came to the same conclusion, although their experimental deviations were far greater.[1] Similar experiments were also made by Ellis,[2] but his experimental variations were also considerably greater than our own.

Our experiments on the temperature coefficient of the cell 8 are also described in the former publication (L. and R.), and it was shown that in this manner an extremely exact determination could be made of the heat of formation of aqueous hydrochloric acid, and even a rough determination of its heat capacity. These measurements have also been reproduced and amplified by Ellis who investigated similar cells containing hydrochloric acid from 0.01 to 4.5 *M*.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 301.]

THE PROPERTIES OF MIXED LIQUIDS. III. THE LAW OF MIXTURES. I.

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Numerous attempts have been made to discover just what happens when two or more liquids mix to form a homogeneous system. Since in such cases neither chemical analysis nor the application of the phase rule can give aid, an answer to the question, if obtainable at all, can only be found from a study of the changes in the various physical properties brought about by the mixing.

All work based upon the change in a physical property which is caused by the mixing of one liquid with others, must necessarily depend upon the assumption that a general law exists, by aid of which, if no chemical interaction takes place between the constituents, and the individual constituents themselves, in the mixture, undergo no change in property due to simple contact with the others, it is possible to calculate from the values of that property for the pure constituents, and their amounts present in the system, the magnitude of the property for any one definite mixture. Such a "law of mixtures" has indeed been postulated in all work of this sort, but a survey of the literature fails to show the existence of any very definite or extensive experimental evidence of the general holding or lack of holding of such a law.

The object of this paper is to present the results of an experimental investigation of such a "law of mixtures," with surface tension as the

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[1] These authors attempt to decide the mechanism of the process of the hydrogen electrode from their experiments. It must be emphasized that no measurements of the potential of a reversible electrode give the slightest clue to the mechanism of the electrode process.

[2] Ellis, THIS JOURNAL, 38, 737 (1916).

property in question. One possible advantage possessed by these measurements, made as they are by the drop-weight method, is that the surface-tension values so found do not require a knowledge of the density of the system, as is necessary with results calculated from the capillary rise, so that they should be more consistent among themselves, and affected by fewer variables, than those found by that method.

The simplest and most logical mixture law, naturally, is that which involves the percentage by weight (in g.) of the constituents, together with their values of the property in question, when in the pure state, and of course at the same temperature.[1]

Such a law is

$$P_{\text{Mix.}} = l_a P_a + l_b P_b + l_c P_c + \text{etc.},$$

where the terms $P_{\text{Mix.}}$, P_a, P_b, P_c, etc., are the surface tensions, respectively, of the mixture, and of the constituents in the pure state, all at the same temperature; and the terms l are the fractions by weight of the constituents in the system, when their summation is equal to 1 g. For such a law to hold, it is generally conceded that in the mixture there must be no chemical interaction between the constituents, and that the value of the property P of each constituent in the mixture must remain what it was in the pure state.[2]

Many investigators, employing various physical properties, after assuming some such ideal mixture law to hold in general, have concluded

[1] This is true, naturally, only when the property is one which does not depend upon the number of molecular weights present, as the volume of a gaseous system does, for example, in which case the percentage in moles (*i. e.*, the molar fraction) would have to be substituted for the percentage by weight in g. In the case of surface tension, however, since it does not depend in any known, direct way upon the molecular weight or the volume, the relation in terms of percentage by weight in g. is the one logical one.

[2] It is difficult to fix the meaning of the terms employed in the various mixture laws which have been used in the past for the surface tension of a mixture, for no definition was given in the original paper, and various interpretations have been made by subsequent investigators. Thus, Rodenbeck (Inaugural Diss., Bonn, 1879) formulated the following approximate, empirical law for the value of the capillary constant of such mixtures as show no change in volume when the constituents are mixed: $a^2_{\text{Mix.}} = \mu_1 a_1^2 + \mu_2 a_2^2$, where μ_1 and μ_2 are called fractions of the constituents present (presumably by volume) and a_1^2 and a_2^2 are the capillary constants of the pure constituents. Fractions by volume are, of course, logical for capillary constants, as are fractions by weight in grams for surface tension.

Volkmann (*Ann. Phys.*, [3] 16, 321 (1882)) found that a similar law applied to surface tension and gave values in somewhat better agreement with experiment. He gives as his equation $\gamma_{\text{Mix.}} = \mu_1\gamma_1 + \mu_2\gamma_2$, where μ_1 and μ_2 are stated as being the same as those of Rodenbeck (by volume!).

