may greatly increase the actual value of p. At the same time, since the radii only of the larger bubbles just on the point of escaping were measured, the value of p for these is probably not far removed from that for the external pressure. It is quite possible that the observations on the increase of efficiency of metal deposition at low pressures may find important technical applications.

It is hoped that the authors will continue their investigations along these lines, taking the precaution to eliminate overvoltage effects by the introduction of a rotating commutator as already suggested.

CAPE TOWN, SOUTH AFRICA.

[CONTRIBUTION FROM THE GAYLEY CHEMICAL AND METALLURGICAL LABORATORY OF LAFAYETTE COLLEGE.]

FLUIDITIES AND SPECIFIC VOLUMES OF MIXTURES OF BENZYL BENZOATE AND BENZENE. XXIX.

BY EUGENE C. BINGHAM AND LANDON A. SARVER.

Received July 15, 1919.

Introduction.

Evidence has been accumulating to prove that the old hypothesis that viscosities are additive is quite untenable. At the same time there is both theoretical and experimental proof that fluidities are additive. The decision as to whether one or the other or neither of these properties is additive is of course absolutely imperative before fluidity can come into use for solving physical chemical problems. Since fluidity is very well suited to solve many such problems, it seems strange to the uninitiated that the fundamental decision has been arrived at so late. The reason, however, is not far to seek. To test the hypothesis that fluidities are additive, it would be most natural and easy to measure the fluidities of mixtures of 2 pure inert liquids. The difficulty comes in finding liquids which are "inert," *i. e.*, individually non-associated as well as without tendency to combine with each other.

We have more or less satisfactory methods for determining when a given liquid is non-associated, but we are unable to predict with certainty when loose combinations may be formed; much less are we able to explain the nature of the "molecular compounds."

It is this complication of "variables" which has hitherto rendered the problem of their separation insoluble. One procedure is that advocated by Bingham of seeking evidence outside of mixtures of liquids in suspensions and pure liquids, which seems to speak more unequivocally in favor of the view that fluidities are additive. If this course is pursued and we boldly maintain that fluidities are additive the number of variables is at once reduced and it becomes possible to calculate the association of liquids and in simple cases the combination in mixtures. It is generally true that combination produces effects on other physical properties which can be used to the greatest advantage in testing out the inherent probability of each of our conclusions. Hence it becomes possible to build up a considerable structure of truth resting upon a foundation which is tested out at every point, in order to determine its stability or instability. This can be well illustrated as follows.

Thorpe and Rodger measured the viscosities of mixtures of chloroform and ether. When the curve was plotted it showed a point of inflection, to explain which made it necessary to assume that (1) in certain mixtures combination took place, whereas (2) in other mixtures the opposite effect was shown, such as might be produced by breaking down of association. When it is noted that in *every* mixture there is contraction in volume and heat evolution, these 2 hypotheses become improbable. However, when we plot the fluidities of chloroform and ether against the volume concentration, the point of inflection disappears and the curve shows positive curvature throughout. This is explained by the *single* hypothesis that chloroform and ether form a loose combination, a conclusion supported by all of the other evidence which we have had at hand.

Kendall,[1] in 1912, examined a considerable portion of the available viscosity data and came to the conclusion that a formula

$$\log \eta = a \log \eta_1 + b \log \eta_2$$

gives better average agreement than any hitherto proposed. It hardly seems likely, however, that the logarithms of the viscosities should be additive. Certainly no physical meaning for such an awkward conception has been put forth. But as one of us has pointed out,[2] if it happens that on mixing combination takes place more frequently than dissociation, it might well be that some purely empirical formula such as the above would show better statistical agreement than the true formula, which we believe to be the additive fluidity-volume concentration formula, $\varphi = a\varphi_1 + b\varphi_2$. But it is important to note that on account of the disturbing factors of association and combination, no single formula, either empirical or otherwise, can apply to all mixtures.

Kendall and Monroe[3] have attempted to settle the question finally by studying "inert" liquids of widely differing fluidities,[4] namely, mixtures of (1) benzene and benzyl benzoate, (2) benzene and ethyl benzoate, (3) toluene and ethyl benzoate, and (4) toluene and benzyl benzoate. In speaking of the mixtures of benzene and benzyl benzoate they say[5] "so far

---

[1] Kendall, *Meddel. K. Vetenskapsakad. Nobelinst.*, **2**, No. 25 (1913).

