

Two pairs of conjugate solutions in the binodal area, not saturated with solid sodium nitrate, were determined by direct and complete analysis of the equilibrium phases formed from known mixtures of the three components (complexes 11 and 12 of Table I). The two tie-lines so obtained are sufficient to indicate that the plait point of the binodal curve must lie considerably over toward the dioxane-rich side. Two other points on the binodal curve (numbers 10 and 13 of Table I) were determined synthetically by a kind of titration: addition of solid sodium nitrate, in successive small portions, with shaking, to known weights of suitable mixtures of water and dioxane. The appearance of a turbidity indicating the formation of a second liquid marked a point on the binodal curve. In experiment no. 13 the liquids so formed were almost immediately approximately equal in volume, indicating proximity to the plait point, which, however, was not further investigated.

The last five values (a-e) listed in Table I were obtained in some earlier more precise work on the effect of water on the solubility of sodium nitrate in dioxane, using more highly purified dioxane and sodium nitrate. These mixtures were rotated for at least two weeks, and were analyzed in duplicate, and only for sodium nitrate, the percentage of water in the equilibrium solutions being calculated from the exact composition of the mixed solvent, prepared by weight. An enlarged plot of these special points for this region of the system is shown in Fig. 2, in which the shape of the curve

is seen to be similar to the corresponding portion of the solubility curve of silver nitrate in dioxane containing small amounts of water.<sup>3</sup>

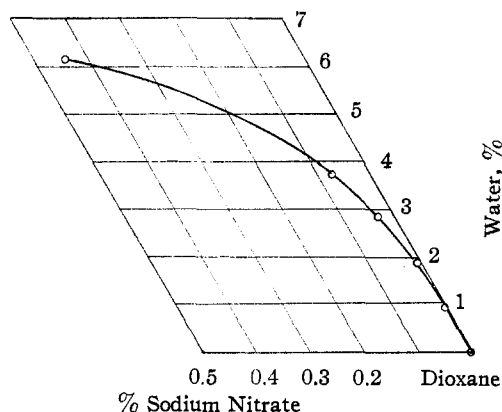


Fig. 2.—Effect of water on solubility of sodium nitrate in dioxane, at 25°.

### Summary

The solubility relationships in the ternary system sodium nitrate–dioxane–water at 25° have been investigated, using a direct analytical determination of water in the equilibrium liquids by means of the Karl Fischer reagent. A small region of immiscible liquids appears, for solutions containing between 52.13 and 93.40% dioxane and between 17.84 and 0.44% sodium nitrate. Exact determinations are also given for the solubility of sodium nitrate in dioxane containing very small percentages of water.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## The Relative Surface Tension of Potassium Chloride Solutions by a Differential Bubble Pressure Method<sup>1</sup>

BY F. A. LONG AND G. C. NUTTING

The surface tensions of dilute aqueous solutions of electrolytes have been investigated recently by a capillary height<sup>2</sup> and by a ring method.<sup>3</sup> Both show a minimum in the surface tension at about 0.001 normal although the depth of the minimum is considerably larger for the ring method. To explain the discrepancy of these results from the theoretical Onsager–Samaras<sup>4</sup> prediction, two

different types of explanations have been advanced. Dole<sup>5</sup> and also Bikerman<sup>6</sup> have developed theories on the assumption that the results are true surface tensions. Langmuir<sup>7</sup> postulated that the true surface tension did not have a minimum and that the experimental results were due to the neglect of the zeta potential at the silica–solution interface. This theory has been discussed in more detail by Jones and Frizzell.<sup>8</sup>

(1) Presented at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) Jones and Ray, *THIS JOURNAL*, **59**, 187 (1937); **63**, 288, 3262 (1941).

(3) Dole and Swartout, *ibid.*, **62**, 3089 (1940).

(4) Onsager and Samaras, *J. Chem. Phys.*, **2**, 528 (1934).

(5) Dole, *THIS JOURNAL*, **60**, 904 (1938).

(6) Bikerman, *Trans. Faraday Soc.*, **34**, 1268 (1938).

