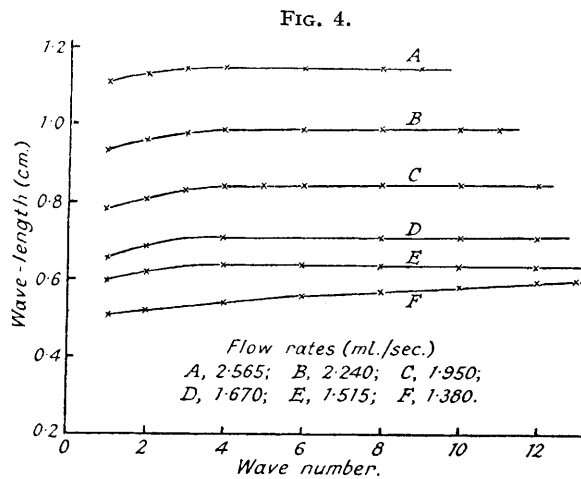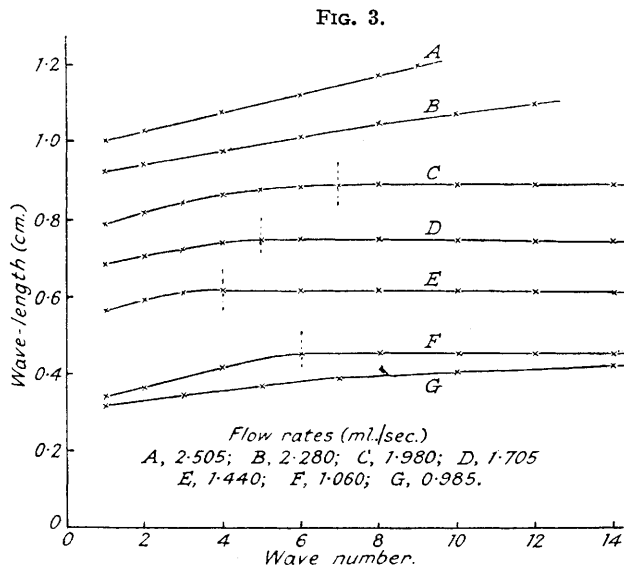
*Temperature Measurement.*—The temperature experiments were carried out by enclosing the whole apparatus in a large wooden box 2 ft. deep, kept by thermostat at approximately the required air temperature. The upper half of the front was formed of glass, and the lower part was open while the readings were being taken. Liquid at approximately the correct temperature was filled into the reservoir, and the liquid allowed to flow for a while before each determination to bring the apparatus to a constant temperature. The temperatures quoted in Table IV were obtained by allowing the jet to impinge directly on the bulb of a thermometer, and the arrangement described above was sufficient to prevent changes in temperature occurring during a determination.

DISCUSSION AND RESULTS.

Apart from the work of Satterly and Strachan (*Trans. Roy. Soc. Canada*, 1935, **29**, 105), who studied the vibrations which develop along a vertical jet of circular cross-section when the jet strikes a solid barrier, and some qualitative experiments by Rayleigh (*loc. cit.*), previous work in this field has been confined to the use of vibrating jets in a horizontal position. Although this renders unnecessary the application of correction factors for changing gravity effect along the jet, the use of a vertical jet offers pronounced practical advantages. The gravity effect in a horizontal jet, although uniform along the length of the jet, acts at right angles to the direction of flow. This force, being in the same plane as the two-dimensional oscillation, gradually upsets the purity of the vibrations, and quickens the break-up of the jet. Under identical reservoir conditions, the change in direction of the jet tube from horizontal to vertical brings about an immediate increase of approximately 30% in the length of unbroken jet stream, with a corresponding increase in the range of surface ages available for measurement. Again, stable conditions for a pure liquid in a horizontal jet can be regarded as holding only

when the wave-length is constant along this jet.   This is not necessarily true of the vertical jet, although the increase in wave-length due to the increasing velocity under gravity is largely compensated for by the decrease due to diminishing area of section.

