A CONTRIBUTION TO THE THEORY OF SOLUTION.

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When two completely miscible liquids, which do not visibly react with each other, are mixed together in any proportion, the physical properties of the mixture are found in general to differ from those calculated according to the simple mixture law. This divergence has been ascribed to changes in the state of aggregation of the molecules of one or both liquids, to the formation of a definite compound between the two liquids, or to both these causes combined. From a qualitative standpoint the theory is quite satisfactory; on the other hand, it is extremely difficult to apply quantitatively, except in the simplest cases. The reason for this lies in our lack of satisfactory knowledge of the molecular condition of most liquids and of the changes in this condition which take place when different liquids are mixed together. Nevertheless, some fairly satisfactory quantitative results have been obtained in a few simple cases.

Dolezalek * endeavours to apply a quantitative theory in the simplest possible cases—

- (i.) Where both liquids are unassociated and one solvate is formed between them.
- (ii.) Where one liquid is normal and the other partly associated, while no solvate is formed.

He exemplifies (i.) with mixtures of acetone and chloroform and (ii.) with mixtures of benzene and carbon tetrachloride. By assuming that neither the solvate molecules nor the associated liquid molecules are volatile as such, he shows that a knowledge of the partial pressures of the two components in the vapour phase enables quantitative data as to the extent of solvate formation or association to be determined and also enables the physical properties of any mixture to be calculated. The only physical properties he considers, however, are vapour pressure and density.

In a later paper, Dolezalek and Schulze † make a careful study of the liquid pair ether-chloroform. This appears to furnish a simple case of two non-associated liquids combining to form a single solvate with equimolecular proportions of the parent substances. The authors show how certain physical properties of these mixtures, such as heat capacity, vapour pressure, specific volume, refractive index, and viscosity, may be calculated with fair accuracy. Additional evidence of the formation of a solvate is given by the fact that an equimolecular mixture of ether and chloroform solidifies as a single substance when cooled to a temperature about 30° above the freezing-point of pure ether.

With a view to applying the theory of Dolezalek, Hubbard ‡ has examined

* *Zeit. phys. Chem.*, 1908, 64.† *Ibid.*, 1913, 83.‡ *Ibid.*, 1910, 74.

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certain physical properties of a number of binary liquid mixtures. The discussion of his results does not seem to have yet appeared.

Denison,* while recognizing the formation of associated molecules of one or both liquids as a possible cause of departure from the mixture law, mainly devotes his attention to solvate formation, and attempts to show that the divergences are to be ascribed to it, that more than one solvate is not likely to be present, and that the composition of the solvate may be inferred from a quantitative study of such divergences. However, the examples chosen by him to illustrate his theory are not suitable for this purpose.

Holmes† and Holmes and Sageman‡ consider a number of aqueous and non-aqueous solutions from the property divergence standpoint. They reject the solvate hypothesis and propound a purely physical theory in explanation of their results.

The work in this present paper was undertaken at the suggestion of Professor Orme Masson, after the publication of Denison's results, in order to afford more suitable tests for his theory.

EXPERIMENTAL WORK.

The experimental work in this paper consists of a series of measurements of the density, heat capacity, and heat change on mixing, of mixtures of selected pairs of liquids. The liquids were carefully purified as follows:—

Ethyl Ether.—This was purified in the manner recommended by Wade and Finnemore.§ A considerable quantity of Merck's pure ether was washed in small portions with ten successive changes of distilled water to remove alcohol. The ether was then dried over granular calcium chloride for some days and afterwards over phosphorus pentoxide for a week. The almost anhydrous liquid was then kept in the dark over shredded sodium and sodium amalgam for several months to remove the last traces of water and also any peroxides. When required for use, portions of this stock were distilled from fresh sodium and amalgam and kept in the dark. A density determination gave—

$$D_4^{20} = 0.71308.$$

The density under the same conditions of the ether used by Dolezalek and Schulze|| was 0.71305.