[2] *J. Phys. Chem.*, **18**, 157 (1913).

[3] Kendall and Monroe, THIS JOURNAL, **39**, 1787 (1917).

[4] *Am. Chem. J.*, **35**, 199 (1906).

[5] THIS JOURNAL, **39**, 1796 (1917).

as can be judged, this system is ideal. Careful calorimetric measurements failed to indicate any heat evolution or absorption on admixture of equal volumes of the two liquids. Density determinations showed that no volume change occurred." The other mixtures appeared to the authors to be equally inert. However, none of the mixtures gave results which would be predicted by any hypothesis given above. As a matter of fact, no empirical formula was found which would fit *all* of the data, although the first 3 mixtures are represented by a formula

$$\eta^{1/3} = a\eta_1{}^{1/3} + b\eta_2{}^{1/3},$$

where the concentrations are molecular. That they have found an empirical formula which will reproduce the viscosities of mixtures of benzene and benzyl benzoate with a divergence of only 3.8% is not remarkable. But it is remarkable that there should be a larger deviation from the fluidity-volume concentration curve, provided that these liquids are inert as they maintain and fluidities are truly additive. This apparent exception, therefore, demanded investigation.

Since Kendall and Monroe have not given their data in regard to the densities of their solutions and only mention the subject in the somewhat vague way quoted above, it seemed best to repeat a portion of their work, as there might have been at least slight changes in volume and in temperature which might have been ascribed to experimental error. If benzene and benzyl benzoate form an ideal mixture as Kendall and Monroe think they do at 25°, then they certainly should also do so at other temperatures. On the other hand, if fluidities are additive and there were combinations taking place, causing the sag from the linear fluidity curve, then it is probable that the amount of combination will be less at the higher temperatures and greater at the lower temperatures, hence there will not be the concordance found by Kendall and Munroe except at the one temperature investigated.

Preparation of Materials.

Benzene.—Pure commercial benzene was shaken repeatedly with sulfuric acid until the latter showed no coloration. It was washed with distilled water, and *N* sodium hydroxide solution, to remove the last traces of acid; and finally 5 times with water to remove the alkali. After drying it was recrystallized 6 times by freezing it in a round-bottomed flask, shaking occasionally with a circular motion and pouring off the last portion each time; in this way the liquid forms a solid cake around the walls of the flasks, freezing at constant temperature until only a few cc. remain. This liquid is poured off, the solid melted and the process repeated. At the end no change of freezing-point temperature could be observed while the last portion was freezing. The benzene, thus purified was dried over freshly cut sodium which had been carefully washed with pure benzene; and it was then fractionated between 80.2° and 80.3° into a carefully cleaned, dust-free bottle.

Benzyl Benzoate.—One mole of pure benzyl alcohol was added drop by drop to one and one-half moles of benzoyl chloride heated to 140° in an oil-bath. Hydrogen chloride was freely evolved, and the reaction was complete in 2 hours. The oil was fractionated to remove the excess of benzoyl chloride, giving a yield of over 90% of nearly pure ester. It could not be dried with phosphoric anhydride, since under the influence of the latter substance the ester passed over almost quantitatively into benzoic acid and benzyl phosphate. To free it from benzoic acid the oil was titrated with 0.05 *N* sodium hydroxide, using one milligram of phenolphthalein dissolved in a known quantity of alkali for an indicator, until the aqueous solution was colored permanently red; the solid phenolphthalein was soluble chiefly in the oil, while the sodium salt was soluble only in the alkaline aqueous solution. The ester was washed many times with water to remove last traces of alkali, and dried by heating for several hours on a water-bath, *in vacuo*, while a current of dry air was being drawn through it. The substance was now recrystallized 3 times to free it from benzyl alcohol; the ester was mixed with $^1/_{10}$ of its volume of ether, frozen, filtered on a platinum cone, melted, and the process repeated. The material, thus purified, was again subjected to the treatment with dry air, *in vacuo*, to remove last traces of ether and water, and finally fractionated 3 times, *in vacuo*, into dust-free apparatus. A large sample of the pure ester was melted, showing a slight softening at 17.55°, and melting at 18.2°. It was absolutely colorless and had a faint odor. The substance decomposed slightly when distilled at atmospheric pressure, giving a pale yellow color and a faint odor; hence it was necessary to conduct all distillations under reduced pressure.