In fact, throughout the literature, no further fixing of μ is indicated, and the various authors have assumed it to mean molecular fraction, weight fraction, or volume fraction. Thus, Whatmough (*Z. physik. Chem.*, **39**, 129 (1902)) uses at times all three of these units, while Worley (*J. Chem. Soc.*, **105**, 267 (1914)) uses volume fractions, both investigators calculating surface tension.

that variations from it, as illustrated by maxima or minima in the so-called property-composition curves (*i. e.*, those in which the values of the property and the compositions of mixture are employed as the coördinates), indicate the presence of chemical compounds formed by the interaction of the constituents, while others have also involved the idea that in part these variations may be due to a mutual breaking down of the polymerization previously existing in the pure constituents. Washburn has shown, however,[1] that although these conclusions *may* be justified, we have no certainty that they are.

Denison,[2] on the other hand, has derived theoretically a relation which enables us to differentiate between the effects due to the formation of chemical compounds, and those due to a disassociation of one or both of the constituents, after showing that a further association of these, due to the mixing, would be impossible. His proposed method of attack consists in plotting the *deviation* of the observed value of the property of the mixture, from the value for the mixture, as calculated from an ideal mixture law (in place of the value of the property itself), against the composition of the mixture. A maximum point of the curve here indicates the presence of the maximum amount of a chemical compound of a composition identical with that of the mixture which exhibits the maximum deviation from the law, while the disassociation of one or more of the constituents is evidenced only by a sagging of the curve.

It will be noted, here, that there is a decided difference in the meaning of a maximum in the two types of curve. Thus, with the property-composition curve, a maximum or a minimum simply shows at what composition of mixture *the property itself attains a maximum or minimum value*, while in the Denison curve, a maximum represents that composition of mixture at which *the deviation from the mixture law is a maximum.* That the latter means something more than the former is certainly evidenced by the experimental fact that the maximum or minimum point of a property-composition curve, in general, shifts with the temperature, *i. e.*, for the same mixed liquids, the maximum point appears at different compositions, depending upon the temperature. With the deviation—of property—composition type of curve, on the other hand, the maximum deviation from the mixture law is always found at the *same* concentration for any one kind of mixture, independent of the temperature—a change in temperature, here, only changing the angle at which the lines, which form the maximum by their junction, meet; in other words, the change in temperature simply accentuating or making less marked the maximum point.

As far as concerns the Denison method, it will be seen from the above

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[1] *Tech. Quart.*, **21**, 360 (1908).

[2] *Trans. Faraday Soc.*, **8**, 20, 35 (1913).

that it is not necessary to postulate a mixture law that always gives for normal liquid mixtures a calculated value exactly in accord with the observed, for it is not the absolute, but the *relative* deviations of the two values at various concentrations which are employed in abnormal mixtures. So long, then, as a mixture law is found, which, assuming the liquids to be normal, allows the calculation of the property value for the mixture (except, of course, in the case of extreme relative concentrations) that differs from the observed value by an approximately *constant* percentage of error for that system—the law would form a satisfactory basis for the Denison method of treating abnormal mixtures.

Experimental Results.

The surface tensions in this work were determined by the falling drop-weight method.[1] Each drop weight used was the mean of at least three results, which agreed with one another to within a few hundredths of 1%. Standard weights and certified thermometers were employed throughout.

All mixtures were made up by weight, and in order to prevent change of composition of the mixture, the more volatile liquids were always added last, the mixtures being cooled before transfer from the supply vessel to the apparatus. Each solution was freshly prepared just before being used, and a fresh portion taken for each determination. By allowing the first drop of the mixed liquid system carried over to remain suspended from the tip for a period of five minutes before causing it to fall, the weighing vessel was saturated with the vapor given off by the mixture. This drop was then allowed to fall with the assurance that all succeeding drops, since their equilibrium vapor pressure was previously attained, would evaporate to a minimum extent, if at all. The incorrectness in the composition of the first drop after hanging, and hence also in its weight, owing to unequal evaporation of the constituents, was of course compensated for in the five-drop blank, made exactly like the thirty-drop determination, and subtracted from it. This form of procedure appeared to give excellent results.

The choice of liquids and mixtures, as well as the number of concentrations of the substances in the mixtures, was unfortunately very materially restricted by the present great difficulty in obtaining pure chemicals, and by the small quantities of most of these which were obtainable at best. No liquid not known to be pure was used, except when experiment gave values of surface tension agreeing with those of previous investigators in this laboratory, whose liquids were known to be of the highest purity. This comparison served as a test both of the purity of the substances used in this work, and of the accuracy of the results.

The surface-tension values for the individual liquids are to be taken as accurate (and reproducible) to within a few hundredths of a dyne, while

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

for the mixtures, taking everything into account, the results are probably accurate to within considerably less than a tenth of a dyne. Attention is called to the fact here, in view of later results, that any change in the composition of a mixture, due to the evaporation of one constituent, would mean a raising of the surface tension, for the more volatile substances used were in general those of the lower surface tension.

