are shown to be in harmony with some of the views of T. W. Richards in regard to the compressibility of atoms.

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THE PROPERTIES OF MIXED LIQUIDS. I. SULFURIC ACID-WATER MIXTURES.

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This paper is the first report upon a somewhat extended series of investigations, started some two years ago, upon the drop weights, or surface tensions, of pure liquids, at many temperatures, and their relationship to the values of that property in their binary or other admixtures in various proportions, at those temperatures. The main object of the work is to provide such a further, perhaps more consistent, set of experimental data that eventually it may perhaps be possible to find the cause of the mutual effects of liquids upon one another; which, although absent in some cases, are great, and yet of widely differing magnitude, in others.

For some binary liquid mixtures it is known that the so-called *law of mixtures* holds more or less rigidly, *i. e.*, the value of a certain physical property of the mixture is equal to the sum of the values of that property for the pure constituents under like conditions, each multiplied by the ratio of its weight in the mixture, to the total weight of the system. Or, expressed as an equation, $P_{Mixt.} = xP_a + (1-x)P_b$, where the terms P represent the values of the property considered, and x is the weight of the constituent a, when the total weight of the mixture is regarded as unity. In all cases of this sort it is generally assumed, apparently with reason, (1) that no chemical reaction has taken place between the constituents, and (2) that the previous molecular state of each constituent in the pure condition still persists in their mixture.

The great mass of binary liquid mixtures, however, not only fails to follow this law, but shows a variation from it which depends solely upon the constituents selected, and upon the proportions in which they are mixed. From the fact that following the law of mixtures is regarded as indicating that a system is free from any chemical interaction between its constituents, and that the molecular states of its constituents are unaltered as a result of the mixing, it is natural to assume that a system which does not follow this law is one in which either a chemical reaction has taken place, or in which the constituents have undergone a molecular change, of the nature of a breaking down of a previous polymerization of one or both of the individuals, for example.

Many investigators, ignoring the second possible cause of change,

have assumed that, from the curve obtained by plotting the results of some one of the various physical properties of a system, which does not follow the mixture law, against the percentage composition of the mixture, it is possible not only to conclude that a chemical compound has been formed, but actually to calculate its formula. Washburn,[1] however, after an exhaustive review of the previous work, has concluded that in all such property-composition curves "supposed points of discontinuity are due to experimental error"......although "striking irregularities sometimes occur." Next, quoting the fact brought out by Tammann that "as regards certain of its physical properties a salt solution resembles the pure solvent under an increased external pressure"....he shows how this might "cause a dissociation of complex molecules into simple ones"......the effect of which would be that "a large part of the abnormal effects of salts upon the physical properties should also be ascribed to changes in the complexity of the solvent." Washburn's final conclusion, which may be regarded as the last word upon the subject of the physical properties of mixed liquids as it was then understood, is that "methods of studying hydration which depend upon the deviation of any physical property of a solution from the law of mixtures are incapable of yielding any *conclusive* information regarding the complexity or even the existence of hydrates in aqueous solution."

The later work of Denison,[2] however, has modified the above conclusion decidedly, at least in so far as it concerns mixtures of liquids, and apparently not only enables us to differentiate between the effects due to a change in the molecular states of the individual constituents, and those due to their chemical interaction, but also actually does make possible the calculation of the formula of the chemical compound formed in the latter case. Denison's method of attack was theoretical, in that he assumed in a hypothetical system that the various possible changes had taken place to different extents, and studied the curves thus obtained. In this manner he showed first, confirming Washburn's statement, that "a maximum or minimum in the property-composition curve must be taken as giving *possible* indication of the formation of a chemical compound, although there is no certainty." At the same time he calls attention to the fact that a sagged curve (without maxima or minima) may be caused by either a dissociation of one of the constituents, or by their chemical combination, but that a process involving increased association of one of the constituents as a result of their mixing is unlikely.

It is not the property-composition curve, however, but that for which the coördinates are composition and *deviation* from the mixture law, that leads to indications of chemical interaction between the constituents

[1] *Tech. Quart.*, **21**, 360 (1908).
[2] *Trans. Faraday Soc.*, **8**, 20, 35 (1912).

of mixed liquids. Denison's conclusions from curves of this form may be summarized briefly as follows:

The magnitude of the deviation from the mixture law is proportional to the amount of new substance formed, and always reaches a maximum when the concentration of the new substance attains a maximum value; and further, when this is true, the mixture as a whole has the same fractional composition as the new substance formed. Although temperature changes may affect the form of the property-composition curve, especially as regards the maximum point, the point of maximum *deviation* from the mixture law is independent of temperature change.