Standardization of Apparatus.

The viscometer used had previously been carefully calibrated;[1] several observations on dust-free water showed the values given there to be correct. In the formula $\eta = Cpt - C'\rho/t$, $\log C = 3.15555 - 10$ and $\log C' = 8.37598 - 10$.

Experimental.

Observations were made upon the 2 pure substances and 3 mixtures over a range of temperature from 5° to 75°. The mixtures were made by first weighing out the benzyl benzoate in a glass-stoppered bottle, then adding the benzene from a capillary pipet; the 2 liquids were then mixed with a circular motion, care being taken not to wet the stopper, lest differential evaporation should change the concentration. Great care was taken at all times to protect reagents and apparatus from dust. A summary of results follows.

---

[1] See Bingham and Jackson, Bur. Standards, *Bull.* 298.

TABLE I.—BENZYL BENZOATE.

Temp. bath ° C.	Time Sec.	p_0.	P.	η in cp.	φ.	v.	ρ.
5	2359.0	401.3	401.3	19.280	5.185	0.8818	1.1134
15	2111.5	401.3	401.3	12.120	8.249	0.8890	1.1249
25	1438.5	403.0	402.9	8.292	12.06	0.8958	1.1163
40	909.6	403.0	402.9	5.243	19.07	0.9058	1.0780
60	566.6	402.6	402.0	3.259	30.68	0.9200	1.0870
80	390.7	402.6	401.5	2.245	44.56	0.9330	1.0546
90	333.4	402.4	400.8	1.912	52.30	0.9430	1.0604
100	289.0	402.4	400.3	1.655	60.42	0.9460	1.0571

TABLE II.—BENZENE.

5	564.1	103.2	102.7	0.8293	120.5	1.1187	0.8939
15	477.5	103.2	102.6	0.7012	142.5	1.1323	0.8832
25	410.1	103.4	102.5	0.6018	166.1	1.1461	0.8725
40	336.9	103.5	102.2	0.4912	203.5	1.1675	0.8565
60	266.9	103.5	101.6	0.3877	257.9	1.1980	0.8347
75	331.6	71.08	69.86	0.3314	301.8	1.2371	0.8083

TABLE III.

Benzyl Benzoate 75%; Benzene, 25% by Weight.

Temp. bath ° C.	Time Sec.	p_0.	P.	η in cp.	φ.	v.	ρ.
5	905.8	410.2	410.0	5.313	18.86	0.9402	1.0640
15	683.0	410.3	409.7	4.004	24.99	0.9483	1.0550
25	524.2	410.3	409.7	3.073	32.54	0.9565	1.0454
40	372.1	410.5	409.4	2.180	45.88	0.9685	1.0325
60	256.7	410.4	407.7	1.556	64.27	0.9854	1.0148
75	209.7	410.4	406.5	1.220	82.00	0.9985	1.0015

TABLE IV.

Benzyl Benzoate, 50%; Benzene, 50% by Weight.

5	534.8	308.4	308.3	2.356	42.44	0.998	1.0016
10	474.0	307.7	307.4	2.084	47.97	1.002	0.9980
15	424.1	307.7	306.7	1.861	53.73	1.008	0.9925
25	345.6	307.7	306.3	1.514	66.04	1.018	0.9825
40	410.4	198.9	197.8	1.161	86.13	1.032	0.9687
60	306.6	198.9	197.2	0.865	115.6	1.053	0.9560
75	255.2	199.0	196.6	0.718	139.3	1.069	0.9359

TABLE V.

Benzyl Benzoate, 25%; Benzene, 75% by Weight.

5	461.1	199.0	198.2	1.308	76.4	1.056	0.9468
15	380.0	199.0	198.0	1.076	92.8	1.068	0.9363
25	320.6	199.0	197.5	0.9057	110.3	1.080	0.9263
40	257.0	199.0	196.7	0.7205	138.8	1.098	0.9106
60	314.2	125.4	123.9	0.5578	179.3	1.123	0.8904
75	266.3	125.5	123.4	0.4702	212.7	1.143	0.8750

TABLE VI.