The change in wave-length along the jet in both vertical and horizontal positions has been studied for distilled water at 20° at various flow rates.   The results are shown graphically in Figs. 3 and 4, in which " wave

FIG. 3.

FIG. 4.



Flow rates (ml./sec.)
A, 2·505;  B, 2·280;  C, 1·980;  D, 1·705
E, 1·440;  F, 1·060;  G, 0·985.

Flow rates (ml./sec.)
A, 2·565;  B, 2·240;  C, 1·950;
D, 1·670;  E, 1·515;  F, 1·380.

number " represents the serial number of the wave, counting along the jet from the orifice.   In both cases the minimum flow rate for visible waves gives rise to a jet having a gradually increasing wave-length.   In an ideal jet (in which the wave-length varies directly as the flow rate) the oscillations are two-dimensional, and this only holds true if the wave-lengths are considerable in comparison with the diameter of the jet.   For small flow rates, either vertical or horizontal, the oscillations will be three-dimensional, and the oscillation frequency will depend upon the wave-length also.   Again, the influence of gravity becomes more pronounced with a vertical jet as the flow rate increases, since the compensation due to decreasing jet radius is less and less able to counteract the increasing flow due to gravity.   The vertical dotted lines in Fig. 3 indicate the position in the jet below which the wave-lengths are not constant, and their changing position along the jet is a measure of the relative predominance of these two effects.   Even with the horizontal jet, however (Fig. 4), an increase in wave-length over the first four waves takes place irrespective of flow rate. Bohr (*loc. cit.*) observed this, and regarded it as being due to a difference between the rate of flow of liquid in the centre of the jet and at the surface, thus giving rise to a velocity potential which increases until balanced by the viscosity of the liquid.   It is improbable that this cause alone is responsible, particularly as the wave-lengths have invariably been found to increase rather than decrease.   No jet will be quite free from turbulent flow over its first few wave-lengths, and in view of the fact that the age of the surface at the end of the fourth wave-length is still less than $10^{-2}$ sec., the establishment of the true surface tension may also be partly responsible.

FIG. 5.



OH - Horizontal jet
OV - Vertical jet
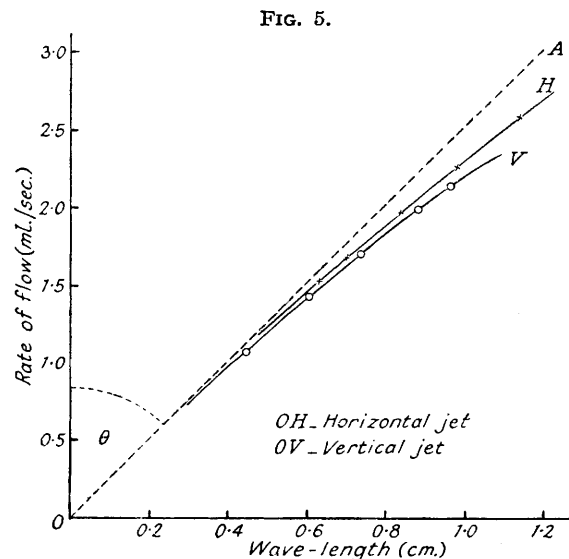
Throughout this work it has therefore been necessary to ignore the first four wave-lengths as representing the period necessary for the establishment of fluid equilibrium.

The flow rate has been plotted against the equilibrium wave-length for both types of jet in Fig. 5.   Although curves of similar type are obtained in each case, yet the gravity effect in the vertical jet results in a greater wave-length over the full range of flow rates.   The surface tension of the liquid under test can be deduced from either of the two curves *OH* or *OV*.   The mathematical treatment given below is applicable to horizontal jets only.   However, where it is of advantage to obtain the maximum length of unbroken jet, a further gravity

factor can be superimposed to make the method applicable to vertical jets, and this will be the subject of a later part.

