the reduced chromium. During the boiling to remove the excess of bromine some of the chromium is precipitated as the phosphate, and the precipitation may be made complete by the addition of ammonia in faint excess and the removal of the excess by boiling. A green precipitate indicates chromium. After the removal of the chromium by filtration the filtrate is made alkaline with ammonia and saturated with hydrogen sulfide, which gives the pink or violet oxysulfide of vanadium if that element is present.

The results are given in the table. Solutions were prepared containing one mg. of V_2O_5 and UO_2[1] to a cc. and 10 mg. of CrO_3 to a cc. The initial volume in every case was 15 cc. when the ammonium phosphate was added, the solution reached a volume of about 50 cc. when the chromium was precipitated, and it was concentrated to about 20 cc. before saturation with hydrogen sulfide.

TABLE I.

	CrO_3 present. G.	UO_2 present. G.	V_2O_5 present. G.	Test for CrO_3.	Test for UO_2.	Test for V_2O_5.
(1).......	...	0.001	..	....	Distinct	....
(2).......	...	...	0.0005	....	....	Distinct
(3).......	0.100	0.001	0.001	Heavy ppt.	Distinct	Distinct
(4).......	0.100	0.001	0.001	Heavy ppt.	Distinct	Distinct
(5).......	...	0.001	0.010	....	Distinct	Strong
(6).......	...	0.010	0.001	....	Strong	Distinct
(7).......	0.100	...	..	Heavy ppt.	....	....
(8).......	0.001	0.100	..	Faint green ppt	Heavy ppt.	....
(9).......	...	0.100	..	Faint white[a] ppt.	Heavy ppt.	....
(10).......	0.001	...	0.010	Green ppt.	....	Strong

[a] Possibly a trace of uranium ammonium phosphate.

NEW HAVEN, CONN.

THE VISCOSITY OF LIQUIDS. V. THE IDEALITY OF THE SYSTEM: BENZENE—BENZYL BENZOATE AND THE VALIDITY OF THE BINGHAM FLUIDITY FORMULA.

BY JAMES KENDALL AND KENNETH POTTER MONROE.

Introduction.

The viscosity curve of the above system at 25° was carefully determined by us[2] in 1917, and the experimental results were shown to agree closely with the empirical formula: $\eta^{1/3} = a\eta_1^{1/3} + b\eta_2^{1/3}$ (where η is the viscosity of a mixture; η_1 and η_2 the viscosities of the 2 components; a and b the mol. fractions of the 2 components in the mixture). The maximum divergence between calculated and observed values was only

[1] The radical uranyl, not the oxide.
[2] Kendall and Monroe, THIS JOURNAL, **39**, 1787 (1917).

3.8%, while with other previously-proposed formulas much larger deviations were recorded. For example, the viscosity—weight composition equation showed divergences up to 204%, the fluidity—volume composition equation of Lees[1] and Bingham[2] showed divergences up to 44.7%, the log η—molecular composition equation of Arrhenius[3] and Kendall[4] showed divergences up to 27%.

The following statements were made with regard to the ideality of the system.

"So far as can be judged, this system is ideal.[5] Careful calorimetric measurements failed to indicate any heat evolution or absorption on admixture of equal volumes of the 2 liquids. Density determinations showed that no volume change occurred. The freezing point of benzene was found to be normally depressed on addition of benzyl benzoate, just as with other esters.[6] The polar natures and internal pressures[7] of the 2 liquids are substantially similar."

Relying upon the above criteria for the essential ideality of the system, the authors were forced to suspect, in view of the magnitude of the divergences recorded above, that *none* of the previously proposed formulas had any claim to be regarded as the correct ideal-mixture equation. They considered themselves to be amply confirmed in this suspicion by the results obtained from 3 other systems of like type, similar extreme divergences between calculated and observed values being uniformly indicated. The data from one system (toluene–benzyl benzoate) cast considerable doubt also upon the general applicability of the $\eta^{\frac{1}{3}}$ equation given above. In a later investigation, therefore, Kendall and Wright[8] examined 6 additional "apparently ideal" systems, and concluded that the average discrepancy between calculated and observed viscosities (7.9% for 62 mixtures) was sufficient to warrant the final rejection of a theoretical basis even for this formula. The log η equation, with an average discrepancy of only 4.8% for these systems, was similarly rejected. All other viscosity and fluidity formulas again gave hopelessly discordant values for every case, and the conclusion was consequently drawn (with natural regret) that the experimental data for ideal mixtures are not reproducible satisfactorily by any known simple formula.