Molecular and Volume Percentages of Mixtures.

Temperature. ° C.	25% benzene.		50%.		75%.	
	Molecular.	Volume.	Molecular.	Volume.	Molecular.	Volume.
5	47.50	29.72	73.10	55.92	89.04	79.19
15	...	29.80	...	56.02	...	79.29
25	...	29.89	...	56.12	...	79.32
40	...	30.06	...	56.31	...	79.45
60	...	30.27	...	56.56	...	79.62
75	...	30.47	...	56.80	...	79.78

The tables are self-explanatory except that the manometer pressure p_0 is the corrected average pressure in grams per square centimeter used in producing the flow, whereas P is the pressure used purely in overcoming viscous resistance. The viscosity[1] is therefore, $\eta = CPt$. The specific volumes are represented by v, the densities by ρ.

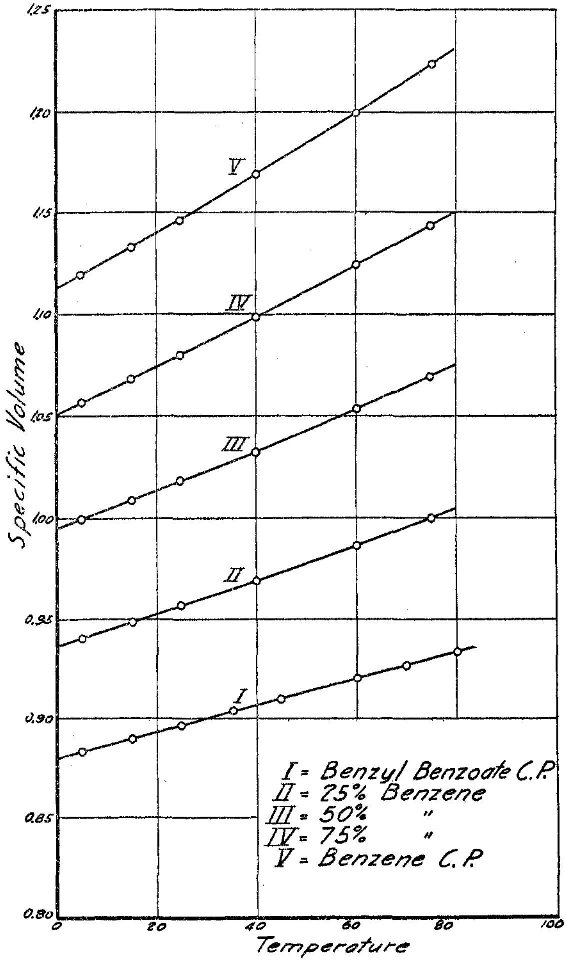

Fig. 1.—The specific volume-temperature curves of mixtures of benzene and benzyl benzoate.

The viscosities are given in centipoises,[2] *i. e.*, absolute c. g. s. units × 10^{-2}. The fluidities φ of benzene are practically identical with the values obtained by Thorpe and Rodger[3] except at the 2 highest temperatures where our fluidities are about 1% higher; thus at 25° our value is 166.2, that of Thorpe and Rodger is 166.1, that of Kendall and Monroe is 165.4. For benzyl benzoate our value is 12.06 as com-

---

[1] Bur. Standards, *Bull.* 14, No. 298, 70 (1917).

[2] *Ibid.*, p. 72.

[3] Thorpe and Rodger, *Phil. Trans.* (*London*), 185A, 521 (1894).

pared with 11.83 found by Kendall and Monroe. We have not used the same mixtures that were employed by Kendall and Monroe, but their values plot on a smooth curve with ours, a fact which is significant, because in using a volatile component like benzene there is need for care in manipulating the mixtures to prevent the composition of the mixture changing subsequent to preparation. It is, however, regarded as impossible that the effects with which we are here concerned can be due to this cause; and it is almost certain that if an error has been inadvertently introduced it would not be proportionately the same for all of the mixtures and for different observers, using presumably different methods of manipulation.

The densities ρ were determined in a special pycnometer devised by Bingham and Van Klooster[1] to be described in another communication. The densities are all corrected for buoyancy of the air and are based on water at 4° as standard. The densities of benzene were not determined by us, the values giving being those of Kopp.

