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]

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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,

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[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).

that this law held; but on trying the "air-bubble" method he found quite different values. The former method also led him to the conclusion that the value of k *could* be nearly the same for salts of quite a different type—which makes his work more or less of a corroboration, perhaps, of Valson's.

Volkman,[1] also working with the capillary rise method, found it impossible to check the results of Quincke, as did also Rother;[2] but Whatmough,[3] using the air-bubble method, came to Quincke's conclusion regarding the solutions of the salts of the same acids. Dorsey,[4] using the "ripple" method, found no such general relation, nor could Forch,[5] who used a drop method.

Morgan and Bole, using the Morgan drop-weight apparatus, have shown that the Valson generalization could not be confirmed, and, in fact, found wide variation in the results of the twenty solutions examined, although there could be no question of the accuracy of the method. We have selected for study solutions of salts of organic acids, mixtures of these salts, and solutions of the acids themselves.

In this investigation, in order that any regularity which does exist might be brought to light, the drop weights of thirty-four separate solutions have been studied, in all cases at two temperatures and usually at three, and the variation of the surface tension with the temperature has been calculated from them in the form of an equation. Since many of the salts of this type are too insoluble to allow the making up of a normal solution, as employed by Valson, and also by Morgan and Bole, the strength of solution selected, in this case, was *one-half* equivalent.

In order that there might invariably be the same actual amount of water in the solution, this one-half equivalent was always dissolved in 1000 grams of water. If simply made up to one liter, the water amount would vary somewhat, according as the solution contracted or expanded; and the results of surface tension would have less meaning than if the same definit amount of water was always affected by the same one-half equivalent of the different substances.

Most of the salts used were made especially for us by the Hoffman and Kropff Chemical Company, while others were from Kahlbaum or Baker. In some cases recrystallization was thought necessary, but no change was caused by that in the results, so the chemicals may be considereed to have been pure.

Here, as in the work of Morgan and Bole, the curve for water, unsatu-

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[1] *Wied. Ann.*, **11**, 177; **17**, 353.

[2] *Ibid.*, **21**, 576 (1884).

[3] *Z. physik. Chem.*, **39**, 129 (1902).

[4] *Phil. Mag.*, **44**, 367 (1897).

[5] *Ann. Physik*, **68**, 801 (1899).

rated with air, just as it was in the case of the salt solutions, is taken for comparison; although for the calibration of the tip, water saturated with air was employed. It was found, after a series of measurements had been made,—first, by the procedure of Morgan and Bole, in having solution in the weighing vessel, before setting up the apparatus; and second, by simply causing the drops to fall into the empty vessel, and after subtracting the weight of this, dividing the remainder by the number of drops—that the results obtained for the weight of a single drop were identical. Furthermore, this was true up to 50°. That but a negligible amount of solvent evaporates from the first drop in this method, is shown by the fact that the weight of a single drop is found to be the same, whether calculated from a total of five drops or from a total of thirty.

But one tip was used in the course of this work—it was standardized against water, employing the results of surface tension of water as found from the equation of Morgan and McAfee[1]. At 30° the average weight of a drop of water, under saturated air conditions from our tip, was 75.210 milligrams, while the surface tension γ calculated, was 71.030 dynes per centimeter. Therefore, K_B is found to be equal to 2.2392 ($K_B = \frac{2.1148}{71.030} \times 75.210$[2]). This calibration was repeated from time to time to make sure that nothing had happened to the tip. To transform results of drop weight, and drop volume, from this tip into surface tension in dynes, γ, and capillary constant, a^2, we have then the relations

$$\gamma_t = \frac{2.1148}{2.2392} \times w = \mathbf{0.9444}\ w_t,$$

and

$$a_t^2 = 0.1837 \times \frac{2.3502}{2.2392} \times \frac{w_t}{d_t} = \mathbf{0.1929}\frac{w_t}{d_t},$$

In the case of twenty of the solutions studied, the density was determined on our own samples, so we are enabled to give the values of a^2 at at least one temperature, for each of these liquids.[3]

No satisfactory densities were found in the literature for either these temperatures or these concentrations.

