[A CONTRIBUTION FROM THE PHYSICAL CHEMISTRY RESEARCH LABORATORY OF NORTHWESTERN UNIVERSITY]

A Twin-Ring Surface Tensiometer. I. The Apparent Surface Tension of Potassium Chloride Solutions

BY MALCOLM DOLE AND JOHN A. SWARTOUT[1]

Introduction

The recently discovered Jones–Ray effect,[2] which is in sharp disagreement with the predictions of the surface tension of potassium chloride solutions based on calculations using the Debye interionic attraction theory of strong electrolytes as developed by Wagner[3] and later more completely by Onsager and Samaras,[4] has been the subject of theoretical papers by Bikerman,[5] Langmuir[6] and Dole.[7] The latter author, assuming that the Jones–Ray data represent true surface tension values, demonstrated by means of a statistical treatment involving the Gibbs adsorption equation that up to a concentration of 0.001 N adsorption of ions in the surface layer is pronounced, but that at higher concentrations further adsorption is negligible, ions being repelled from the surface although the concentration of ions in the surface layer is comparatively small. Because there is no good explanation for this required reversal in the behavior of the ions at 0.001 N, Bikerman in effect abandoned the Gibbs adsorption equation, postulating that in the low concentration range the work of separating positive and negative charges under the surface as the surface is increased, a factor which falls with rising concentration, outweighs the Debye theory work of repelling the ions from the surface, a term in the surface tension equation which rises with rising concentration, and so produces the Jones–Ray effect. Langmuir found it unnecessary to question the validity of the Gibbs equation; instead he states that the Jones–Ray experiment is subject to a methodical error which is due to a water film held on the glass or quartz surface of the capillarimeter by electric forces related to the ζ-potential. On addition of salt to the water the electric pressure responsible for the water film decreases (even at constant ζ-potential), the water film becomes thinner, and the radius of the quartz capillary effectively increases, thus causing a drop in the height of rise and an apparent decrease in surface tension, the Jones–Ray effect.[8] Langmuir calculates a decrease of 0.035 dyne cm.$^{-1}$ for the maximum effect while Jones and Ray find 0.015 dyne cm.$^{-1}$; so it is clear that Langmuir's theory accounts adequately for the magnitude of the apparent lowering of the surface tension.

It occurred to us that it would be interesting to measure the surface tension of aqueous solutions by an entirely independent method such as the ring method. We desired a method which did not involve the Langmuir film, or at least one in which the Langmuir film entered into the calculations in an entirely different way. But the ring method has never been developed to a very high accuracy; it is difficult to measure the breaking weight at the exact instant that the ring separates from the surface. Surface contaminations seem to collect on the ring each time it is torn from the surface, thus changing the contact angle and the magnitude of the pull. Nietz and Lambert[9] covered their rings with various solids such as hydrocarbons, alcohols, aldehydes, ketones, acids, etc., and in this way were able to demonstrate that the pull on the ring, P, varied with the contact angle θ, according to the equation

$$\log P = a + n \log (1 + \cos \theta) \qquad (1)$$

For certain wire sizes the pull may be independent of contact angle and *vice versa.* An advantage of using platinum–iridium rings is that it is possible to ignite the rings before each measurement, burning off the organic matter and restoring the ring to a chemically pure condition. In fact, a good test of the purity of water surfaces is to make a series of measurements with the ring not ignited; if no variation in pull is observed, particularly after a final measurement with a clean, ignited wire, the absence of surface contamination is proved.

Other difficulties of the ring method involve

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[1] University Fellow, 1939–1940.

[2] Grinnell Jones and W. A. Ray, THIS JOURNAL, **59**, 187 (1937).

[3] C. Wagner, *Physik Z.*, **25**, 474 (1924).

[4] L. Onsager and N. N. T. Samaras, *J. Chem. Phys.*, **2**, 528 (1934).

[5] J. J. Bikerman, *Trans. Faraday Soc.*, **34**, 1268 (1938).

[6] I. Langmuir, *Science*, **88**, 430 (1938).