[1] Lees, *Phil. Mag.*, [6] 1, 128 (1901).
[2] Bingham, *Am. Chem. J.*, 34, 481 (1905).
[3] Arrhenius, *Z. physik. Chem.*, 1, 285 (1887).
[4] Kendall, *Meddel. K. Vetenskapsakad. Nobelinst.*, 2, No. 25 (1913).
[5] (Original note.) No system, of course, can be absolutely ideal; even 2 saturated hydrocarbons will not be altogether indifferent to each other. The tests made above, however, are sufficient to establish the fact that any abnormality is here inappreciable.
[6] Unpublished work by Dr. J. E. Booge, see p. 120 of this article.
[7] Hildebrand, THIS JOURNAL, 38, 1459 (1916).
[8] Kendall and Wright, *ibid.*, 42, 1776 (1920).

A recent article by Bingham and Sarver,[1] however, re-opens the subject. These investigators claim to have demonstrated, from an examination of the system benzene–benzyl benzoate at different temperatures, that Kendall and Monroe were in error in asserting that the system is essentially ideal, since the 2 components unite with contraction of volume on admixture. It is owing to this presumable solvation that the experimental viscosities are not in accordance with the values calculated from the Bingham fluidity—volume composition formula. The lack of agreement must be considered, indeed, as strong evidence in favor of the fundamental validity of this fluidity formula for truly ideal liquid mixtures.

A direct conflict of opinion therefore exists between Bingham and Sarver and the present authors, both with respect to the actual experimental data for the system and also with respect to the bearing of these data upon the question of the general validity (or nonvalidity) of the fluidity—volume composition equation. We maintain in this article that the criticisms of Bingham and Sarver are not justified by the experimental facts, and that their own theoretical conclusions are also open to serious objection. The several points of difference which enter into the discussion are taken up separately below.

The Ideality of the System.

Purity of Materials.—It will obviously be useless to perform accurate measurements of any physical property upon any system unless the materials employed are of a degree of purity commensurate with the errors of experiment. In a repetition of previous experimental work, a purity of materials at least equal to that already recorded is essential, since otherwise it will not be legitimate to challenge either the results or the conclusions arrived at in such work. With these 2 postulates in mind, let us compare the materials used by Bingham and Sarver with those employed by Kendall and Monroe.

The benzene was apparently of equally high purity in either case; both pairs of authors quote a boiling point for their samples of between $80.2°$ and $80.3°$. The freezing point furnishes a much more exact criterion of purity.[2] Kendall and Monroe give the value $5.480°$; Bingham and Sarver unfortunately omit to state the freezing point of their product.

The preparation of pure benzyl benzoate is a far more difficult task.[3] Kendall and Wright,[4] however, using a specially devised form of apparatus[5] which allowed change of receivers without breaking the vacuum,

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[1] Bingham and Sarver, THIS JOURNAL, **42**, 2011 (1920).
[2] See Richards and Barry, *ibid.*, **37**, 993 (1915).
[3] Compare Berkeley, *J. Chem. Soc.*, **109**, 520 (1916).
[4] Kendall and Wright, *loc. cit.*, p. 1778.
[5] To be described in a later article (P. M. Gross and A. H. Wright).

recently succeeded after repeated fractionations under constant low pressure (about 20 mm.) in obtaining benzyl benzoate which is certainly, as its physical constants listed below will indicate, a very close approximation to a pure product. The samples employed by Bingham and Sarver and by Kendall and Monroe compare with this as follows.