Curve *OH* in Fig. 5 indicates that the wave-length $\lambda$ increases more rapidly than the flow rate, $f$. The time of oscillation (which in an ideal jet is independent of flow rate) therefore increases as flow rate increases. This effect has been found to occur in all liquids tested, and has been attributed by Rayleigh and Bohr to (*a*) the damping effect on the oscillations caused by the viscosity of the liquid, (*b*) the increasing magnitude of wave amplitudes which occurs with increasing flow rate, and (*c*) the inertia of the air phase. It is considered here that with liquids of low viscosity the velocity gradient set up at the orifice will be maintained throughout the jet, and will represent a further factor accounting in part for the disproportionate extension of wave-length which occurs. The restoring force (*i.e.*, surface tension, $\gamma$) acting on a particle on the surface of the jet will normally act at 90° to the direction of flow in the absence of a velocity gradient. A velocity gradient extending from the centre to the surface of the jet will cause the force $\gamma$ to act at an angle of 90° + α° to the direction of flow. As α will be small, tan α will vary in proportion to the flow rate $f$. Although the point on the equivalent circle about which the particle oscillates is not quite at the centre of the amplitude, it is sufficiently near in the case of the small amplitudes used for the oscillation of the particle (mass $m$) to approach simple harmonic. The time of oscillation $t$ (secs.) will then be given by

$$t = C(m/\gamma \cos \alpha)^{\frac{1}{2}} = C_1/(\cos \alpha)^{\frac{1}{2}}$$

where $C$ and $C_1$ are constants. Now, since $tf = C_2\lambda$, then $f = \lambda C_3(\cos \alpha)^{\frac{1}{2}}$. This relationship between $f$ and $\lambda$ is the equation of a curve of the type shown in Fig. 5, but in the absence of a suitable practical method for determining the angle $\alpha$ and the velocity gradient, it is not yet possible to apply this equation quantitatively.

*Relation between Wave-length, Flow Rate, and Surface Tension.*—Rayleigh (*loc. cit.*) has shown that for an ideal jet, the expression for the time of oscillation takes the general form $t = K_1(dr^3/\gamma)^{\frac{1}{2}}$, where $d$ is the density of the liquid and $r$ the radius (in cm.) of the jet where its cross-section is circular; if $\lambda$ is expressed in cm. and $f$ in ml./sec., then $t = \pi r^2\lambda/f$, whence

$$\gamma = (K_1^2/\pi^2 r)d(f/\lambda)^2.$$

The value of $r$ is that of the jet, not the orifice. Although there are reasons for believing that the extension of wave-length at the beginning of the jet is due to factors other than a change in linear velocity (with consequent reduction in jet radius), yet the assumption that the radius of a circle equivalent to the orifice can be used for $r$ is not justified. As the apparatus is to be calibrated by using liquids of known surface tension, the term $r$ can conveniently be incorporated in the constant in the above equation. Again, the value of $\lambda/f$ for an ideal jet and any liquid is given by the slope of the tangent to the $\lambda$–$f$ curve (Fig. 5) at the origin and can thus be replaced by tan $\theta$. Hence

$$\gamma = K_2 d/\tan^2 \theta \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$\theta$ has, of course, no significance as an angle, and is significant only when referred directly to its tangent; tan $\theta$ for water was found by accurate construction to be 0·400 at 20°. By substituting the values $\gamma = 72\cdot8$ dynes/cm. and $d = 0\cdot9982$ at 20°, we find $K_2 = 11\cdot68$. This value varies, of course, with the jet used, but when once determined by this means, $K_2$ is a fixed property of the apparatus. Results given below indicate that $K_2$ is constant for all liquids and is independent of temperature.

*Determination of* tan $\theta$.—The large number of measurements required before tan $\theta$ can be obtained by geometrical construction prohibits the use of this method for routine measurements, and where changes in wave-length occur along the jet, the method is not possible. It is therefore essential to obtain tan $\theta$ from a single measurement of $\lambda$ and $f$. The lower range of flow rates over which $\lambda$–$f$ proportionality holds varies with the size of orifice and the nature of the liquid, but even in limiting cases where the departure from proportionality is just negligible the flow rate is still so small that a constant wave-length is not obtained even with pure liquids. Again, true two-dimensional oscillations do not operate until the flow rate is so large that the wave-length is appreciably affected by the factors mentioned above. There are therefore no practical conditions under which tan $\theta$ can be obtained as the direct ratio of measured values of $\lambda$ and $f$; it can, however, be obtained as follows.