The results observed, and the values derived from them, are given below, where, in order that space may be saved, only the average weight of the drop is given, although this was determined usually three separate times, all three agreeing within less than one unit in the second decimal place. *All solutions contain one-half of one equivalent dissolved in 1000 grams of water.*

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[1] THIS JOURNAL, 33, 1060–71 (1911).

[2] See *Ibid.*, 33, 1716 (1911).

[3] Our thanks for this are due to Mr. A. P. Sachs.

DROP WEIGHTS AND SURFACE TENSIONS.

t.	w.	γ (0.9444 × w).	$\gamma_{H_2O} = 75.76 - 0.1576t$
0	80.48	76.02	**Ammonium acetate**
30	75.38	71.13	$\gamma_t = \mathbf{76.02 - 0.1629}t$
50	71.84	67.87	
0	80.52	76.05	**Sodium acetate**
20	77.24	72.92	$\gamma_t = \mathbf{76.05 - 0.1565}t$
30	75.54	71.35	$d_{30.12^\circ} = 1.01525$, $a^2_{30.12} = \mathbf{14.35}$
0	78.40	74.04	**Potassium acetate**
20	75.36	71.17	$\gamma_t = \mathbf{74.04 - 0.1433}t$
50	73.86	69.74	$d_{30.1^\circ} = 1.01523$, $a^2_{30.1} = \mathbf{14.03}$
0	80.53	76.06	**Calcium acetate**
20	77.20	72.89	$\gamma_t = \mathbf{76.06 - 0.1585}t$
30	75.49	71.30	$d_{30.2^\circ} = 1.01764$, $a_{30.2} = \mathbf{14.30}$
0	80.20	75.75	**Zinc acetate**
20	76.84	72.55	$\gamma_t = \mathbf{75.75 - 0.1602}t$
30	75.01	70.94	
0	79.84	75.40	**Lead acetate**
20	76.39	72.15	$\gamma_t = \mathbf{75.40 - 0.1624}t$
30	74.68	70.53	
30	75.93	71.71	**Ammonium oxalate**[1]
50	72.34	68.31	$\gamma_t = \mathbf{76.79 - 0.1695}t$
30	75.70	71.52	**Sodium oxalate**
40	74.03	69.87	$\gamma_t = \mathbf{76.46 - 0.1648}t$
50	72.21	68.22	
0	80.37	75.90	**Ferric oxalate**
20	77.00	72.74	$\gamma_t = \mathbf{75.90 - 0.1582}t$
30	75.35	71.15	$d_{30.1} = 1.0126$, $a^2 = \mathbf{14.35}$
30	76.62	73.98	**Ferric oxalate, 5 normal**
50	73.21	69.15	$\gamma_t = \mathbf{77.20 - 0.1610}t$
			$d_{30} = 1.1482$, $a^2_{30} = \mathbf{12.87}$
20	76.58	72.33	**Oxalic acid**
30	74.95	70.75	$\gamma_t = \mathbf{75.50 - 0.1583}t$
50	71.56	67.58	$d_{30} = 1.0060$, $a^2_{30} = \mathbf{14.37}$
0	80.74	76.26	**Sodium tartrate**
20	77.49	73.17	$\gamma_t = \mathbf{76.26 - 0.1547}t$
30	75.82	71.62	$d_{30.1} = 1.0278$, $a^2_{30.1} = \mathbf{14.23}$

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[1] This solution could not be used at lower temperatures without the separation of solid, so it was used at these temperatures in preference to working with a weaker solution that could exist at 0°. This is true of several other salts.