	Melting point. °C.	Boiling point. °C.	Density. 25°/4°.	Viscosity. 25°.	Spec. conductivity. 25°.
Bingham and Sarver........	18.2	....	1.1163	0.08292	.....
Kendall and Monroe........	18.8	....	1.1150	0.08454	.....
Kendall and Wright........	19.4	323.0 ± 0.2	1.1121	0.08504	<1 ×10⁻⁹ mhos.

The inferior purity of Bingham and Sarver's material is evident from its low melting point; softening is admitted even at 17.55°. The impurity present is a substance of higher density and lower viscosity, very probably benzyl chloride.[1]

The total amount of impurity present in any sample can be estimated from the freezing-point depression curve of benzyl benzoate. The slope of this curve, on addition of trichloro-acetic acid, has been determined by Kendall and Booge.[2] For the initial portion of the curve, the freezing point is lowered 1° for every 3.5 mol % of acid added. Now trichloro-acetic acid combines very extensively with benzyl benzoate, hence the slope of the curve (even in its initial portion) will be greater than normal;[3] in other words *more* than 3.5 mol % of an inert impurity must be present to lower the freezing point 1°. Bingham and Sarver's material, with a m. p. 1.2° below that obtained by Kendall and Wright, therefore contains at least 4% of impurities. The experimental results obtained with such material can scarcely be regarded either as accurate in themselves or as capable of furnishing any decisive proof as to the non-ideality of the system.

The Contraction on Mixture.—Bingham and Sarver have plotted, from their experimental data, the specific volume—volume concentration curves for the system at different temperatures, and conclude that the sagging exhibited by these curves indicates that benzene and benzyl benzoate unite with contraction of volume on admixture. The amount of sag in the central portion of the curves (2 to 6%) is too great to be ascribed to impurity of their materials, so that at first sight a valid objection to ideality is hereby raised. A brief consideration of the definitions of density and specific volume, however, discloses the fact that *a sag in the specific volume—volume concentration curve is a mathematical necessity for all mixtures of 2 components with different specific volumes, which show no change*

[1] Gomberg and Buchler, THIS JOURNAL, **42**, 2061 (1920). The final samples of Kendall and Wright were entirely free from benzyl chloride.

[2] Kendall and Booge, *ibid.*, **38**, 1721 (1916).

[3] Kendall, *ibid.*, **36**, 1731 (1914); Kendall and Booge. *loc. cit.*

of volume on admixture. The function which is linear with respect to specific volume is not volume concentration, but weight concentration. The function which is linear with respect to volume concentration is not specific volume, but density. The ideal specific volume—volume concentration curve is not linear but hyperbolic, sagging towards the composition axis.[1]

Let us now test Bingham and Sarver's data against a *true* linear curve: specific volume—weight concentration.[2] The results at 25° are as follow.

Wt. benzene. %.	Spec. vol. (expt.)	Spec. vol. (calc.)	Deviation. %.
0	0.8958	..	...
25	0.9565	0.9584	0.2
50	1.018	1.0209	0.3
75	1.080	1.0835	0.3
100	1.1461	..	...

When it is remembered that the benzyl benzoate employed contained at least 4% of impurities, the small contractions actually obtained cannot be considered to establish the non-ideality of the system.

The results of Kendall and Monroe (not previously published *in extenso*) may be similarly tested.

Wt. benzene. %.	Spec. vol. (expt.)	Spec. vol. (calc.)	Deviation. %.
0	0.8969	..	...
9.27	0.9183	0.9199	0.2
34.40	0.9791	0.9824	0.3
61.29	1.0457	1.0492	0.3
100.0	1.1454	..	...

Small deviations from the calculated values (identical, indeed, with those obtained by Bingham and Sarver) are still indicated. In our opinion, however, these are due not to contraction on admixture, but to systematic experimental errors, since it is extremely difficult to guard adequately against slight "fractional evaporation" of benzene from the mixtures during the necessary manipulations. A careful repetition of the experiments (with benzyl benzoate of m. p. 19.4°) gave the following results. Special pycnometers[3] were employed and all possible care taken to reduce loss by evaporation to a minimum.

[1] The reader may verify these statements (if he feels it necessary) by actual numerical examples. Their negation involves the creation or destruction of matter by mere admixture of 2 liquids.