When referred to its tangent *OA* as ordinate, the equation for curve *OH* (Fig. 5) has the general form $y^n = K_3 x$. When referred to flow rate ($f$) and wave-length ($\lambda$) axes, the equation for the curve becomes

$$(\lambda \sin \theta + f \cos \theta)^n = K_3(\lambda \cos \theta - f \sin \theta) \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $\theta$ is the angle between the tangent and the $f$ axis. Throughout this work tan $\theta$ is related to $f$ in ml./sec. and $\lambda$ in cm. The flow rate $f$ is expressed in volume rather than linear units to avoid reference to the accurate radius of the jet. The value of tan $\theta$ for water (0·400) was substituted in the above equation in order to determine appropriate values for $K_3$ and $n$. Table I shows that as the wave-length increases the value to be given to $n$ in order to maintain $K_3$ constant changes from 3 to 2, which is consistent with the change from three- to two-dimensional oscillation which takes place as the wave-length increases with respect to jet diameter. The table also indicates that for accurate determinations the ratio wave-length/jet diameter should be above 10 in order that true two-dimensional oscillation can operate.
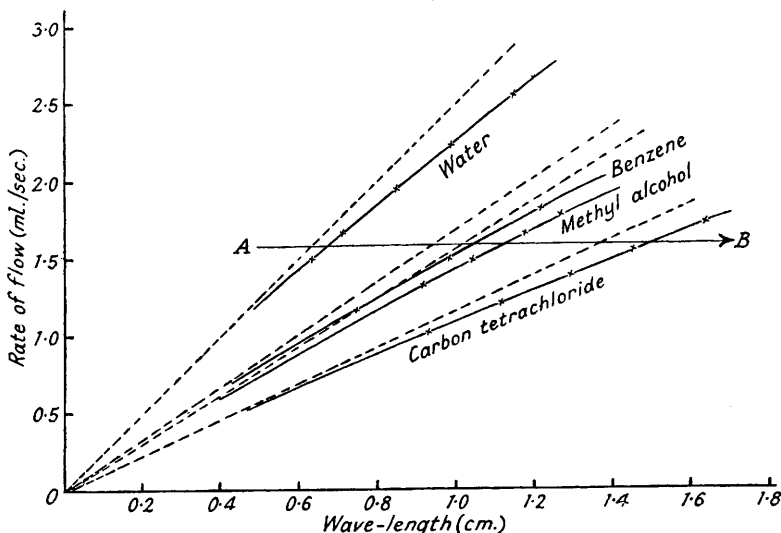
TABLE I.

| | | | | | |
|---|---|---|---|---|---|
| λ, cm. ............................................ | 0·640 | 0·714 | 0·850 | 0·990 | 1·150 |
| f, ml./sec. ...................................... | 1·515 | 1·670 | 1·950 | 2·240 | 2·565 |
| $K_3$, assuming $n = 2$ .......................... | 87·3 | 79·2 | 68·8 | 68·8 | 68·5 |
| $K_3$, assuming $n = 3$ .......................... | 143 | 143 | 146 | 168 | 192 |
| Approx. ratio, λ/jet diameter .............. | 8 | 9 | 10 | 12 | 14 |

With the apparatus used, therefore, the relationship between λ, f, and θ for water is

$$(\lambda \sin \theta + f \cos \theta)^2 = 68\cdot7\ (\lambda \cos \theta - f \sin \theta).$$

*Variation of* $K_3$ *with Properties of Liquid under Test.*—The relationship expressed in equation (1) provides a suitable means of determining the variations which occur in $K_3$ when equation (2) is applied to various liquids. Fig. 6 shows the relation between λ and f for benzene, carbon tetrachloride, and methyl alcohol under the same experimental conditions. The curve for water is reproduced for comparison. The known values for the surface tension being assumed, the value of θ was calculated for each of the three liquids from equation (1). This value was substituted in equation (2), with $n = 2$, and the values obtained for $K_3$ compared against $K_3$ for water, three separate values of λ and f being used in each case. The results are given in Table II, where $K_4$ is defined by $K_3 = K_4 d/\tan \theta$. The value of $K_3$ is a measure of the extent to which the wave-length departs

FIG. 6.



from the ideal proportionality with flow rate, and the results in col. 3 indicate that there are considerable variations from liquid to liquid.