Nitrobenzene.—This substance was made by nitrating benzene under the proper conditions, and, after separating and washing the product, fractionally distilling several times until the boiling-point was constant (209°)—

$$D_4^{20} = 1.20369.$$

Aniline.—A sample of Schuchardt's pure aniline was repeatedly fractionally distilled through an air condenser until the boiling-point was constant (184°). It was preserved in the dark until required, and was perfectly clear and colourless.

$$D_4^{20} = 1.02197. \quad D_4^{25} = 1.01744.$$

Methyl Alcohol.—A sample of Schuchardt's pure acetone-free methyl alcohol was boiled for seven hours with metallic calcium under a reflux condenser, closed with a calcium chloride tube, to remove water. It was

* *Trans. Faraday Soc.*, 1912, VIII, Pt. 1.

† *Trans. Chem. Soc.*, 1906, 1774.

§ *Ibid.*, 1909, 1842.

‡ *Ibid.*, 1909, 1919.

|| *Loc. cit.*

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then fractionally distilled from fresh calcium, and the fraction coming over between 65.15° and 65.24° (bar. 756 mm., cor.) was collected.

$$D_4^{25} = 0.78740.$$

Carbon Tetrachloride.—A sample of Schuchardt's pure reagent was available, but it proved to contain some considerable amount of carbon disulphide. The method of purification advocated by W. Schmitz-Dumont* was used. This consists in adding to the sample a saturated solution of potassium hydroxide in alcohol and then heating to 60° for half an hour. If carbon disulphide is present, the liquid turns brown and potassium xanthate is precipitated. The liquid is then washed repeatedly with water until all the alcohol is removed. This process was carried out and, after drying over calcium chloride for some hours, the carbon tetrachloride was fractionated. The product coming over between 76.22° and 76.38° (bar. 741 mm., cor.) was collected.

$$D_4^{25} = 1.58469.$$

The density and heat capacity of each pure liquid were then determined at the temperature at which the series of mixtures was to be examined (20° or 25°). Each mixture of the chosen pair was accurately made up by weighing in a glass-stoppered Erlenmeyer flask, the less volatile liquid being invariably weighed first. The properties of the mixture were then studied.

Density.—This was determined in a narrow-necked density bottle of 25 c.c. capacity, provided with a well-fitting glass stopper. The bottle was carefully calibrated with distilled water beforehand, and was always used with a suitable counterpoise. The measurements were made in a well-regulated water thermostat provided with a standard (Kew certificate) thermometer. The mixture was introduced into the bottle directly from the mixing flask by blowing it through a fine capillary tube. After bringing the level of the liquid in the bottle to a fixed mark on the neck, the inside of the neck above the liquid was carefully dried with narrow strips of filter paper and the stopper inserted, prior to weighing. All density measurements refer to water at 4° as the standard.

Heat Capacity.—This was determined by a method previously described by the present author.† After the density of the mixture had been determined, the remainder of the liquid in the mixing vessel was introduced by gentle suction into a weight pipette of special form (Fig. 1), and from this into the calorimeter, and the heat capacity was determined. The weight pipette consisted of a cylindrical vessel of 100 c.c. capacity, provided with a tap (A) and a long, suitably bent delivery tube (B), closed by a well-fitting ground-glass cap (C), and carrying a rubber stopper (D) to fit into the opening in the calorimeter.

Heat Change on Mixing.—This was determined by directly mixing the two liquids in known amount in a modified form of the calorimeter used for the heat capacity measurements. The calorimeter (Fig. 2) consisted of an internally silvered thin copper vessel (A) (for one series of mixtures a thin glass calorimeter was used), fixed by means of a rubber ring (C) resting on a cardboard ring (D) in the interior of a silvered Dewar tube (B), which was closed by a well-fitting rubber stopper (E). The temperature was read by a calibrated Beckmann thermometer (F). The liquids were introduced by means of the weight pipette (Fig. 1) through a hole in the stopper, ordinarily

* *Chem. Zeit.*, 1897, 21.

† *Trans. Faraday Soc.*, 1915, XI, Pt. 1.