[2] This change can be visualized very readily by transposing the small circles in Fig. 4 of Bingham and Sarver's paper (p. 2019) to concentrations 25%, 50% and 75% respectively. It will be seen that the circles now fall only very slightly under the straight lines.

[3] Of the type described by Findlay ("Practical Physical Chemistry," 1914, p. 39), with ground-glass stoppers. The first few cc. of liquid drawn through was always rejected.

Wt. benzene. %	Spec. vol. (expt.).	Spec. vol. (calc.).	Deviation. %.
0	0.8992	..	..
24.52	0.9593	0.9596	0.03
50.07	1.0221	1.0225	0.04
75.20	1.0835	1.0843	0.07
100.0	1.1454	..	..

It may confidently be re-asserted therefore that, so far as volume change is concerned, the system is essentially ideal.[1]

The possibility exists, nevertheless, that extensive interactions between the 2 components occur on admixture (either compound formation or dissociation) which involve no appreciable change in volume. Decisive evidence on this point is to be obtained from freezing-point depression data.

Freezing-Point Depression Experiments.—The freezing point of a pure liquid, on addition of an ideal solute, will be depressed according to the equation:[2]

$$ln\ x = (-Q/RT_o).(\Delta T/T)$$

(where x is the mol. fraction of solvent in the solution, Q the mol. heat of fusion of the solvent, T_o and T the absolute freezing points of the pure solvent and the solution respectively, ΔT the freezing-point depression, and R 1.9852). For benzene,[3] Q is 2370 cal.; T_o is 5.480°. Washburn and Read[4] have shown that naphthalene and diphenyl form ideal solutions with benzene by establishing the agreement of the experimental freezing-point curve with that derived from the above equation. The ideality of the present system may be tested in the same way.

The experimental method employed has been described in a previous article.[5] The results obtained are compared with the calculated values in the following table.

Mol. fraction benzyl benzoate.	ΔT(expt.).	ΔT(calc.).	Divergence.
0.00814	0.516	0.530	—0.014
0.01274	0.830	0.831	—0.001
0.02164	1.424	1.414	+0.010
0.03129	2.032	2.050	—0.018
0.04270	2.800	2.807	—0.007
0.05008	3.310	3.298	+0.012

The agreement throughout is within the limits of experimental error (0.01–0.02°). If compound formation occurred on admixture, the ex-

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[1] The actual "contractions" in the above table are about 1% of those indicated in the diagram of Bingham and Sarver.

[2] Roozeboom, "Heterogene Gleichgewichte," 2, 273 (1904).

[3] Demerliac-J. Meyer, see Washburn, "Principles of Physical Chemistry," 1915, p. 172.

[4] Washburn and Read, *Proc. Nat. Acad. Sci.*, 1, 191 (1915).

[5] Kendall, Booge and Andrews, THIS JOURNAL, 39, 2317 (1917).

perimental depressions would be abnormally large; for example, the existence of a stable compound of the type $C_6H_5COO.CH_2.C_6H_5,3C_6H_6$ suggested by Bingham and Sarver[1] would involve a depression, for the last solution tested, of $3.897°$. In the absence of any indication of deviations from the ideal curve, we must conclude that "solvation" is non-existent or inappreciable.

A last possible source of non-ideality (association of the pure components, with consequent disassociation on admixture) may be considered. Bingham and Sarver state that "benzene and many esters are associated." The evidence adduced[2] in support of this statement, however, is inconclusive. All known methods for the estimation of association in the liquid state are admittedly imperfect,[3] yet the most commonly accepted test (surface tension) definitely places benzene and the higher esters among the non-associated liquids.[4] Certainly the extreme divergences existent between the experimental data and the values calculated from the Bingham fluidity formula cannot be ascribed to association, as will be seen below.

The Validity of the Fluidity—Volume Composition Equation.

In view of the results of the preceding section we see no reason for rescinding our rejection of the Bingham equation as a possible ideal-solution formula. The divergences of over 40% between experimental and calculated values in the system benzene—benzyl benzoate cannot be explained away by "non-ideality of the system," since the evidence adduced regarding contraction in volume and solvation on admixture (according to which the lack of agreement in this particular system was held to confirm the fundamental validity of the formula for truly ideal mixtures) possesses no foundation in fact. The system is by all tests essentially ideal.