(7) Langmuir, *Science*, **88**, 450 (1938).

(8) Jones and Frizzell, *J. Chem. Phys.*, **8**, 986 (1940).

The present paper reports an investigation of the surface tension of dilute potassium chloride solutions using another method of measurement. The procedure employed is a differential adaptation of the maximum bubble pressure method and is in essence a modification of the method devised by Warren.<sup>9</sup>

**The Method.**—For a capillary tube small enough so that the bubble formed is a true hemisphere the equation for the maximum bubble pressure method is

$$P_{\max.} = gd\rho + (2\gamma/r) \quad (1)$$

where  $d$  is the depth of immersion of the tube,  $\rho$  is the density difference between the liquid and the gas,  $\gamma$  is the surface tension and  $r$  is the radius of the tube. As this equation indicates the method is free from any assumption about the contact angle. Warren evolved a differential adaptation of this method by using two identical capillaries connected to a single source of gas under a slight pressure. These capillaries were immersed below the liquid surfaces of two different vessels, one containing pure solvent and the other the solution whose relative surface tension was to be measured. The heights of the vessels and thus the depths of immersion of the capillaries were varied with micrometer screws until bubbles came alternately from the two tubes. The maximum pressure in the bubbles is then the same and by measuring the depths to which the two tubes are immersed and the densities of the solutions, the ratio of the two surface tensions can be obtained.

The method used in the present work eliminates the difficult task of measuring the depths of immersion with precision and substitutes a measurement of surface areas and volumes. A sketch of the apparatus is given in Fig. 1. In this figure A and A' are two similar circular glass vessels of about two-liter capacity and inner cross sections of about 250 sq. cm. The walls of these vessels are very nearly perpendicular. C is a bent T made of Pyrex glass through which gas flows. The two ends of this T that dip into the solutions have identical capillary exits from which the bubbles emerge. Saturated nitrogen gas under a pressure of a few cm. of water enters the other opening of the T and its rate of flow is regulated by a valve V which is an ordinary Hoke needle valve. The glass rod R which dips into the right vessel is attached to a screw of known pitch. Each vessel contains a stirrer, S and S'. In the actual setup the two vessels rest on a very rigid framework which allows them to be immersed in a constant temperature water-bath. The T apparatus is attached rigidly to the same framework. The stirrers and the rod R are attached to a separate rigid frame. L and L' are close fitting glass lids with holes for the tubes and rods.

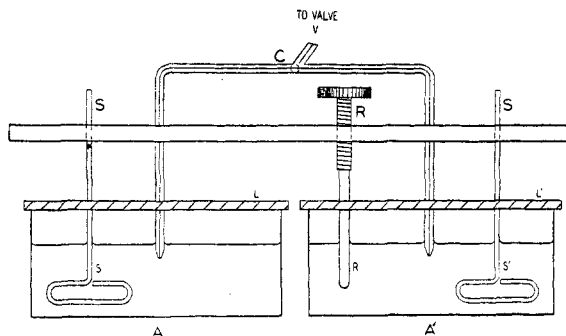


Fig. 1.—Differential bubble pressure apparatus.

The cross sectional areas of the two vessels were obtained by eight measurements of their diameters, taken at the height to which 1000 ml. of solution came. The net areas were obtained by subtracting the cross sectional areas of the rods and tubes that were present in the actual setup.

The tips of the T apparatus were obtained by breaking a selected piece of capillary tubing with a very nearly circular cross section. Tubes were used only if the breaks were smooth and perpendicular to the axis of the tube. By using two ends of a given break it was certain that the two orifices had the same diameter. The circularity and the diameter of the orifices were determined by six different measurements with a traveling microscope. Tubes were rejected if any diameter differed by more than 1% from the average. The diameter of the capillaries as measured by a traveling microscope is certainly not accurate to more than a few tenths of a per cent. but as will appear later, this is sufficient. Before use the area of the ends of the capillaries was reduced to approximately four sq. mm. by tapering the ends on a grinding wheel.