Discussion.

The specific volume-temperature, the fluidity-temperature, and fluidity-specific volume curves are given in Figs. 1, 2 and 3, respectively. The fluidity-temperature curves, Fig. 2, are approximately linear but, never-

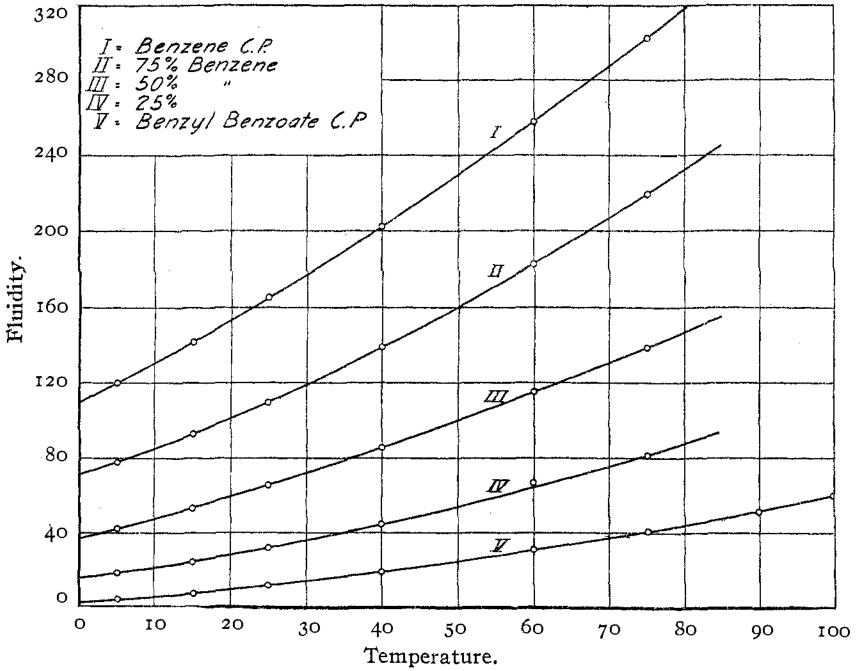

Fig. 2.—The fluidity-temperature curves of mixtures of benzene and benzyl benzoate.

---

[1] Bingham and Van Klooster, *J. Phys. Chem.*, **24**, 6 (1920)

theless, definitely and distinctly sagged. The volume-temperature curves, Fig. 1, are still more nearly linear, the curve for benzoyl benzoate not departing noticeably from a straight line. The law of Batschinski, which says that the fluidity of a liquid is directly proportional to its free volume,[1] is fairly well substantiated by Curves I, II, III, IV and V of Fig. 3, representing the fluidities of a given liquid over the range of temperature from 5° to 75°; but when this law is applied to the various mixtures at a given temperature (Curves VI, VII, VIII, IX, X, and XI) it breaks down badly, although Batschinski in a private communication reports that the law holds in certain cases tried by him.