TABLE II.

| γ, cm. | f, ml./sec. | $K_3$. | $K_3/d$. | $K_4$. | γ, cm. | f, ml./sec. | $K_3$. | $K_3/d$. | $K_4$. |
|---|---|---|---|---|---|---|---|---|---|
| $H_2O$; γ used = 72·8 dynes/cm. at 20°; tan θ = 0·400. | | | | | $CCl_4$; γ used = 26·7 dynes/cm. at 20°; tan θ = 0·835. | | | | |
| 1·150 | 2·565 | 68·5 | 68·6 | 27·5 | 1·728 | 1·875 | 51·8 | 32·4 | 27·6 |
| 0·990 | 2·240 | 68·8 | 68·8 | 27·6 | 1·606 | 1·750 | 51·4 | 32·2 | 27·4 |
| 0·850 | 1·950 | 68·8 | 69·0 | 27·6 | 1·422 | 1·570 | 51·9 | 32·6 | 27·8 |
| $C_6H_6$; γ used = 28·9 dynes/cm. at 20°; tan θ = 0·596. | | | | | MeOH; γ used = 22·6 dynes/cm. at 20°; tan θ = 0·640. | | | | |
| 1·220 | 1·820 | 40·9 | 46·6 | 27·8 | 1·312 | 1·790 | 34·8 | 43·9 | 27·9 |
| 0·980 | 1·495 | 41·1 | 46·8 | 27·9 | 1·206 | 1·660 | 34·4 | 43·5 | 27·5 |
| 0·800 | 1·240 | 41·5 | 47·3 | 28·2 | 1·062 | 1·480 | 34·0 | 42·9 | 27·3 |

As the period of oscillation in a jet is a direct function of the density of the liquid, the deviations from ideal behaviour must also vary with density. The values of $K_3/d$ are therefore listed in col. 4. These represent the true basis on which to compare the various liquids, and again they vary considerably from liquid to liquid.

The broken-line tangents in Fig. 6 represent the ideal λ–f ratio for each of the four liquids. The major causes of deviation from these lines, *i.e.*, air-phase inertia, velocity gradient, viscosity potential, and variations in wave amplitude, are each functions of the flow rate, and their influence upon wave-length must necessarily depend upon the frequency of vibration. As the wave-length increases for any given flow rate (say, along the line $AB$ in Fig. 6) the rate of oscillation decreases and the factors causing deviation will play a less significant part. It was therefore to be expected that the value $K_3/d$ would decrease with increase in tan θ. The respective values given in Table II show that, in fact, a clear inverse proportionality exists, and that if $K_3$ in equation (2) be replaced by $K_4 d/\tan \theta$ the value of $K_4$ is constant for all four liquids.

*Determination of Surface Tension of any Liquid.*—The results set out above indicate the probability that

surface tension values for any liquid can be determined by the following method : (1) Accurate determination of wave-length and flow rate. (2) Substitution of these results in the expression : $(\lambda \sin \theta + f \cos \theta)^2 - K_4 d (\lambda \cos \theta - f \sin \theta)/\tan \theta$. (The value $K_4$ depends upon the dimensions of the apparatus used and can be obtained as shown above.) (3) $K_4$, $d$, $\lambda$, and $f$ being known, it is possible to find the value of $\theta$ at which the expression has zero value. This is readily done by substituting into the expression two near values of $\theta$, plotting the values obtained for the expression against the angle, and reading off the value of $\theta$; $\tan \theta$ then has direct significance in terms of wave-length per unit flow rate. (4) Substitution of the value of $\tan \theta$ so obtained in the expression $\gamma = K_2 d/\tan^2 \theta$.