If the above be true, and aside from any consideration of the merits of the theoretical reasoning involved, the few applications of it by Denison himself are convincing, it will be seen that it is possible to determine the formula of a compound formed by the interaction of the constituents of a mixed-liquid system by aid of the physical properties alone, since the composition of the compound formed must invariably be identical with the composition of that mixture which exhibits the maximum deviation from the value calculated by aid of the mixture law. In other words, if Denison's conclusion be true, we can get as definite information from it for homogeneous liquid systems, as we can by the application of the phase rule to non-homogeneous systems.

In the course of the present series of investigations it is intended, among other things, to apply this proposed method of plotting results, not only with respect to surface tension, but also to all other physical properties that can be readily measured at the time, or for which results are given in the literature; in other words, to subject the method to a thorough experimental test.

The Determination of the Surface Tension.

The surface tensions of the sulfuric acid-water mixtures were determined by the drop-weight method,[1] the dropping tip, which in all cases gave drops for these solutions that were "normal" in profile, being standardized by aid of water at three temperatures, with the following result, each drop-weight value being the mean of several measurements, agreeing to within a few hundredths of one per cent.

t.	w_{H_2O} (mgs.).	γ_{H_2O} (dynes).	Constant $= \dfrac{\gamma_{H_2O,t}}{w_{H_2O,t}}$.
0	80.93	75.75[2]	0.9360
30	75.88	71.03	0.9361
50	72.21	67.59	0.9360
		Average,	0.9360

[1] See Morgan, THIS JOURNAL, **37**, 1461 (1915).

[2] This value is for water unsaturated with air. If air is bubbled through the liquid just before the determination, the values of both γ and w are slightly larger at 0°, *viz.*, $\gamma = 75.87$; but since this process is impossible in the later work with solutions, owing

The surface tension of a liquid can thus be found in dynes per centimeter at any temperature, from its drop weight in milligrams from this tip at that temperature, by aid of the equation

$$\gamma_{l,t} = 0.9360 \times w_{l,t}.$$

The value of this constant was redetermined frequently during the course of the work and found to remain unchanged. From the value of this constant the mean diameter of the tip used is calculated to be approximately 5.35 millimeters.[1]

Owing to the very viscous nature of sulfuric acid solutions from 60 to 90% content, and their consequent lack of what might be called covering power, difficulty was at first experienced in driving the drop out to the extreme edge of the tip. This trouble can be readily avoided in the case of all viscous liquids, however, by forcing the first drop out rapidly and nearly to maturity, and then quickly withdrawing it. This process is to be repeated perhaps a dozen times, until the tip is seen to be completely covered, after which each new drop, formed in the usual way, goes out of itself to the same extent, i. e., to the extreme edge of the tip, just as non-viscous liquids do without aid.

As in all previous work with solutions, the weighing vessel is first charged with a small amount of the liquid, the vessel and contents being weighed before it is attached to the apparatus and placed in the thermostat. When the proper temperature is attained, the desired number of drops are allowed to form and fall, and the vessel removed and again weighed with its contents. The difference in the two weighings thus gives the weight of the fallen drops. In this way, the concentration of the first and succeeding drops remains unchanged, for evaporation is prevented by the vapor already present from the inclosed liquid.

The thermometer used in the work was a certified one, the temperatures being fixed to within ±0.05°, while the weights employed had been compared with a standard set.

The sulfuric acid which served as a basis for the solutions was a good "C. P." acid of specific gravity 1.84. Both gravimetric and volumetric analyses of this sample showed that it contained 96.12% of H_2SO_4, and therefore, 3.88% of water, by weight. Solutions up to 96.12% acid were made from this by the addition of calculated amounts of distilled water, while those of higher concentration were prepared by adding various amounts of pure sulfur trioxide. The 100% acid thus produced had a melting point of 10.40°. All the solutions, in addition, were analyzed gravimetrically, with the result that no appreciable differences were found to exist.

to the loss of vapor and consequent change in concentration, the above procedure is to be preferred here. At higher temperatures, the effect of contained air is negligible.

[1] See Morgan, loc. cit., p. 1466.

The results for surface tension, as well as for specific cohesion, of the various solutions studied at three temperatures, are given in the following table. As the actual drop weights observed can be found, of course, from the surface tension results given, by division by the factor 0.9360, to save space, these are omitted in the table. All concentrations are expressed in weights of acid per 100 g. of solution.

TABLE I.—RESULTS.