[7] M. Dole, THIS JOURNAL, **60**, 904 (1938).

[8] The authors are indebted to Professor Grinnell Jones for the opportunity of reading his analysis and mathematical refinement of the Langmuir theory in advance of publication.

[9] A. H. Nietz and R. H. Lambert, *J. Phys. Chem.*, **33**, 1460 (1929).

variations in the angle of pull, errors due to vibrations, and uncertainties inherent in the geometry of the apparatus and surface curvature which the Harkins F-factor attempts to eliminate.[10]

We have developed a new relative ring method, described in the next section, which overcomes many of these difficulties, thereby reducing the relative error to 0.002%.

The New Twin-Ring Method

Although differential methods involving identical apparatus such as the Joule twin-calorimeter have been used many times before, no one seems to have adapted this idea to relative surface tension measurements. If two rings are hung from each end of a balance beam so that they dip below pure water surfaces and if the two liquids are simultaneously lowered, the ring on the side of the weakest net tension will break from the surface first. By adding weights to that side of the balance, it is possible to balance the forces until a small change of weight, in our experiment 0.1 mg., will cause one or the other ring to break from the surface. After the equilibrium weight for pure water has been found, dilute aqueous solution can be substituted for water in one of the pans and the balancing process repeated. The change in weight divided by the total pull gives at once the apparent change in the relative surface tension in passing from water to the dilute solution.

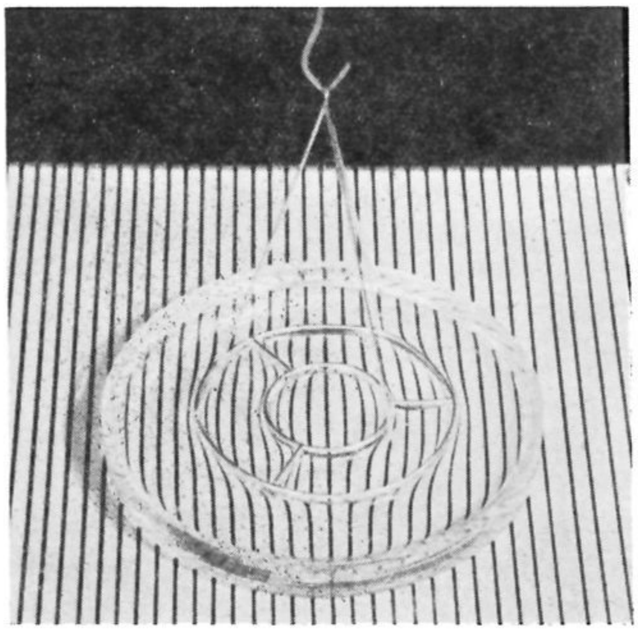

Fig. 1.

This method, which can be made as accurate as the Jones–Ray differential method, has the theoretical advantage of not involving a vertical film of the type discussed by Langmuir. It is unnecessary to know the weight at the exact moment that the maximum pull is reached as in the Harkins–Young method, or at the moment that the film breaks from the surface; keeping the weight constant, *observation is made only of the side at which the ring breaks*. Because of the twin-ring feature of the method, many difficulties appear equally on both sides of the apparatus and thus cancel; also by virtue of the substitution technique the angle of pull and orientation of rings need not be considered, provided, of course, that they remain constant for different measurements. The necessity for applying a Harkins F-factor correction seems to be eliminated, at least for dilute solutions.

The chief difficulties of the method are its tediousness and, because of the frequency with which the rings must be pulled from the surface, the requirement of scrupulous cleanliness of surface. This last difficulty might, on the other hand, be considered an advantage as the experimental necessity for dealing with uncontaminated surfaces lends credibility to the final data.

