602. *The Properties of Freshly Formed Surfaces. Part XV. The Application of the Contracting Liquid-jet Technique to the Measurement of Tensions at Liquid–Liquid Interfaces.*

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An experimental technique is described for the production and measurement of a stable contracting jet of carbon tetrachloride flowing into water. The technique should be applicable to any pair of immiscible liquids of different densities. The method given in Part X (*J.*, 1949, 2789) for the calculation of surface tension at various positions along the surface of a liquid → air jet.has been extended to the calculation of liquid–liquid interfacial tensions.

IT has been shown in Part X (*J.*, 1949, 2789) that the dimensions of a contracting jet of liquid flowing vertically from a circular orifice may be used to determine the surface tension of pure liquids and aqueous solutions of surface-active compounds, at surface ages up to about 0·3 second. The present paper describes the practical modifications necessary in order that the technique may be applied to the study of a contracting jet of one liquid flowing into another. The mathematical treatment of the dimensions of the liquid→liquid jet is given, and the physical properties of the jet are compared with those of the liquid→air jet.

The only other available technique for the study of interfaces at small surface ages is that employing an oscillating jet (Addison, *Phil. Mag.*, 1945, **36**, 73). The most important points of comparison between the two techniques are as follows : (*a*) The upper age limit of the oscillating jet surface is about 0·01 sec. This imposes a severe restriction on the systems which may be studied. The contracting-jet method applied to interfaces permits measurement of tensions at surface ages up to the same maximum, *i.e.*, 0·3 sec., as for liquid→air jets. (*b*) Whereas surface-area changes in the oscillating jet are negligible, the surface of the contracting jet is continually changing in area. Dynamic tensions at a stationary surface are not therefore directly available from the contracting-jet method, though such values may be calculated from knowledge of the rate of change of surface area. However, these rates are so greatly in excess of the rates available by trough or drop methods that the technique provides a valuable means of studying the effect of area change on surface tension in those systems where adsorption rates are rapid.

The experimental work and calculations described in this paper refer to a jet of carbon tetrachloride flowing into water. Although other liquid–liquid systems have not been investigated quantitatively, the general treatment should be applicable to (*a*) jets of any liquid more dense than, and immiscible with water, flowing into water or aqueous solutions, and (*b*) jets of water or aqueous solution flowing into less dense immiscible liquids.

The treatment of results given below is applicable to mobile liquids only, since it has been assumed throughout that the jets may be regarded as conservative systems with respect to energy. It has been shown in Part X (*loc. cit.*) that any dissipation of energy which may occur with mobile liquids is not sufficient to influence the calculated tensions by more than the experimental error arising from measurement of jet dimensions.

<div align="center">EXPERIMENTAL.</div>

Apparatus.—The carbon tetrachloride (about 12 l.) was contained in a 20-l. reservoir *D* (Fig. 1). In view of the high density and volatility of carbon tetrachloride, it was necessary to modify the apparatus described in Part X (*loc. cit.*). The modified apparatus used for measurements at liquid–liquid interfaces is shown in Fig. 1. This apparatus has also been found preferable to that described in Part X for measurements in air, when volatile liquids are under examination. In the earlier apparatus the valve controlling the flow of liquid was placed in the long vertical arm *A* (Fig. 1). With the valve in this position and the apparatus filled with carbon tetrachloride, the negative pressure exerted by the long column of liquid in *A* gave rise to bubbles of vapour below the valve. Once formed, these bubbles increased rapidly and varied the flow rate. This difficulty was overcome by placing the valve (*B*) on the reservoir side of the syphon tube *A*. *A* had a uniform internal diameter of 1·4 cm. and was 150 cm. long. All taps were lubricated with silicone grease. As a further precaution against the inefficiency of tap (5), the Buchner flask *C* and tap (3) were introduced. The water (or aqueous solution) was contained in a rectangular glass tank *E*, 30 × 30 × 15 cm., of which one 30 × 30-cm. vertical face was optically plane.