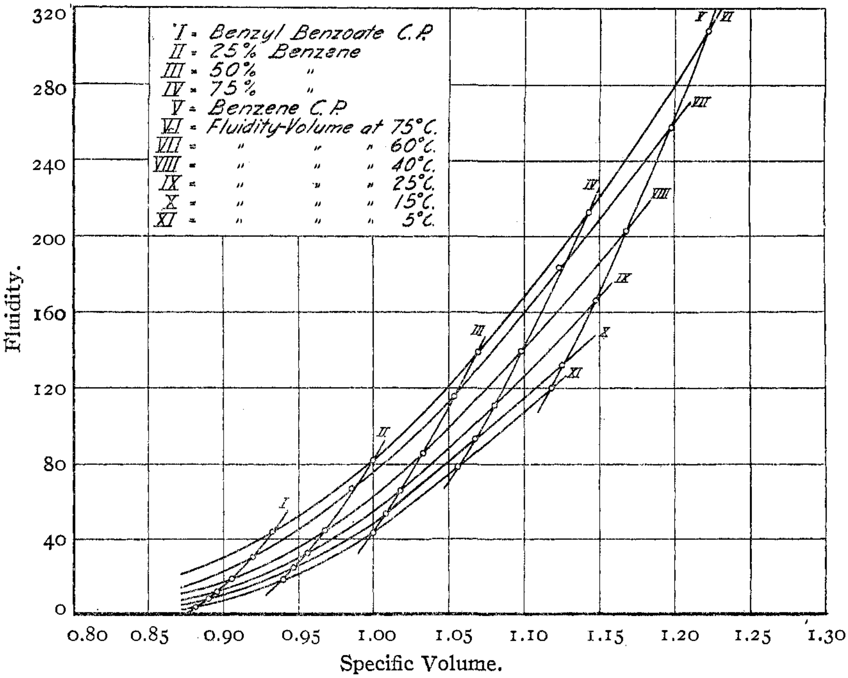

Fig. 3.—The fluidity-specific volume curves of mixtures of benzene and benzyl benzoate at different temperatures.

The specific volume-volume concentration curves, Fig. 4, show that contraction in volume has taken place on mixing at every temperature. Therefore, we are justified in the conclusion that combination has certainly taken place; hence the fluidity-volume concentration curves should deviate from a straight line according to the hypothesis that fluidities are additive, and in Fig. 5 this is observed to be the case. The sag in the specific volume-volume concentration curves is least at the lowest temperature, and it would seem that the sag in the fluidity-volume con-

---

[1] This Journal, 39, 1787 (1917).

centration curves would also be likely to be least at the lowest temperature, as Fig. 5 shows to be true.

We have plotted the observed and calculated curves of fluidity against molecular concentration. Whereas there is good agreement between the two at 25°, as Kendall and Monroe have pointed out, there is no such agreement at other temperatures, the observed values being too high at low temperatures and too low at high temperatures, the deviation of the calculated values from the observed in the 50% mixture by weight being 34% at 25°, 15.6% at 5°, and —6.0% at 60°.

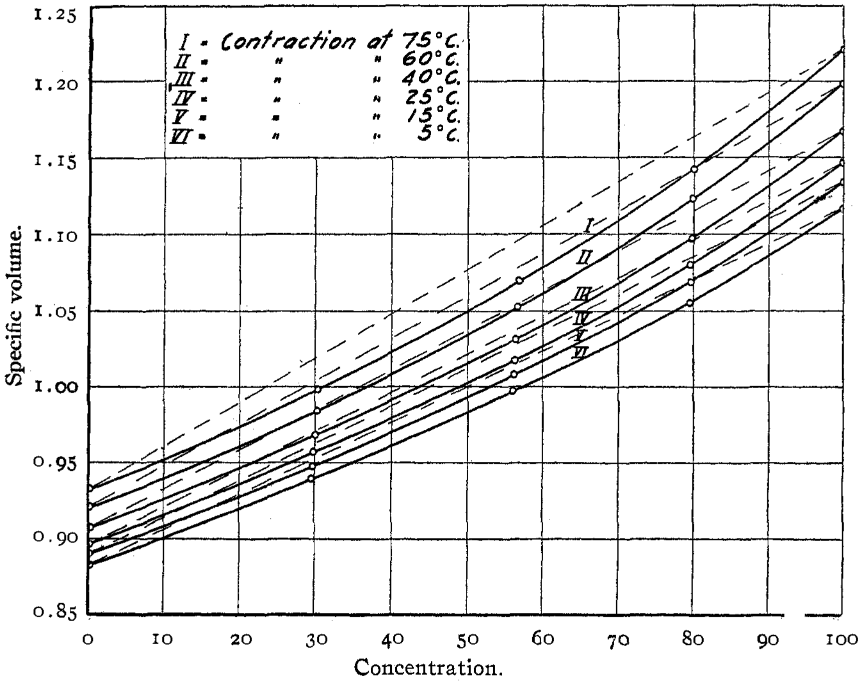

Fig. 4.—The specific volume-volume concentration curves of mixtures of benzene and benzyl benzoate for different temperatures. The sagging of the curves shows that benzene and benzyl benzoate unite with contraction in volume, solvation probably taking place.

If benzene and benzyl benzoate form an ideal pair of liquids, as Kendall and Monroe maintain, and the cube roots of viscosities are truly additive, then it is hard to explain why mixtures demonstrate it at one temperature only. We, therefore, return with renewed confidence to the hypothesis that fluidities are normally additive. When fluidities are not a linear function of the volume concentration we may safely predict that evidence of abnormality may also be found in the other physical properties.