Column 1, grams H_2SO_4 per 100 g. of solution; 2, mols of SO_3 per 100 mols of mixture; 3, temperature; 4, surface tension in dynes from $\gamma_t = $ constant $\times w_t;$ 5, specific cohesion, a^2, from γ and $d;$ 6, specific cohesion from interpolation formulas; 7 and 8, the values of the coefficients α and β of the interpolation formula for the variation in surface tension with temperature, for the concentration in question, viz., $\gamma_t = \gamma_0 + \alpha t + \beta t^2$, where γ_0 in very case is the value presented for that concentration at 0° in Column 4.

1.	2.	3.	4.	5.	6.	7.	8.
0	0	0°	75.75	15.46	15.44		
		30	71.03	14.56	14.46	—0.1485	—0.000294
		50	67.59	13.96	13.90		
4.67[1]	0.89	0	75.35	14.87	14.91		
		30	71.15	14.15	14.14	—0.1283	—0.00039
		50	67.96	13.64	13.63		
8.93	1.74	0	75.27	14.42	14.40		
		30	71.31	13.80	13.83	—0.1197	—0.00041
		50	68.26	13.34	13.37		
16.40	3.36	0	75.66	13.76	13.79		
		30	71.87	13.25	13.24	—0.1154	—0.000378
		50	68.95	12.84	12.88		
22.73	4.88	0	76.07	13.24	13.23		
		30	72.62	12.84	12.84	—0.0994	—0.00052
		50	69.80	12.48	12.49		
28.18	6.30	0	76.56	12.83	12.84		
		30	73.10	12.46	12.46	—0.1071	—0.000274
		50	70.52	12.16	12.15		
32.90	7.63	0	76.91	12.49	12.48		
		30	73.60	12.16	12.16	—0.1057	—0.000154
		50	71.24	11.91	11.90		
37.05	8.89	0	77.02	12.16	12.16		
		30	73.97	11.89	11.89	—0.0946	—0.000237
		50	71.70	11.66	11.66		

[1] This concentration corresponds within less than 0.1% to that solution investigated in 1912 by Morgan and Bole (THIS JOURNAL, **35**, 1756), who used a larger tip, standardized with both water and benzene. An idea of the reproducibility of the surface tension results by the drop-weight method can perhaps be best obtained from the comparison of the two sets of values given below:

t.	M. & B.	M. & D.
0°	75.39	75.35
15	73.33	73.34 (interpolated)
30	71.15	71.15

TABLE I (*continued*).

1.	2.	3.	4.	5.	6.	7.	8.
40.71	10.07	0	77.05	11.88	11.88		
		30	74.27	11.65	11.65	—0.0838	—0.000297
		50	72.12	11.44	11.44		
		70	69.50	. . .	. . .		
42.38	10.63	0	77.11	11.75	11.74		
		30	74.34	11.53	11.53	—0.0880	—0.000145
		50	72.35	11.34	11.33		
43.97	11.18	0	77.02	11.61	11.61		
		30	74.39	11.41	11.41	—0.0800	—0.000257
		50	72.38	11.23	11.23		
45.46	11.72	0	76.97	11.49	11.48		
		30	74.42	11.30	11.30	—0.0766	—0.00028
		50	72.44	11.12	11.13		
46.88	12.24	0	76.80	11.36	11.36		
		30	74.46	11.19	11.19	—0.0663	—0.00039
		50	72.51	11.02	11.03		
48.06	12.68	30	74.37	11.09	11.10		
48.23	12.75	0	76.57	11.21	11.24		
		30	74.34	11.07	11.09	—0.0637	—0.00036
		50	72.50	10.92	10.93		
49.51	13.24	0	76.41	11.09	11.12		
		30	74.30	10.97	10.98	—0.0582	—0.00041
		50	72.49	10.82	10.84		
54.10	15.11	0	75.82	10.65	10.67		
		30	74.06	10.59	10.59	. . . .	. . . . . .
		50	72.41	10.46	10.48		
57.86	16.76	0	75.17	10.28	10.29		
		30	73.80	10.27	10.25	—0.0263	—0.00065
		50	72.24	10.16	10.16		
61.08	18.28	0	74.45	9.95	9.92		
		30	73.29	9.96	9.97	—0.0235	—0.00051
		50	72.01	9.90	9.90		
66.23	20.94	0	73.39	9.45	9.45		
		30	72.47	9.49	9.52	—0.0152	—0.00052
		50	71.34	9.45	9.45		
70.18	23.18	0	72.21	9.03	9.06		
		30	71.63	9.12	9.14	—0.0058	—0.00084
		50	70.41	9.06	9.06		
72.95	24.89	0	71.49	8.77	8.75		
		30	71.00	8.86	8.85	+0.0085	—0.00083
		50	69.85	8.81	8.81		
75.84	26.78	0	70.63	8.48	8.48		
		30	70.03	8.56	8.53	+0.0028	—0.00076
		50	68.87	8.51	8.52		
79.69	29.51	0	69.06	8.08	8.09		
		30	68.66	8.18	8.16	+0.0214	—0.0012
		50	67.24	8.10	8.12		

TABLE I (continued).

