of cane sugar, which was officially stated by the United States Bureau of Standards to have a heat value of 3,945 calories per gram, plus or minus three calories.

The amount of water used was such, that its weight, plus the hydrothermal equivalent, was the equivalent of 3,000 grams of water.

Specimen of Combustion:

Substance, cane sugar. Bureau of Standards = 3.945 ± 3 calories.
Weight of substance taken 1.1466 grams.

Weight of water in cup	2,530 grams
Hydrothermal equivalent	470
Water equivalent of apparatus	3,000 grams

Before firing.		After firing.	
Time.	Reading.	Time.	Reading.
3.00	1.500	3.06	3.025
3.01	1.500	3.07	3.030
3.02	1.500	3.08	3.030
		3.09	3.030

Temperature of water at start 26°.
Temperature of room 28.5°.

Ignition heat	60 calories
Nitric acid	4.6 calories
	64.6 calories

3.030—1.500 = 1.530 total rise.
1.530 × 3,000 = 4590 calories.
4590—64.6 = 4525.4 calories.
4525.4 divided by 1.1466 = 3947 calories.

These results demonstrate the value of the use of the vacuum cup and of the method of ignition for bomb calorimeter work. It has the further recommendation of being less expensive than other bomb calorimeters of equal accuracy.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, No. 218.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. XIII. THE DROP WEIGHTS OF AQUEOUS SOLUTIONS AND THE SURFACE TENSIONS CALCULATED FROM THEM.[1]

BY J. LIVINGSTON R. MORGAN AND GEORGE A. BOLE.

Received August 1, 1913.

The object of this investigation[2] was, *first*, to apply the Morgan drop-

[1] For other papers in this series see THIS JOURNAL, 30, 360–76, 1055–68; 33, 349–62, 643–57, 657–72, 672–84, 1042–60, 1060–71, 1275–90, 1713–27; 35, 1249–62, 1505–24.

[2] The experimental work in connection with this paper was carried out during the winters of 1910–11 and 1911–12.

weight apparatus to the study of aqueous solutions, for the securing of data which might, at any rate ultimately, be used in formulating the laws governing the surface tension of salt solutions; and *second*, to test out, as carefully as might be, the relationship proposed by Valson[1] which, although never more than partially corroborated by other observers, seems to have had wide acceptance, *viz.*, that *normal aqueous solutions of all salts lead to practically identical values of the surface tension.*

Valson's expression was:

$$D \times H = 61.7,^2$$

where D is the density of the normal solution, and H its height of capillary ascension in a tube with an internal bore of 0.5 millimeter, all at 15° D × H, here, of course, is proportional to surface tension, for the actual surface tension in dynes per centimeter would be

$$\gamma = {}^1/_2 \left(D \times \frac{H}{10} \times \frac{0.05}{2}\right) \times 980.1,$$

where the radius and height are expressed in centimeters.

This law was contradicted by some investigators, and partially corroborated, in isolated cases only, by others; but apparently it is still widely accepted as a most important generalization concerning solutions. Without going into a discussion of the results of other investigators here,[3] we shall proceed at once to a description of the means employed to determin the drop weight of a solution in such a way as to avoid error due to evaporation of solvent (which would make the solution more concentrated) and to lead to constant, consistant results.

In the case of pure liquids, the procedure has been to allow evaporation to take place unchecked, and then to compensate for it by employing a blank with a different number of drops, but which has stood for the same period of time, and consequently has lost the same total weight by the evaporation. Thus, thirty drops are first allowed to form and fall in the dry weighing vessel, and the total weight of drops plus vessel determined. Then in the same dry weighing vessel, five drops are allowed to form and fall, and the sixth drop to hang, before being drawn back, until the same total time has elapsed in the "5" determination as in the "30." Subtracting the total weight of the vessel with the five, from that of the vessel with the thirty, gives us, then the weight of twenty-five drops, free from any effect of evaporation. In both cases here, the first drop is allowed to hang, before falling, for five minutes in order to saturate the weighing vessel at once with vapor, and all vapor in the vessel is condensed in both

[1] *Compt. rend.*, **74**, 103 (1872).

