VISCOSITY AND FLUIDITY—A SUMMARY OF RESULTS.[1] II.

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FLUIDITY AND OTHER PHYSICAL PROPERTIES.

Fluidity and the Boiling-Point.—Thorpe and Rodger[2] have measured the viscosities of a very large number of liquids and with great care from 0° to nearly the boiling-point of each liquid. The corresponding fluidities have been calculated by Miss Harrison and the writer. When a line is drawn through the fluidities of a given class at the boiling temperatures as extrapolated, the resulting curve in a surprising number of cases turns out to be a straight line, as shown in Figs. 12–16. In those classes of

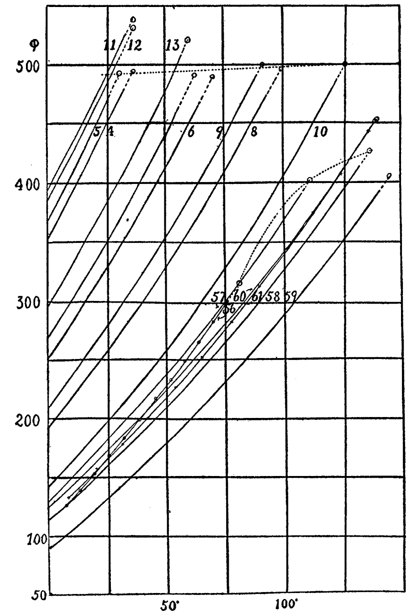

Fig. 12.

The fluidities of various hydrocarbons at different temperatures. 4, pentane; 5, isopentane; 6, hexane; 7, isohexane; 8, heptane; 10, octane; 11, trimethylethylene; 12, isoprene; 13, diallyl; 56, benzene; 57, toluene; 58, ethylbenzene; 59, (*o*)-xylene; 60, (*m*)-xylene; 61, (*p*)-xylene.

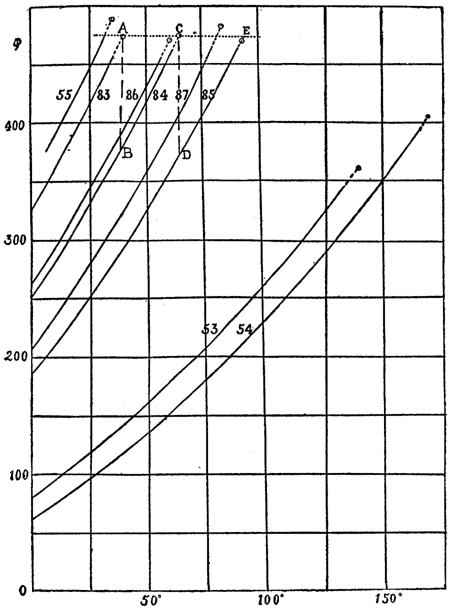

Fig. 13.

The fluidities of various ethers and acid anhydrides at different temperatures. 53, acetic anhydride; 54, propionic anhydride; 55, diethyl ether; 83, methylpropyl ether; 84, ethylpropyl ether; 85, dipropyl ether; 86, methylisobutyl ether; 87, ethylisobutyl ether.

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[1] For Part I., see the PHYSICAL REVIEW, December, 1912.

[2] Phil. Trans. (London), *185A*, 397 (1894); *Do.*, *189A*, 71 (1897).

compounds which are usually regarded as associated, as the aromatic hydrocarbons, acids, alcohols, esters, and ketones, the fluidities of a homologous series at the boiling-point still fall on a smooth curve, but this curve is no longer a straight line, as seen in Figs. 12, 16 and 17.

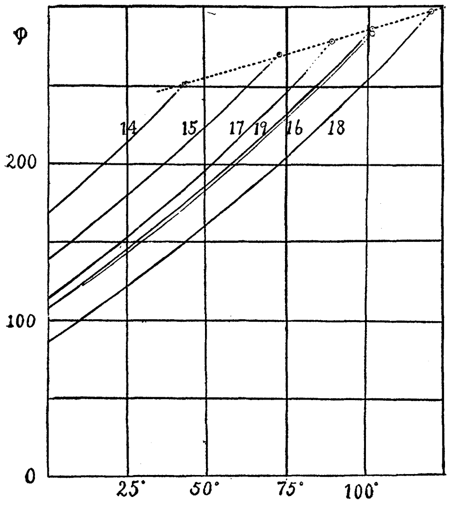

Fig. 14.

The fluidities of various alkyl iodides at different temperatures. 14, methyl iodide; 15, ethyl iodide; 16, propyl iodide; 17, isopropyl iodide; 18, isobutyl iodide; 19, allyl iodide.

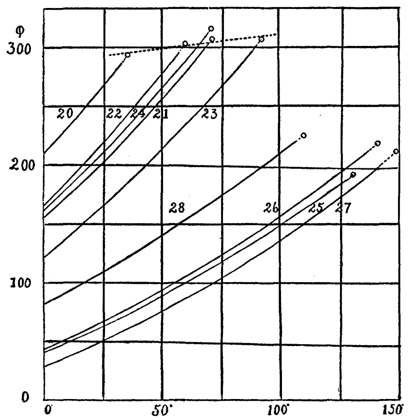

Fig. 15.

The fluidities of various bromine derivatives of the hydrocarbons at different temperatures. 20, ethyl bromide; 21, propyl bromide; 22, isopropyl bromide; 23, isobutyl bromide; 24, allyl bromide; 25, ethylene bromide; 26, propylene bromide; 27, isobutylene bromide; 28, acetylene bromide.