1.	2.	3.	4.	5.	6.	7.	8.
83.06	32.14	0	67.22	7.70	7.71		
		30	66.72	7.78	7.78	+0.0108	—0.00092
		50	65.47	7.73	7.72		
86.26	34.89	30	64.12	7.36	7.38		
87.29	35.80	0	64.12	7.19	7.19		
		30	63.29	7.23	7.25	—0.0114	—0.00054
		50	62.20	7.19	7.18		
89.29	37.70	0	62.06	6.91	6.92		
		30	61.24	6.94	6.97	—0.0094	—0.00060
		50	60.10	6.90	6.92		
91.82	40.25	30	58.34	6.57	6.60		
92.62	41.09	30	57.53	6.46	6.48		
		50	56.70	6.44	6.46		
93.63	42.20	0	57.06	6.29	6.29		
		30	55.56	6.33	6.33	—0.0083	—0.00044
		50	56.42	6.30	6.30		
94.49	43.16	0	56.18	6.19	6.19		
		30	55.44	6.21	6.18	—0.0165	—0.00028
		50	54.67	6.19	6.20		
95.15	43.89	30	54.68	6.12	6.13		
95.66	44.51	0	54.98	6.05	6.04		
		30	54.28	6.07	6.06	—0.0171	—0.00021
		50	53.61	6.06	6.06		
96.12	45.05	0	54.44	5.99	5.99		
		30	53.67	6.00	6.01	—0.0235	—0.000075
		50	53.08	6.00	6.01		
96.89	45.98	30	52.79	5.90	5.91		
97.32	46.51	30	52.33	5.85	5.86		
99.20	48.92	30	50.23	5.62	5.61		
99.46	49.27	30	50.08	5.61	5.60		
99.80	49.72	30	49.63	5.56	5.56		
		50	49.06	5.56	5.54		
100.00	50.00	30	49.62	5.56	5.52		
100.80		30	49.47	...	...		
101.60		30	49.53	...	...		
102.40		30	49.62	...	...		
102.60		30	49.72	...			
103.05		30	49.91	...			
103.10		30	49.98	...	...		
103.45		30	50.01	...	...		

As it was found impossible to express directly the variation in surface tension with percentage composition at any one temperature, by aid of an equation, various indirect methods were tried which would enable one ultimately to interpolate with accuracy the value of γ at any desired concentration. The method which was finally adopted was one employ-

ing the values of specific cohesion (α^2), which were obtained by aid of the densities of Domke and Bein,[1] from the general equation

$$a_t^2 = \frac{2\gamma_t}{9.80d_t}.$$

The values of a^2 so obtained, when plotted against the molar percentage of SO_3 (i. e., mols of SO_3 per 100 mols of mixture), were found to give a curve which could be broken up into a series of straight lines for interpolation purposes. In this way it is possible to find a^2 at any desired concentration and 0°, 30° or 50°, to calculate from it and the density the corresponding value of γ, and then from the temperature variation of γ (found from the values at the three temperatures) to calculate γ at the desired temperature and concentration.[2]

The two values of a^2 thus found are given in Columns 5 and 6 of the table, and are included for the reason that only through the variation of a^2 with the composition can values of γ be interpolated at concentrations and temperatures other than those given.

Discussion of the Results.

In Fig. 1 the above results are shown graphically, the ordinates being surface tensions in dynes and the abscissas percentages of sulfuric acid (grams in 100 g. of solution). As will be observed, there is a decided maximum of surface tension in each of the isotherms, which shifts materially in terms of concentration with a change in temperature, and becomes more marked as the temperature increases, showing that the surface tension of all solutions is less influenced by a change in temperature than is that for water. Furthermore, since both the addition of sulfuric acid to water, as well as that of water to sulfuric acid, increases the surface tension, solutions of different concentrations may have the same surface tension value at the same temperature: for example, at 0°, when the concentrations of acid are approximately 28% and 48%, the surface-tensions are identical. In a similar way, the addition of sulfur trioxide to absolute sulfuric acid ($SO_3 \cdot H_2O$) also increases its surface tension.

[1] Landolt-Börnstein-Roth, *Tabellen*, 1912, pp. 265–6.

[2] The equations for this purpose are to be obtained by aid of the following table:

$$a_c{}^2 = x - yc.$$

(c = mols SO_3 per 100 mols of mixture.)