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closed by a small rubber stopper (G). A thin glass stirring rod (H), terminated by a thin flat disc of glass about 1.5 cm. in diameter, ensured rapid mixing of the two liquids. This stirring rod was lubricated through the stopper with a little vaseline or phosphoric acid. The under side of the stopper (E) was heavily coated with several layers of tinfoil to protect it from the action of vapours in the calorimeter.

The method of experiment was as follows :—

The two pure liquids were introduced into weight pipettes of similar form (Fig. 1) and each carefully weighed. The Dewar tube and calorimeter had been immersed meanwhile in a water thermostat at the temperature of experiment until the reading shown by the Beckmann thermometer was constant (somewhat lower than that shown by the thermostat thermometer). This condition took some considerable time to attain, as the Dewar tube was

FIG. 1.

an efficient insulator. The thermostat was provided with a perforated cardboard cover to diminish radiation. The pipette containing the more volatile liquid was then immersed in the thermostat for half an hour or so with the mouth of the delivery tube over the edge of the bath so that it should not get wet. The glass cap (Fig. 1, C) was then removed and the delivery tube inserted into the calorimeter through the hole in the rubber stopper, into which its own stopper fitted. The liquid was introduced by gentle blowing through a calcium chloride tube attached to the other end of the pipette. The calorimeter was then closed and the pipette weighed after again putting on its cap. The pipette containing the second liquid was then immersed in the thermostat, and after half an hour, when the calorimeter temperature was

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quite constant, the calorimeter was opened, the delivery tube of the pipette inserted as before, and the liquid blown in. The two liquids were rapidly mixed by the stirring rod and the temperature changes noted. Radiation corrections were then applied and the second pipette weighed. The water equivalent of the calorimeter being known, the number of calories evolved or absorbed on mixing was then calculated.

FIG. 2.

THEORETICAL CONSIDERATIONS.

In attempting to establish a theoretical basis on which to consider experimental results one is met at the outset with the difficulty of expressing suitably the concentrations of the various substances present in the chosen mixtures. The molar fraction method recommends itself as being perhaps less open to objection than either the mass or the volume method of calcu-

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lating concentration ; in any case, it is the method which lends itself most simply to mathematical treatment from the mass action standpoint. However, one must remember that the molar fraction method is quite useless in the case of liquids in which the state of molecular aggregation in the liquid state is unknown. This will considerably limit in practice the application of a theory founded on it. In the following discussion the molar fraction method has been adopted.

Let us suppose that we are dealing with two simple unassociated liquids A and B, the mixing of which results in the partial formation of a solvate $A_\alpha B_\beta$. Denison * has shown, in the special case of a solvate AB_β , that the concentration of the solvate is a maximum when the liquid mixture has the synthetic composition denoted by the formula of the solvate. The proof can be extended to any solvate $A_\alpha B_\beta$. Thus we have

Let N molecules of A be mixed with $1 - N$ molecules of B with the formation of x molecules of the solvate $A_\alpha B_\beta$. The total number of molecules present is

$$1 - (\alpha + \beta - 1)x.$$

Applying mass action considerations, the equilibrium conditions require that

$$(N - \alpha x)^\alpha (1 - N - \beta x)^\beta = Kx [1 - x(\alpha + \beta - 1)]^{\alpha + \beta - 1}.$$

Differentiating this, we obtain—

$$\frac{dx}{dN} = \frac{(N - \alpha x)^{\alpha-1} (1 - N - \beta x)^{\beta-1} [a(1 - N) - \beta N]}{[1 - (\alpha + \beta - 1)x]^{\alpha + \beta - 2} [1 - (\alpha + \beta)(\alpha + \beta - 1)x] + (N - \alpha x)^{\alpha-1} (1 - N - \beta x)^{\beta-1} [\alpha^2(1 - N - \beta x) + \beta^2(N - \alpha x)]}.$$

Hence

$$\frac{dx}{dN} = 0 \text{ when } \frac{N}{1 - N} = \frac{\alpha}{\beta}.$$

This means that, if we plot the number of molecules of solvate formed per one total synthetic molecule of the mixture against the number of molecules of A present per one total synthetic molecule, we obtain a curve which reaches a maximum at the concentration corresponding to the composition of the solvate.