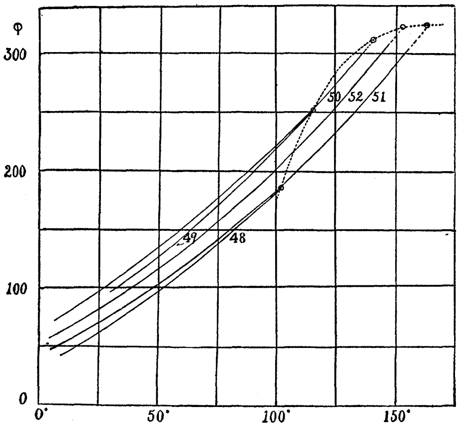

Fig. 16.

The fluidities of various organic acids at different temperatures. 48, formic acid; 49, acetic acid; 50, propionic acid; 51, butyric acid; 52, isobutyric acid.

It is quite improbable that these relationships are due only to accident. They have remained undiscovered for the most part, because of the hyperbolic nature of the viscosity curves and because the viscosities at the boiling-points are very small, making the relation uncertain. Finally the linear fluidity-boiling-point curves of the unassociated classes would themselves be hyperbolas when changed on to the viscosity basis, thus adding to the complication.

The effect of adding a methylene group to any compound is to raise the boiling-point and to lower the fluidity. The meaning of the relation which we have noted seems to be that the ratio between these effects is constant, or in Fig. 13 $AB/AC = CD/CE$.

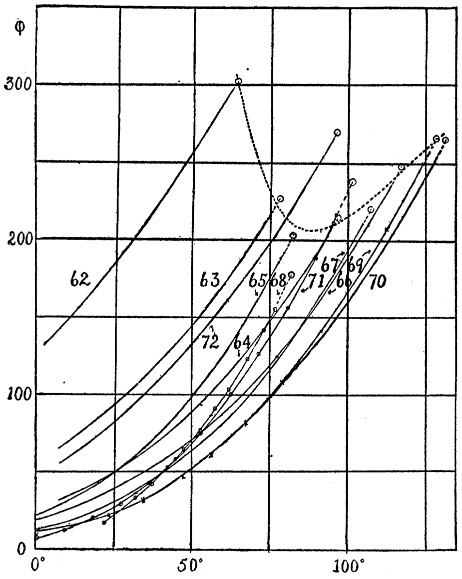

Fig. 17.

The fluidities of various alcohols at different temperatures. 62, methyl alcohol; 63, ethyl alcohol; 64, propyl alcohol; 65, isopropyl alcohol; 66, butyl alcohol; 67, isobutyl alcohol; 68, trimethylcarbinol; 69, active amyl alcohol; 70, inactive amyl alcohol; 71, dimethylethylcarbinol; 72, allyl alcohol.

Fluidity and Vapor Pressure.[1]—It is better perhaps to regard it merely as a coincidence that for the classes of aliphatic hydrocarbons and ethers the fluidity of every member of the class at its boiling-point is nearly identical. But it is quite unlikely that this coincidence is peculiar to the vapor-pressure of 760 mm., therefore it is desirable that it be shown that this relation holds for all vapor-pressures. If it be true for a given

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[1] Cp. ninth and thirteenth papers.

class that, at any given vapor-pressure, the fluidities are identical, it follows that the vapor-pressure-fluidity curves of the whole class should fall together into a single curve, for the fluidities of all of the different members of the class at any given vapor-pressure would form but a single point of the curve. How far this is the case is shown in Fig. 18 for the class of ethers so far as the requisite data have been obtained. The fluidities were measured by Thorpe and Rodger, the vapor-pressures were measured by the author by the method of Ramsay and Young.[1] A similar relation is found to hold for the aliphatic hydrocarbons.

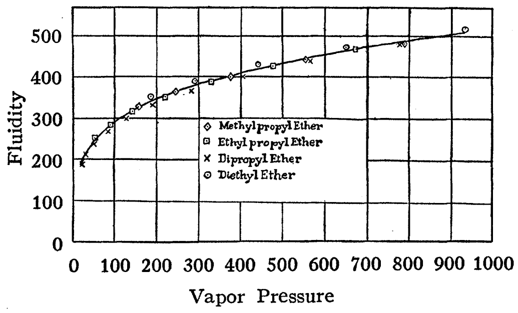

Fig. 18.

Fluidity-vapor-pressure curve of ethers.

This relation does not hold true for the other classes, but it has been pointed out that the other classes of unassociated substances also have linear boiling-point-fluidity curves and that it may be regarded as a coincidence that the fluidity of the classes of ethers and hydrocarbons are identical; hence it seemed desirable that a method be worked out for comparing the fluidity-vapor-pressure curves of these other classes.

The fluidity-vapor-pressure curves of all unassociated compounds are similar but not coincident. The fluidity of the aliphatic hydrocarbons at their boiling points is around 500 cm.g.$^{-1}$ sec. units. Taking the round number 500 as the standard, all other fluidities may be reduced to those of a substance which has a fluidity of 500 at the boiling-point—the general properties of the curve remain the same as before. Thus heptane has a fluidity at the boiling-point (98.4° C.) of 503.9. At 90° C. heptane has a fluidity of 468.3 absolute units and a vapor-pressure of 588.8 mm.

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[1] Professor Alexander Smith has kindly called my attention to the omission in my paper of the correction for the depression of the mercury in the thermometer due to the expansion of the glass under the diminished pressure. Probably the error in this case was relatively small because the pressures were not very low, but it should not have been neglected.

I may here call attention to a correction in my twelfth paper, Am. Chem. J., *46* (1911). On page 288, column three of Table XII. should read, "Volume per cent. of clay 1.015, 1.009, 1.003, 0.991, 0.977, 2.570, 2.565, 2.552, 2.542, 2.531, 4.603, 8.390."