Range of c.	x.	y.	Range of c.	x.	y.	Range of c.	x.	y.
	0°.			30°			50°	
0–1.74	15.444	0.601	0.885–3.36	14.457	0.362	1.74–3.36	13.903	0.305
1.74–4.88	15.056	0.377	3.36–6.30	14.156	0.269	3.36–6.30	13.738	0.257
4.88–7.63	14.567	0.274	6.30–16.76	13.755	0.209	6.30–16.76	13.341	0.189
7.63–18.28	14.272	0.238	16.76–26.78	13.062	0.169	16.76–23.18	12.994	0.169
18.28–24.89	13.167	0.177	26.78–43.16	12.446	0.145	23.18–35.80	12.525	0.149
24.89–42.20	12.287	0.142	43.16–48.92	10.606	0.102	35.80–42.20	12.054	0.136
42.20–45.05	10.802	0.107	48.92–49.72	9.354	0.076	42.20–49.72	10.515	0.100

If this curve were examined by one who believes that the property-composition curve can lead to definite information as to the existence of compounds in solutions, he would possibly fix the apparent point of inflection existing at a concentration of about 85% acid as indicating the presence of the hydrate $H_2SO_4.H_2O$. It is true that such a compound
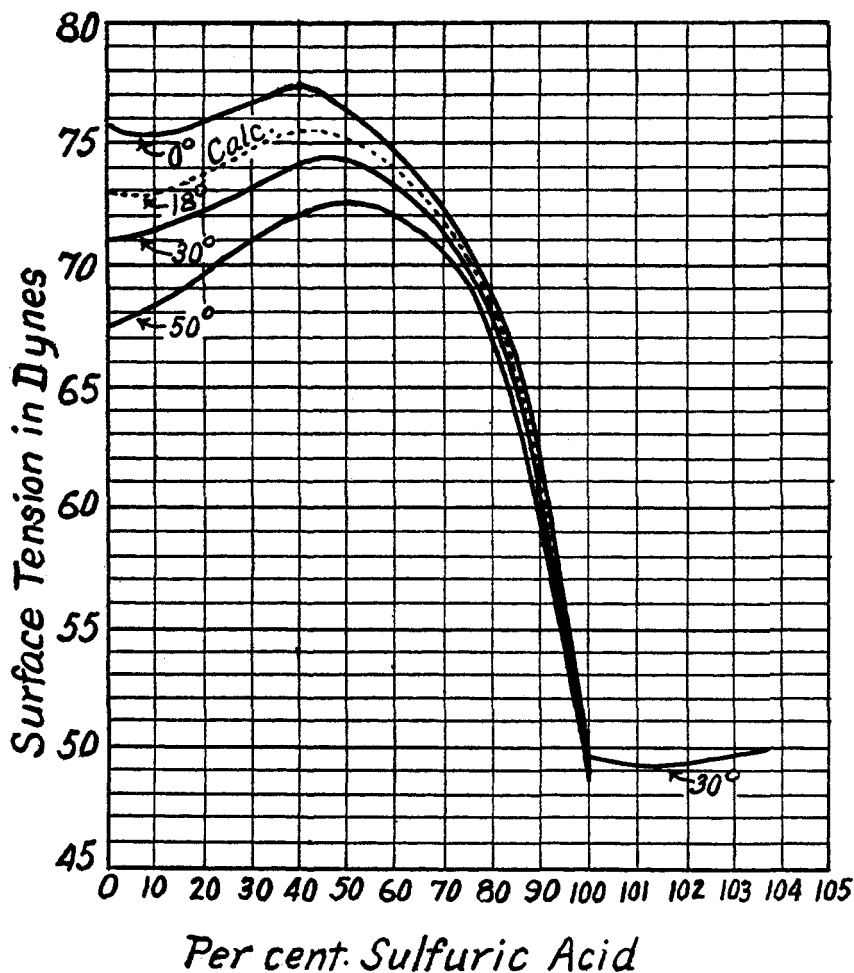

Fig. 1.

is proven to exist by the phase rule, and further, at least one other physical property shows irregularities at this concentration when so treated;[1] but as far as this one curve is concerned the indication must be regarded as altogether too faint for the drawing of any definite conclusion.

In Fig. 2 is presented a graph similar to that given by Röntgen and

[1] See Washburn, *loc. cit.*, p. 407.