The assumption that the fluidity-volume concentration curve is linear is represented by Curve I in Fig. 6. The assumption that the logarithmic-molecular concentration curve should be linear is represented by Curve II. The assumption that the cube roots of the viscosities should be a linear function of the molecular composition is represented by Curve III. There are, of course, an indefinite number of other curves depending upon the function of the fluidity which is arbitrarily selected and also dependent upon whether we choose the volume, weight, molecular, or some other concentration as the second variable. For example, the viscosity-molecular concentration would be much lower than any of those shown.

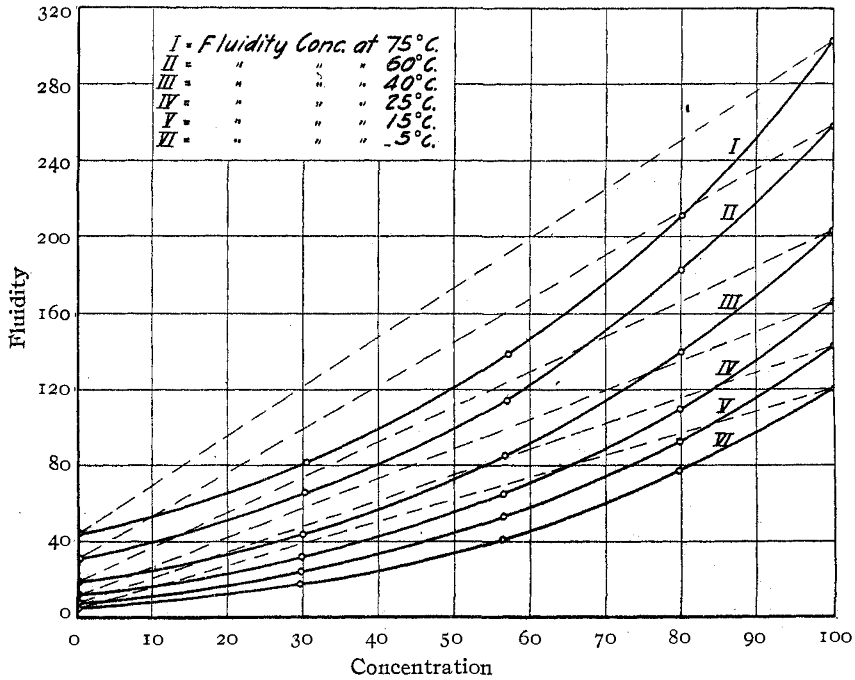

Fig. 5.—The fluidity-volume concentration curves of mixtures of benzene and benzyl benzoate. According to the hypothesis that fluidities are additive, the sagging of these curves is a confirmation of the solvation which was indicated by the sagging of the specific volume-volume concentration curves, Fig. 4.

The observed fluidities are plotted in full lines instead of dashes, Curves IV, V and VI, according to weight, volume, and molecular concentrations, respectively. Curve VI lies close to Curve III, for this particular pair of liquids at 25°, but this fact certainly does not warrant the conclusion that the normal fluidity-volume concentration curve is not linear. A study of the nature of viscous flow[1] which can only be referred to here

---

[1] Bur. Standards, *Bull.* 13, 321 *et seq.* (1916).

shows that we must employ volume concentrations. On the other hand, being convinced that fluidities and volume concentrations are related to each other in a linear manner, the divergence between Curves I and V can be used to calculate the degree of solvation, and this result can be compared with the solvation as calculated by other methods.

In this particular case, one must be cautious in interpreting results due to the fact that benzene and benzyl benzoate are probably both associated[1] to some extent, which complicates the problem. However, we note that all temperatures the greatest deviation of the fluidity-volume concentration curve from the linear curve is in a mixture which contains about 58% of benzene which corresponds to a molecular compound of the formula $C_6H_5.COO.CH_2.C_6H_5.3C_6H_6$. The fact that the maximum deviation does not shift at the different temperatures is also taken as strong evidence of the correctness of the hypothesis that fluidities are