Reducing this fluidity to standard we have $468.3 \times 500 \div 503.9 = 464.7$. By plotting the curves of a large number of substances we could obtain a composite curve which might then be regarded as the standard curve. There are obvious reasons, however, for choosing the curve of a known substance as the standard curve for reference, hence we have chosen heptane, since its fluidities and vapor-pressures are known over a considerable range and its fluidity-vapor-pressure curve is close to the composite curve.

We have elsewhere[1] given a table of vapor-pressures corresponding to the various fluidities of heptane, reduced as indicated above. By comparing the observed vapor-pressures of any substance with the values calculated by the use of this table, one can prove that the relation between fluidity and vapor-pressure in the different classes of substances is quite general, the highly associated substances alone being exceptional. The agreement is shown for a single substance, methyl isobutyrate, in the following table. The fluidity at the boiling-point (92.3°) is 397.3.

TABLE I.

The Vapor-Pressures (p) of Methyl Isobutyrate Calculated from Its Fluidities Reduced to 500 *C.G.S. Units at the Boiling Point.*

Temp.	ϕ Red.	p Obs. in Cm.	p Calc. in Cm.	Per Cent. Diff.	Temp.	ϕ Red.	p Obs. in Cm.	p Calc. in Cm.	Per Cent. Diff.
0	187.3	1.22	1.02	−17	50	338.3	16.20	16.20	0
10	214.7	2.24	1.98	−12	60	372.8	24.38	24.44	0
20	243.3	3.89	3.55	− 6	70	409.6	35.53	35.93	1
30	273.0	6.54	6.17	− 6	80	449.2	50.50	51.76	2
40	304.7	10.47	10.29	− 2	90	490.9	70.70	71.60	1

There is general agreement when the vapor-pressures are not too small and the compound not highly associated. From a study of a considerable number of compounds, we have found that for vapor pressures of more than ten centimeters, the calculated values differ from the observed by only a little over three per cent.

Since this relation exists, it is possible to calculate unknown vapor-pressures of unassociated compounds, when the boiling-point of the compound is known. Conversely, if the vapor-pressures of a substance and its fluidity at the boiling point are known, it becomes possible to construct the fluidity curve. Thus suppose that the fluidity of ethylpropyl ether at 20° C. is desired, it being known that the fluidity of this substance at the ordinary boiling-point is 479.9 and that its vapor-pressure at 20° is 14.26 cm. The corresponding fluidity interpolated

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[1] Am. Chem. J., *47*, 187 (1912).

from the table for heptane, the standard substance, is 328.0; but these fluidities are reduced, so that they must be corrected back. Thus $328.0 \times 479.9 \div 500 = 314.8$, which is practically identical with the observed value of 314.9.

A priori, one would hardly expect to find any relation at all existing between the fluidity of a liquid and the pressure of the vapor above it. Yet it is proved that a relation does exist of a very simple character. This is doubtless the result of both of these properties being similarly dependent upon another property of the liquid, which is probably its molecular volume.

As has been already hinted, the calculated values of the vapor-pressure differ very widely from the observed values in the case of highly associated liquids. A discussion of these interesting cases would carry us beyond the limits of this paper.

Finally it is important to point out that the above relation could hardly have been discovered on the assumption that viscosities are additive. The viscosity-vapor-pressure curves must be hyperbolic in character, although like the viscosity curves some of them might appear to be linear, as would indeed those of the ethers and aliphatic hydrocarbons.

Fluidity and Chemical Composition and Constitution.[1]—As soon as any considerable amount of viscosity data had been collected, it became evident to the early workers in this field that there is a relation between viscosity and chemical composition. At the hands of Pribram and Handl[2] the number of empirical relations became quite extended, although their experimental material lacked great precision. This seemed to Thorpe and Rodger to indicate that results of great importance might be obtained if very accurate data were available for a sufficient variety of substances of unquestioned purity. Consequently these investigators began the accumulation of viscosity data considering carefully every detail of the purification of material, precision in measurement, and accuracy in the calculation of results. Their monumental work[3] finally embraced some 85 substances. To bring out new relationships, it became necessary to find the proper basis of comparison. For this purpose Thorpe and Rodger studied their data from every point of view which occurred to them. They compared viscosity coefficients, molecular viscosities, and molecular viscosity work, at the boiling-point, critical temperatures, temperatures corresponding to a given slope of the viscosity curves, and viscosities corresponding to a given slope of the viscosity

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[1] Cp. sixth paper.

[2] Sitzungsber. der math.-naturwiss. Klasse der Kais. Akad. d. Wiss. Wien, *78*, II., 113 (1878); *Do.*, *80*, II., 17 (1879); *Do.*, *84*, II. 717, (1881).

[3] *Loc. cit.*

curves. They confirmed the conclusion that different atoms and groupings have, in general, an additive effect upon the viscosity, but as a whole their results are disappointing, for the value of an atom or grouping is sometimes arbitrarily assumed to vary from class to class. Thus oxygen has one value for ethers, another for alcohols, and still another for acids. But even with these assumptions, a considerable number of substances fail to give satisfactory results upon any basis of comparison. They obtained best results in comparisons at equal slope, although their argument to prove that this should be the case is scarcely conclusive.

If the fluidities are additive, and not viscosities, it seems probable that the true basis of comparison should be worked out in comparing fluidities and not viscosities as has been done uniformly heretofore. Inspection of Figs. 12–16 shows that in homologous series, the fluidity-temperature curves form a family of approximately straight and parallel lines. Were they actually linear and parallel, their slopes and intercepts would of course completely define them, and give us therefore a true basis of comparison. Hence it seems certain that we should either compare fluidities at a given temperature or temperatures of equal fluidity together with the slopes of the fluidity curves. Since the curves in a given class are nearly parallel, it is evident that the slope is characteristic of the class to which a compound belongs. The molecular weights of the compounds determine the values of the intercepts. But the fluidity-temperature curves are neither perfectly linear nor parallel. The lack of linearity may be ascribed to association, using that term broadly. It should be recalled at this point that metallic mercury gives a fluidity curve which is quite linear and apparently cuts the temperature axis at absolute zero. It is probable that all fluidity curves would unite at absolute zero, so that exact parallelism is not to be expected even within a given class.