[2] Another form of this expression is H = 118.5–56.8D, where for a normal solution D can never be very much larger than 1.

[3] In the next paper of this series, where thirty-four other solutions are studied a more extended discussion of the various methods will be found.

cases by dipping the vessel in cold water. This method has given very satisfactory results with pure liquids, even up to temperatures within a few degrees of the boiling point.

It was feared that this procedure might not give the most satisfactory results possible when applied to solutions, as all the vapor to saturate the air space of the weighing vessel, would have to come from the first drop as it hangs for five minutes, and this loss of solvent might so change the concentration of the solution as to alter the weight of the drop. To make sure of avoiding any such difficulty in this investigation, an amount of the solution was always put into the dry weighing vessel before setting up the apparatus, and the weight of liquid and vessel determined. In this way, the vapor necessary to saturate the small air space of the weighing vessel was taken from a comparatively large amount of solution (10 to 20 drops) before a drop was run over to hang; the concentration of this was not, therefore, affected appreciably. Tests showed here that the liquid, vapor and vessel, weighed the same (after having been put on the apparatus and kept at the temperature of observation for a period equal to the average length of a determination) as it did originally. The difference between the weight of the vessel, containing the liquid plus a number of drops that had been allowed to form and fall, and the original weight of vessel and liquid was then taken as the weight of the number of drops which had fallen. With pure water, this procedure led to the same result as that given by the usual blank of five drops.[1]

In the original determination of the drop weight and surface tension of water,[2] the sample was always saturated with air before the determination, by allowing a current of dry air to bubble through it for some time. Naturally this could not be done with solutions, for the consequent loss of solvent would change the strength of the solution decidedly. In order to compare the values of the surface tension of salt solutions with the surface tension of water at that temperature, it was necessary to first determin the value for water as free from air, practically, as was the water used to make up the solutions. The value of surface tension found in this way is slightly lower (0.15% about) than the value found for an air-saturated sample.

The tip was cleaned before each determination in practically the same way as that employed by Morgan and McAfee, *viz.*, first with water, then with a warm, weak sulfuric-chromic acid mixture, then again with water, being finally dried by a current of filtered, dry air. It is only in this way that satisfactorily constant values for any one liquid can be obtained—

[1] It was found in a later piece of work (see the following article) that these precautions were really unnecessary, for the same results can be obtained by simply subtracting from the weight of drops plus vessel, found in the usual way, the weight of the empty glass weighing vessel itself.

[2] Morgan and McAfee, THIS JOURNAL, 33, 1279.

though when this precaution is taken there is no reason why the difference in weight between two successive "30" determinations should be more than a few tenths of a milligram.

Two tips were used in the course of this investigation, and, as is usual, were re-standardized at frequent intervals to make sure that no change in the tip had taken place. The K_B values as found by comparison with the surface-tension value for water, calculated from the Morgan-McAfee equation, are given in the following table. Here, of course, the water was saturated with air, since the calculated values were for such a sample:

t.	w (mg.).	γH_2O (M. and McA.).	$K_B = 2.1148 \times \gamma/w$.
	TIP NO. 1.		
34.8	78.310	70.24	**2.3577**
	TIP NO. 2.		
30.0	79.403	71.03	**2.3641**

Tip No. 2 was also calibrated against benzene, with the following exceedingly satisfactory result: At 30°, $w = 29.750$, $d = 0.8679$, from which

$$K_B = \frac{w(M/d)^{2/3}}{288.5 - 30 - 6} = \mathbf{2.3640}$$

From these values of K_B it follows that surface tension (γ) and capillary constant (a^2) can be calculated from the drop weight and drop volume, from these tips, by aid of the relationships.

$$\left.\begin{aligned} \gamma_1 &= 0.8970 \times w_1 \\ a_1^2 &= \mathbf{0.1831} \times w_1/d \end{aligned}\right\} \textbf{Tip No. 1}$$

$$\left.\begin{aligned} \gamma_2 &= \mathbf{0.8946} \times w_1 \\ a_2^2 &= 0.\mathbf{1827} \times w_1/d \end{aligned}\right\} \textbf{Tip No. 2}$$

The salts used in this work were Baker's "analyzed," and each was tested for impurity and recrystallized so that the correct content of water of crystallization was assured.