To make a surface tension determination the two vessels are filled with just less than 1000 ml. of water, placed in the water-bath and the stirrers, rod, lids and T apparatus are put in place. After an hour or so has elapsed, to ensure temperature equilibrium, a slow current of gas is allowed to pass into the T apparatus. This gas is at a constant pressure of 10 to 12 cm. of water and the valve V is adjusted so that bubbles form from one of the orifices at a constant rate of one bubble every twenty to forty seconds. Water is added to the vessels until a single drop will cause the bubbles to shift from one orifice to the other. The water in the two vessels is stirred, allowed two to four minutes to equilibrate and then the rod R is turned so that bubbles come with equal frequency from the two orifices. This indicates equal maximum bubble pressures and represents the zero point for the apparatus. The position of the rod R (which is equipped with a scale to measure the distance it is immersed) is a measure of this balance point. Three or four further determinations of this zero point are made. Usually the apparatus will show a constant balance for an hour or more. Since the two vessels contain only water, at the balance point the depths of immersion of the two tips are identical.

After the zero point is established, a few ml. of a potassium chloride solution of known concentration is added to one of the vessels from a weight pipet. This shifts the bubbling entirely over to the other orifice. Water is added to the other vessel, again from a weight pipet, until

(9) Warren, *Phil. Mag.*, [7] 4, 358 (1927).

the bubbles just shift back to the first orifice. The two vessels are then stirred and the final adjustment to a new balance, the condition where bubbles come from both orifices with equal frequency, is made by changing the position of the rod R. This new balance is checked as before to see whether it remains constant. If so the apparatus is disassembled, the depths to which the tips are immersed is determined to about 0.1 mm. and the final volume of the dilute potassium chloride solution in the one vessel is determined to about two ml.

The equation for the calculation of the relative surface tension follows directly from equation (1). At the initial balance since both vessels contain water and since the orifices are identical the equality of maximum pressures means that  $d_0 = d_1 = d$ . At the final balance point there is again a state of equal maximum bubble pressure. Hence

$$P_{\max.} = g\rho_0(d + \Delta d_0) + \frac{2\gamma_0}{r_0} = g\rho_1(d + \Delta d_1) + \frac{2\gamma_1}{r_1} \quad (2)$$

where the subscript zero refers to the water and the subscript one to the potassium chloride solution. Neglecting for the moment the zeta potential effect,  $r_0 = r_1$ .  $\Delta d_0$  and  $\Delta d_1$  are the increases in depth of immersion of the two tips. These can be calculated precisely from the surface areas of the two vessels and the volume increases caused by the additions of water and salt solution and by the change in position of rod R. A transformation gives

$$\frac{\gamma_1}{\gamma_0} = RST = 1 + \frac{gr}{2\gamma_0} [d(\rho_0 - \rho_1) + (\Delta d_0\rho_0 - \Delta d_1\rho_1)] \quad (3)$$

For dilute electrolyte solutions, when the capillaries are immersed only slightly, the last term involving the precisely known  $\Delta d$ 's is considerably larger than the one involving  $d$  which is less precisely known.

For large capillaries the measured radius should not be used in the above equation; instead the problem should be solved by the use of the Bashforth and Adam tables.<sup>10</sup> For water solutions and for tubes of radius smaller than 0.07 cm., a corrected radius can be obtained from the Schrödinger<sup>11</sup> approximation

$$\frac{2\gamma}{g\rho} = rh \left( 1 - \frac{2r}{3h} - \frac{r^2}{6h^2} \right)$$

For the capillaries used in the present work an effective radius was calculated for water by means of this equation and then used for the work with dilute solutions. This corrected radius differs so slightly from the measured value that the calcu-

lation is hardly necessary. More important is the fact that the difference in the correction for pure water and for dilute electrolyte solutions is quite negligible so that it is justifiable to use the same value of the radius for both.

**Precision of the Method.**—In order to illustrate the errors of the method, the data and calculations for a determination of the relative surface tension of a solution of 0.0048 molar potassium chloride are given in Tables I, II and III. The errors given for the original data are estimated but they are subsequently treated as probable errors.