There are several reasons for comparing the temperatures of equal fluidity rather than fluidities at a given temperature.

1. The slopes are more nearly equal when the fluidities are the same.

2. At a given fluidity the members of at least two classes have the same vapor-pressure, and experience has proved that substances are comparable at temperatures corresponding to equal vapor-pressure.

3. The fluidity curves for associated compounds depart widely from linearity at low fluidities, but approach linearity at high fluidities, as do the curves of other compounds.

4. A yet more cogent reason grows out of the fact, mentioned above, that exact parallelism in the curves of a given class is not to be expected. A methylene group added to pentane, for example, lowers the fluidity a

certain amount, but a methylene group added to decane cannot lower the fluidity by the same amount, since as the molecular weight increases the fluidity must approach zero asymptotically. Otherwise, it would require no very high molecular weight to give a negative fluidity, which is inconceivable.

The fluidity of 200 was chosen for the basis of comparison since most substances could then be included. The temperatures and slopes of several unassociated compounds corresponding to the fluidity of 200 are given in Table II.

Table II.

Absolute Temperatures and Slopes of Non-Associated Substances Corresponding to a Fluidity of 200 C.G.S. Units.

Substance.	Abs. Temp. ($\phi = 200$) Observed.	Diff. CH_2.	Slope at ($\phi = 200$).	Abs. Temp. ($\phi = 200$) Calc.	Per Cent. Diff.
Hexane	(255.1)[1]	(21.0)	(2.88)	254.6	0.2
Heptane	276.1	23.0		277.3	0.4
Octane	299.1		2.44	300.0	0.3
Isohexane	(249.0)	(20.2)	(2.79)	247.0	0.8
Isoheptane	269.2		2.68	269.7	0.2
Methyl iodide	290.2	19.0	1.92	287.4	1.0
Ethyl iodide	309.2	23.5	1.80	310.1	0.3
Propyl iodide	332.7		1.82	332.8	0.0
Isopropyl iodide	324.5	21.0	1.92	325.2	0.2
Isobutyl iodide	345.5		1.86	347.9	0.7
Allyl iodide	330.5		1.82	328.8	0.5
Ethyl bromide	268.7	27.9	2.22	273.5	1.8
Propyl bromide	296.6		2.08	296.2	0.1
Isopropyl bromide	289.4	25.6	2.22	273.5	1.8
Isobutyl bromide	315.0		2.08	311.3	1.1
Ethyl propyl ether	(255.0)	(24.0)	(2.70)	256.1	0.5
Dipropyl ether	279.0		2.62	278.8	0.1
Methylissbutyl ether	(251.1)	(19.0)	(2.75)	248.5	1.0
Ethylisobutyl ether	270.1		2.68	271.2	0.4

Table III.

The Value of the Iso-Grouping.

Substance.	Temp. Obs. Normal Grouping.	Temp. Obs. Iso-grouping.	Diff.
Hexane	255.1	249.0	6.1
Heptane	276.1	269.2	6.9
Propyl iodide	332.7	324.5	8.2
Propyl bromide	296.6	289.4	7.2
Propyl chloride	261.5	255.2	6.3
Butyric acid	381.6	371.6	10.0
Methyl butyrate	304.2	295.8	8.4

[1] Values in parentheses are extrapolated.

Column 3 of Table II. shows that the value of a methylene group varies around a mean value of 22.7. The effect of an iso-grouping is to decrease the fluidity of a compound some 7.6 units, as shown in Table III.

The value of the hydrogen atom is calculated as follows:

TABLE IV.

The Value of the Hydrogen Atom.

Substance.	Temp. Obs.	$n \times CH_2$ Calc.	Diff.
Hexane	255.1	136.2	118.9
Heptane	276.1	158.9	117.2
Octane	299.1	181.6	117.5
Isohexane	249.0	128.6	120.4
Isoheptane	269.2	151.3	117.9

The mean value for H_2 is 118.4. Hydrogen has therefore a value of 59.2 and carbon of − 95.7.

The value of the "double bond" in allyl compounds is obtained from Table V.

TABLE V.

The Value of a Double Bond.

Substance.	Temp. Obs. Normal Propyl.	Temp. Obs. Allyl.	Diff.
Iodide	332.7	330.5	2.2
Bromide	296.6	292.2	4.4
Chloride	261.5	256.0	5.5

To raise the fluidity of an allyl compound to 200 it is therefore only necessary to raise it to a temperature which is some four degrees lower than is required for the corresponding normal compound, containing two more hydrogen atoms. Thus the "double bond" has a value of 114.4, the absence of the hydrogen atoms being nearly compensated for by the "condition of unsaturation."

Assuming that the ethers are unassociated, we may obtain the value of the oxygen atom.

TABLE VI.

The Value of the Oxygen Atom.

Substance.	Temp. Obs.	C_nH_{2n+2}.	Oxygen.
Ethylpropyl ether	254.9	231.9	23.0
Dipropyl ether	279.0	254.6	24.4
Methylisobutyl ether	251.4	224.3	27.1
Ethylisobutyl ether	270.3	247.0	23.3

This gives an average value for oxygen of 24.2. The values of sulphur and the halogens are obtained similarly but need not to be given here.

From these values, the temperatures corresponding to a fluidity of 200 may be calculated. Some of these calculated values are given in the fifth column of Table II. A comparison between the observed and calculated values for 35 substances gives an average percentage difference of less than 0.8 per cent. The constants found at a fluidity of 300 are entirely consistent with these found at a fluidity of 200. The association is smaller at the higher temperatures as would be expected, and thus the temperature coefficients of association have been calculated,[1] but need not be given here.