The barrier. A stream of carbon tetrachloride did not " wet " a solid glass barrier placed below water level, and a steady jet could not be obtained under these conditions. A liquid barrier was therefore used. The carbon tetrachloride from orifice *G* flowed into a funnel *H* ; the stem of the funnel was bent as shown, and the tip cut at an angle, to form a constant level device which provided a stationary liquid interface in funnel *H*. The overflow of liquid from *H* passed down the outside of the stem into a rectangular glass vessel *K* (11 × 11 × 7 cm.) This arrangement eliminated agitation of the liquid barrier surface. The modified funnel *H* was suspended by a glass rod, which was bent into an appropriate shape at the bottom to hold the funnel *H* firmly and was secured at the top by clamp *M*. By movement of the glass rod in *M*

it was possible to displace *H* either vertically or horizontally, so that the barrier could be moved into the desired position after formation of the jet.

Liquid levels. The water level in tank *E* was maintained constant by the use of syphon and constant-level device *F*. In order that the measured flow rate should be accurate it was essential that the liquid level in *K* should also remain steady. This was achieved by the use of a second syphon and constant-level device *L*, which was shielded to prevent evaporation.

Method of Forming the Jet.—Because of the low surface tension of carbon tetrachloride (compared with water) the critical flow rate of a jet of carbon tetrachloride flowing into air is so high that it was impracticable to form the jet in air and then to raise the water level above the orifice. The following technique was therefore employed. Vessels *K*, *H*, and *L* were filled with carbon tetrachloride, and a further vessel, similar to *K* and also containing carbon tetrachloride, was placed round the orifice *G* so that *G* was immersed below the liquid surface. The tank *E* and overflow *F* were then filled with water,

FIG. 1.
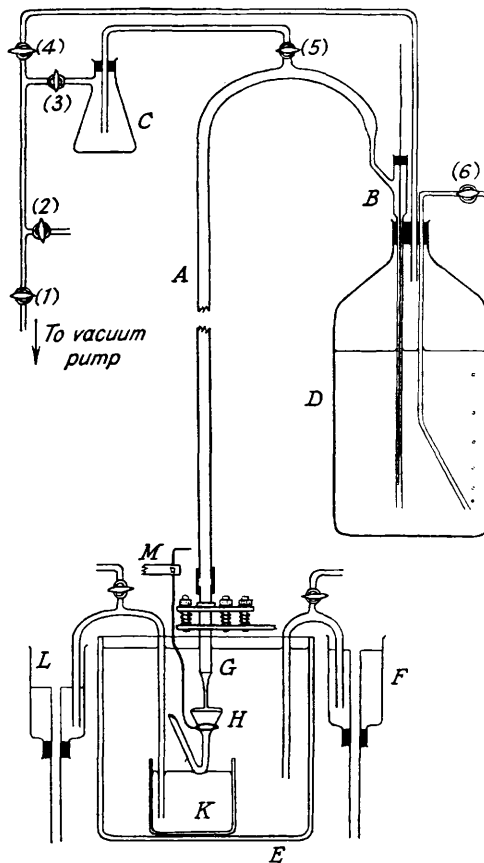
and the syphons leading to *F* and *L* were filled by suction. Taps (1) and (4) were opened, and the vacuum thereby applied to the air space in *D*, until the carbon tetrachloride rose in *A* to a position a few cm. below the liquid level in *D*. Tap (4) was then closed, taps (3) and (5) were opened, and the syphon in *A* was completed by drawing liquid up to tap (5). Taps (5), (3), and (1) were then closed, and taps (6), (2), and (4) opened. This resulted in a rapid flow of carbon tetrachloride down *A* into the vessel surrounding *G*. This vessel was then carefully lowered to bring *G* into contact with the water phase, and thus to form the liquid→liquid jet. The vessel was then removed from tank *E*, and the barrier *H* was moved into position. Taps (2) and (4) were closed, and the flow rate was adjusted by means of valve *B* to the desired value. Finally, the water level in tank *E* was adjusted so that orifice *G* was immersed to a depth of about 2 cm.

The Orifice.—The orifice used was similar to that previously described (Part *X*, *loc. cit.*), and the same levelling device was used. Under the conditions described, the carbon tetrachloride did not wet the lip of the orifice tube. The operative radius is therefore the internal radius, which was 0·600 cm.