DROP WEIGHTS AND SURFACE TENSIONS (*continued*).

	w.	$\gamma (0.9444 \times w)$.	$\gamma_{H_2O} = 75.76 - 0.1576t$
0	80.83	76.34	**Potassium tartrate**
20	77.44	73.13	$\gamma_t = 76.34 - 0.1607t$
30	75.72	71.52	$d_{4°} = 1.0308$, $a^2_{4°} = 15{,}01$
0	79.96	75.51	**Tartaric acid**
20	76.77	72.50	$\gamma_t = 75.51 - 0.1503t$
30	75.19	71.00	
0	75.15	70.99	**Ammonium salicylate**
20	72.34	68.29	$\gamma_t = 70.99 - 0.1352t$
30	70.84	66.93	$d_{30} = 1.0150$, $a^2_{30} = 13.47$
0	75.40	71.21	**Sodium salicylate**
20	72.45	68.42	$\gamma_t = 71.21 - 0.1396t$
30	70.96	67.02	
0	80.73	76.26	**Potassium citrate**
20	77.47	73.13	$\gamma_t = 76.26 - 0.1567t$
30	75.74	71.56	$d_{30.1} = 1.0208$, $a^2_{30.1} = 14.21$
0	77.33	73.03	**Citric acid**
30	73.60	69.51	$\gamma_t = 73.03 - 0.1147t$
0	78.04	73.73	**Sodium butyrate**
20	74.32	70.16	$\gamma_t = 73.73 - 0.1785t$
30	72.41	68.37	
50	68.60	64.80	
0	80.35	75.88	**Manganese lactate**
20	76.97	72.71	$\gamma_t = 75.88 - 0.1586t$
30	75.32	70.12	$d_{30.1} = 1.0248$, $a^2_{30.1} = 14.17$
0	80.32	75.85	**Sodium carbonate**
30	75.16	70.99	$\gamma_t = 75.85 - 0.1620t$
40	73.46	69.37	
50	71.74	67.75	
0	80.71	76.22	**Potassium carbonate**
30	75.41	71.31	$\gamma_t = 76.22 - 0.1669t$
50	71.88	67.87	
0	80.84	76.36	**Lithium formate**
20	77.59	73.23	$\gamma_t = 76.36 - 0.1563t$
30	75.86	71.67	$d_{30} = 1.0081$, $a^2_{30} = 14.52$
0	80.77	76.30	**Ammonium formate**
20	77.64	73.28	$\gamma_t = 76.30 - 0.1511t$
30	75.95	71.77	$d_{30} = 1.0040$, $a^2_{30} = 14.60$
0	80.83	76.35	**Sodium formate**
20	77.64	73.30	$\gamma_t = 76.35 - 0.1526t$
30	75.97	71.78	$d_{30} = 1.0157$, $a^2_{30} = 14.43$

Drop Weights and Surface Tensions (*Continued*).

t.	w.	$\gamma(0.9444 \times w)$.	$\gamma_{H_2O} = 75.76 - 0.1576t$.
0	80.81	76.33	**Potassium formate**
20	77.63	73.29	$\gamma_t = \mathbf{76.33 - 0.1518}t$
30	75.98	71.78	$d_{30.1} = 1.0183$, $a^2_{30.1} = \mathbf{14.39}$
0	80.70	76.21	**Calcium formate**
20	77.48	73.16	$\gamma_t = \mathbf{76.21 - 0.1526}t$
30	75.85	71.63	$d_{30} = 1.0178$, $a^2 = \mathbf{14.38}$
0	80.71	76.22	**Magnesium formate**
20	77.50	73.19	$\gamma_t = \mathbf{76.22 - 0.1515}t$
30	75.90	71.67	$d_{30.1} = 1.0150$, $a^2_{30.1} = \mathbf{14.41}$
0	80.60	76.14	**Barium formate**
20	77.44	73.10	$\gamma_t = \mathbf{76.14 - 0.1520}t$
30	75.76	71.58	$d_{30} = 1.0409$, $a^2_{30} = \mathbf{14.05}$
0	80.74	76.27	**Strontium formate**
20	77.59	73.23	$\gamma_t = \mathbf{76.27 - 0.1521}t$
30	75.89	71.71	$d_{30.1} = 1.0355$, $a^2 = \mathbf{14.14}$
0	80.40	75.94	**Cupric formate**
20	77.16	72.69	$\gamma_t = \mathbf{75.94 - 0.1546}t$
30	75.48	71.28	$d_{30} = 1.0166$, $a^2 = \mathbf{14.32}$
0	79.34	74.93	**Mixture of Sodium acetate and potassium acetate,** 1/4 equivalent of each
30	74.70	70.55	$\gamma_t = \mathbf{74.93 - 0.1461}t$
0	76.94	72.66	**Mixture of sodium salicylate and ammonium formate, 1/4 equivalent of each**
30	72.56	68.56	$\gamma_t = \mathbf{72.66 - 0.1379}t$
0	77.15	72.86	**Mixture ammonium salicylate and potassium formate, 1/4 of an equivalent of each**
30	72.63	68.59	$\gamma_t = \mathbf{72.86 - 0.1423}t$