The first solutions studied were of sodium chloride in the dilutions 0.5, 1.0, 2.0 and 2.5 normal, *i. e.*, 1 equivalent was made up to 1 liter with water. The results of these determinations (Tip No. 1) are given in the following table.

SOLUTIONS OF SODIUM CHLORIDE.[1]

t.	w.	γ (= 8970 × w).	
0.0	85.47	76.68	**0.5 normal**
34.3	79.45	71.27	$\gamma_t = 76.67 - 0.1577t$
0.0	86.21	77.34	**1 normal**
34.2	80.38	72.09	$\gamma_t = 77.34 - 0.1536t$
0.0	87.86	78.81	**2 normal**
33.2	82.16	73.69	$\gamma_t = 78.81 - 0.1543t$
0.0	88.78	79.64	**2.5 normal**
33.9	83.23	74.65	$\gamma_t = 79.64 - 0.1469t$

[1] As usual the drop weight is the average of three or more very closely agreeing results—only the average is given here, however, to save space.

The relationship of surface tension to concentration at any one temperature here is shown to be curvilinear and impossible to express by any simple formula, especially if the attempt is made to calculate it by aid of the surface tension of water, unsaturated with air as the solutions are, *viz.*, $\gamma_0 = 75.76$ dynes. It will be noted that, at 0°, the value of the increase due to the presence of 0.5 mole, as calculated from the various values, is not constant, but increases with increased concentration. Thus, for example, we find the successive values, due to ½ an equivalent added, to be 0.67, 0.735 and finally 0.83, as between the twice and the twice and a half normal solutions. This curvilinear relationship of surface tension with concentration is probably general.

Four other "normal" solutions were studied, with the results given below (Tip No. 2).

"NORMAL" SOLUTIONS.

Potassium Bromide

t.	w.	$\gamma = 0.8946 \times w$.	
0	85.43	76.43	$\gamma_t = 76.43 - 0.1434t$
30	80.62	72.11	

Potassium Chloride.

0	85.80	76.76	$\gamma_t = 76.76 - 0.1493t$
30	80.84	72.28	

Ammonium Chloride.

0	86.14	77.05	$\gamma_t = 77.05 - 0.1510t$
30	81.08	72.52	

Potassium Iodide.

0	84.97	76.02	$\gamma_t = 76.02 - 0.146t$
30	84.09	71.64	

There can hardly be any question of identity of the values for surface tension here, for the values at 0° for the salts NaCl, KBr, KCl, NH_4Cl and KI are respectively, 77.34, 76.43, 76.76, 77.05 and 76.02. The error in this work, in no case, can exceed the value of a few units in the second place in decimals—in fact, such agreements are obtained by two observers, using different tips.

The results obtained (Tip No. 2) and the surface tensions calculated, as well as the formula for the variation of the latter with the temperature, are given in much condensed form below: In every case here the concentration, unless otherwise noted, represents *one equivalent of the anhydrous salt, dissolved in 1000 grams of water.* In this way the real effect of the salt added should be more readily observed for the water content of all solution would then be the same.

DROP WEIGHTS AND SURFACE TENSIONS.