Illumination and Measurement of Jet Dimensions.—Jet dimensions were measured with a travelling microscope fitted with vertical and horizontal vernier scales and an objective of 2″ focal length. The jet was viewed through, and in a direction at right angles to, the optically plane glass side of the tank *E*.

9 M

The position of G was so arranged that the jet was about 2 cm. from the plane side of tank E. The jet was illuminated directly from behind, using a strip light and diffuse screen.

Flow Rate.—The flow rate of carbon tetrachloride was determined by measuring the rate of flow from the outlet of vessel L. When the apparatus had reached equilibrium, the flow rate was constant within 0·25%.

Critical Flow Rate.—In general it appears possible to study jets of liquid-in-liquid at flow rates lower than those available in liquid–air systems of the same surface tension. For instance, for a jet of aqueous solution, $\gamma = 46$ dynes/cm., flowing into air, the minimum (or critical) flow rate is 4·4 ml./sec., whereas a jet of carbon tetrachloride flowing into water will remain stable at flow rates as low as 0·9 ml./sec. This is probably owing in part to the smaller density difference between the two phases.

Carbon Tetrachloride.—The carbon tetrachloride used was redistilled before each experiment, and its interfacial tension against water (44·8 dynes/cm. at 20°) checked after each distillation by the drop-volume method.

Temperature.—The measurements were carried out at room temperature, which did not vary beyond the limits 17° $\pm$ 1·5° during the experiments. This temperature variation is not significant.

DISCUSSION AND RESULTS.

Shape of Jet.—For any given orifice, the extent to which a jet of liquid narrows depends (*inter alia*) on the density of the jet liquid, the density difference between the two phases, and the surface or interfacial tension operating. At comparable flow rates, it has been found that a

FIG. 2.
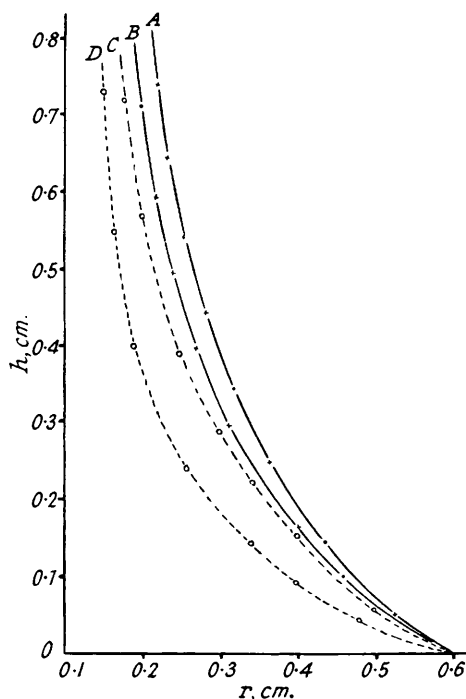
Curve.	Type of jet.	γ, dynes/cm.	Δ density, g./ml.	Flow rate, ml./sec.
A	CCl$_4$→H$_2$O	44·8	0·602	2·175
B	CCl$_4$→H$_2$O	44·8	0·602	1·495
C	H$_2$O→air	73·3	1·00	2·00
D	Ideal liquid→air	44·8	1·00	2·00

jet of carbon tetrachloride flowing into water narrows less rapidly than a jet of water flowing into air. Fig. 2 shows two liquid→liquid and two liquid→air curves relating horizontal jet radius (r) with distance from the orifice (h). Curves A, B, and C were obtained experimentally, and curve D shows the shape of a jet of " ideal " liquid (see Part X, *loc. cit.*) having unit density and a surface tension equal to the carbon tetrachloride–water interfacial tension, calculated for comparison with curve A. The influence of the factors referred to above on jet dimensions are clear from Fig. 2. As with the liquid→air jets, decrease in interfacial tension results in a

narrowing of the liquid→liquid jet. Although the two types of jet are of somewhat different shape, the influence of tension changes on radius is similar in the two cases, and the order of experimental error is comparable.