Further, at one end of the curve (the pure B end) where $N = 0$ and $x = 0$

$$\frac{dx}{dN} = \frac{1}{K + 1} \text{ if } \alpha = 1;$$

$$\text{for any other value of } \alpha, \frac{dx}{dN} = 0.$$

At the other end of the curve (the pure A end), $N = 1$ and $x = 0$; therefore

$$-\frac{dx}{dN} = \frac{1}{K + 1} \text{ if } \beta = 1;$$

$$\text{for any other value of } \beta, -\frac{dx}{dN} = 0.$$

In words, if the formula of the solvate is the simplest possible, i.e. if α and β each equal 1, the gradient of the solvate-concentration curve at the pure A

* Loc. cit.

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end must be equal, but of opposite sign, to the gradient at the pure B end. If α has a value greater than 1, then the gradient at the pure B end is 0; similarly for β at the pure A end. If α and β are each greater than 1, then the gradients at both ends of the curve equal 0.

Now, it is easily shown that the extent of any deviation is directly proportional to the number of solvate molecules formed, or

$$\Delta = kx,$$

where k is a constant depending on the molecular values for the particular

FIG. 3.

property of A, B and $A_\alpha B_\beta$. Hence the deviation curve also attains its maximum (or minimum in the case of negative deviations) point when

$$\frac{N}{1-N} = \frac{\alpha}{\beta}, \text{ and again } \frac{d\Delta}{dN} = 0,$$

at both ends for any values of α and β respectively greater than 1; but

$$\frac{d\Delta}{dN} = \frac{k}{K+1}$$

at the pure B end if $\alpha = 1$, and it equals $-\frac{k}{K+1}$ at the pure A end if $\beta = 1$.

Thus we have three types of curves (Fig. 3), representing the formation of solvates of the composition AB, $A_\alpha B$ and $A_\alpha B_\beta$ respectively. Obviously also the deviation curves for all properties of mixtures of a particular pair of liquids must, in general, be similar to each other.

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For the simple case where $\alpha = \beta = 1$, the equilibrium equation simplifies to—

$$(N - x)(1 - N - x) = Kx(1 - x)$$

or—

$$x(1 - x) = \frac{1}{K + 1} \cdot N(1 - N).$$

Since $\Delta = kx$, it follows that—

$$k = \frac{\Delta}{1 - \frac{k}{K + 1} \cdot \frac{N(1 - N)}{\Delta}}$$

From this equation we can calculate k , the property constant, and K , the equilibrium constant, since values of N and Δ may be read from the curve, while $\frac{k}{K + 1}$ is the gradient at each end of the curve and can be measured.

Or, in order to avoid the inaccuracy of measuring tangents to the curve, we may solve the equation by treating k and $\frac{k}{K + 1}$ as two unknown constants and choosing two values of N on the same property curve. Thus we can evaluate k and K and, knowing k , we can calculate x values from those of Δ for any mixture and thus plot the true x curve. Further, we can treat different property curves of the same liquid-pair in this way and evaluate the k value for each; and they all should give the same x curve.

It is very doubtful whether any actual cases agree with the simple AB theory, as above, although some may be found to approximate to it closely enough to afford a test. Dolezalek and Schulze* claim that mixtures of ether and chloroform supply such a case, but plotting of their results shows a considerable deviation from perfect symmetry, although this is neglected by them. Notwithstanding Denison's argument to the contrary, it seems probable that, in most cases, two or more solvates are formed, and it becomes very difficult to apply a simple working theory quantitatively. The deviation curves for many pairs of unassociated liquids are quite different for different properties of the same pair, and this makes an explanation on a single solvate basis quite impossible. The assumption of the presence of two or more solvates in such cases gives a satisfactory qualitative explanation at least, for then the deviation curves would be compounded from two or more variables.