Experimental Details

The Rings and Pans.—Each ring (see Fig. 1) was actually a double ring; that is, it was made of two concentric rings of 3 and 6 cm. in diameter, respectively, which were connected by three equally spaced wires, the rings, cross wires and supports being made of a platinum–10% iridium alloy, 1 mm. in diameter. Three equally placed vertical supports connected to the outer rim met at an apex consisting of a small 5-mm. ring which enabled the ring system to be hung on the hook of the long rod attached to the balance. Total dry weight of the rings was about 12.5 g. each. The surface tension pull on each ring was approximately 5.7 g., being about 16% greater than one would calculate theoretically (this is the Harkins F-correction). These large ring systems were used in order to give a relative accuracy to 0.002%, corresponding to 0.1 mg.—the accuracy of the balance. This accuracy is necessary in a study of the Jones–Ray effect which itself amounts only to 0.02%.

The ends of the long wires on which the rings were hung were bent into a hook and filed to a sharp V (see Fig. 1) so that each ring would always hang in the same plane both vertically and horizontally. The pans holding the water and solution were made as large (11 cm. in diameter) as the length of the balance beam and the size of auxiliary apparatus would allow. Harkins and Jordan[11] demonstrated that, within the accuracy of their experiments, the pull on their ring of 3.65 cm. in diameter became independent of the size of the pan for pan diameters of 8

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[10] W. D. Harkins and H. F. Jordan, THIS JOURNAL, **52**, 1751 (1930); B. B. Freud and H. Z. Freud, *ibid.*, **52**, 1772 (1930).

[11] W. D. Harkins and H. F. Jordan, *ibid.*, **52**, 1751 (1930).

or 9 cm. or greater; in other words, when 2.5 cm. of liquid separated the ring from the side of the pan. In our experiments the separation also amounted to approximately 2.5 cm.

Containing Vessel and Water-Bath.—The vessel containing each pan and surrounding water-bath illustrated in Fig. 2, where the general arrangement of the whole apparatus may be seen, was modeled after that of Harkins and Jordan.[12] Water or solution could be run into the pans through tubes A and A′ while the excess overflow was sucked out at B and B′. The level of liquid in the two pans was controlled by the height of mercury in the two bulbs C and C′ and these heights of mercury were in turn controlled by the air pressure produced by the exterior column of mercury with leveling bulb D. Slight variations in the height of the liquid level in each pan made no detectable difference in the final equilibrium weight; yet the levels were always adjusted to bring the pointer of the balance within one small division of the zero mark during the lowering operation. In the actual experiments the liquid levels could be lowered uniformly and slowly making use of a screw adjustment attached to the leveling bulb D.

The level of water in the surrounding bath is indicated in the illustration; usually temperature equilibrium was attained in one hour or less. Evaporation at the liquid surface in the pans was retarded if not entirely eliminated by the presence of saturated vapor arising from the overflow liquid in the jars holding the pans and also from the water of the water-bath. Evaporation of the whole system was prevented by metal covers between A and B and A′ and B′. The jars holding the pans were not covered and there may have been diffusion of vapor from one jar to the other; perhaps our difficulty in obtaining reproducible data in the case of the most concentrated solution studied, the 1 *N*, may have been due to this effect.

The temperature was maintained at 25.00 ± 0.01° with the aid of a new cold cathode type tube relay invented by Dr. A. A. Frost and Dr. P. G. Smith of this Laboratory. The circuit for this relay, which is remarkably simple, will be published elsewhere; here it is sufficient to say that the tube was a OA 4-G tube, argon filled, containing a small ring anode and disk cathode. The whole circuit is the most efficient and fool-proof with which the authors have had experience.

Balance.—An ordinary analytical balance whose zero point could be reproduced to 0.1 mg. was used; for the direct tension measurements, a simple chain mechanism (not shown in Fig. 2) was built into the balance and calibrated. The absolute surface tension determinations, made in the usual way, using one ring only, were accurate to ±5 mg. The pans of the balance were removed for the relative measurements and small stirrups, E, E′, Fig. 2, to hold the weights were hung on the beam hooks. The position of the balance was not fixed as experience showed it should have been. Most of the time the balance was stationary, but when the apparatus had been entirely taken apart for cleaning and reassembled, the water balancing weight usually had changed, indicating that the balance had probably not been returned to its exact original position (the total pull on the rings depended on the angle and orientation of the rings because the rings were neither exactly plane nor the direction of pull exactly vertical). The entire apparatus was placed on a large cement block which was separated from the floor by rubber to reduce vibrations.