t.	w.	γ (= 0.8946 × w).	
0	86.10	77.02	**Sodium chloride**
30	81.15	72.59	$\gamma_t = 77.02 - 0.1437t$
0	85.99	76.93	**Ammonium chloride**
30	80.97	72.41	$\gamma_t = 76.94 - 0.1507t$
			At 18° $w = 83.00$, $\gamma = 74.25$. Calculated $\gamma_{18} = 74.22$
0	84.88	75.93	**Barium chloride**
30	79.98	71.52	$\gamma_t = 75.93 - 0.1137t$
0	85.03	76.07	**Cadmium chloride**
30	79.96	71.52	$\gamma_t = 76.07 - 0.1517t$
0	85.67	76.65	**Sodium nitrate**
30	80.62	72.11	$\gamma_t = 76.65 - 0.1513t$
0	83.96	75.11	**Ammonium nitrate**
30	79.41	71.04	$\gamma_t = 75.11 - 0.1357t$
0	85.48	76.47	**Ammonium nitrate, 2 equivalents per 1000 grams of H_2O**
40	79.18	70.82	$\gamma_t = 76.47 - 0.1412t$
			w at 21.5° = 82.07, $\gamma = 73.41$. $\gamma_{21.5}$ calculated = 73.34
40	78.03	69.81	**Barium nitrate**[1]
50	76.38	68.32	$\gamma_t = 75.77 - 0.1490t$
0	85.02	76.07	**Sodium iodide**
30	79.99	71.55	$\gamma_t = 76.07 - 0.1507t$
0	84.87	75.93	**Potassium iodide**
30	79.86	71.44	$\gamma_t = 75.93 - 0.1497t$
0	85.68	76.65	**Potassium bromide**
30	80.64	72.13	$\gamma_t = 76.65 - 0.1507t$
0	85.56	76.54	**Sodium sulfate**
30	80.35	71.88	$\gamma_t = 76.54 - 0.1553t$
20	82.32	73.64	**Potassium sulfate**[2]
40	78.82	70.50	$\gamma_t = 76.78 - 0.1570t$
0	86.12	77.03	**Magnesium sulfate**
30	81.14	72.57	$\gamma_t = 77.03 - 0.1487t$

[1] It was found that this concentration could not be used at lower temperatures so the 0° value was extrapolated in the formula, rather than use a smaller concentration, such as could be used experimentally at that temperature. The relationship, for this extrapolation, was assumed to be linear, as for other solutions it had been shown to be.

[2] Here, as with barium nitrate, we used higher temperatures rather than lower concentrations—the value of γ at 0° in the equation, thus, is also extrapolated.

DROP WEIGHTS AND SURFACE TENSIONS—(*continued*).

t	w.	γ (= 0.8946 × w).	
0	85.17	76.19	**Potassium ferrocyanide**
30	80.11	71.66	$\gamma_t = 76.19 - 0.1510t$
0	83.51	74.71	**Tri-potassium phosphate (K_3PO_4)**
30	79.17	70.82	$\gamma_t = 74.71 - 0.1297t$
18	82.10	73.43	**Hydrogen-disodium phosphate (Na_2HPO_4)**[1]
30	80.13	71.68	$\gamma_t = 76.05 - 0.1458t$
0	82.69	73.98	**Mono-potassium phosphate (KH_2PO_4)**
30	78.38	70.11	$\gamma_t = 73.98 - 0.1209t$
0	83.53	74.74	**Hydrochloric acid** (1.0022 normal)
30	79.09	70.74	$\gamma_t = 74.74 - 0.1333t$
0	84.69	75.77	**Phosphoric acid** (0.9977 normal)
30	79.49	71.11	$\gamma_t = 75.77 - 0.1553t$
0	84.28	75.39	**Sulfuric acid** (1.008 normal)
15	81.97	73.33	$\gamma_t = 75.39 - 0.1413t$
30	79.53	71.15	

The actual values of the product H × D, according to Valson, are given below for the sake of comparison, for normal solutions of some of the salts we have studied at 15°, the bore of the capillary being 0.5 millimeters. Under γ will be found the value of surface tension in dynes per centimeter, calculated by aid of the equation

$$\gamma = 1.225 \times H \times D.^2$$

VALSON'S RESULTS FOR NORMAL SOLUTIONS AT 15°, γ_{H_2O} = 73.50,

Substances.	H × D.	γ (dynes).	γ (M. and B.).
Cadmium chloride	61.8	75.70	73.80
Ammonium chloride	61.8	75.70	74.67
Sodium chloride	62.0	75.95	74.81
Barium chloride	62.0	75.95	73.73
Ammonium nitrate	61.6	75.46	73.64
Sodium nitrate	61.8	75.70	74.38
Barium nitrate	61.6	75.46	73.53
Potassium iodide	61.5	75.34	73.69
Sodium iodide	61.5	75.34	73.81
Potassium bromide	61.8	75.70	74.40
Magnesium sulfate	61.7	75.58	74.80
Potassium sulfate	62.0	75.95	74.42
Sodium sulfate	62.0	75.95	74.21