In comparing viscosities, it has been customary to give an important special value to a ring grouping, but we have found that in comparing fluidities the value of the ring grouping is of small importance and may perhaps be neglected in a first approximation; for it would diminish the immediate usefulness of the method if a special value had to be assigned for each constitutive difference.

From the constants at different fluidities it is evidently possible to construct the entire fluidity curve of any unassociated substance.

Fluidity and Association.[2]—In the above calculations of constants it has been assumed that the compounds chosen are non-associated. This is probably not entirely warranted, but they must be associated to nearly the same extent since the agreement between the calculated and observed

Table VII.

Absolute Temperatures and Slopes of Some Associated Compounds Corresponding to a Fluidity of 200 C.G.S. Units.

Substance.	Abs. Temp. for ($\phi = 200$) Obs.	Abs. Temp. for ($\phi = 200$) Calc.	Slope for ($\phi = 200$).	Association.
Water	328.9	142.6	3.04	2.31
Formic acid	(380.2)	185.5	(2.18)	2.05
Acetic acid	363.8	208.2	2.06	1.77
Propionic acid	362.0	230.9	1.92	1.57
Butyric acid	381.6	253.6	1.92	1.57
Isobutyric acid	371.6	246.0	2.00	1.51
Methyl alcohol	305.2	165.3	2.78	1.84
Ethyl alcohol	343.4	188.0	3.24	1.83
Propyl alcohol	365.6	210.7	3.76	1.74
Butyl alcohol	377.0	233.4	3.44	1.62
Ethyl formate	273.8	230.7	2.40	1.19
Ethyl acetate	284.0	253.4	2.50	1.12
Ethyl propionate	298.1	275.1	2.44	1.08

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[1] Cp. ninth paper.

[2] Cp. sixth and ninth papers.

values is very good in most cases, and it is a general belief that some of these compounds are indeed unassociated. If we now consider the manifestly associated compounds, the method of comparison outlined above gives us a means of calculating the magnitude of the association. For we have seen that the absolute temperature required to produce the given fluidity is directly proportional to the molecular weight. The assumption that this holds true as molecules unite with each other is rather a deduction than an assumption. Its contradiction would involve

TABLE VIII.

A Comparison of the Values of Association as Determined by Different Investigators.

Substance.	R. & S.[1] 16–46°.	R. & S. Corr. by Traube.	Traube.[2] 15°.	Longinescu.[3]	B.&H.[4], Temp. of ($\phi = 200$).
Water	3.55 1.64	1.79	3.06	4.67	2.31
Ethylene chloride	——	——	1.46	1.00	1.21
Dimethyl ketone	1.26	1.18	1.53	1.60	1.23
Diethyl ketone	——	——	——	1.25	1.16
Methyl propyl ketone	1.11	1.10	1.43	1.25	1.14
Formic acid	3.61	2.41	1.80	1.80	2.05
Acetic acid	3.62 2.13	2.32	1.56	1.75	1.77
Propionic acid	1.77	1.45	1.46	1.55	1.57
Butyric acid	1.58	1.35	1.39	1.36	1.51
Isobutyric acid	1.45	1.28	1.31	——	1.51
Benzene	1.01	1.05	1.18	——	1.17+
Toluene	0.94	1.01	1.08	——	1.08+
Methyl alcohol	3.43 2.32	2.53	1.79	3.17	1.84
Ethyl alcohol	2.74 1.65	1.80	1.67	2.11	1.83
Propyl alcohol	2.25	1.70	1.66	1.67	1.74
Isopropyl alcohol	2.86	2.00	1.53	——	1.75
Butyl alcohol	1.94	——	——	1.47	1.62
Isobutyl alcohol	1.95	1.53	1.54	——	1.66
Active amyl alcohol	1.97	1.54	1.53	——	1.54
Allyl alcohol	1.88	1.50	1.55	1.80	1.69
Methyl formate	1.06	1.07	(1.60)	1.12	1.25
Ethyl formate	1.07	1.08	1.39_0°	——	1.19
Methyl acetate	1.00	1.04	1.48_0°	1.09	1.17
Ethyl acetate	0.99	1.04	1.25	1.00	1.12
Propyl acetate	0.92	1.00	1.31	1.00	1.11
Ethyl propionate	0.92	1.00	1.27	0.94	1.08
Methyl butyrate	0.92	1.00	1.30_0°	1.00	1.10

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[1] Ramsay and Shields, Zeitschr. f. physik. Chem., *12*, 464 (1893); Do., *15*, 115 (1894).

[2] Traube, Ber. d. deutsch. chem. Gesell., *30*, 273 (1897).

[3] Journ. Chim. Phys., *1*, 289 (1903).

[4] Bingham and Harrison, *loc. cit.*

an assumption for which we do not at present see any justification. The average molecular weight or association of a liquid is therefore measured by the ratio of the observed absolute temperature to the calculated absolute temperature at the fluidity chosen as the basis of comparison.

The observed and calculated absolute temperatures corresponding to the fluidity of 200 and the calculated association of some supposedly associated compounds are given in Table VII. The slopes of these compounds are also given in the fourth column.

In Table VIII. is given a comparison of the association as calculated by the fluidity method with that obtained by other methods.