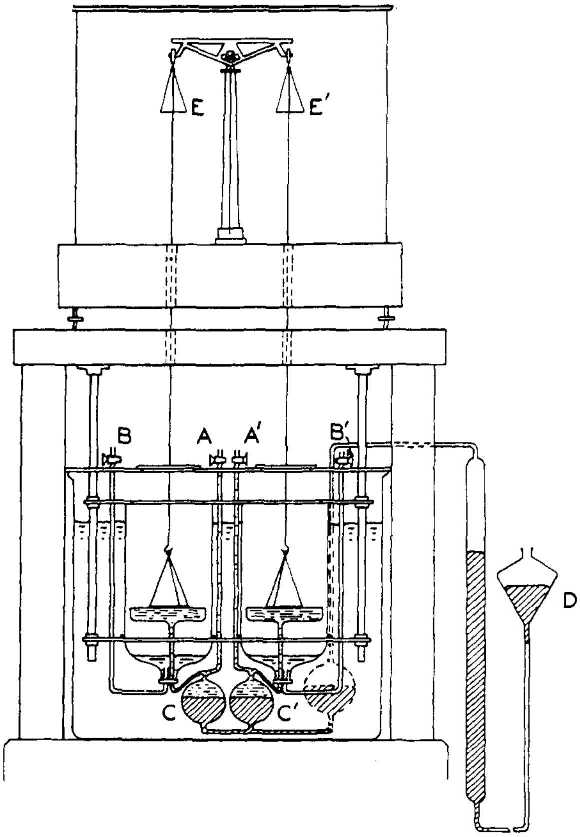

Fig. 2.

Solutions.—Using the density data of Jones and Ray, all the potassium chloride solutions were made up according to the volume-normal scale at 25°. Weights were reduced to vacuum. Commercial c. p. potassium chloride was used as the salt without further recrystallization. Repetition of some of the work using once-recrystallized and twice-recrystallized salt showed no significant difference. The chief impurities causing irregularities in the results are organic compounds inasmuch as most salts behave alike in respect to their influence on the surface tension of the solvent. The salt was freed of organic matter by fusion.

Purity of the water or rather freedom of the water surface from organic contamination is vital for the success of the twin-ring method. Conductivity water distilled in a Kraus still and stored overnight in a tall grease-separating column after the manner of Jones and Ray proved to be satisfactory. Impurities present on the water surface in some of the rejected experiments probably were introduced into the water from unclean receptacles.

Cleaning Technique.—Not only is purity of the water and salt important, but the most rigorous cleanliness of flasks and pans is absolutely essential. In fact it was not until a satisfactory cleaning procedure had been adopted

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[12] This apparatus was originally designed by T. F. Young; see Harkins, Young and Cheng, *Science*, **64**, 333 (1926).

that the twin-ring method appeared at all possible. Many surface chemists sweep their aqueous surfaces free of grease immediately before the surface tension measurements using barriers either coated with di-cetyl or of pure metal, but attempts by us to apply this purification technique were unsuccessful because of the inaccessibility of the surface and because the twin-ring method requires a whole series of measurements for the determination of one balance point. We were forced, therefore, to use clean apparatus and clean water, materials which would remain clean throughout the experiment. The elimination of grease from our apparatus was finally accomplished by the following routine: Hot boiling 1:1 mixture of nitric and sulfuric acids was poured into the pans in the constant temperature-bath and allowed to stand overnight. After removal of the acid and rinsing with distilled water, steam generated from water which had previously been refluxed over alkaline potassium permanganate for six hours was forced through the filling tubes A and A′, thereby steaming out all the glass surface with which the solutions were later to come into contact (the solutions and water were run into the apparatus directly from the tall grease-separating towers). After the steaming process, which served chiefly to remove acid vapors, the constant temperature water-bath was refilled and the pans rinsed with the purest water. The *p*H of the water in each pan was then determined with a Cameron *p*H meter and the rinsing continued until the *p*H of the water in the pans equalled that in the tall columns, about *p*H 6.0. In this way complete removal of acid could be secured.