Apart from this one system, however, Bingham and Sarver claim "both theoretical and experimental proof that fluidities are additive." The experimental proof, being more tangible, may first be investigated.

A careful search through the whole of the available literature fails to elicit a single binary-liquid system with apparently-ideal components for which the experimental data follow the linear fluidity—volume composition formula.[5] The deviations are invariably far in excess of possible experimental errors,

[1] Bingham and Sarver, *loc. cit.*, p. 2021.

[2] Bingham and Harrison, *Z. physik. Chem.*, **66**, 28 (1909). See Dunstan and Thole, "The Viscosity of Liquids," **1914**, p. 31.

[3] Compare Turner, "Molecular Association," **1915**, p. 84.

[4] Morgan, "Elements of Physical Chemistry," **1914**, p. 116. See also Meyer and Mylius, *Z. physik. Chem.*, **95**, 353 (1920).

[5] The proviso should be added that the fluidities of the 2 components of the mixture are not nearly identical. If such is the case, deviations from the linear curve may be but small, but all other formulas also give equally satisfactory results. Agreement with the experimental data is here a matter of necessity rather than of merit (compare Kendall and Monroe, *loc. cit.*, p. 1793).

and increase uniformly as the ratio between the fluidities of the 2 com-
ponents is widened.[1] Thus for the system ether–benzene,[2] where the
ratio is 2.5 to 1, the maximum divergence is over 10%; for the system
benzene—benzyl benzoate, where the ratio is 14 to 1, the maximum diverg-
ence is over 40%; for the system ethyl benzoate—benzyl benzoate,[3] where
the ratio is 20 to 1, the maximum divergence is over 60%. It is signifi-
cant that these large divergences are *always* in the same direction; the
calculated fluidities are consistently too high. In other words, the for-
mula is systematically in error.

The excuse[4] that this is due to the fact that none of the systems cited
is sufficiently ideal ("solvation" being the predominant disturbing factor)
is entirely inadequate when the magnitude of the deviations and our
total lack of evidence regarding such solvation are considered, as (for ex-
ample) in the system benzene—benzyl benzoate discussed in detail above.
A still more striking illustration is afforded by the system hexane—decane.[5]
If the fluidity formula is ever to fit the experimental facts, 2 saturated
hydrocarbons should certainly furnish a fair test, since opportunity for
solvation here is entirely absent. The curve, however, is not linear, but
typically sagged.

Apparently ideal solutions, therefore, yield no support for the fluidity
equation. Disagreement between calculated and experimental values in
the case of admittedly non-ideal solutions has, however, also been postu-
lated as evidence in its favor.

Such solutions fall, in general, into 2 types.[6] In the first,[7] extensive
compound formation between the 2 components occurs on admixture,
and the viscosity (owing to the production of more viscous complexes) is
abnormally high. In the second,[8] disassociation of an associated com-
ponent takes place, and the viscosity (owing to the production of less
viscous simple molecules) is abnormally low.[9] In certain systems the 2

[1] The systems ethyl alcohol—methyl alcohol (Bingham *et al.*, *Z. physik. Chem.*, 83,
653 (1913)); and ethyl alcohol—acetone (Dunstan, *J. Chem. Soc.*, 85, 822 (1904)), give
approximately linear curves, yet their components are certainly not ideal. The most
plausible explanation is that the 2 opposing factors of compound formation and
disassociation (see text above) happen to counterbalance.

[2] Getman, *J. chim. phys.*, 4, 498 (1906).

[3] Kendall and Wright, *loc. cit.*, p. 1780.

[4] Bingham, *J. Phys. Chem.*, 18, 162 (1914).

[5] Bingham *et al.*, *Z. physik. Chem.*, 83, 651 (1913).

[6] See Dunstan and Thole, "The Viscosity of Liquids," 1914, p. 44.