So far as one is able to judge, the result seems to be all that could be desired. We believe that the fluidity method is freer from assumptions to which question may be raised, than the other methods, and we hope that it may prove of use in calculating association. However that may be, it seems certain that the above concordance ought to add very greatly to the weight of the reasoning of this paper as a whole; for it is especially to be noted that similar results have not and probably cannot readily be obtained from a comparison of viscosity data as such. Lest this statement appear unsupported, we shall attempt to prove it as follows. Let *AB* and *A'B'* in Fig. 19 represent two fluidity curves, parallel to each other and therefore presumably representing members of the same class of substances, and let a third fluidity curve *CD* be at an angle to the other two to represent a substance in another class. Since we have elected to compare absolute temperatures at a fluidity of 200, this amounts to comparing the intercepts of the curves on the line *AD*, whose equation is $\varphi = 200$. The corresponding viscosity curves obtained by taking the reciprocal values of the above fluidities and multiplying by 10,000 are represented by *ab*, *a'b'*, and *cd*; and *ad* is of course the reciprocal of the line *AD*. But the point *a* and the point where the curve *a'b'* crosses *ad* are points of equal slope on the viscosity curves, hence we conclude that within a given class it makes no difference whether we compare temperatures corresponding to a given fluidity or temperatures corresponding to a given slope on the viscosity curves. The latter is exactly the method of comparison which Thorpe and Rodger found very advantageous. But between different classes they found difficulties.

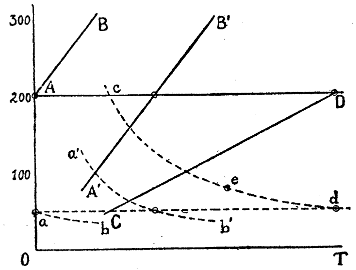

Fig. 19.

Diagram illustrating the relationship between viscosity and fluidity-temperature curves.

This is now easily explained, for *d* is the reciprocal of the point *D* which we believe should have been used; but they selected the point *e*, which has the same slope as the point *a*, and for this choice we think that there is not adequate reason. However it is advantageous for our point of view that they unwittingly proved that a comparison of temperatures corresponding to a given fluidity gives the best results even if they did not make it perfectly general.

Fluidity and Hydration.[1]—It is but a step from the consideration of the complexes which exist in homogeneous liquids to that of the loose combinations in solution, which are most common in aqueous solutions and are called hydrates. An increase in the average molecular weight usually, but not necessarily invariably, takes place and this increase should under favorable circumstances be capable of detection and measurement by means of the fluidity method.

The queston of hydration was in the minds of the earliest investigators in the field of viscosity, hence it is useless to hope to add anything of moment to their work without an advance in the underlying theory. Our study of the problem has led to the belief that there are three misconceptions prevalent, which have stood in the way of its solution.

1. It has invariably been assumed that viscosities and not fluidities are additive, causing the simplest mixtures to appear abnormal, as already discussed.

2. By common consent the concentrations of solutions have been reckoned on the weight-percentage or molecular percentage basis. But we have already pointed out that concentrations must be reckoned in terms of volume percentage, since it is the total space occupied by a liquid of given fluidity which is of importance, and not its density or molecular volume.

3. It has been assumed that a maximum, or minimum, in a viscosity curve had peculiar significance and that it coincided with the composition of the hydrate formed. Neither part of this assumption appears to be true, as we shall now attempt to prove by the consideration of the following simple cases.

Case I. The fluidity-temperature curves of two similar substances are represented by *A* and *B* in Fig. 20*a*. Let it be supposed that a combination takes place between the two substances on mixing, which is a maximum in the 50 per cent. mixture; so that for this mixture the fluidity is lowered from the curve *C* (dotted), which would be expected were there no combination, to the curve .5*B*. Plotting these points, the fluidity-concentration curves of these same substances for the various

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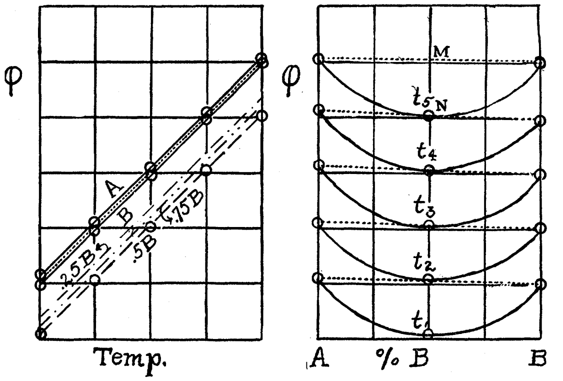
[1] Cp. fourteenth paper.

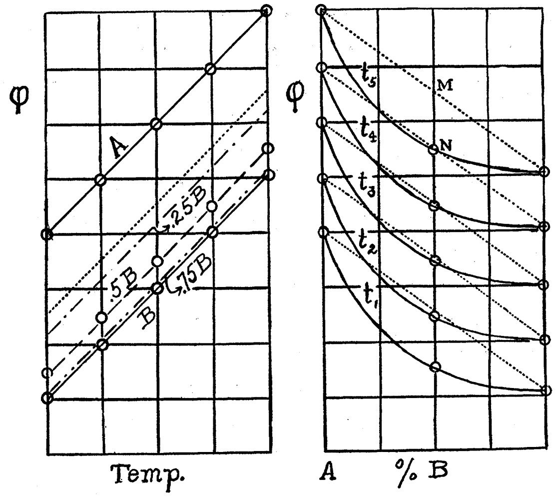
temperatures t_1, t_2, t_3, etc., may be interpolated as shown in Fig. 20*b*. The curves .25*B* and .75*B* may be added to Fig. 20*a* for the 25 per cent. and 75 per cent. mixtures respectively. In this case there is a well-defined minimum in the fluidity-concentration curves in the 50 per cent. mixture corresponding to the composition of the hydrate.



a *b*

Fig. 20.