General Procedure.—Water was run into the apparatus through tubes A and A′ until the pans overflowed. After standing for twenty to thirty minutes for temperature equilibrium to be attained, the dishes were overflowed again to renew the surface and the water levels were lowered slightly. The platinum–iridium rings, after ignition to red heat, were suspended on the long rods attached to the balance beam (see Fig. 2) and any difference in the dry weight of the two carefully balanced by the addition or removal of weights to ±0.1 mg. The liquid levels were then raised until contact was made with each ring when the beam of the balance was lowered to put the balance into operation. By a gradual lowering of the mercury leveling bulb, the liquid levels were then slowly lowered over a five-minute interval until one ring broke free. Weights were next added to that side of the balance and the process repeated until the addition or subtraction of 0.1 mg. would cause either the right-hand ring or the left-hand ring to break first from the surface. After four or five such observations the rings were usually removed from the apparatus and ignited to remove any trace of organic matter that might have accumulated on them, and the final adjustment of the weights made.

TABLE I

TYPICAL WATER BALANCE-WEIGHT STANDARDIZATION

Apparatus filled at 1:50 P. M.; pans overflowed with water at 2:25; temperature 25.00 ± 0.01°.

Time	Weight on left balance arm, g.	Ring breaking (L = left, R = right)
2:40	0.0078	L
2:43	.0082	R
2:46	.0080	R
	Rings removed and ignited	
2:57	0.0079	R
3:00	.0078	R
	Pans overflowed and rings ignited	
3:20	0.0080	L
3:25	.0082	R
3:31	.0081	R
	Rings removed and ignited	
3:45	0.0080	L
3:52	.0081	R

Accepted balance-weight, 0.00805.

Table I illustrates one such determination of the water balancing point (see Table IV for another example). When the water balancing weight was approximately known in advance, the final balancing point could be reached rapidly, in half an hour or sometimes in fifteen minutes.

In Table II we have collected all of the water standardization weights so that the agreement in the results from day to day may be seen. That these weights differ from zero is due, of course, to the fact that the rings were not exactly symmetrical in shape or in orientation. The sudden changes in the water standardization values observed after February 22, March 28, April 15 and 25 are probably to be explained by shifts in the position of the balance or by slight changes in the shapes of the rings. Within these periods satisfactory constancy of the experimental observations was attained; particularly were the results quite gratifying and within the experimental sensitivity of the balance during the interval February 22 to March 28 when ten measurements were made having a maximum fluctuation of only 0.2 mg. In fact it was easier to attain a constant water balance-weight value than a constant zero point of the balance.

TABLE II

WATER STANDARDIZATION WEIGHTS

Date	Weight on left balance arm, g.	Date	Weight on left balance arm, g.
1/22/40	−0.0161	3/14/40	+0.00815
1/30/40	− .01600	3/16/40	.00805
1/31/40	− .01635	3/28/40	.00805
2/ 8/40	− .01610	4/ 3/40	.01825
2/19/40	− .01605	4/ 3/40	.01830
2/22/40	− .01610	4/ 4/40	.01805
2/26/40	+0.00795	4/10/40	.01805
2/28/40	.00805	4/15/40	.01805
2/29/40	.00805	4/25/40	.01930
3/ 2/40	.00815	6/ 6/40	.01375
3/ 4/40	.00805	6/ 7/40	.01385
3/ 6/40	.00805	6/10/40	.01385
3/ 8/40	.00805		

After completing the water standardization the left-hand pan was emptied and solution added. The process of determining the equilibrium weight was then repeated. The results of all our experiments are given in Table III.