TABLE I

PRELIMINARY MEASUREMENTS AND ESTIMATED ERRORS

Net surface area of left dish	= 247.74 ± 0.3 sq. cm.
Net surface area of right dish	= 247.06 ± 0.3 sq. cm.
Capillary radius	= 0.0427 ± 0.0002 cm.
One turn of rod R	= 0.0407 ± 0.0004 cc.

TABLE II

Data for a determination of the relative surface tension of 0.0048 *M* potassium chloride. The initial potassium chloride solution was 1.086 ± 0.001 *M* and its density was 1.04667 ± 0.00005.

Data

Initial balance of R	= 16.2 ± 0.1 turn
KCl solution added to left	= 4.6385 ± 0.0002 g.
	= 4.4316 ± 0.0002 cc.
Water added to right	= 4.4737 ± 0.0002 g.
	= 4.4869 ± 0.0002 cc.
New balance of R	= 18.4 ± 0.2 turns
Final volume of KCl solution	= 1000 ± 2 ml.
Final immersion of capillaries	= 0.67 ± 0.01 cm.

Derived data

Volume on right due to rod R	= 0.0895 ± 0.0085 cc.
Net volume increase on right	= 4.5784 ± 0.0090 cc.
$\Delta d_0$ , inc. of immersion on right	= 0.018481 ± 0.00005 cm.
Molar volume change on left (due to dilution of KCl)	= -0.0097 ± 0.0001 cc.
Net volume increase on left	= 4.4219 ± 0.0003 cc.
$\Delta d_1$ , inc. of immersion on left	= 0.017849 ± 0.00002 cm.
Concentration of final KCl	= 0.00481 ± 0.00001 <i>M</i>
Density of final KCl	= 0.997304 ± 0.000005

TABLE III

CALCULATION OF *RST* BY EQUATION 4 FROM THE DATA OF TABLE II

$$\begin{aligned} RST &= 1 + \frac{gr}{2\gamma_0} [d(\rho_0 - \rho_1) + (\Delta d_0\rho_0 - \Delta d_1\rho_1)] \\ &= 1 + 0.289[0.65(-0.000230) + (0.018481\rho_0 - 0.017849\rho_1)] \\ &= 1 + 0.289[-0.000149 + 0.000626] \\ &= 1.000138 \pm 0.000016 \end{aligned}$$

An inspection of the data in Tables II and III shows that the largest errors arise from the determination of the position of the rod R and from the measurement of the surface areas. Errors in concentration, density and molar volume correction, which are unimportant in this example, become more important as the concentration increases

(10) Adam, "Physics and Chemistry of Surfaces," 2nd edition, p. 365.

(11) Schrödinger, *Ann. Physik*, **46**, 413 (1915).

but remain relatively small up to 0.05 molar potassium chloride.

The error in the surface areas can be examined by making a determination in the same way as for a salt solution but adding water to both vessels. For solutions of equal density equation 3 reduces to

$$RST = 1 + \frac{g^2 \rho_0}{2\gamma_0} (\Delta d_0 - \Delta d_1) \quad (4)$$

Thus if the vessels both contain water ( $\Delta d_0 - \Delta d_1$ ) should be zero. For one pair of vessels, a series of fourteen water determinations gave an average  $\Delta d$  difference of only 0.00002 cm. and it was concluded that the measured areas were mutually consistent. For a second pair of vessels, a series of twelve water determinations gave a  $\Delta d$  difference of 0.0015 cm. and this value was used to reduce the value of the area of one vessel by 0.38 sq. cm.

A more important function of these water determinations is to test the over-all behavior of the apparatus. For example, a series of fourteen water determinations gave a mean deviation of ( $\Delta d_0 - \Delta d_1$ ), irrespective of sign, of 0.000032 cm. This figure agrees fairly well with the estimated error listed in Table III and clearly indicates that the apparatus shows a rather consistent behavior.