In addition to these on which we also have worked, Valson studied twenty-nine others. Only three of this entire forty-two were found by him to be below 61.4, and only three above 62. The lowest value he found

[1] This case is similar to those of barium nitrate and potassium sulfate.

[2] See page 1751.

was for cadmium iodide, *viz.*, 60.7, which gives $\gamma = 74.34$ dynes. The highest value was 62.1, equal to 76.07 dynes, which he found for lithium chloride, sodium chloride and lithium sulfate.

The first striking thing concerning these γ values of Valson, is that they are all so high; since water itself, at 15° (he gives no experimental value for water), is only 73.50 dynes, his lowest value 74.34 is still very much above water. Further, according to his work, none of his salts seem to cause the surface tension of the solution to fall below that of water itself. Our results in this respect for ammonium nitrate, 75.11, as compared to 75.76 for water, both at 0°, are characteristic of this salt and many others; this is true not only according to the drop-weight method, but by all other methods which have proven at all satisfactory with salt solutions. As a matter of fact, we find that tri-potassium phosphate and mono-potassium phosphate also depress the surface tension, the values at 0° being 74.71 and 73.98, respectively.

Valson's agreements, and the fact that no results below water were obtained by him (though his work has never been checked) may be due to a phenomenon noted by several observers, *viz.*, the lowering of the capillary height of a solution on standing for some time. These were cases of salt solutions which had *greater* surface tensions than water and the lowering was apparently justly attributed to a separation of the solution and solvent at the surface, having the meniscus itself, finally, pure water. Zemplén[1], in making optical observations of the shape of the meniscus of salt solutions, noted that in time that the meniscus became practically the same as that for pure water, even changing during the reading. If such a change in the surface does take place with the capillary rise (Valson's method) solutions with higher surface tensions would be lowered in value, while those giving lower values would be raised; so that all would *ultimately tend* to the same value, which would be practically that of water at that temperature. The only difficulty with such an explanation of Valson's results is that his constant value is much higher than the value of water at that temperature. It is possible, of course, since he was not calculating any *absolute* value from his results, that his capillary tube, which he speaks of as having a bore of 0.5 mm., was only roughly that, since the knowledge of its exact diameter was not necessary. If, however, his results were really found with some other tube and calculated to one with a bore of 0.5 mm., this explanation fails. Whatever be the explanation, however, it is quite certain that the generalization proposed by Valson cannot be confirmed by the results of drop weight any more than it can by other methods. It is difficult to find results in the literature with which to compare ours, for usually higher concentrations than ours have been employed.

[1] *Ann. Physik*, **20**, 783 (1906).

Jäger,[1] however, gives results which lead to the following surface tensions in dynes; p represents grams per 100 grams of water, and the temperature is 13.5°:

$$\gamma_{NaCl} = \gamma_{H_2O}\,(1 + 0.0026p + 0.000025p^2).$$
$$\gamma_{NH_4Cl} = \gamma_{H_2O}\,(1 + 0.0032p + 0.000003p^2).$$
$$\gamma_{KCl} = \gamma_{H_2O}\,(1 + 0.0023p - 0.000036p^2).$$

In this form these equations simply give the surface tension of the solution in terms of a percentage of the surface tension of water. Since our value for water at 13.5° is 73.74, when it is in the condition in which it is in the solutions, we find as the comparison of values:

COMPARISON OF RESULTS AT 13.5°

Substance in solution.	γ (Jäger).	γ (M. and B.).	Δ
NaCl	74.96	75.08	+0.12
NH_4Cl	75.08	74.91	—0.17
KCl	75.15	74.75	—0.40

A further comparison is possible from the results of Volkmann[2] and Pann,[3] both by capillary rise, coming from the same laboratory and agreeing together, in general, to within 0.5% and usually very much better.