Schneider,[1] and showing the relationship between surface tension and compressibility of sulfuric acid-water solutions. Although a direct comparison of our surface-tension results with theirs is impossible, as they employ arbitrary units for the expression of surface tension, the close similarity of the two surface-tension curves can be taken as showing that the results would agree very closely if expressed in the same units. Since their compressibility results are given at 18°, it was necessary for us to interpolate values of γ for that temperature by aid of columns 7 and 8 of Table I; it is from these that our surface-tension curve here is
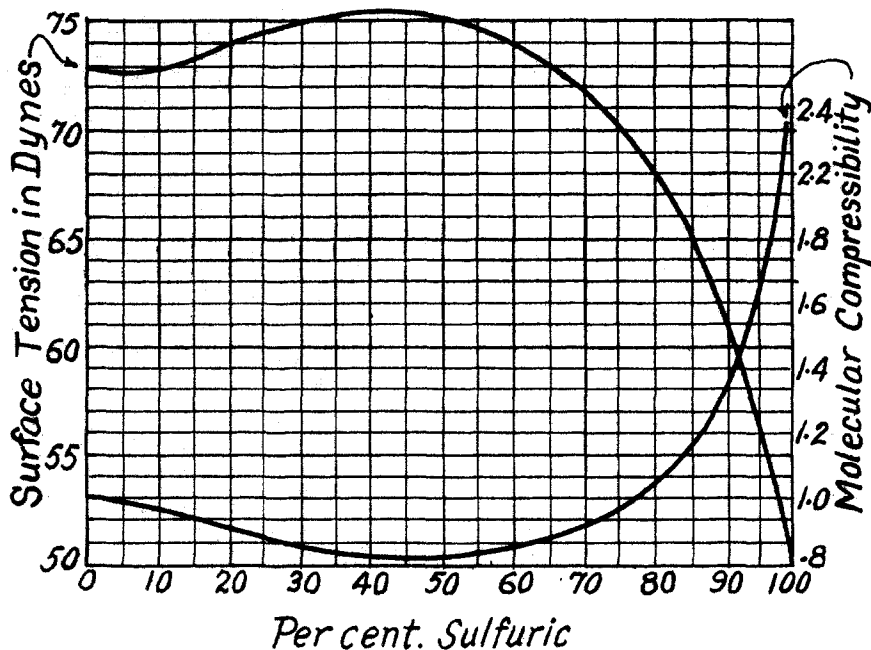
Fig. 2.

made up, and from which the dotted curve in Fig. 1 was plotted. Owing to the artificial unit selected by Röntgen and Schneider for the expression of the compressibility results in their curve, viz., *molecular compressibility*, which is the relative compressibility expressed in terms of water, when the change in volume is measured as taking place, not in equal volumes, but in volumes which contain an equal number of mols, it is difficult to see what significance they hoped to show by the fact that the two curves form such a symmetrical figure, for when plotted in any other terms they show no such relationship.

In Fig. 3 are grouped the curves plotted according to the Denison method,

[1] *Ann. Physik. u. Chem.*, **29**, 65 (1886). See also Whatmough, *Z. physik. Chem.*, **39**, 165 (1901).
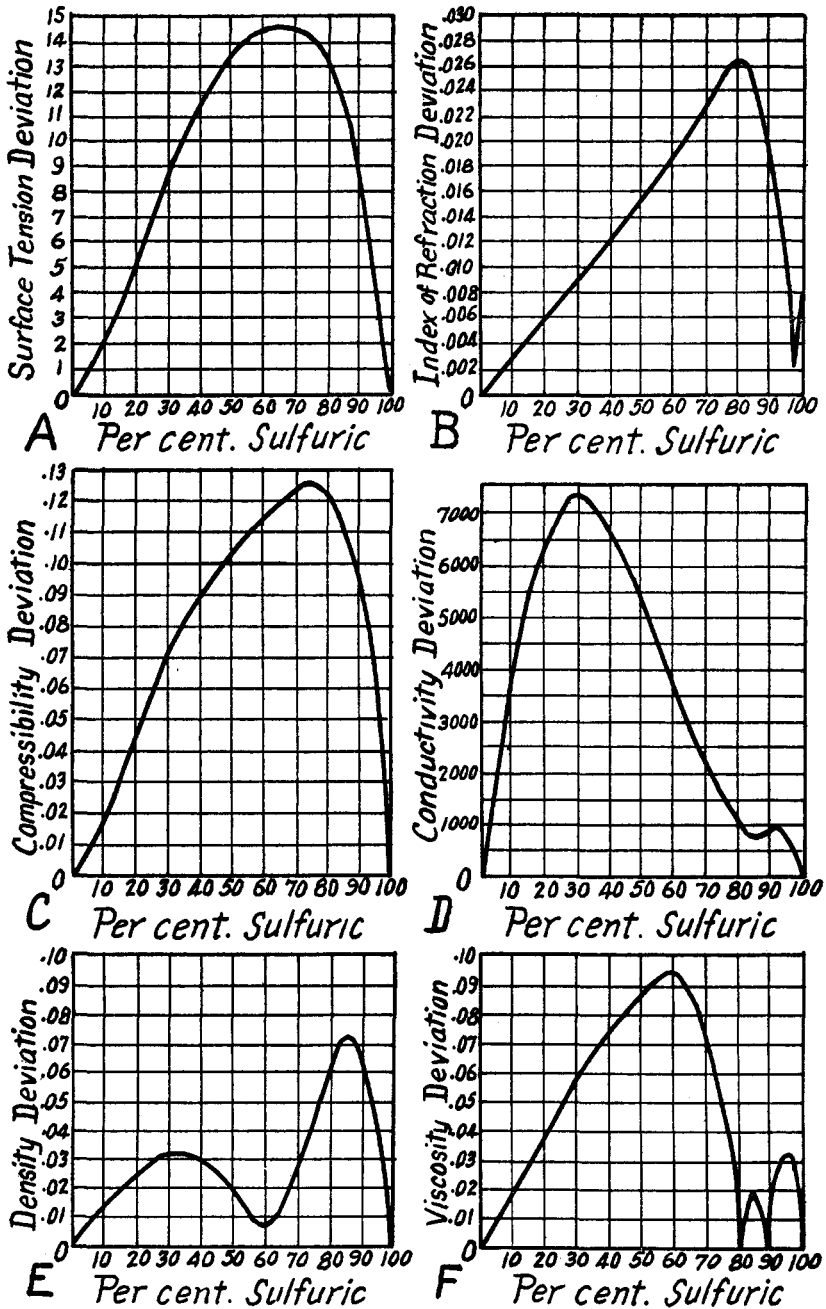
Fig. 3.