Practically no data on the surface tension of the above solutions are to be found in the literature. Forch[1] made one determination on a solution of sodium formate, and gives an increase of 0.170 mg. mm. caused by 1.25 gram equivalents at 18°. This corresponds to a change of 0.67 dynes /cm. for a half-normal solution, assuming the change in concentration to be constant. Calculating the corresponding value from our results we find for sodium formate $\gamma = 73.60$ and for water $\gamma = 72.92$, both at 18°, which gives a difference of 0.68 dynes per centimeter. This agreement is excellent, although the value Forch finds for sodium acetate is quite different from ours. He found, as we do, that sodium butyrate

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[1] *Ann.* 68, 801 (1899).

lowers the surface tension of water; the amount of lowering due to a half-normal solution, calculated from his results, being about 2.89 dynes per centimeter, as against 2.51, as found from our results. In this connection it may be mentioned that he noticed that a trace of free acid present in the salt had a large effect on the result. The influence of the acid is to lower the surface tension of water, and this may have been the cause of his excessive lowering.

Jäger,[1] by capillary rise, found for sodium carbonate the relationship $\gamma = 73.035\ (1 + 0.0016\ p)$ at 13.5°, where p = the percentage of salt present. In our case a half equivalent in 1000 grams means a 2.65 per cent solution, which would give a value of γ of 73.35 dynes, while our results calculated at 13.5° give $\gamma = 73.66$. These are the only comparisons that can be made of our results with those of other observers, but the differences here are not large, excluding the butyrate, the larger being but 0.4 per cent.

A comparison of the values of surface tension among themselves shows that the formates, tartrates, carbonates, oxalates, the citrate, the lactate, and a part of the acetates raise the surface tension of water; while the salicylates, the butyrate, part of the acetates, and all the acids lower it. The degree of change for the different classes of salts are, for the most part quite different. Thus, *such a relationship as that proposed by Valson, does not hold at all for such solutions.*

Although there is no apparent *general* relation between all the salts, there is a noticeable relationship in some cases between the salts of the same acid. Especially is this evident with the formates. With the exception of the barium and copper salts, they can be quite accurately expressed in one formula. And the character of the curve for the barium and copper salts is the same as for the other seven. This formula would correspond to Quincke's equation for chlorides, and to relations which other investigators have found for salts of the same acid. The equations for the two salicylates show that the lines representing them are close together and are practically parallel. The same is true of the tartrates; but with the carbonates and oxalates the agreement is not so close, although there is an evident similarity. In view of these evident relations, the divergence of the values for the different acetates was not to be expected; nor was the fact that the lead and zinc acetates lower the surface tension of water.

The results would seem to indicate, then, that the effect which these salts have on the surface tension of water is determined, for the most part, by the acid radical. The variations in the values of similar salts would indicate, however, that there are other factors as well, which have a marked effect. The liberation of free acid by hydrolysis in the case of

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[1] *Wien. Ber.*, 101, [2*a*] 158, 954 (1892).

salts of weak acids may be the cause of their negative effect on water. Experiments have shown that the fatty acids lower the surface tension of water and that the lowering is proportional to the carbon content of the acid. The salts investigated here show some such regularity in their effect upon the surface tension of water.