Two features arise from the less rapid contraction of the liquid→liquid jet : (1) The surface age at any given distance from the orifice is greater than that of the corresponding water→air jet. On the basis of tension changes only, the decrease in tension from the water–air to the carbon tetrachloride–water value should result in a decrease in the available surface age (cf. Fig. 7, Part X). However, this effect is outweighed by the density factor, and the measured age–h curves are compared in Fig. 3. (2) The initial contraction in surface area is less pronounced. This aspect is considered in detail in the following paper.

FIG. 3.
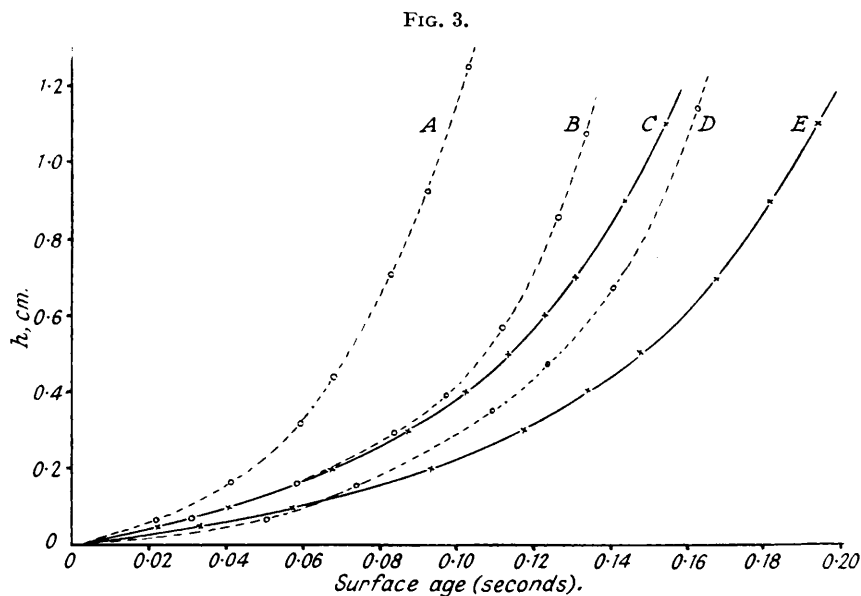
Type of jet.	Curve.	Flow rate, ml./sec.
$CCl_4 \rightarrow H_2O$	C	2·175
	E	1·495
$H_2O \rightarrow air$	A	3·0
	B	2·0
	D	1·0

Derivation of Equation applicable to Liquid–Liquid Interfaces.—Consider a jet of liquid (1), density ρ_1, flowing at a rate of f ml./sec. into a liquid (2), density ρ_2 (where $\rho_1 > \rho_2$) from an orifice submerged to a distance x below the surface of liquid (2). At a point A on the jet at a distance h_1 below the orifice, where the interfacial tension is γ_1 and the horizontal radius r_a, the total energy of unit mass of liquid is given by :

$$E = \text{Kinetic energy} - \text{potential energy} + \text{pressure energy} + \text{tension energy} . \quad . \quad (1)$$

It is assumed initially that (a) the external radius of curvature is sufficiently large that its reciprocal may be neglected, (b) the true internal and the horizontal radii are equal, and (c) the horizontal component of the kinetic energy is negligible. The pressure energy per unit volume of jet liquid at point $A = \rho_2 g(h_1 + x) + P$, where P is the atmospheric pressure, and the vertical kinetic energy is $f^2/2\pi^2 r_a^4$. Then the total energy (E_1) of unit mass of liquid at A is

$$E_1 = \frac{f^2}{2\pi^2 r_a^4} - (H + h_1 + x)g + \frac{1}{\rho_1}\left\{\rho_2 g(h_1 + x) + P\right\} + \frac{\gamma_1}{\rho_1 r_a}$$

where H is the head of liquid (1) required to produce the flow rate f. A similar expression will hold for the energy E_2 at a point B at a distance h_2 below the orifice, where the horizontal radius is r_b and the interfacial tension γ_2.