To calculate the apparent relative surface tension, it is necessary to know the total surface pull on the left-hand ring. This weight, also given in Table III, was obtained by direct observation; the uncertainty is ±5 mg., which is negligible for the dilute solutions, and which amounts only to 0.00002 unit in the relative surface tension, γ/γ_0, for the 1 N potassium chloride solution the relation being

$$\Delta(\gamma/\gamma_0) = -(w/g^2)(\Delta g) \qquad (2)$$

where w is the change in weight between the water and solution balance weights, g is the total pull on the ring, and Δg the uncertainty in g (holding w constant).

The relative surface tension, neglecting any consideration of the Harkins F-factor correction, is calculated from the simple equation,

$$\gamma/\gamma_0 = (g + w)/g \qquad (3)$$

TABLE III

APPARENT RELATIVE SURFACE TENSION AS DETERMINED BY THE TWIN-RING METHOD AT 25°

N of KCl	g	w	γ/γ_0	γ/γ_0 (Jones and Ray)
1	5.699	0.1309	1.0230	1.0230
1 (once recr.)	5.770	.1340	1.0232	
1 (once recr.)	5.706	.1436	1.0252	
1 (twice recr.)	5.706	.1378	1.0242	
0.09937	5.770	.0148	1.00257(?)	
.1	5.770	.01570	1.00272	1.00273
.02	5.770	.0017	1.00030	1.00047
.01	5.770	− .0003	0.99993	1.00013
.005	5.770	− .00105	.99982	0.99998
.002	5.770	− .0013	.99977	.99988
.002		− .0010	.99982	
.001	5.699	− .00175	.99969	.99982
.001	5.770	− .00170	.99970	
.001 (once recr.)	5.706	− .0016	.99972	
.0005	5.770	− .00045	.99992	.99983
.0001	5.770	− .00035	.99994	.99997

Some uncertainty is attached to the value for the 0.09937 N solution because considerable difficulty was experienced in finding the equilibrium weights. All the data of Table III were obtained using commercial C. P. salt except in the cases indicated. Since Jones and Ray's data showed a maximum of their effect at 0.001 N, solutions of this concentration were studied three times under different conditions of salt purity and different values of g. The maximum deviation between all three data amounted only to 0.00003 unit in γ/γ_0 or 0.003%. Thus it is apparent that the twin-ring method is as precise as the differential capillary-rise method of Jones and Ray. Our inability to obtain closely agreeing values in the case of the most concentrated solution where the maximum deviation is 0.2% remains unexplained at the present time; the fact, however, that the average of our four values, 1.0239, agrees within 0.09% with that of Jones and Ray indicates that our differential method practically eliminates the necessity of considering the Harkins F-factor correction in the dilute solution range.

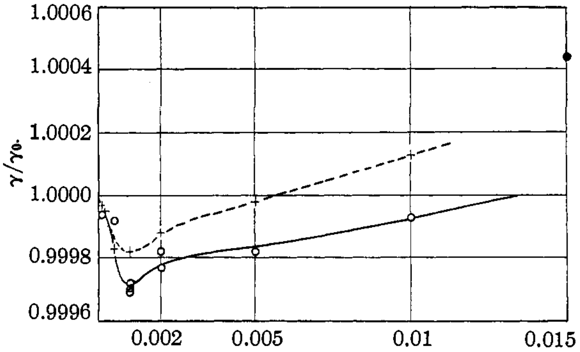

Fig. 3.—Apparent relative surface tension of potassium chloride solutions at 25°: ○, Dole and Swartout; +, Jones and Ray; ●, Schwenker at 0°.

Discussion of Data

A study of the data in Table III and in Fig. 3 shows that at low concentrations our values are slightly lower than those of Jones and Ray and Schwenker[13] (the latter's value determined at 0°),[13] but at 0.1 N almost identical with Jones and Ray's and probably somewhat higher at 1 N. However, the most interesting feature of our work is that the Jones–Ray effect is definitely confirmed, in fact not only is the magnitude of the surface tension lowering greater in our case, but the concentration of the minimum is also 0.001 N, the same concentration for the minimum as found by Jones and Ray. There is no doubt in our minds that the Jones–Ray effect exists in the case of surface tension measurements made using rings as well as capillary tubes. But the difference in the data for the two methods, amounting to 0.01% in relative surface tension at

(13) G. Schwenker, *Ann. Phys.*, [5] **11**, 525 (1931). See also the earlier investigation of A. Heydweiller, *Ann. Physik*, [4] **33**, 145 (1910).