The inherent sensitivity of the apparatus can be tested by finding the least change in the immersion of the rod R, and thus the least height change, that will cause the bubble flow to shift from predominantly one capillary to predominantly the other. Lack of sensitivity is the cause of the error in the position of R which is shown in Table II to be the most important source of error in a determination. It has been found that various pairs of capillary tips show quite different sensitivities. For a good set of tips 0.1 turn of R will shift the bubble flow and the shift is reversible in the sense that a constant zero is maintained. For a poor set as much as 0.8 turn of R may be necessary. Tips that needed over 0.4 turn to cause a shift of bubble flow were not used in the surface tension determinations and one of the functions of the frequent water determinations was to test the sensitivity.

Errors from contamination are decreased in the present apparatus due to the fact that the bubbles are formed below the main surface of the liquids and are formed continuously. Even so, all parts of the apparatus were cleaned with hot chromic acid solution before every experiment. The only

exception to this was that a surface tension determination was often preceded by a water run. No lubricated valves of any sort were used. The weight pipets used to introduce solutions were constructed on a siphon principle to eliminate stopcocks.

**Temperature Control.**—The temperature coefficients of the surface tension of water and of salt solutions are quite similar so that for this type of differential apparatus it is only important that the temperature of a given determination be constant. Actually the water-bath was maintained at  $25 \pm 0.01^\circ$  and since any temperature fluctuations are damped by the lagging effect of the thick glass vessels errors due to temperature variation are well within the limit of other errors.

One factor which might affect the temperature equality is the heat of dilution of the added solution. The data<sup>12</sup> for potassium chloride and for sucrose indicate that for solutions below 0.01 molar this factor is negligible. However for more concentrated solutions or for solutions with large heats of dilution this effect can be of some importance.

**Bubble Rate.**—Since the present procedure involves a continuous flow of gas it is a dynamic method as contrasted with a truly static method like the capillary rise. Whether such a dynamic method will measure the true equilibrium surface tension of a solution depends upon the rate at which the bubbles flow and upon the speed with which the final surface tension is established. It seems reasonable that for solutions of materials like simple salts or sucrose where the adsorption is small and for which no barrier to diffusion seems probable the surface tension will be established in a very short time. Some experimental evidence is available which justifies this. Working with fairly concentrated sodium chloride solutions, Bond and Puls<sup>13</sup> concluded that the equilibrium surface tension is established in less than 0.003 second. From a fairly rough equation they calculated that the actual time is probably of the order of  $10^{-10}$  seconds.

If the work of Bond and Puls gives the correct order of magnitude for the time required to reach equilibrium, then a bubble rate of the order of one every few seconds should allow ample time. To test this, experiments have been done with bubble rates ranging from one every five seconds to one

(12) Landolt-Börnstein, *Erg. IIb*, pp. 1538, 1545.

(13) Bond and Puls, *Phil. Mag.*, [7] 24, 864 (1937).

every two minutes. Table IV gives the surface tension results for four potassium chloride solutions, all close to 0.0024 molar. As nearly as possible these four runs were carried out in an identical fashion. The same apparatus assembly and the same initial potassium chloride solution were used. The only difference was in the bubble rate. The constancy of the results for a ten-fold variation of bubble rate strongly suggests that both bubble rates are slow enough to allow the equilibrium surface tension value to be reached.

TABLE IV

COMPARISON DETERMINATIONS OF THE SURFACE TENSION OF 0.0024 *M* POTASSIUM CHLORIDE

Seconds per bubble	Molar concn.	RST
90	0.00229	1.000097
100	.00235	1.000099
9	.00249	1.000072
9	.00241	1.000106

Measurements of the surface tension of sugar solutions also afford evidence that the equilibrium surface tension is attained. The results obtained for sucrose with a rate of one bubble every twenty to forty seconds are in quite good agreement with Jones and Ray's truly static results. Since sucrose is a large molecule with a rather small diffusion coefficient it would be expected to afford a more severe test than electrolytes like potassium chloride. Consequently on the basis of these results and the previously mentioned work, it is concluded that for solutions of simple salts, sucrose and similar molecules a bubble rate of one every twenty seconds or slower will give equilibrium surface tension values.