A quantitative explanation is not yet possible, because the equations obtained by applying mass action considerations contain several constants for which values cannot be calculated. However, by assigning arbitrary values to these constants it is possible to calculate deviation curves which approximate closely to those obtained by experiment. Further, it is improbable that only one solvate will be present in a given mixture, because the original solvate formed must have some tendency to combine with further molecules of one or both pure components, with the formation of new solvates. Repetitions of this process are possible, but the concentrations of these higher solvates will probably be so small as to be inappreciable.

Throughout the foregoing argument solvate formation alone has been considered and no account has been taken of changes in the state of association of the component liquids on mixing. This limits the testing of the theory in practice to the examination of mixtures of known unassociated liquids, in which mixtures one may reasonably suppose solvate formation to be the predominating factor. In the case of associated liquids it is

* Loc. cit.

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extremely difficult to develop a satisfactory quantitative theory, owing to the complexity of the phenomena. Dolezalek* has made an attempt to do so in the case of very simple mixtures, but his method can have only a very limited application.

DISCUSSION OF THE RESULTS.

For various reasons, the choice of suitable experimental liquids has been somewhat limited. A few words are necessary as to the suitability of the liquids actually chosen for the testing of the solvate theory.

Ether is well known as a typical unassociated liquid.

Aniline and nitrobenzene are found by Dutoit and Mojoiu† to be slightly associated, while the Ramsay and Shields' method‡ indicates that both liquids are normal or slightly dissociated. Also Beckmann§ finds that the molecular weight of aniline dissolved in ether is normal.

Methyl alcohol is well known to be strongly associated, the association factor by Ramsay and Shields' method being 3·43.

FIG. 4.

Carbon tetrachloride is found to be normal by Dutoit and Mojoiu,|| and this is also indicated by the Ramsay and Shields' method. Dolezalek,¶ on the other hand, calculates a value 1·15 at 50° for the association constant, which fits in with his theory of the conditions obtaining in mixtures of carbon tetrachloride and benzene.

The following symbols are used in the tables of results :—

- M the percentage by weight of the more volatile component in the mixture.
- N the number of molecules of this component per one total synthetic molecule of the mixture.
- D the density of the mixture at the temperature of experiment, referred to water at 4°.
- V the molecular volume of the mixture in c.c.
- S the specific heat of the mixture.

*. Loc. cit.

†, ‡, Trans. Chem. Soc., 1893, 63, 1089.

|| Loc. cit.

† J. Chim. Phys., 1909, 7, 169.

§ Zeit. phys. Chem., 1889, 3, 603.

¶ Zeit. phys. Chem., 1908, 64.

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C the molecular heat of the mixture (from a smooth curve).

E the heat change on mixing per 100 gm. of the mixture, in calories.

Δ_v the contraction in volume of the mixture on mixing per one total synthetic molecule, in c.c.

Δ_c the rise in molecular heat on mixing, in calories.

Δ_E the heat change in calories on mixing per one total molecule of the mixture, positive or negative as indicated.

Nitrobenzene and Ether.

The experimental results for this liquid-pair are given in the following tables :—

TABLE I.

Contractions at 20°.

M.	N.	D.	V.	Δ_v .
0	0	1'20369	102'23	0
10'35	0'1609	1'13401	101'55	0'93
20'21	0'2962	1'07293	101'17	1'54
34'34	0'4649	0'99462	100'83	2'17
48'85	0'6134	0'92116	100'98	2'26
65'87	0'7623	0'84297	101'69	1'78
84'21	0'8985	0'77099	102'52	1'18
100	1'0000	0'71322	103'87	0

TABLE II.

Heat Capacity at 20°.

M.	N.	S.	C.	Δ_c .
0	0	0'342	42'1	0
10'35	0'1609	0'362	41'7	0
20'21	0'2962	0'382	41'5	0
34'34	0'4649	0'408	40'9	— 0'2
48'85	0'6134	0'443	41'2	+ 0'3
65'87	0'7623	0'473	40'5	+ 0'1
84'21	0'8985	0'512	40'5	— 0'2
100	1'0000	0'540	40'0	0

The heat change on mixing was found to be very small and no systematic series of measurements of this property was made.