using the extents of the deviation from the mixture law as the ordinates, and percentages by weight of the liquid mixture as the abscissas. The surface tensions, according to the mixture law, as stated above, are calculated here from the values of that property for the constituents at the temperature in question, and the proportions in which they are present. Thus for a solution containing 4.67 g. of sulfuric acid to 95.33 g. of water, since the γ values at $0°$ are, respectively, 50.2 and 75.75 dynes, we have

$$\gamma_{mixt.} = (0.0467 \times 50.2) + (0.9533 \times 75.75) = 74.55 \text{ dynes.}$$

In this way the deviations shown in Table II are obtained, from which the above curve, A of Fig. 3, is obtained.

TABLE II.—SURFACE-TENSION DEVIATIONS.

Column I gives g. H_2SO_4 per 100 g. of solution.   II gives value of γ obs. minus γ calc., where γ calc. is found from the mixture law.

I.	II.	I.	II.	I.	II.	I.	II.
0	0.0	40.71	11.7	57.86	14.2	87.29	10.7
4.67	0.8	42.38	12.2	61.08	14.3	89.29	9.1
8.93	1.8	43.97	12.5	66.23	14.6	93.63	5.2
16.40	4.1	45.53	12.9	70.18	14.4	94.49	4.6
22.78	6.1	46.88	13.0	72.95	14.4	95.66	3.7
28.18	8.0	48.23	13.1	75.84	14.3	96.12	3.2
32.90	9.6	49.51	13.3	79.69	13.7	100.00	0.0
37.05	10.7	54.15	13.9	83.06	12.7	....	..

The values for viscosity are taken from Dunstan;[1] the electrical conductivities are those at $18°$ as given by Kohlrausch;[2] the densities are those of Domke and Bein[3] as reproduced in the above Tabellen (265–266); the refractive indices are those found by Veley and Manley;[4] while the relative compressibilities are those already mentioned of Rontgen and Schneider. In all cases the deviations of these results have been calculated in the same way as that illustrated above, so it will be unnecessary to present the actual values here.

As will be observed, maxima are exhibited by all the properties considered in the figure which, according to Denison's theory, should indicate that compounds are formed in every case by the interaction of the constituents, the composition of a compound always being identical with that of the mixture at the point of maximum deviation.

The deviation-of-property-composition curve for surface tension interpreted in this way would show the existence in solution of a compound of the formula $H_2SO_4.3H_2O$, which corresponds to about 65% sulfuric acid.