**Preparation of Materials.**—The water used in all this work was conductivity water prepared in a Barnstead

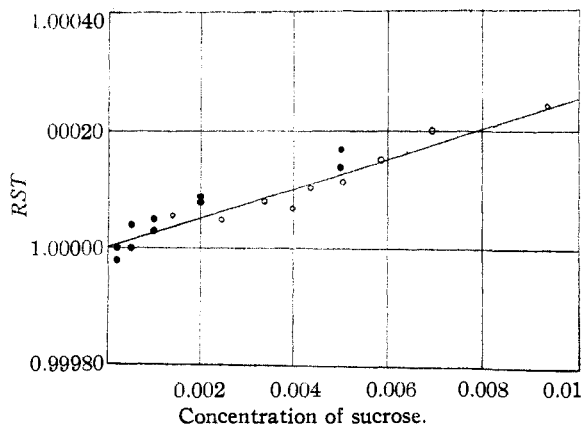


Fig. 2.—The relative surface tension of sucrose solutions. The open circles are from this investigation; the solid circles are taken from the results of Jones and Ray.

conductivity water still. No attempt was made to free the water from carbon dioxide. Occasional determinations of the conductivity of the water gave an average value of  $0.8 \times 10^{-8}$  mho. This water was stored in a settling tower similar to the type used by Jones and Ray.<sup>2</sup>

The nitrogen gas used for the bubbles was taken from a tank of water-pumped nitrogen and was passed through absorbent cotton and then through washing towers containing chromic acid and sodium hydroxide. It was finally passed through several washing towers containing water to saturate it with water vapor, into a twelve liter reservoir flask and so to the valve. The pressure of the gas was maintained at a constant value by maintaining a continuous flow of about 1 cc. per minute and letting the excess flow out of the system through a T tube immersed to a depth of 15 cm. in mineral oil.

Reagent grade potassium chloride was used without any preliminary recrystallization since the work of Jones and Ray indicated that small amounts of other salts would not affect the results. The salt was, however, fused in platinum dishes to remove any organic matter. Solutions were obtained by transferring weighed amounts of the fused potassium chloride to volumetric flasks and making the solutions up to the required volumes.

**Sucrose Measurements.**—Several measurements were made with sucrose in the range 0.001 to 0.01 molar. The capillary tips used in this work had radii of 0.0427 cm. The necessary density and molar volume data were obtained from Landolt-Börnstein.<sup>14</sup> The experimental results are shown graphically in Fig. 2 in which the data of Jones and Ray are plotted as solid circles for comparison. It is obvious that the values are a quite linear function of concentration and also that they agree rather well with the Jones and Ray data.

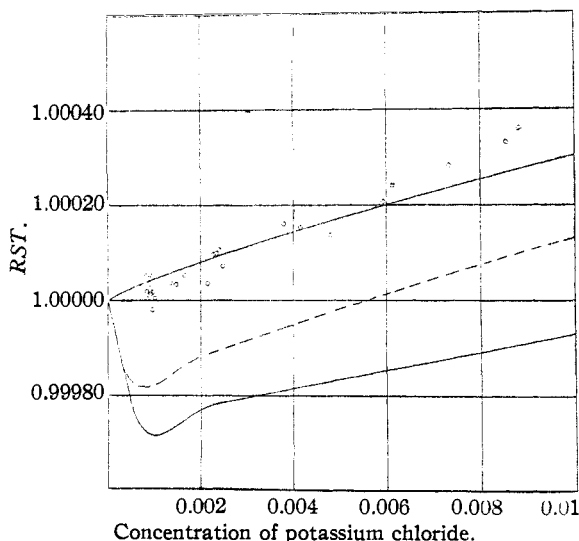


Fig. 3.—The relative surface tension of potassium chloride solutions. The points give the results of this research. The uppermost curve is the theoretical Onsager and Samaras prediction; the dotted curve is that given by Jones and Ray; the lowest curve is the one given by Dole and Swartout.

(14) Landolt-Börnstein, Vol. I, p. 428; p. 463.