This simple procedure, which had so far been shown to give true surface-tension values for four liquids of widely different density, surface tension, and chemical nature, was then applied to the determination of the surface tensions of other liquids. The results are given in Table III and are in good agreement with results obtained by other methods.

TABLE III.

| Liquid. | $\lambda$, cm. | $f$, ml./sec. | $\tan \theta$. | $\gamma$, dynes/cm. at 20°. | Liquid. | $\lambda$, cm. | $f$, ml./sec. | $\tan \theta$. | $\gamma$, dynes/cm. at 20°. |
|---|---|---|---|---|---|---|---|---|---|
| $Et_2O$ ......... | 1·320 | 1·640 | 0·700 | 17·0 | $CHCl_3$ ......... | 1·480 | 1·690 | 0·801 | 27·2 |
| $C_7H_{16}$ ......... | 1·060 | 1·495 | 0·630 | 20·1 | PhMe ......... | 1·206 | 1·815 | 0·595 | 28·5 |
| EtOH ......... | 1·060 | 1·480 | 0·640 | 22·5 | $m\text{-}C_6H_4Me_2$ ... | 1·000 | 1·510 | 0·594 | 28·7 |
| $COMe_2$ ......... | 1·104 | 1·580 | 0·620 | 23·8 | | | | | |

*Influence of Temperature.*—Surface-tension measurements have been made for four liquids over a range of temperature, in order to verify that the method and constants which have been shown to give satisfactory results at 20° are applicable over the range of temperature required. The flow rates chosen were such that at the lowest temperature the wave-lengths were still sufficiently long to ensure pure two-dimensional vibration. The results are given in Table IV. The height of the capillary air inlet $B$ into the reservoir was adjusted at each temperature so that the flow rate was constant throughout the tests on any one liquid. Thus the variation of wave-length with temperature is immediately available from Table IV.

TABLE IV.

| Liquid. | Temp. | $f$, ml./sec. | $\lambda$, cm. | $\tan \theta$. | $\gamma$, dynes/cm. | $-d\gamma/dt$. |
|---|---|---|---|---|---|---|
| $H_2O$ | 13° | 2·025 | 0·874 | 0·398 | 73·8 | 0·150 |
| | 33 | 2·025 | 0·900 | 0·406 | 70·6 | 0·160 |
| | 45 | 2·025 | 0·916 | 0·410 | 68·7 | 0·166 |
| | 60 | 2·025 | 0·940 | 0·417 | 66·0 | 0·180 |
| $CCl_4$ | 7 | 1·620 | 1·432 | 0·816 | 28·3 | 0·120 |
| | 32 | 1·620 | 1·520 | 0·854 | 25·1 | 0·135 |
| | 48 | 1·620 | 1·580 | 0·884 | 23·0 | 0·140 |
| $C_6H_6$ | 11 | 1·690 | 1·106 | 0·587 | 30·0 | 0·120 |
| | 35 | 1·690 | 1·180 | 0·611 | 27·0 | 0·130 |
| | 50 | 1·690 | 1·240 | 0·630 | 24·9 | 0·140 |
| MeOH | 8 | 1·715 | 1·214 | 0·628 | 23·8 | 0·080 |
| | 18 | 1·715 | 1·238 | 0·635 | 23·0 | 0·085 |
| | 38·5 | 1·715 | 1·304 | 0·656 | 21·0 | 0·105 |
| | 50 | 1·715 | 1·340 | 0·671 | 19·8 | 0·115 |

Thermal agitation in the jet was responsible for a progressive shortening of the unbroken jet as temperature increased. It was possible in each case to shorten the jet to less than 5 waves, and the highest temperature recorded in Table IV represents the limit to which the temperature could be raised without reducing the unbroken jet to less than 5 waves.

The results obtained indicate that the method can be applied over a range of temperature, and that the constants as defined are independent of temperature.

HARRIS INSTITUTE TECHNICAL COLLEGE, PRESTON.