The similarity of the results on equivalent solutions of the formates, for instance, shows that the degree of change of surface tension is proportional to the number of moles present and not to the number of grams of the substance used. It is not likely that the positive ion is altogether without effect. In the case of the formates, the good agreements may be due to the fact that the positive ions are similar, *i. e.*, are either alkalies or alkaline earths. The copper salt, which has a positive ion of a different nature from the others, shows the greatest divergence. Lack of data here makes it impossible to test out Heydweiller's[1] suggestion, that the effect of a salt upon the surface tension of water is dependent upon the ionized portion, the un-ionized portion and the viscosity of the solution.

Some mixtures were investigated, so selected that one of the solutes in each case tends to lower the surface tension and the other to raise it. The mixture of sodium and potassium acetates shows a surface tension which is practically the mean of that of the two separate solutions. In this case the degree of change caused by the two solutes is not very large for either. But when one solute changes the surface tension much more than the other, the surface tension of the mixture lies closer to that of the solution showing the greatest change and is *not* additive. Srebnitzkii[2] investigated such mixtures by the capillary rise method, and found much the same results. It is also probable that, in the last two above-named mixtures, the solute causing the large decrease in surface tension causes a larger proportional change with a decrease of concentration; *i. e.*, the change for $^1/_4$ an equivalent is probably much more than half that for a $^1/_2$ equivalent solution.

Summary.

The result of this piece of work may be summarized as follows:

1. From the determination of the drop weights and surface tensions of the thirty half-normal solutions, at two and usually more temperatures, the change in surface tension with the temperature is found to be linear, within the limits of temperature studied.

2. Some salts are found to raise the surface tension of water, while others lower it: facts which make Valson's generalization—*that all normal salt solutions at the same temperature have identical values of surface tensions*—impossible.

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[1] *Ann. Physik*, 33, 145 (1910).

[2] *J. Russ. Phys. Chem. Soc.*, 44, 145.

3. The acids studied, citric, tartaric and oxalic, lower the surface tension of water, so that hydrolysis in such salts would tend to lower the surface tension.

4. Salts of the same acid, for the most part, show a marked agreement in their values for the surface tension at the same temperatures; but there are decided exceptions even to this generalization.

5. The surface tension of a solution of two salts, one of which raises the surface tension and the other lowers it, is an additive property of the two separate solutions—provided no chemical reaction takes place between them and the values for the two are not very far removed from the value for water. If one of the solutes causes a much larger effect than the other, the value for the mixture lies closer to the one with the greater effect.

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NOTES.

A Method for Electrolytic Heating and Regulation of Thermostats.—Of the many methods suggested for heating thermostats, electrical heating by resistance wires has gradually displaced the other methods because of the cleanliness, safety and little attention necessary. Electrical heating has been accomplished principally by coils of resistance wire or by incandescent bulbs of the ordinary kind, or of special design, placed within the bath. If the coils are well insulated, there is a lag in the transmission of the heat. Bare wires usually corrode, unless of platinum, and this is too expensive to be available in the average laboratory. Also, some particular place in the bath must be reserved for the bulbs or coils. The ideal heater would be one which heated all parts of the bath simultaneously and which was free from lag. Such heating is most closely realized by dipping electrodes into an electrolyte, thus utilizing the resistance of the bath itself and making it the heating circuit.

L. Ehrman[1] has tried an electrical method for heating, in which he used the liquid (dilute sulfuric acid) in the bath for the resistance, and passed the current between two platinum points sealed in glass tubes. He states that he obtained good results for twenty hours.

Without a previous knowledge of Ehrman's work, the authors made use of copper plates—later replaced by graphite plates—in aqueous solution with the 110 volt alternating current. Sheets of copper, 8 cm. square and 6.5 cm. apart, in series with a relay interrupter, were first tried in a 17 liter thermostat at 40°. The relay *a b*, was a modified telegraph pony relay of 20 ohms resistance, which served to make and break the heating circuit as the temperature of the bath fluctuated. Relays with metal con-

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[1] *Bull. assoc. chim. sucr. dist.*, **26**, 272.