The dropping tip used in this work gave drops for all the liquids studied that were normal in profile. The standardization of the tip (*i. e.*, the ascertaining of the factor which would transform drop weights from this tip in milligrams into surface tensions in dynes per centimeter) was made against *benzene* at three temperatures, and against *water* at two temperatures. The following equations[1] give the values of the surface tensions of benzene and water that were used in the standardization:

$$\gamma_{C_6H_6,t} = 30.514 - 0.132t + 0.000082t^2,$$

$$\gamma_{H_2O,t} = 75.872 - 0.1547t + 0.00022t^2$$

The equation for benzene represents the average results found by five investigators using the capillary rise method, while that for water is the generally accepted one.

A comparison of the drop weights and surface tensions, together with the values of the calculated ratio, is given in the following table:

STANDARDIZATION OF TIP.

Liquid.	t.	Av. drop wt. in mg. (w).	Surface tension in dynes per cm. (γ).	Constant ($= \gamma/w$).
Benzene...........	25°	28.253	27.26	0.9650
Benzene...........	30	27.592	26.63	0.9650
Benzene...........	35	26.926	25.99	0.9653
Water............	25	74.491	71.87	0.9648
Water............	30	73.647	71.03	0.9645
				Average, 0.9649

From these experiments, it is shown that the surface tension at any temperature, of any liquid, expressed in dynes per cm. can be found by multiplying its drop weight from this tip in mg. at that temperature, by the constant 0.9649. Or, for any liquid,[2] at any temperature, from this tip,

$$\gamma_{l,t} = 0.9649\, w_{l,t}.^{3}$$

The toluene, chlorobenzene and acetone used in this research, although the purest obtainable, were redistilled, and that fraction collected of

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[1] Morgan, *Loc. cit.*

[2] The liquid here is assumed to be such, of course, as to give on this tip a normal, bag-like drop.

[3] From Morgan (*Loc. cit.*, p. 1466) calculation shows the mean diameter of this tip to lie very close to 5.18 mm.

which the boiling point was constant to within 0.1°. The esters were those which had been especially prepared for previous researches.[1]

Since no determination of the surface tensions of specially purified toluene or chlorobenzene have been made previously in this laboratory, the results for these two liquids and the equations calculated for them are given below.

TOLUENE.

t.	w.	γ.
15°	29.160	28.14
25	27.976	27.00
50	25.026	24.15

$$\gamma_t = 29.843 - 0.1138t.$$

In the table below a comparison is presented of the values of γ, calculated from this equation to the temperatures employed by other observers, with those found directly by them. The values marked with a star are extrapolated.

COMPARISON OF γ VALUES FOR TOLUENE.[5]

t.	Ramsay and Aston.[2]	Renard and Guye.[3]	Walden and Swinne.[4]	M. and G.
13.1°	...	28.21	...	28.35*
15.2	28.18	...	...	28.11
21.2	...	...	27.39	27.43
27.1	...	...	26.73	26.76
29.1	...	26.33	...	26.53
46.6	24.60	...	...	24.54
48.0	...	24.15	...	24.38
59.0	...	23.10	...	23.13*
65.3	...	...	22.48	22.41*
78.4	20.93	...	...	20.92*
79.0	...	20.92	...	20.85*

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[1] By the Hoffman and Kropff Chemical Co.

[2] *Z. physik. Chem.*, **15**, 39 (1894).

[3] *J. chim. phys.*, **5**, 81 (1907).

[4] *Z. physik. Chem.*, **80**, 700 (1912).

[5] According to the capillary rise of Richards and Combs (THIS JOURNAL, **37**, 1856, (1915)), the surface tensions of the liquids benzene, toluene, ethyl alcohol, methyl alcohol and isobutyl alcohol should be higher than the values found by other observers, using the same method, although they find the conventional value for water.

It is of interest here, in connection with the above results for toluene, to make a comparison of the surface-tension values of the above liquids, excluding water, as found by Richards and Combs, with those that would have been found by the various investigators working in this laboratory with the *purely relative* drop-weight method for surface tension, if they had used the Richards-Combs value of γ for benzene at 20°, in place of the value calculated by the benzene equation given above, for the standardization of the tip.

The two individual values found by Richards and Combs at 20° for benzene were 28.94 and 28.88, *i. e.*, a mean value of 28.91 dynes per cm., while the benzene equation used throughout in standardizing a tip leads at that temperature to 27.91 dynes per cm. By multiplying the results for γ for any liquid, as given by the drop-weight investi-

CHLOROBENZENE.

t.	w.	γ.
10°	34.544	33.33
25	32.640	31.49
40	30.784	29.70

$$\gamma_t = 34.535 - 0.1210t.$$

This equation leads to a result at 39° which agrees exactly with that found by Renard and Guye, and, in general its results differ but slightly from the values of other observers using the capillary rise method.