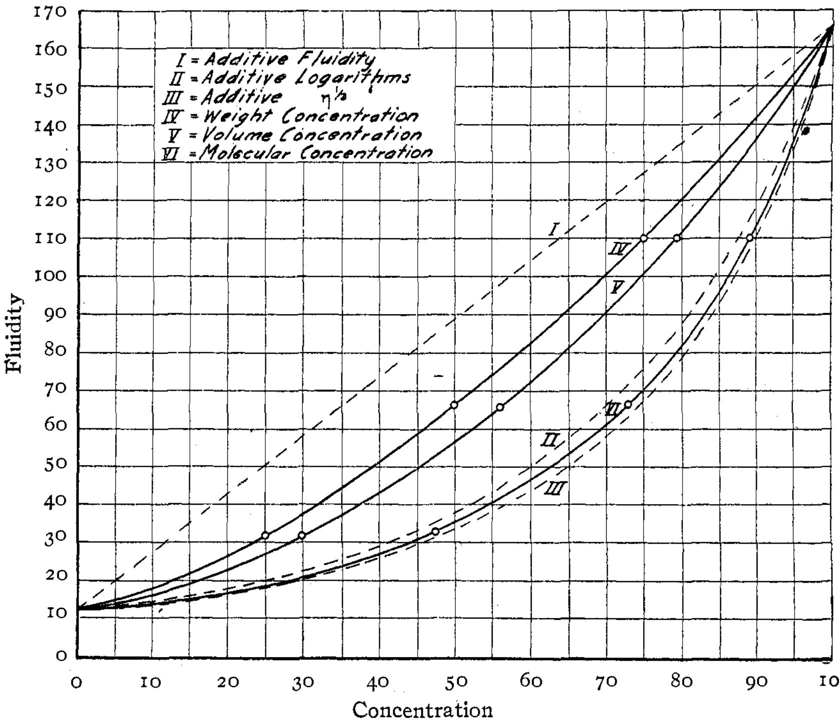

Fig. 6.—A few of the indefinite number of empirical curves are shown by dashes, and observed fluidities, as plotted against weight, volume, and molecular concentrations, are shown by full lines. To base any fundamental conclusion upon the accidental proximity of two of these curves, would be manifestly unwarranted, unless it was supported by other proof of a very strong character.

---

[1] Benzene and many esters are associated (*Z. physik. Chem.*, 66, 28 (1909)).

additive. It would be rather embarassing to have to explain a pronounced shift of the maximum deviation.

Summary.

When inert liquids are mixed it is assumed that the fluidity is a linear function of the volume composition. It had been reported that benzene and benzyl benzoate are inert as indicated by absence of contraction or heat evolution on mixing, yet at 25° their fluidity-volume concentration curve is not linear, and the cube roots of the viscosities are a linear function of the molecular concentrations.

This paper proves that benzene and benzyl benzoate show quite perceptible concentration on mixing, which is proof of aggregation which we would expect from the fluidity-volume concentration curve.

Furthermore, the cube root equation applies at only the one temperature used in the earlier work, but it does not apply at either higher or lower temperatures. This example is, therefore, not only not evidence against the fundamental hypothesis that fluidities are additive, but it is strong evidence in its favor.

EASTON, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

A DETERMINATION OF THE ATOMIC WEIGHT OF THULIUM.

BY C. JAMES AND O. J. STEWART.

Received August 6, 1920.

The material used in this work was obtained and purified as described under Thulium.[1] Owing to the fact that the fractions were very small, several of them were united. All the purest material was combined to form oxalate A, while B and C were two other sets containing small amounts of neoytterbium.

These oxalates A, B and C were converted to the hydrated chloride in a manner identical with that used for samarium. Since a detailed description of this process has already been given in a paper from this laboratory,[2] it need not be repeated here.

Dehydration of the hydrated chloride then followed, using the same method that was employed for samarium. The fused chloride dissolved quickly and completely in pure water.

The ratio, $TmCl_3 : 3Ag$, was then calculated from results obtained from the chloride analyses which were in every respect similar to those mentioned for samarium, silver and other reagents of equal purity being used.

Since each fraction contained only enough material for one analysis, Fractions A and B, after being analyzed once, were again purified as chloride for the second analysis.

---

[1] THIS JOURNAL, 33, 1332 (1911).

[2] *Ibid.*, 39, 2605 (1917).