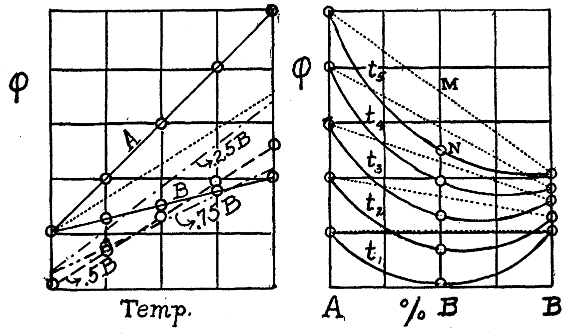
Case II. In Fig. 21*a*, the same conventions are employed, the curves *A* and *B* being still parallel and the maximum lowering of the fluidity being in the 50 per cent. mixture and the same in amount as in Case I. The only difference is that the two curves *A* and *B* are sufficiently



a *b*

Fig. 21.

distant from each other so that the curve .5*B* falls above the curve *B*. The result is that the fluidity-concentration curves, shown in Fig. 21*b*, no longer give a minimum, although by assumption the hydration is the same as before both in relative composition and in amount. However it is clear that the deviation of the fluidity-concentration curves from the linear curves, which would be expected were there no combination, and as measured vertically *MN*, is the same as in the preceding case.



a *b*

Fig. 22.

Case III. In Fig. 22*a* and *b* is depicted the case where the fluidity-temperature curves of the components are no longer parallel so that the result is practically a combination of cases I. and II. At low temperatures there is a good minimum in the fluidity-concentration curves, but it gradually shifts to the right as the temperature is raised, until at the highest temperatures there is no minimum at all. It is manifestly erroneous to assume that the composition of the hydrate changes on this account. On the other hand the deviation from the expected linear curves as measured vertically is everywhere the same as in the simpler cases.

In practice the hydration will generally be less at the higher temperatures so that the deviation should grow smaller as the temperature is raised, but the cases given are perhaps sufficient to show that the *deviation* of the observed fluidity-concentration curve from the linear curve, which would be expected were there no combination between the components of the solution, can alone furnish trustworthy information.

If the above reasoning is correct it seems possible that the way may now be open to use the property of fluidity to throw important light upon the question of hydration and other similar combination in solution. For example, certain puzzling contradictions may be immediately disposed of. Thorpe and Rodger[1] measured the viscosities of mixtures

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[1] J. Chem. Soc., *71*, 366 (1897).

of methyl iodide and carbon disulphide and of carbon tetrachloride and benzene at several temperatures. In each case they found sagging in the viscosity curves, which they accounted for by assuming that the components of the mixtures united with each other to some extent. But they themselves noted that when methyl iodide and carbon disulphide are mixed, quite a marked expansion takes place, with the absorption of heat. With carbon tetrachloride and benzene there is no expansion but perhaps a very slight contraction. The evidence is therefore puzzling if not absolutely contradictory. When the fluidities of these pairs are plotted against volume concentrations, on the other hand, we find that the curves are slightly bent upward in the case of methyl iodide and carbon disulphide, and slightly sagged downward in the case of carbon tetrachloride and benzene. Moreover the sagging in the latter case is greatest at the lower temperatures where the conditions are most favorable to combination. This is shown by the continuous curves in Fig. 23. The curves indicated by dashes represent the result of plotting fluidities against the weight concentrations as given by Thorpe and Rodger. The result is contradictory, because an increase in fluidity would not be expected to accompany even a very slight contraction. Moreover the departure from the linear (dotted) curve, which we should expect if there were no combination, should not increase as the temperature is raised as is apparently the case. For an increase in fluidity in the mixture would seem to be due to one component causing

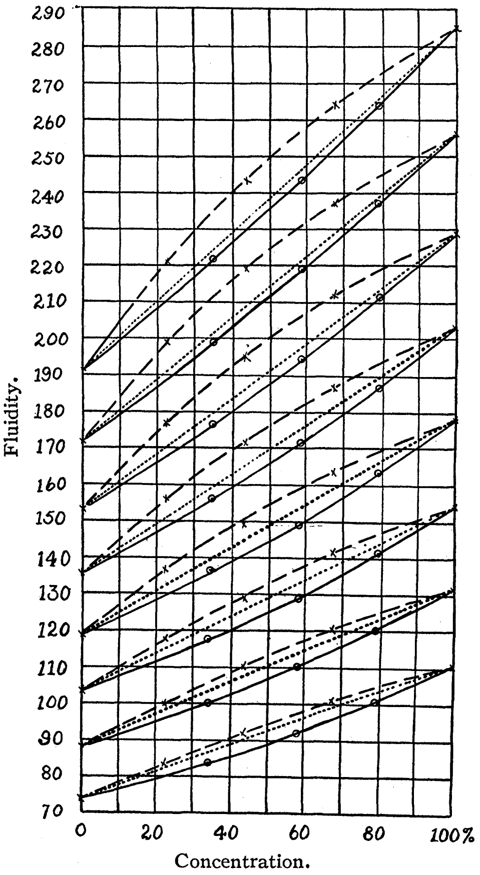

Fig. 23.

The fluidities of mixtures of carbon tetrachloride and benzene plotted against volume concentrations (continuous lines) and weight concentrations (dashes) as compared with the linear curves (dotted).

the destruction of the association of the other, and this effect would naturally be greatest at low temperatures where the association is greatest. Fortunately these contradictions are cleared up as we have seen by plotting fluidities against volume-concentrations, for which there is ample justification.