All the other liquids studied were those prepared for previous researches, the results agreeing with those obtained earlier, with the one exception of amyl hydrocinnamate, which though in stock had never been previously studied.

The values of the surface tension of the individual liquids, at the tem-

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gators on the basis of the other standardization, then by the ratio 28.91/27.91 = 1.0358, we should obtain values based upon the Richards and Combs' value as a standard. These values should then be comparable with those of Richards and Combs—and an agreement would show that drop weights from a proper tip are indeed proportional to their surface tensions. In the table below is shown the very remarkable agreement in the values of surface tension by the two methods, the largest deviation being equal only to the deviation of the Richards and Combs' mean from the two individual values for benzene, *i. e.*, 0.03 dyne per cm.

COMPARISON OF γ VALUES AT 20°.

		Drop weight.	
Liquid.	Capillary rise. γ R. & C.	γ based on the R. and C. value.	γ based on the average value.
Ethyl alcohol	22.27	22.30	21.53[1]
Methyl alcohol	22.61	22.63	21.85[1]
Isobutyl alcohol	22.85	22.86	22.07[2]
Toluene	28.58	28.56	27.57[3]

[1] Morgan and Neidle, THIS JOURNAL, **35**, 1862 (1913); direct result at 20°.

[2] Morgan and Stone, *Ibid.*, p. 1510; interpolated value from $\gamma = 23.569 - 0.07497t$, the temperature being incorrectly given there as $0.025t$.

[3] Morgan and Griggs. Interpolated result.

The above values are also, naturally, those that would be obtained directly by multiplying the drop weight of the liquid by the ratio $\gamma_{C_6H_6}$, R. & C./$w_{C_6H_6}$ at 20°, in place of by the customary $\gamma_{C_6H_6}$, equation/$w_{C_6H_6}$, both at one identical temperature, the constant so obtained being 1.0358 times the one always employed in the past in the drop-weight work. And the same general result could be shown by finding the ratios of the surface tension of benzene to those of the other liquids, and comparing them with the ratios of the drop weight of benzene to the drop weights of the other liquids, from, of course, the same tip and at 20°—for the corresponding ratios would show the same identity in value exhibited above. As far as these liquids are concerned, the above table is to be taken as proof positive, then, that drop weights from a proper tip are also rigidly proportional to the larger surface tensions as found by Richards and Combs—and that as a *relative* method the one based upon the drop weight is a correct one. The agreement in the table is indeed most remarkable, in view of the fact that *three* different sized tips were used in the drop-weight work, and the measurements made by three different individuals.

peratures employed for the mixtures, as determined directly by the drop-weight method in this work are given below. These are the values of γ to be used in the law of mixtures for the calculation, with the percentages by weight, of the theoretical values of the surface tension of the mixtures, which are then to be compared with the values directly observed. It will be seen from this that every value considered in this paper is either determined directly at the temperature considered, or calculated from those which are so determined by but a very small interpolation.

VALUES OF γ USED IN MIXTURE-LAW CALCULATIONS.

Liquid.	t.	γ.	Liquid.	t.	γ.
Benzene	10.0	29.201	Methyl propionate	15.0	24.636
Benzene	10.8	29.097	Methyl propionate	40.0	21.699
Benzene	15.0	28.550	Ethyl formate	15.0	23.505
Benzene	40.0	25.361	Ethyl formate	40.0	20.502
Toluene	10.0	28.705	Propyl acetate	15.0	24.080
Toluene	10.8	28.614	Propyl acetate	40.0	21.347
Toluene	15.0	28.136	Methyl butyrate	15.0	24.667
Toluene	40.0	25.291	Methyl butyrate	40.0	21.903
Chlorobenzene	10.0	33.325	Ethyl lactate	15.0	29.449
Chlorobenzene	15.0	32.720	Ethyl lactate	40.0	26.990
Chlorobenzene	40.0	29.695	Amyl hydrocinnamate	15.0	31.359
Ethyl propionate	10.0	24.468	Amyl hydrocinnamate	40.0	29.275
			Acetone	15.0	23.335

In the following tables, in which all the percentage values are *by weight* (in g.), the observed values for the mixtures are compared with those calculated by aid of the above surface tensions and the percentages, using the mixture law already stated:

MIXTURES OF TWO LIQUIDS.