[7] For example, the system acetic acid—aniline (Faust, *Z. physik. Chem.*, 79, 106
(1912)).

[8] For example, the system acetone-carbon disulfide (Faust, *loc. cit.*, p. 105).

[9] It is for this reason that the assumption of association in the system benzene-
benzyl benzoate could not explain the failure of the Bingham fluidity formula for this
system, but would only accentuate the divergences already existent. The experi-
mental fluidities, far from being abnormally high, fall considerably below the linear
curve (see Bingham and Sarver, *loc. cit.*, Fig. 5, p. 2020).

effects may both be existent, but usually one or the other will predominate sufficiently to give a curve quite distinct from the normal type, often indeed with a maximum or a minimum point.

Now it is perfectly true that pronounced deviations from the Bingham fluidity formula are regularly obtained with such systems—in one direction when compound formation is very marked and in the opposite direction when disassociation is the main disturbing factor. Such cases of disagreement, however, form a very frail foundation for a general formula, especially when it is noted that the same regularities exist if any one of an indefinite number of alternative formulas is chosen as a basis for comparison. If it is manifestly unwarranted (as Bingham and Sarver claim) to base fundamental conclusions in this field upon the accidental proximity of curves, it is obviously still more dangerous to base such conclusions upon their accidental remoteness, unless supported by other proof of a very strong character.

Is the experimental proof adduced by Bingham from other fields (pure liquids and suspensions) sufficiently strong to substantiate the formula in spite of its failure at home? With full recognition of the valuable pioneer work which Bingham has performed in these fields,[1] and with especial admiration for the various relationships connecting fluidity with other physical properties which he has elaborated, we venture to remain unconvinced. Similar relationships between alternative functions (*e. g.*, logarithmic viscosity)[2] and other physical properties have also been deduced, and if they are not so numerous as fluidity relationships it is presumably only because the industry or enthusiasm of their sponsors has been inferior. We have as yet no reason to regard any of these relationships as other than empirical; their approximate agreement through a limited range gives us no grounds at all for investing them with extended theoretical significance.

It is impossible, for space considerations, to sift the evidence for each particular case here. As a single illustration, however, the formula of Batschinski[3] connecting fluidity with free volume may be critically examined, since this has been repeatedly cited[4] in support of the fluidity-volume concentration formula.

Batschinski has shown that the simple formula,

$$\phi = k(v - \omega)$$

(where ϕ is the fluidity; v is the specific volume; k and ω are constants) holds very closely for a great many liquids over a small temperature range, and that the constant ω agrees fairly well with the limiting volume

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[1] For a summary of this work see *Phys. Rev.*, **35**, 407 (1912); **1**, 96 (1913).

[2] Dunstan and Thole, "The Viscosity of Liquids," **1914**, p. 32, *et seq.*

[3] Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

[4] Bingham, *J. Phys. Chem.*, **18**, 163 (1914); Bingham and Sarver, *loc. cit.*, p. 2018.

derived by other methods (e. g., van der Waals' constant b). The direct proportionality between fluidity and free volume thus established is an exceedingly useful relationship, but that it is not necessarily fundamental is evident when we note that: (a) the formula is apt to break down very badly[1] when the temperature range is extended over 100°; (b) an in-definite number of alternative equations, using functions other than fluidity, can readily be constructed to fit the experimental data just as well as the Batschinski formula.[2] As an example, the equation recently proposed by Arrhenius:[3]

$$\text{d} \log \eta . v^{1/2} / \text{d} T = k / T^2$$

may be cited.

Without theoretical support, therefore, Batschinski's equation cannot be considered as more than an ingenious interpolation formula, accurate over a restricted range of temperature. Its bearing upon the fundamental validity of the Bingham equation for ideal liquid mixtures is zero.