0.001 *N* and 0.02% at 0.01 *N*, a difference apparently greater than the experimental uncertainty, suggests that the Jones–Ray effect is not identical as measured by the two methods. Furthermore, if this difference is real, we can conclude that either the ring or the capillary method does not give true relative surface tension data, or perhaps that neither does.

We now have to ask ourselves whether the Langmuir[6] vertical film theory postulated to account for the Jones–Ray effect can in any way be applicable to surface tension data obtained by our twin-ring method. Consider a possible increase in the diameter of cross section of the wire forming the rings as a result of a Langmuir film between platinum alloy and water. It is easy to calculate in this case that any "thickening" of the wire of the ring decreases the internal periphery to the same extent that the external periphery is increased with a consequent cancelling of effects; furthermore, the large ring radius is so great that the Langmuir "Δr" is negligible in comparison. The Harkins F-factor correction is also a function of the ring thickness, but a change in diameter amounting to 10% would be required to give the Jones–Ray effect; this is roughly 1000 times greater than the change in diameter expected on the basis of the Langmuir theory.

In considering the possibility that the weight of the rings might be increased by a Langmuir film, it should be remembered that water does not wet or adhere to platinum in the way that it wets glass; when the platinum ring is torn from the water surface, the water collects on the platinum in little drops and the vertical supports of the ring seem to shed water completely, leaving them apparently dry, whereas when a glass rod is drawn out of the water it remains "wet." We have attempted to answer this question experimentally by drying both rings, then submerging the right-hand ring as far as possible, vertical supports submerged to the depth of a centimeter, while the left-hand ring was allowed just to touch the surface. If a Langmuir film adhered to the right-hand ring, it should have become heavier, causing the left-hand ring to break from the surface. Three experiments were carried out, the first indicating a change in weight equal to 1.7 mg., the value of *w* for 0.001 *N* potassium chloride, but the second and third indicating no significant change in weight. Data for the last experiment are given in Table IV. We conclude, therefore, that the Langmuir film theory cannot be applied to our method.

TABLE IV

EXPERIMENT TO TEST EXISTENCE OF VERTICAL FILM

Wt. on left, g.	Ring breaking
Pure water in both pans	
0.0139	R
.0138	R
Rings ignited	
0.0138	L
.0139	R
.0138	L
Balance point for pure water 0.01385	
Both rings ignited, right ring submerged	
0.0139	L
.0145	R
Weight of film not greater than 0.7 mg.	
Both rings ignited, right ring submerged	
0.0140	R
Weight of film not greater than 0.2 mg.	

One other rather rough experiment was carried out to test the applicability of Langmuir's theory. A 10^{-6} *M* thorium nitrate solution was added to the left dish when the balance-weight was found to have changed by only 0.3 mg., an almost negligible amount. Thorium nitrate solutions are believed to have a marked influence on the ζ-potential, but the thorium may have been in the colloidal state in our experiment.

We are not yet ready, however, to assert that our measurements represent solely true variations in surface tension although the fact that the Jones–Ray effect is observed with the ring as well as the capillary rise method lends strength to this possibility. It may be that the contact angle between the platinum alloy–solution interface and the solution–air interface changes with addition of salt to water; for example, organic impurities on the rings raise the contact angle, and so lower the net tension. This is equivalent to assuming that the Harkins F-factor, which amounts to 16% and which we have assumed to be constant, changes with the concentration. It would be interesting to have the Jones–Ray effect confirmed by still a third independent method, such as the drop-weight method or the pendant drop method. Until we know whether the Jones–Ray effect is a true surface tension effect or not, it is rather futile to attempt to invent theories to explain it; the chief purpose of this paper is the description of the twin-ring tensiometer.

Summary

1. A new twin-ring tensiometer enabling the error of relative surface tension measurements to be reduced to 0.002% is described.