1. Benzene-Toluene:

t.	Benzene.	Toluene.	γ obs.	γ calc.	Deviation.
10.8°	24.98%	75.02%	28.76	28.74	+0.02
	50.07%	49.93%	28.85	28.86	−0.01
	75.06%	24.94%	29.01	28.98	+0.03
40.0°	24.99%	75.01%	25.21	25.31	−0.10
	47.69%	52.31%	25.22	25.32	−0.10
	74.98%	25.02%	25.25	25.34	−0.09

2. Benzene-Ethyl Propionate:

t.	Benzene.	Ethyl propionate.	γ obs.	γ calc.	Deviation.
10.0°	42.93%	57.07%	26.42	26.50	−0.08
	54.55%	45.45%	26.94	27.05	−0.11

3. Benzene-Chlorobenzene:

t.	Benzene.	Chlorobenzene.	γ obs.	γ calc.	Deviation
10.0°	30.18%	69.82%	31.70	32.08	−0.38
	46.94%	53.06%	31.00	31.39	−0.39
	71.19%	28.81%	30.13	30.39	−0.26
40.0°	30.18%	69.82%	27.99	28.39	−0.40
	44.54%	55.46%	27.27	27.77	−0.50
	72.67%	27.33%	26.16	26.55	−0.39

MIXTURES OF TWO LIQUIDS (*continued*).

4. Benzene-Methyl Butyrate:

t.	Benzene.	Methyl butyrate.	γ obs.	γ calc.	Deviation.
15.0°	33.62%	66.38%	25.91	25.97	—0.06
	50.77%	49.23%	26.55	26.64	—0.09
	77.25%	22.75%	27.67	27.67	0.00
40.0°	33.62%	66.38%	22.99	23.07	—0.08
	50.77%	49.23%	23.54	23.66	—0.12
	77.25%	22.75%	24.52	24.57	—0.05

5. Benzene-Propyl Acetate:

t.	Benzene.	Propyl acetate.	γ obs.	γ calc.	Deviation.
15.0°	54.97%	45.03%	26.39	26.54	—0.15
40.0°	54.97%	45.03%	23.40	23.55	—0.15

6. Benzene-Acetone:

t.	Benzene.	Acetone.	γ obs.	γ calc.	Deviation.
15.0°	45.22%	54.78%	25.44	25.69	—0.25

7. Toluene-Ethyl Propionate:

t.	Toluene.	Ethyl propionate.	γ obs.	γ calc.	Deviation.
10.0°	51.87%	48.13%	26.64	26.67	—0.03

8. Toluene-Chlorobenzene:

t.	Toluene.	Chlorobenzene.	γ obs.	γ calc.	Deviation.
10.0°	21.99%	78.01%	32.01	32.31	—0.30
	51.08%	48.92%	30.55	30.97	—0.42
	77.30%	22.70%	29.53	29.75	—0.22
40.0°	21.99%	78.01%	28.44	28.73	—0.29
	51.08%	48.92%	27.03	27.45	—0.42
	77.30%	22.70%	26.02	26.29	—0.27

9. Toluene-Methyl Propionate:

t.	Toluene.	Methyl propionate.	γ obs.	γ calc.	Deviation.
15.0°	32.67%	67.33%	25.74	25.78	—0.04
	46.20%	53.80%	26.16	26.25	—0.09
	74.99%	25.01%	27.21	27.26	—0.05
40.0°	32.67%	67.33%	22.72	22.87	—0.15
	46.20%	53.80%	23.23	23.36	—0.13
	74.99%	25.01%	24.27	24.39	—0.12

10. Toluene-Ethyl Formate:

t.	Toluene.	Ethyl formate.	γ obs.	γ calc.	Deviation.
15.0°	27.33%	72.67%	24.47	24.77	—0.30
	51.13%	48.87%	25.39	25.87	—0.48
	82.02%	17.98%	26.99	27.30	—0.31
40.0°	27.33%	72.67%	21.49	21.81	—0.33
	51.13%	48.87%	22.48	22.95	—0.47
	82.02%	17.98%	24.12	24.43	—0.31

11. Chlorobenzene-Acetone:

t.	Chlorobenzene.	Acetone.	γ obs.	γ calc.	Deviation.
15.0°	50.25%	49.75%	26.56	28.05	—1.49

12. Chlorobenzene-Ethyl Propionate:

t.	Chlorobenzene.	Ethyl propionate.	γ obs.	γ calc.	Deviation.
10.0°	50.25%	49.75%	27.93	28.92	—0.99

MIXTURES OF TWO LIQUIDS (*continued*).

13. *Ethyl Lactate-Propyl Acetate:*

t.	Ethyl lactate.	Propyl acetate.	γ obs.	γ calc.	Deviation.
15.0°	28.68%	71.32%	25.19	25.62	—0.43
	51.59%	48.41%	26.19	26.85	—0.66
	78.83%	21.17%	27.78	28.31	—0.53
40.0°	28.68%	71.32%	22.48	22.97	—0.49
	51.59%	48.41%	23.54	24.26	—0.72
	78.83%	21.17%	25.21	25.80	—0.59

14. *Chlorobenzene-Methyl Butyrate:*

t.	Chlorobenzene.	Methyl butyrate.	γ obs.	γ calc.	Deviation.
15.0°	53.51%	46.49%	28.13	28.98	—0.85
40.0°	53.51%	46.49%	25.28	26.07	—0.79

15. *Amyl Hydrocinnamate-Methyl Propionate:*

t.	A. h.	M. p.	γ obs.	γ calc.	Deviation.
15.0°	51.52%	48.48%	27.25	28.10	—0.85
40.0°	51.52%	48.48%	24.50	25.60	—1.10

16. *Acetone-Propyl Acetate:*

t.	Acetone.	Propyl acetate.	γ obs.	γ calc.	Deviation.
15.0°	49.70%	50.30%	23.63	23.71	—0.08

MIXTURES OF THREE LIQUIDS.