**Potassium Chloride Measurements.**—A fairly large number of measurements on potassium chloride solutions were made. Several different starting solutions of the salt were used, ranging from 0.2 to 1 *M*. Four different sets of capillary tips were used but their size was close to  $r = 0.042$  cm. Densities were calculated from the equation of Jones and Ray and the molar volume data were taken from the work of Geffcken.<sup>15</sup> The results are shown graphically in Fig. 3, where for comparison the curves of Jones and Ray and of Dole and Swartout as well as the theoretical Onsager-Samaras curve are also given.

The data in Fig. 3 show a wide deviation from the other two experimental curves. The minimum at 0.001 *M* is not present although there does seem to be a slight concavity in the curve near this concentration. For concentrations greater than 0.001 *M* the results roughly parallel those of Jones and Ray but they lie much higher. The deviation is, of course, well outside the experimental error and there seems to be no constant error which will explain the difference.

In order to see if the variation between the present results and those of the previous workers was maintained at higher concentrations, two determinations were made for approximately 0.05 molar solutions. The data are given in Table V where, for comparison, the figures of Jones and Ray and of Schwenker<sup>16</sup> ( $0^\circ$ ) are also given. The determinations at this concentration are less accurate than those for more dilute solutions primarily because the heat of dilution of the initial 3.86 molar potassium chloride solution is large enough to introduce an error due to temperature changes. Because of this error the first two surface tension values in Table V may be too large by as much as five in the last figure but even so the data show that the parallelism between the Jones and Ray data and the present work is approximately maintained.

TABLE V  
POTASSIUM CHLORIDE RESULTS FOR MORE CONCENTRATED SOLUTIONS

Work	Concentration	RST
Present	0.0437	1.00142
Present	.0512	1.00179
Jones and Ray	.0437	1.00123 (interpolated)
Jones and Ray	.0512	1.00146 (interpolated)
Schwenker at ( $0^\circ$ )	.05	1.00141

### Discussion

The most obvious feature of the data for the relative surface tension of potassium chloride is

(15) Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931); Geffcken and Price, *ibid.*, **B26**, 81 (1934).

(16) Schwenker, *Ann. Physik*, [5] **11**, 525 (1931).

the wide variation from the results of Jones and Ray and of Dole and Swartout. There is no minimum in the surface tension-concentration curve and in general the values agree fairly well with the Onsager and Samaras predictions.

There are several possible explanations for the disagreement. A conceivable one is that the data obtained with the bubble pressure apparatus are not true equilibrium values due to the speed with which bubbles are formed. If this were true the results could not be compared with the static values of Jones and Ray. However, for several reasons this explanation seems unlikely. The previously mentioned experiments with sucrose and with varying bubble rates both indicated equilibrium. The fact that the values parallel those of Jones and Ray at higher concentrations also indicates equilibrium since even if equilibrium were attained slowly in the region of the Jones and Ray minimum it should be attained much more rapidly in the region of negative adsorption where presumably the image forces predominate.

Another explanation for the discrepancy that suggests itself is that the contact angle does not stay at zero with salt solutions and that the minimum found by Jones and Ray and Dole and Swartout arises from failure to consider the variation of the contact angle. However, this explanation also seems rather unlikely. The contact angle of pure water against glass or fused silica is undoubtedly zero.<sup>17</sup> To account for the Jones and Ray minimum a change in contact angle to about  $1^\circ$  would be necessary. Although small, this is an angle which should be easily detected. More serious is the implication with respect to the spreading coefficient of water on silica or glass. A change of contact angle from 0 to  $1^\circ$  in going from water to a dilute salt solution would indicate either a large change in the spreading coefficient or an initial condition of  $W_{st}$ , the work of adhesion, almost identical with  $2\gamma$ . Neither of these seems very probable.