2. Surface tension measurements of potassium chloride solutions at 25° have been made over a wide concentration range. Agreement with similar data of Jones and Ray is so close that no consideration need be made of the Harkins F-factor.

3. The data confirm the Jones–Ray effect; the minimum of the surface tension occurs at 0.001 *N* potassium chloride solution as in Jones and Ray's work, but we find the apparent lowering of the surface tension to be 0.03% instead of 0.02%.

4. We have not been able to demonstrate any applicability of the Langmuir film theory to our data, and conclude, therefore, that the validity of the Langmuir theory as an explanation of the Jones–Ray effect, is questionable.

EVANSTON, ILLINOIS RECEIVED AUGUST 13, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE UNIVERSITY OF MARYLAND]

Combustion of Methane: Displacements of Mixtures Giving Maximum Flame Velocities[1]

BY A. R. T. DENUES[2] WITH WILBERT J. HUFF

I. Introduction

In the slow propagation of flame in gases it has long been recognized and generally accepted that mixtures giving maximum flame velocities[3] are displaced toward excess combustible from the stoichiometric mixtures for complete combustion.[4,5] These displacements[6] are a fundamental characteristic that must be accounted for by any adequate theory of the mechanism of flame propagation. In practical applications where the maximum thermal or mechanical output must be secured from minimum gas volumes, or where variations in thermal output may be critical, an understanding of the magnitude of this displacement and its variation with changes in mixture composition may be important.

Despite the long and general recognition of displacements, some recent writers have apparently doubted their existence for methane and for natural gas consisting principally of methane[7]; this called attention to the phenomenon for this gas. Computations based upon published data for carbon monoxide and hydrogen[8] give regular relationships between the displacements and the content of oxygen in the atmosphere. In contrast, the analogous relation for methane was not established by available data.

Thus, it was noted from Jahn's data,[8] which are perhaps the most complete measurements, made by the burner method, of flame velocities pertinent to this discussion, that curves relating the displacements and the oxygen content of the atmosphere used for the combustion of hydrogen and of carbon monoxide could be derived that appeared continuous and exhibited maxima, but that a similar relation for methane was quite uncertain. The positions of the maxima of flame velocity reported by Jahn for methane, excluding apparently extrapolated values, lead to displacements of 0.9, 1.1, 1.2, 1.3, 1.2, 0.9 and 0.0 in order as the oxygen content of the atmosphere increases in the series 21, 25, 30, 40, 60, 80, and 98.5 volume-per cent. Except for the value for combustion with substantially pure oxygen, these displacements average 1.1 with an average deviation of about 0.1. In view of the lack of precision measures in Jahn's paper and the magnitude of the precision measures recorded for similar work in a later section of the present discussion, it must be concluded from Jahn's data that the displacements for methane in atmospheres other than pure oxygen are substantially independent of the oxy-

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[1] Abstracted from a thesis submitted by A. R. T. Denues, Research Fellow in Chemical Engineering, 1938–1939, in partial fulfillment of requirements for the degree of Doctor of Philosophy in June, 1939.

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[3] "Flame velocity" as used here denotes the rate of movement of flame during the slow, uniform period, relative to the unburned gas and in a direction normal to the flame surface.

[4] E. Mallard, *Ann. Mines*, [7] **7**, 355 (1875).

[5] W. Michelson, *Ann. Phys. Chem.*, [3] **37**, 1 (1889).

[6] This divergence of mixture giving maximum flame velocities from the stoichiometric mixtures for complete combustion will be abbreviated in this paper to the term "displacement."

[7] Thus: Haslam and Russell, "Fuels and their Combustion," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 268, state that the maximum speed occurs when the methane and oxygen are in combining proportions, and "Combustion," American Gas Association, New York, N. Y., 1932, p. 92, gives a curve of flame speed *vs.* primary air–gas ratio that indicates that the maximum speed natural-gas–air mixture is displaced toward excess air.

[8] G. Jahn, "Der Zündvorgang in Gasgemischen," R. Oldenbourg, Berlin, 1934.