17. *Benzene-Toluene-Ethyl Propionate:*

t.	Benzene.	Toluene.	Ethyl propionate.	γ obs.	γ calc.	Deviation.
10.0°	34.29%	33.43%	32.28%	27.48	27.51	—0.03

18. *Benzene-Toluene-Chlorobenzene:*

t.	Benzene.	Toluene.	Chlorobenzene.	γ obs.	γ calc.	Deviation.
10.0°	31.34%	32.78%	35.89%	30.11	30.52	—0.41
40.0°	30.36%	33.66%	35.97%	26.46	26.89	—0.43

19. *Benzene-Toluene-Methyl Propionate:*

t.	Benzene.	Toluene.	Methyl propionate.	γ obs.	γ calc.	Deviation.
15.0°	33.07%	33.68%	33.25%	27.03	27.11	—0.08
40.0°	33.07%	33.68%	33.25%	23.96	24.12	—0.16

20. *Benzene-Toluene-Acetone:*

t.	Benzene.	Toluene.	Acetone.	γ obs.	γ calc.	Deviation.
15.0°	30.99%	32.87%	36.15%	26.24	26.53	—0.29

MIXTURES OF FOUR LIQUIDS.

21. *Benzene-Toluene-Ethyl Propionate-Chlorobenzene:*

t.	Benzene.	Toluene.	E. p.	Chlorobenzene.	γ obs.	γ calc.	Deviation.
10.0°	23.18%	27.62%	18.45%	30.74%	28.97	29.46	—0.49

22. *Benzene-Toluene-Methyl Propionate-Ethyl Lactate:*

t.	Benzene.	Toluene.	M. p.	E. l.	γ obs.	γ calc.	Deviation.
15.0°	24.60%	24.09%	27.74%	23.58%	27.33	27.58	—0.25
40.0°	24.60%	24.09%	27.74%	23.58%	24.32	24.72	—0.40

23. *Benzene-Toluene-Methyl Butyrate-Propyl Acetate:*

t.	Benzene.	Toluene.	M. b.	P. a.	γ obs.	γ calc.	Deviation.
15.0°	23.57%	26.28%	24.56%	25.59%	26.28	26.34	—0.06
40.0°	23.57%	26.28%	24.56%	25.59%	23.34	23.47	—0.13

MIXTURES OF FIVE LIQUIDS.

24. *Benzene-Toluene-Methyl Butyrate-Propyl Acetate-Methyl Propionate:*

t.	Benzene.	Toluene.	M. b.	P. a.	M. p.	γ obs.	γ calc.	Deviation.
15.0°	17.61%	20.50%	20.17%	21.01%	20.72%	25.84	25.94	—0.10
40.0°	17.61%	20.50%	20.17%	21.01%	20.72%	22.88	23.05	—0.17

Discussion of Results.

Of the twenty-four differently constituted mixtures studied in this research, almost all being considered in several proportions and at two temperatures (*viz.*, 16 of two constituents, 4 of three, 3 of four, and 1 of five), the mixture law, depending upon the relative weights *in g.* of the constituents, may be said *to hold rigidly* in ten cases if we accept 0.1 dyne per centimeter as a plausible experimental error (*viz.*, 6 mixtures of two constituents 2 of three, 1 of four, and 1 of five). A similar result is also obtainable from the drop-weight measurements of Morgan and Thomssen[1] of an equal weight mixture of another system, benzene and carbon tetrachloride, where the deviation of the observed from the calculated value is but 0.03 dyne per cm., a fact that is confirmed for this system in a different relative proportion by the work of Ramsay and Aston.[2] The latter investigators find also that a similar following of this law is exhibited by two mixtures of different proportions of toluene and piperidine.

For the other fourteen systems studied above, the calculated result is found to deviate from that observed, by amounts varying from 0.15 to 1.5 dynes per cm., *the observed result being consistently and invariably smaller than that calculated.* Further, the deviation here is always greater at 40° than at 10°.