COMPARISON OF RESULTS. 1 EQUIVALENT IN 1000 GRAMS.

Substance.	t.	γ (V).	(γ P).	γ (M. and B.).	Δ.
K_2SO_4	10	...	75.07	75.21[4]	+0.14
K_2SO_4	16	74.67	...	74.27	—0.40
K_2SO_4	30	...	72.00	72.07	+0.07
Na_2SO_4	10	...	75.50	74.98	—0.52
Na_2SO_4	16	74.54	...	74.06	—0.48
$NaNO_3$	10	...	75.24	75.14	—0.10
$MgSO_4$	16	74.52	...	74.66	+0.14
NH_4Cl	16	74.24[4]	...	74.53	+0.29
NaCl	16	74.74	...	74.72	—0.02
$BaCl_2$	16	74.67	...	74.27	—0.40

It must be confessed that the agreements here are very satisfactory, the greatest discrepancy being in the case of Na_2SO_4, where the difference from Volkmann is 0.48 and from Pann is 0.52 dynes. These amounts however, are roughly but 0.7% where in some cases Pann's results vard as much as 0.5% from Volkmann's, although by the same method any practically a repetition of Volkmann's work. There would seem to be some difficulty, perhaps, with respect to Na_2SO_4, for it disagrees in this way from both observers. So far as we know, our sample was pure, and there is no more reason for casting doubt on the results for it than on those of any other salt.

[1] *Wien Ber.*, **101**, [2a] 158, 954 (1892).
[2] *Wied. Ann.*, **1**, 177; **17**, 353.
[3] Dissertation, Königsberg i. Pr. 1906.
[4] Extrapolated.

The values obtained by Valson, then, as will be observed by inspection of the three above comparison tables, must be regarded as incorrect, and the rule that he proposed as to the constancy of the surface tension of normal salt solutions as untrue. By our work it is only in the case of the iodides, that the results of surface tension are identical.

The results of this investigation may be summarized as follows:

(1) It is shown that the Morgan drop weight apparatus can be satisfactorily used for the determination of the surface tensions of salt solutions, and when so used gives results which are in excellent agreement with the best results found by other standard methods.

(2) By the study of the solutions of some twenty salts, one equivalent of each being dissolved in 1000 grams of water, it was shown that Valson's proposed law—that the surface tension of normal salt solutions is identical—is untrue, and the results upon which he based it are incorrect.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, NO. 219.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE; XIV. THE DROP WEIGHTS OF AQUEOUS SOLUTIONS OF THE SALTS OF ORGANIC ACIDS.[1]

BY J. LIVINGSTON R. MORGAN AND WALTER W. MCKIRAHAN.

Received August 1, 1913.

The object of this investigation, was, primarily, to continue the work of Morgan and Bole[2] in testing the relationship suggested by Valson[3], *viz: that aqueous solutions of equivalent amounts of salts have the same surface tension, independent of the nature of the salt.*

Sometime after Valson's work Quincke[4] suggested a relationship holding for aqueous salt solutions which is expressed by the equation.

$$A_s = A_w + ky$$

where A_s is the surface tension of the solution, A_w is the surface tension for water, and y is the "salt equivalents" in every 100 molecules of water, k being a constant depending on the nature of the substance in solution. It will be seen, therefore, that he was modifying quite decidedly Valson's relationship in this proposal, for with him constancy of surface tension depended upon the "nature" of the substance dissolved. By capillary rise (the same method used by Valson) Quincke found, indeed,

[1] Other papers of this series have appeared in THIS JOURNAL, **30**, 360–376, 1055–1068; **33**, 349–362, 643–657, 657–672, 672–684, 1042–1060, 1060–1071, 1275–1290, 1713–1727; **35**, 1249–62, 1505–24, and the preceding paper.

[2] THIS JOURNAL, see preceding paper.

[3] *Compt. rend.*, **74**, 103 (1872).

[4] *Pogg. Ann.*, **160**, 560 (1877).