If a conservative system is assumed, E_1 and E_2 may be equated whence

$$\frac{f^2}{2\pi^2}\left(\frac{1}{r_a{}^4} - \frac{1}{r_b{}^4}\right) + \frac{1}{\rho_1}\left(\frac{\gamma_1}{r_a} - \frac{\gamma_2}{r_b}\right) = g(h_1 - h_2)\left(1 - \frac{\rho_1}{\rho_2}\right)$$

A more general form of this equation, which allows for the three approximations made above, may be developed, as described in Part X (equation 7). Thus, if at jet positions A and B the external radii are $r_{1(a)}$ and $r_{1(b)}$, the internal radii are $r_{2(a)}$ and $r_{2(b)}$, and the slopes of the $h–r$ curves are $(dh/dr)_a$ and $(dh/dr)_b$ respectively, then the equation becomes

$$\frac{f^2}{2\pi^2}\left(\frac{1}{r_a{}^4} - \frac{1}{r_b{}^4} + \frac{1}{r_a{}^4(dh/dr)_a{}^2} - \frac{1}{r_b{}^4(dh/dr)_b{}^2}\right) +$$

$$\frac{\gamma_a}{\rho_1}\left(\frac{1}{r_{2(a)}} - \frac{1}{r_{1(a)}}\right) - \frac{\gamma_b}{\rho_1}\left(\frac{1}{r_{2(b)}} - \frac{1}{r_{1(b)}}\right) = g(h_1 - h_2)\left(1 - \frac{\rho_2}{\rho_1}\right) . \quad . \quad (2)$$

For a jet of liquid of density ρ_1 equal to unity, flowing into air, ρ_2 may be neglected, and equation (2) then reverts to the equation applied in Part X (equation 7) to jets of aqueous solutions in air.

Application of equation (2) to the determination of interfacial tension requires a knowledge of the value of the energy at some point on the jet. The following two methods are possible.

(1) *Using a point of known tension as reference.* (a) If the surface is known to establish equilibrium early in the jet, any point lower in the jet may be taken as reference. In practice, this information is not generally available, and it is more frequently necessary to use the orifice as a reference point.

(b) *Using the orifice as reference point.* If A is considered as the orifice, and B a point sufficiently far down a jet of pure liquid that the external radius can be ignored, the sum of the B energy terms in equation (2) can readily be calculated, and the sum of the A (or orifice) energy terms obtained by difference. For a given orifice this energy sum (termed K_f) will depend only on the flow rate. If the measurement is repeated over a range of flow rates, it is possible to obtain a K_f–f calibration curve for the apparatus. Thus in systems where adsorption rates are slow, so that the surface tension at the orifice may be regarded as the pure liquid value, the sum of the energies at the orifice may be obtained from the K_f value at that flow rate. This was the method found to be most suitable for liquid→air jets (Part X); because of the rapid contraction which occurs with such jets in the neighbourhood of the orifice, it was difficult to measure directly, with sufficient accuracy, the internal and external radii at the orifice, and the dependent energy terms. However, with liquid→liquid jets, the reverse appears to be the case. In order to obtain a K_f–f calibration curve, it is necessary to carry out a series of experiments in which the depth of the orifice below the water surface is kept exactly constant, and this has proved difficult experimentally. On the other hand, the liquid→liquid jets contract less rapidly at the orifice. The various energy terms at the orifice can therefore be obtained with greater accuracy by direct measurement, and a K_f–f curve becomes of less importance.

(2) *Employing the point of intersection of internal and external radii.* At any point on the jet, the tension energy is expressed as $\gamma\left(\dfrac{1}{r_2} - \dfrac{1}{r_1}\right)$. If the point at which $r_2 = r_1$ is found, then at this point on the jet the tension energy makes no contribution towards the total energy E, which is then represented by the kinetic, potential, and pressure energies as shown in equation (1). By plotting the external and internal radii against h, the position on the jet at which the tension energy disappears is readily found. Fig. 4 shows typical $r–h$ curves. Point P may then be taken as the point of reference, and E readily evaluated from jet dimensions. The interfacial tension at any other point may then be calculated by means of equation (2).