The curve obtained by plotting Δ_v against N is shown in Fig. 4. It will be seen that, although the contraction on mixing is considerable, the heat capacity shows practically no deviation from the mixture law. Also, the heat change on mixing is very small. A simple inspection of the contraction curve makes it clear that more than one solvate must be formed in this case, since the curve is not symmetrical and does not reach a maximum at $N = 0.5$ (thus disposing of the simple AB supposition), and also since the gradients at both ends of the curve have definite values (thus disposing of the $A_\alpha B_\beta$ supposition). However, the experimental results are too meagre to permit further conclusions to be drawn.

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Aniline and Ether.

The experimental results for this liquid-pair are given in the following tables :—

TABLE III.
Contractions at 20°.

M.	N.	D.	V.	Δ_v .
0	0	1'02197	91'07	0
14'54	0'1761	0'97322	92'19	1'13
30'78	0'3584	0'92101	93'66	2'00
44'45	0'5013	0'87845	95'11	2'38
54'20	0'5979	0'84874	96'28	2'46
55'85	0'6138	0'84373	96'49	2'44
62'19	0'6738	0'82466	97'34	2'37
71'76	0'7615	0'79606	98'75	2'08
80'38	0'8373	0'77054	100'15	1'65
100	1'0000	0'71308	103'90	0

TABLE IV.
Heat Capacity at 20°.

M.	N.	S.	C.	Δ_c .
0	0	0'472	43'94	0
14'54	0'1761	0'490	43'84	0'59
30'78	0'3584	0'507	43'72	1'18
44'45	0'5013	0'520	43'36	1'39
55'85	0'6138	0'528	42'90	1'47
62'19	0'6738	0'531	42'64	1'34
71'76	0'7615	0'537	42'15	1'20
80'38	0'8373	0'535	41'50	0'84
100	1'0000	0'540	40'02	0

TABLE V.
Heat Change at 20° (Positive).

M.	N.	E.	Δ .
8'38	0'1031	33'82	30'82
16'02	0'1933	54'94	49'12
25'98	0'3060	92'50	80'72
33'10	0'3833	112'98	96'93
43'80	0'4947	142'07	118'88
54'02	0'5901	158'53	129'60
62'88	0'6802	160'51	128'64
75'27	0'7927	141'06	110'05
82'76	0'8579	110'01	84'48
91'30	0'9294	71'31	53'79

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The curves drawn from these three sets of results are given in Figs. 5, 6, and 7 respectively. The departure of each property from the mixture law is strongly marked. The curves of contraction (Fig. 5), of heat capacity deviation (Fig. 6), and of heat evolution (Fig. 7) are similar to each other in general form, but they are not symmetrical and do not reach a maximum at $N = 0.5$, but rather in the neighbourhood of $N = 0.6$. Also, the gradients at the ends of all the curves have definite values. Hence, here again no single solvate supposition will explain the experimental facts, and we are forced to assume the presence of two or more solvates.

Aniline and Methyl Alcohol.

The experimental results for this liquid-pair are given in the following tables:—

TABLE VI.
Contractions at 25°.

M.	N.	D.	V.	Δ_v .
0	0	1.01744	91.47	0
8.21	0.2063	0.99904	80.52	0.49
14.22	0.3252	0.98602	74.26	0.70
19.95	0.4199	0.97271	69.34	0.82
24.58	0.4863	0.96193	65.90	0.87
29.40	0.5474	0.95056	62.75	0.91
36.62	0.6267	0.93360	58.72	0.93
42.00	0.6777	0.92097	56.13	0.91
54.10	0.7740	0.89283	51.33	0.82
57.71	0.7986	0.88416	50.13	0.78
74.71	0.8956	0.84489	45.45	0.53
100	1.0000	0.78740	40.68	0

TABLE VII.
Heat Capacity at 25°.

M.	N.	S.	C.	Δ_c .
0	0	0.484	45.02	0
8.21	0.2063	0.512	41.35	1.62
14.22	0.3252	0.534	38.95	2.27
19.95	0.4199	0.547	36.85	2.59
24.58	0.4863	0.553	35.15	2.59
29.40	0.5474	0.568	33.55	2.56
36.62	0.6267	0.571	31.35	2.39
42.00	0.6777	0.577	30.95	2.30
54.10	0.7740	0.595	27.00	1.82
57.71	0.7986	0.587	26.30	1.75
74.71	0.8956	0.601	23.15	1.09
100	1.0000	0.605	19.39	0

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FIG. 5.