Perhaps the most important experimental result obtained in this work, in connection with the fact that the deviation, when it exists, is invariably in the same direction, is the further fact that the *maximum* deviation is also invariably exhibited by those mixtures which contain approximately equal parts by weight of the constituents. So consistent was this result that those mixtures, which for one reason or another could not be studied in more than one proportion by weight, were invariably measured on an equal weight basis, since plainly that mixture would show the maximum possible deviation of such a system, and would present the worst possible condition for the holding of the mixture law.

It is possible that such deviations as those found above may be dependent upon two factors, one of which is certainly of great importance, while the other may perhaps ultimately be found to merge completely and invariably into it. The factor, of doubtful meaning, is the magnitude of the difference existing between the surface-tension values of the constituents themselves, when in the pure state—the other being the specific

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[1] THIS JOURNAL, 33, 667 (1911).

[2] *Loc. cit.*

chemical nature of the substances. That the difference in magnitude of the constituents' surface tension may have no effect in some cases at least, and the specific nature a large effect, is shown by contrasting the mixtures of toluene and ethyl propionate on the one hand, where the constituents differ in surface tension by 4.24, and yet the deviation of the observed from the calculated values of the mixture is but 0.03 dyne per cm., with those of toluene and ethyl formate, on the other, which, while exhibiting a difference of 4.63 themselves, lead to a deviation of the mixture of 0.48 dyne per cm.

This naturally points to a decided difference in effect, when mixed with toluene, of ethyl propionate and ethyl formate, which can only be due to a difference in the specific nature of the two. Further, *all* mixtures containing chlorobenzene invariably show large deviations from the mixture law, while those containing benzene show none at all, or at worst much smaller ones, although the surface tensions at 10° are, respectively, 33.33 and 29.20 dynes per cm. This result for chlorobenzene mixtures is confirmed by the work of Ramsay and Aston, who find that the mixture of chlorobenzene and ethylene dibromide gives large variations from the calculated values—the deviation in this case, contrary to the ones above, seeming to decrease at a higher temperature. In the same way, chloroform and carbon disulfide mixtures as found by them give large deviations, but whether this is due to the chloroform or the carbon disulfide, or to both, cannot be stated, as no other mixtures of either were studied.

It will be noted from the tables above that in all binary mixtures, the maximum deviation is at a concentration of approximately equal weights of the constituents, and, except at extreme relative concentration of the constituents, is roughly constant. As was mentioned above, this would not affect the result obtained from the deviation-of-property—composition curve nearly as much as it would affect the comparison of the calculated and observed values of the mixture; for it is the *relative* deviations at various dilutions employed in this curve, and the differences in the deviations at various concentrations are very much smaller than the deviations themselves at any one concentration. In this case, however, this conclusion could only be drawn for mixtures which are not extreme (relatively) in concentration, for a very small amount of one liquid could not affect the value of the mixture so considerably and consequently would cause the law to hold to a better, absolute degree.

The study of mixtures containing more than two constituents, makes evident that the law still holds most satisfactorily in certain cases. The deviations here, when they are present, are never additive, but rather of the same order of magnitude as those of the pairs of constituents of which they could be made. Thus the deviation of a benzene-methyl butyrate-toluene-propyl acetate mixture is of the order of the deviation of the benzene-methyl butyrate or the benzene-propyl acetate or the benzene-toluene binary mixtures, and is not equal to the summation of their deviations.

Since we cannot prove by any known, direct method that the liquids used in the mixtures studied in this research either react chemically with one another in the mixture or fail to react, or whether the constituents are really associated when pure or not, or whether such a possible state of association is changed or not on mixing, we are free to make two assumptions as to the holding of the mixture law, and to choose the more plausible and consistent to serve as a temporary guiding principle which may aid in obtaining a definite answer to the question ultimately.

I. If *all* these mixtures studied are really free from chemical reaction between the constituents, and no change of the individual constituents of any sort results from the mixing—then the mixture law in the above form is plainly a failure, capable of errors which are certainly far beyond the experimental errors of even the roughest of methods. It could still be used as a basis for the Denison method, however, even in this form, for the *difference* in the deviations at various concentrations is much smaller than the deviation of any one concentration from the law—and it is of such *relative* deviations with concentration that the Denison law has to do.

II. If, on the other hand, we are free to assume in some of the above mixtures that slight changes are possible, of the nature perhaps of a change in the property of the constituents themselves due to the mixing, rather than the formation of a new compound, then the mixture law can be considered as a rigid law in those cases in which no changes of this sort occur.

The experimental results here show that in ten cases the law holds rigidly, while in the other fourteen there is always a negative deviation of the experimental from the calculated value, with a maximum deviation invariably at an equal weight (in g.) concentration of the mixture. Further than this, certain definite liquids are found to invariably affect their mixtures with *every* other liquid in such a way as to lead to an abnormal result similar to the above.