A third explanation for the difference between the bubble pressure results and those obtained by Jones and Ray is that the reason for the minimum observed by the latter is the one proposed by Langmuir, a change in the effective radius of the capillary as the concentration of electrolyte changes. Since this change of effective radius is caused by the zeta potential at the glass-solution

(17) Richards and Carver, *THIS JOURNAL*, **43**, 827 (1921); Bosanquet and Hartley, *Phil. Mag.*, [6] **43**, 456 (1921).

interface it should enter for the bubble pressure method also. But there are reasons why the effect should be smaller for the bubble pressure apparatus. The capillaries are of Pyrex instead of fused silica and it is probable that the Pyrex-solution zeta potential is smaller than for fused silica. In addition the capillary is larger by a factor of three than that of Jones and Ray and this will also decrease the importance of the zeta potential contribution. A third point is that the position of the meniscus is quite different for the bubble pressure method. In the capillary height apparatus the meniscus is formed completely within the capillary tube. In the bubble pressure apparatus the bubble extends down into the bulk of the solution and is in contact with glass only at the end of the tube. Although as formulated by Langmuir the effect of the zeta potential is treated in terms of a layer of solution along the capillary it can alternatively be discussed in terms of its effect on the radius at the lowest point of the meniscus. Because the region of close approach of the meniscus to the capillary wall is much less for the bubble pressure method it is

very probable that the perturbation from the wall-solution zeta potential will be less. Thus the difference between the two methods of measurement seems likely to be due to a difference in the extent of the contribution of the zeta potential.

### Summary

1. A differential maximum bubble pressure apparatus for the precise measurement of relative surface tensions is described. The relative surface tension values for dilute aqueous sucrose solutions, obtained with the apparatus, are similar to those obtained by the capillary height method.

2. The relative surface tension of potassium chloride solutions is considerably different from that obtained by previous workers. No minimum in the surface tension-concentration curve is observed and the results agree fairly well with the Onsager-Samaras predictions.

3. Explanations for the lack of agreement of the various results are considered and it is concluded that the most likely is the effect of the zeta potential as postulated by Langmuir.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

## The Heat Capacity of Benzene- $d_6$ <sup>1,2</sup>

BY WALDEMAR T. ZIEGLER AND D. H. ANDREWS

Several years ago Lord, Ahlberg and Andrews made a semitheoretical calculation<sup>3</sup> of the heat capacities of crystalline benzene and benzene- $d_6$  based upon the spectroscopically determined frequencies<sup>4</sup> of the molecules in the gaseous state and certain assumptions concerning the contribution of lattice vibrations and the process of lattice expansion to the heat capacity. The agreement between the calculated and experimental values of  $C_p$  for crystalline benzene over the temperature range 4-270°K. may be described as very good, clearly indicating the general correctness of the frequency assignments for benzene.

(1) From a dissertation submitted to the Board of University Studies of the Johns Hopkins University in 1938 by W. T. Ziegler in conformity with the requirements for the degree of Doctor of Philosophy.

(2) Part of this research was presented in a paper with Dr. R. C. Lord, Jr., at the Boston meeting of the American Chemical Society, September, 1939.

(3) Lord, Ahlberg and Andrews, *J. Chem. Phys.*, **5**, 649 (1937). For a more complete exposition of the method used see Lord, *J. Chem. Phys.*, **9**, 693, 700 (1941).

(4) Lord and Andrews, *J. Phys. Chem.*, **41**, 149 (1937).

At that time certain of the fundamental frequencies of both benzene and benzene- $d_6$  were in doubt. Since then, the work of Langseth and Lord on the deuterated benzenes<sup>5</sup> has appeared which resulted in several changes in the frequency assignments previously made. These changes produce an almost insignificant change in the calculated values of  $C_p$  for crystalline benzene,<sup>6</sup> but decrease the calculated  $C_p$  values for benzene- $d_6$  by about 2% at 270°K.

It seemed to us of interest to determine the heat capacity of crystalline benzene- $d_6$  in order that the results might be compared with those predicted by a calculation of the type described above. Through the kindness of Dr. C. K. Ingold of University College, London, we obtained a loan of about 5 ml. of benzene- $d_6$  with which to carry out the measurements. The semi-micro heat conduction

(5) Langseth and Lord, *Kgl. Danske Videnskab. Selskab. Math-fys. Medd.*, Vol. 16, No. 6 (1938).

(6) Brucksch and Ziegler, *J. Chem. Phys.*, to be published shortly.