FIG. 6.

FIG. 7.

TABLE VIII.
Heat Change at 25°.

M.	N.	E.	Δ_E .
3.12	0.0855	— 4.89	— 4.30
6.32	0.1639	— 4.59	— 3.81
10.58	0.2558	+ 4.69	+ 3.63
14.48	0.3297	+ 17.4	+ 12.7
21.01	0.4359	+ 41.9	+ 27.8
27.65	0.5261	+ 58.2	+ 35.5
36.01	0.6205	+ 81.2	+ 44.8
47.30	0.7228	+ 104.9	+ 51.4
60.61	0.8172	+ 115.1	+ 49.7
64.32	0.8397	+ 114.7	+ 47.9
83.49	0.9362	+ 80.1	+ 28.8
86.42	0.9486	+ 63.7	+ 22.4

The curves drawn from these three tables are shown in Figs. 8, 9, and 10 respectively. This case is quite unsuitable for consideration from the simple solvate standpoint, since methyl alcohol is notoriously associated. In fact, a solution of aniline in methyl alcohol shows some similarity to one of ammonia in water in that it is capable of dissolving small amounts of copper oxide,

FIG. 8.

giving a green solution. The deviation curves for this mixture are, however, very interesting, although it is quite impossible to fit any simple theory to the experimental results. The contraction curve (Fig. 8) has quite a different maximum to the heat capacity deviation curve (Fig. 9), while the heat change on mixing curve (Fig. 10) is remarkable in showing both a maximum and a minimum. Qualitatively, this behaviour is easily understandable. We may suppose that two simultaneous sets of actions occur on mixing the component liquids—

- (i.) Formation of one or more solvates, accompanied by heat evolution.
- (ii.) Partial dissociation of the methyl alcohol, accompanied by heat absorption.

When the mixture is rich in alcohol, (i.) predominates and we have a maximum near the alcohol end of the curve. When the mixture is rich in

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aniline, (ii.) predominates and we have a corresponding minimum near the aniline end of the curve. A quantitative theory must be extremely difficult to

FIG. 9.

FIG. 10.

apply, in consequence of our lack of knowledge of the association changes which take place when methyl alcohol is mixed with its partner.

Aniline and Carbon Tetrachloride.

The experimental results for this liquid-pair are given in the following tables :—

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TABLE IX.
Contractions at 25°.

M.	N.	D.	V.	Δ_v .
0	0	1'01748	91'468	0
15'46	0'0996	1'07856	91'898	0'129
29'60	0'2028	1'14087	92'382	0'232
41'03	0'2962	1'19636	92'843	0'293
51'87	0'3947	1'25364	93'372	0'316
62'08	0'4976	1'31273	93'930	0'330
71'17	0'5990	1'36962	94'527	0'303
79'06	0'6955	1'42275	95'110	0'250
87'05	0'8027	1'48057	95'791	0'167
93'51	0'8971	1'53065	96'403	0'080
98'14	0'9696	1'56853	96'876	0'006
99'39	0'9896	1'57938	96'991	0'005
100	1'0000	1'58469	97'068	0

TABLE X.
Heat Capacity at 25°.

M.	N.	S.	C.	Δ_c .
0	0	0'484	45'02	0
15'46	0'0996	0'446	44'18	0'52
29'60	0'2056	0'409	43'05	0'83
40'47	0'2915	0'377	42'05	1'00
51'87	0'3947	0'349	40'84	1'19
62'08	0'4976	0'321	39'50	1'25
71'17	0'5990	0'295	38'20	1'33
79'99	0'7075	0'268	36'45	1'06
87'05	0'8027	0'244	34'78	0'68
93'85	0'9022	0'223	33'16	0'42
100	1'0000	0'204	31'41	0

TABLE XI.
Heat Change at 25° (Negative).