It is important that, irrespective of the mathematical treatment involved, the accuracy with which tensions may be measured by the contracting-jet method depends on the magnitude of the tension term $\gamma\left(\dfrac{1}{r_2} - \dfrac{1}{r_1}\right)$, and thus upon the difference between the internal and the external jet radius. It is clear from Fig. 4 that the tension at point P is not available and that there is a portion of the jet in the neighbourhood of P over which r_1 and r_2 are so close as to give rise to considerable errors in the calculated tensions. Results calculated for such points are in parentheses in the Table. Interfacial tensions calculated for the carbon tetrachloride–water system, employing three different reference points, are shown in this Table. The apparatus

required for the production and study of a liquid→liquid jet is more difficult to manipulate than for the simpler liquid→air systems, and in consequence the experimental errors arising from measurement of jet dimensions are greater. Further refinement of the experimental technique should reduce such errors. In addition, it should be noted that any error in the

			Interfacial tension (dynes/cm.) calculated :		
f (ml./sec.).	h (cm.).	Horiz. r (cm.).	(a), if $\gamma = 44\cdot8$ at h value denoted by *.	(b), with orifice used as reference.	(c), with point of intersection of r_2 and r_1 used as reference.
1·495	0	0·600	(50·7)	—	(49·4)
	0·095	0·4575	(53·0)	(45·8)	(49·5)
	0·295	0·310	(36·5)	(39·7)	(35·5)
	0·395	0·2675	40·4	45·0	41·6
	0·495	0·2415	44·3	47·7	45·2
	0·595	0·215	41·7	44·4	42·5
	0·695	0·2005	48·5	47·3	45·7
	0·795	0·1875	45·8	47·1	45·6
	0·895	0·1775	45·9	47·9	46·5
	0·995	0·1710	47·7	49·5	46·5
	1·095	0·162	* 44·8	48·0	46·2
	1·195	0·156	47·0	48·8	46·2
1·597	0·998	0·1743	* 44·8		
	1·098	0·1667	45·3		
	1·198	0·1597	47·3		
	1·298	0·1533	43·6		
	1·398	0·1475	44·0		
3·289	1·007	0·241	43·8		
	1·107	0·233	* 44·8		
	1·207	0·224	45·0		
	1·307	0·217	46·2		

determination of the energy of unit mass (K_f) at the reference point is reflected in the calculated tensions throughout the jet. The somewhat high tensions calculated when using the orifice as reference probably arise from errors in the determination of r_1 and r_2 at the orifice. However, at

FIG. 4.

Flow rate, 1·495 ml./sec.
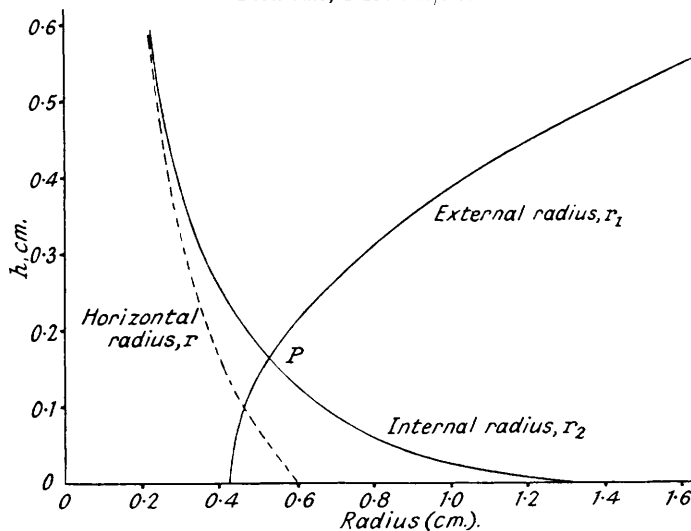
point P in the jet (Fig. 4) the energy of unit mass of liquid is independent of r_1 and r_2, and the use of P as reference point is considered to be the most reliable method of calculation. Nevertheless, the results in the Table are regarded as confirming that equation (2) may be applied to liquid→liquid jets, and that the order of accuracy is adequate to permit the study of adsorption rates and dynamic tensions, where tension changes of the order of 20—30 dynes/cm. may occur.

As the derivation of equation (2) was independent of the numerical values of the tension and density, the equation has general applicability.   Again, the liquid→air equation given in Part X (equation 7) is a special aspect of the present more general equation, and its applicability over a range of tension values has already been confirmed.