As no one liquid could conceivably be assumed to interact chemically with *all* others, and as a chemical interaction, if it take place, could not possibly lead in all cases and invariably to the greatest amount of a compound formed at an *equal-weight* (in g.) mixture of the constituents, it would seem that a chemical interaction of the constituents as the cause of the deviation would be a thing very far indeed from the facts.

This conclusion would leave only an effect of one liquid upon the property of the other, or a similar mutual effect of the constituents upon one another, as a possible explanation of the observed deviation. That explanation, however, would seem to lead directly and exactly to just such results as those above. For if $P_{\text{Mix.}}$ in the equation $P_{\text{Mix.}} = l_aP_a + l_bP_b$ is to vary to a maximum, through, for example, a change in the value of P_b, as caused by the presence of the other, unchanged liquid, and naturally, proportional to the amount of this, it is clear that the maximum effect on $P_{\text{Mix.}}$ must be due to a maximum change in the whole term l_bP_b, and not in P_b alone. And since to produce this, l_b would have to be as large as possible, and P_b would have to be affected as much as possible (*i. e.*, l_a would have to be as large as possible), it is clear that the maximum effect on $P_{\text{Mix.}}$ (*i. e.*, on l_bP_b) would be observed at a concentration of 50% each of the two constituents. For the greatest change in the term l_bP_b must necessarily be brought about, and only then, when the maximum possible amount of liquid is affected to the greatest extent possible, *i. e.*, by the greatest amount of the other; and since $l_a + l_b = 1$ by definition, l_a in the mixture must equal l_b, and each equal 0.5.

Since the higher temperatures indicate increased abnormality in result over those at the lower, although the maximum point remains at the 50% concentration, the effect of one liquid upon the property of another, or the neutral effect of the liquids upon one another, must increase with increased temperature.

This reasoning it is thought makes supposition II above the one which is to be regarded as probably true, at least with regard to such mixtures as have been studied in this work.

With respect to other forms of the mixture law applied to the above results, it must be noted here that using either the volume per cent. or the molar per cent., in place of the weight per cent. (in g.), fails to lead to as satisfactory a general result as that given above. As no theoretical reasons exist for the selection of either of these over the latter for the property of surface tension, although, for example, the molar fractions might be necessary for some properties, as volume of a gaseous mixture, the matter need not be discussed further here, although all values have been calculated.

Ramsay and Aston and Kremann and Meingast[1] have studied the additive property of the function $\gamma(M/d)^{2/3}$ in place of γ, with some success. It must be confessed, however, that this relationship complicates the question somewhat, in that a change of density on mixing could conceivably counteract and render invisible a real effect on the surface tension. It would seem that something of this sort often occurs, for Kremann and Meingast find the value of this function in the mixture to be additive for 22 out of the 24 liquids studied. For purposes of segregating groups of liquids according to their effect when mixed, the relationship can hardly be said to be as useful as the one we have used.

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[1] *Monatsh.*, **35**, 1323 (1914).

Summary.

The results obtained in this research may be very briefly summarized as follows:

I. From the surface tensions by the drop-weight method, of *twenty-four* homogeneous mixtures in various proportions and at two temperatures, it was found that *ten* follow rigidly the law of mixtures in the form $P_{Mix.} = l_aP_a + l_bP_b +$ etc. (where the summation of the relative weights l_a, l_b, etc., is equal to 1 g.). Of these mixtures, *six* were of two constituents, *two* of three, *one* of four, and *one* of five.

II. Whenever variations appear (the other *fourteen* mixtures) the observed value is invariably less than that calculated from the law. These deviations increase in magnitude with increased temperature, and are always at a maximum at both temperatures for that mixture which contains equal weights (in g.) of the constituents.

III. Although the deviations might be due to the magnitude of the difference in the surface-tension values of the constituents when pure, the effect is probably negligible and merges into the more important factor—the nature of the constituent. An example of this latter is chlorobenzene, which renders every mixture, in which it is, abnormal. The deviation of a complex mixture is not a summation of the deviations of the pairs of liquids of which it could be made, but is of the same order as these.

IV. It is shown that chemical interaction for binary mixtures could not be the cause of the maximum deviation invariably found at a composition of mixture of 50% by weight (in g.) of the two constituents—whereas this behavior is shown to be exactly that which might be expected if the one liquid by its simple, physical, presence influenced the value of the property of the other (or each affected the other), and the conclusion is consequently drawn that the mixture law considered is a rigid law, provided no chemical interaction takes place between the constituents, and neither liquid influences the value of the property of the other. The effect of this latter action is invariably to produce the maximum deviation at a 50% mixture by weight (in g.) of the two constituents.

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THE PROPERTIES OF MIXED LIQUIDS. IV. THE LAW OF MIXTURES. II.

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This investigation is a continuation of the work of Morgan and Griggs,[1]

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[1] See preceding paper.