M.	N.	E.	Δ_E .
14'67	0'0942	98'6	97'4
27'26	0'1848	162'1	169'0
41'52	0'3005	212'7	236'8
53'99	0'4152	238'7	282'3
60'67	0'4827	237'8	291'0
66'93	0'5504	235'1	297'5
73'08	0'6215	220'9	288'9
80'76	0'7175	197'3	269'7
86'07	0'7888	174'6	246'2
91'22	0'8627	129'2	188'0
94'31	0'9092	100'3	148'8

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FIG. 11.

FIG. 12.

FIG. 13.

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The curves drawn from these three sets of results are given in Figs. 11, 12 and 13 respectively. The contraction curve (Fig. 11) shows a relatively small volume change, the maximum effect being in the neighbourhood of $N = 0.46$; also, the curve exhibits a point of inflection towards the carbon tetrachloride end and the gradient possibly becomes equal to 0 at the termination of the curve. The reality of this point of inflection has been carefully verified by repeated experiments. However, the heat capacity deviation curve (Fig. 12) shows no sign of this peculiarity; it also reaches a maximum at $N = 0.52$. The heat change curve (Fig. 13) is similar in these respects, but is remarkable for the very large heat absorption which it exhibits. This is peculiar when contrasted with the small volume contraction shown, instead of a not unreasonably expected expansion.

Again, the single solvate theory is inadequate to explain the results. It is not quite clear why the contraction curve is the only one showing the point of inflection. If it were due to a solvate containing more than one molecule of aniline in its composition, one might expect the deviation curves of other properties to show some evidence of a similar peculiarity. On the other hand, it may be due to slight association of the carbon tetrachloride, which influences the density of the mixtures to a greater extent than it does the heat capacity and the heat absorption on mixing.

Ether and Chloroform.

This case has been investigated by Dolezalek and Schulze,* and they claim to have shown that the supposition of the presence of a solvate of equimolecular composition explains the experimental results determined for several properties of mixtures of these liquids. However, their curves show considerable deviations from perfect symmetry, which is required by their argument. Their figures for the contractions observed are given in Table XII, their notation having been changed into that adopted in this Paper.

N represents the synthetic molar fraction of chloroform in the mixture and Δ the contraction per one total synthetic molecule of the mixture, in c.c.

TABLE XII.
Contractions at 20°.

N.	Δ .
0.1	0.45
0.2	0.79
0.3	1.06
0.4	1.27
0.5	1.30
0.6	1.16
0.7	0.97
0.8	0.72
0.9	0.42

The deviation from symmetry is apparent from a simple inspection of these figures; again, if k (the property constant) and K (the equilibrium constant) are calculated as indicated in the theoretical part of this Paper,

* Loc. cit.

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different results are obtained according to where the two points on the curve necessary for the calculation are selected.

Thus, using as data

$$\begin{array}{ll} N = 0.2 & \Delta = 0.79 \\ N = 0.5 & \Delta = 1.30 \end{array}$$

we get

$$k = 10.2 \quad \text{and} \quad K = 1.24 ;$$

but if we use as data

$$\begin{array}{ll} N = 0.4 & \Delta = 1.27 \\ N = 0.7 & \Delta = 0.97 \end{array}$$

we get

$$k = 3.35 \quad \text{and} \quad K = 0.02.$$

The value for K obtained by Dolezalek and Schultze from vapour pressure considerations is $K = 2.96$.

It is evident that this case also cannot be treated from a single solvate standpoint, and we must postulate the existence of two or more solvates.

The evidence adduced in this Paper shows that, in the cases examined, no simple solvate theory will suffice to explain the experimental results, even though the liquids used, with one exception, are little associated. Also, a study of the deviation curves obtained from many other liquid-pairs by various authors leads to the conclusion that only in rare cases, if at all, will the conditions be simple enough to permit of an explanation of the deviations by single solvate formation. In the great majority of cases, the molecular condition of a mixture of two liquids is much more complex, and it becomes very difficult to develop and apply any satisfactory quantitative theory.

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