What, finally, is the *theoretical* proof in favor of the fluidity formula? Several derivations, with minor points of difference, may be found in the literature.[4] All, however, depend upon the assumption that in a binary liquid mixture under viscous flow the components A and B are arranged in alternate layers of pure A and pure B, parallel to the direction of flow. Why an originally homogeneous liquid should assume this peculiar struc-ture we find it impossible to conceive. It is quite true that a non-homo-geneous mixture in which the alternate layers were originally oppositely arranged (i. e., perpendicular to the direction of flow) would tend to trans-form to a mixture of the type indicated, through shearing of the layers, but this is entirely beside the point. In a homogeneous binary mixture we have no layers, either horizontal or vertical; the ultimate "structure" is necessarily an altogether haphazard arrangement of the molecules of the 2 components (approximating to the "checkerboard" arrangement indicated by Lees[5] and Bingham,[6] but in 3 dimensions) and no amount of shearing during viscous flow could possibly effect a separation into layers of a single molecular species. The actual law relating viscosity with composition under this haphazard arrangement still remains to be formulated,[7] yet it should obviously be between the 2 limits of additive viscosity and additive fluidity, which are respectively derivable from the

[1] Compare, for example, the data for hexane and octane (Batschinski, *loc. cit.*, pp. 659-61).

[2] Compare Kendall and Monroe, THIS JOURNAL, **39**, 1799 (1917).

[3] Arrhenius, *Meddel. K. Vetenskapsakad. Nobelinst.*, 3, No. 20 (1918).

[4] Lees, *Phil. Mag.*, [6] **1**, 128 (1901); Bingham, THIS JOURNAL, **33**, 1257 (1911); *Phys. Rev.*, **35**, 408 (1912); Bur. Standards, *Bull.* **13**, 321 (1917).

[5] Lees, *loc. cit.*

[6] Bingham, *Phys. Rev., loc. cit.*

[7] Some interesting suggestions are to be found in a recent monograph by Kleeman ("A Kinetic Theory of Gases and Liquids," John Wiley and Sons, **1920**).

assumptions of perpendicular and parallel layering.[1] The experimental facts are in accordance with this reasoning; in ideal solutions $d\eta/dx$ is not a constant (as additive viscosities demand) nor, on the other hand, does it increase as rapidly as η^2 (as additive fluidities would necessitate).

The utmost that can now be said in favor of the Bingham fluidity formula is that it is not so widely in error as the additive viscosity formula which it supplanted. Other empirical formulas which are in far better agreement with the experimental facts, however, are now in common use.[2] These also will necessarily yield, in time, to the true ideal equation, as yet unknown.

In this connection, one point of primary importance in Bingham and Sarver's recent paper should not be overlooked. The agreement of the cube root viscosity formula with the experimental data for a given system at any one temperature cannot be claimed as establishing the formula for other temperatures, since wide divergences may there be recorded.[3] This is a strong argument for the rejection of fundamental validity for this formula, a step, however, already taken by the present authors[4] on other grounds.

Summary.

It has been claimed by Bingham and Sarver that the system benzene–benzyl benzoate is not ideal (perceptible contraction, presumably owing to solvation, occurring on admixture) and that consequently the conclusions drawn by Kendall and Monroe from their examination of the system (particularly their rejection of the fluidity—volume composition formula as the true ideal equation for binary liquid mixtures) are not valid.

An examination of Bingham and Sarver's experimental data (which are necessarily somewhat inaccurate owing to the impurity of the benzyl benzoate employed) shows that the contraction claimed is non-existent. Freezing-point depression determinations also indicate the absence of compound formation. The system is, as previously asserted, essentially ideal.

A critical investigation of the experimental and theoretical evidence for the validity of the linear fluidity—volume composition formula for ideal mixtures has not, in our opinion, disclosed any facts which warrant its reconsideration. The formula is systematically in error; other equations are known which are in far better agreement. The true ideal equation, however, still remains to be discovered.

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[1] The assumption of a 2-dimensional checkerboard arrangement, which results in a log η-volume composition formula (see Lees, *loc. cit*), is nearer to the truth, but still inconsistent with the facts.

[2] Herschel (Bur. Standards *Tech. Paper*, **164** (1920)) has recently employed the log η formula in computing the viscosities of blended oils.

[3] Bingham and Sarver, *loc. cit.*, p. 2019.

[4] Kendall and Monroe, *loc. cit.*, p. 1801; Kendall and Wright, *loc. cit.*, p. 1782.