According to the deviation-composition curve for the index of refraction,

[1] *J. Chem. Soc.*, **91**, 85 (1907); *Proc. Chem. Soc.*, **30**, 104 (1914).
[2] Landolt-Börnstein-Roth, *Tabellen*, 1912, pp. 1099–1100.
[3] *Z. anorg. Chem.*, **43**, 125 (1905).
[4] *Proc. Roy. Soc.*, (A) **76**, 469–87 (1905).

a compound is indicated in the vicinity of 80%, while 85% would indicate $H_2SO_4.H_2O$ and 73% acid corresponds to $H_2SO_4.2H_2O$—the former composition being indicated by a maximum deviation in the compressibility deviation curve at that point also. The curves for the deviation of the other three properties considered show either two or three maxima each. Those for density indicating compounds of the formula $H_2SO_4.12H_2O$ (30% acid) and $H_2SO_4.H_2O$ (85% acid), while conductivity also leads to $H_2SO_4.12H_2O$ (30% acid) as well as to $3H_2SO_4.H_2O$ (94% acid); and, finally viscosity shows its three maxima at $H_2SO_4.4H_2O$ (58% acid), $H_2SO_4.H_2O$ (85% acid) and either $3H_2SO_4.H_2O$ (94%) as with conductivity, or $4H_2SO_4.H_2O$ (95%), $5H_2SO_4.H_2O$ (96%), it is impossible to decide which from the data.

It is to be remembered here that the phase rule consideration of this system, SO_3 in water, indicates the existence of the following solid hydrates: $H_2SO_4.4H_2O$, $H_2SO_4.2H_2O$, and $H_2SO_4.H_2O$, only the latter existing as a solid above $-15°$.

Unless the approximate position of the point of maximum deviation is first found, and later examined very closely, at small concentration intervals, errors in fixing the real maximum point up to perhaps 5% might well be present, which could account for some of the only approximate agreements in concentration noticeable at the maxima above. This would also account for the uncertainty as to which compound is shown by viscosity by the last maximum point considered, and by compressibility.

In connection with the finding of certain compounds indicated by the aid of one physical property, which are not shown by others, Denison calls attention to the fact that the compound formed may well be undistinguishable from the constituents, using one physical property as the criterion, whereas on the basis of some other property, it may vary widely. If this be true, a study of all properties would be necessary to fix all existing compounds.

Whether or not Denison's theory solves the question as to the existence of compounds in mixed liquids, the method does, at any rate, call attention to the various concentrations at which the maximum variation from the mixture law is found, according to which of the various physical properties is selected as a criterion. In this way, at any rate, the contemplated work of this series will call attention to those mixtures which are characteristic in producing the maximum variation from the mixture law, *i. e.,* will determine those mixtures which are most abnormal, so that in time, perhaps, not only will it be possible to prove the Denison theory to be correct or incorrect, but in the latter case, by a statistical study, to make an equivalent step forward in answering the question as to what happens when two liquids are mixed.

Summary.

The results of this research may be summarized briefly as follows:

(1) More than one hundred determinations of the surface tension of forty-eight concentrations of sulfuric acid in water, at various temperatures, have been made by aid of the drop-weight method, and formulas provided by which the surface tension and specific cohesion can be calculated at any concentration and temperature between 0° and 50°. A method is also given which obviates any difficulty produced in the drop-weight method by high viscosity and poor covering power.

(2) It is found that both the addition of sulfuric acid to water, as well as that of water to sulfuric acid, causes an increase in the surface tension, so that different concentrations of sulfuric acid may have identical surface-tension values at the same temperature. The addition of SO_3 to sulfuric acid ($SO_3.H_2O$) also increases the surface tension.

(3) If the property-composition curve means anything as to chemical interaction, it can be assumed, perhaps, from the surface-tension results to indicate the existence of the hydrate $H_2SO_4.H_2O$ at 85% acid.

(4) The application of the theory of Denison, that the deviation of a property from the mixture law plotted against the composition, shows at the point of maximum deviation the presence of a compound identical in composition with that of the solution leading to that maximum deviation, indicates the following hydrates in water solutions of sulfuric acid, according to the property which is taken as a criterion:

$H_2SO_4.H_2O$ by density, compressibility viscosity (and refraction);

$H_2SO_4.2H_2O$ (by refraction);

$H_2SO_4.3H_2O$ by surface tension;

$3H_2SO_4.H_2O$ by conductivity (and viscosity);

$H_2SO_4.12H_2O$ by conductivity and density;

$4H_2SO_4.H_2O$ or $5H_2SO_4.H_2O$ (by viscosity).

NEW YORK CITY.

THE TERNARY SYSTEM CaO–Al₂O₃–MgO.

BY G. A. RANKIN AND H. E. MERWIN.

The study of a three-component system can be undertaken only if the equilibrium relations in the three systems of two components have previously been ascertained, a prerequisite of which again is that the properties of the pure components be adequately known. Similarly, before one can proceed to the investigation of a four-component system—at least with the hope of a successful outcome—one must have elucidated the equilibrium relations in the four possible systems made up of combinations