The viscosity curves for chloroform and ether as measured by Thorpe and Rodger[1] show a point of inflection. To explain this they were forced to assume that at some concentrations one of the liquids destroyed the association of the other, while at other concentrations the two components united with each other to form complexes. On its face this assumption seems somewhat improbable and this improbability is further increased by other facts obtained by the same experimenters. For in the case of chloroform and ether there is "a considerable evolution of heat and a notable contraction," the greatest contraction taking place in the mixture containing 40.14 weight percentage of ether. But the point of inflection in some of the viscosity curves occurs in this mixture, the exact point varying considerably as the temperature is raised. So viscosity tells a tale which is different from that of any of the other properties, and this fact tells heavily against viscosity comparisons as an aid in investigation. When rightly viewed the testimony of all of the properties must agree, since all of the properties of a substance must be the outgrowths of its chemical composition and constitution together with the physical conditions imposed upon it. In the case under discussion, if we plot fluidities against concentrations, we obtain curves for the different temperatures, which no longer show a point of inflection, but are considerably sagged, the greatest deviation from the linear curve occurring in the mixture where the greatest contraction and presumably the greatest heat evolution also occur. Thus the different kinds of evidence agree in indicating that there is some kind of a combination between the components of the mixture.

Were the components of the mixture non-associated, it would not be difficult to calculate the average molecular weight of the mixture by the fluidity method. But substances which form the feeble combinations on mixing which we have under consideration are usually associated and it is quite likely that this association is altered in the mixture, so that the result is considerably complicated thereby. This change in the association of the components may indeed shift the point of greatest deviation from the linear curve, so that this point will not exactly correspond to the composition of the hydrate. The familiar problem of hydrates in aqueous solution is therefore a complicated one, which we

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[1] Loc. cit.

are not yet in a position to handle very satisfactorily, although it does seem possible to clear the way for a solution. To fix our attention upon this problem more closely, let us consider the case of ethyl alcohol and water. The former at the fluidity of 200 requires an absolute temperature of 343.6 and has an average molecular weight of 1.83 times the empirical formula. The latter requires an absolute temperature of 328.9 and the association is 2.31. With ethyl alcohol and water there is a definite minimum in the fluidity curves, which at some temperatures occurs in the mixture corresponding to the composition $C_2H_6O.3H_2O$, *i. e.*, about 52 volume per cent., hence earlier workers on the viscosity of these mixtures concluded that this hydrate is actually formed. The greatest deviation from the linear curves, which would be expected were there no combination, occurs in the mixture which corresponds to the hydrate $C_2H_6O.4H_2O$, or in the mixture containing 44.79 volume per cent. of alcohol. It has been objected that the maximum in viscosity (or the minimum in fluidity) migrates as the temperature is changed, but so far as we have been able to observe, this is not true of the maximum deviation from the linear curves.

On mixing, it seems altogether likely that the diminished frequency of collision between molecules of the same kind will lessen the tendency toward association. Whether this action occurs and whether it obeys the law of mass action can probably be determined and will be discussed later. But for the moment let us consider this breaking down of association as negligible.

The temperature corresponding to a fluidity of 200 in the 52.08 volume per cent. mixture which we should expect were there no combination, would be $.4479 \times 343.6 + .5521 \times 328.9 = 335.5$. On the other hand, from the constants already given, the temperature required to give the pure hydrate $C_2H_6O.4H_2O$ a fluidity of 200 would be $14 \times 59.2 + 5 \times 24.2 - 2 \times 95.7 = 758.4$. But the observed absolute temperature at which the 44.79 volume per cent. mixture has a fluidity of 200 is 362.3. Hence if we let x represent the fraction of the volume of the mixture combined as $C_2H_6O.4H_2O$, the rest remaining unchanged, we have $335.5 (1 - x) + 758.4x = 362.3$ or $x = 0.06337$. But this value has no great significance for the following reasons.

1. It has been assumed that the hydrate has the simplest possible formula, but it may be a polymer of the value given. This would make the percentage of hydration lower than that given.

2. The association of the components may be less after mixing. This would raise the percentage.

3. In mixtures other than the one considered, the percentage of hydration would certainly be different, if the law of mass action applies.

It may now be shown that the hydrates in solution are qualitatively at least subject to the law of mass action. The mixture of alcohol and water in the ratio corresponding to $C_2H_6O.3H_2O$ has at 25° C. a fluidity of 42.5 and a mixture of acetic acid and water corresponding to $C_2H_4O_2.H_2O$ has at 25° C. almost exactly the same fluidity; so that were there no chemical change, these two mixtures might be combined with each other in any proportion without altering the fluidity. But we have noticed that when acetic acid and ethyl alcohol are mixed there is a drop in the fluidity and we may remark in passing that this cannot be due to the formation of ethyl acetate, because this substance has a high fluidity—236.3 at 25°. However, the dilution of the mixture of alcohol and water by adding acetic acid will cause a marked decrease in the amount of combination between the alcohol and water, because according to the law of mass action four molecules of water must meet a molecule of alcohol in order to form a hydrated molecule, and the presence of the acetic acid lowers the concentration of the water. As a matter of fact, the fluidity of the mixture is raised by 10 per cent. above the expected 42.5 or less, if this law had been inoperative. This is not the only possible explanation of the increase in fluidity in this case. It may be due to the dissociation of the acetic acid on dilution.

The same point may have light thrown upon it from another source. The values of μ_∞ measure the sums of the velocities of the cations and anions $u + v$ in ionic migration. In mixtures of alcohol and water these values suffer a gradual falling off as the percentage of alcohol is increased, but there is no minimum to correspond with the minimum in the fluidity of the mixtures. The reason seems to be that in the mixture with the smallest fluidity, the components of that mixture are united with each other to their very fullest extent, hence the "atmosphere" around the ion is reduced to the smallest amount and the migration velocity is therefore relatively large. If the atmosphere about the ions were uniform in size, conductivity would be directly proportional to the fluidity of the solution.

Since writing the above, an instance has occurred to us where two apparently slightly associated substances unite with each other with considerable vigor to form complex molecules, which seems to give us the simplest possible case for determining whether the formation of solvates follows the Law of Mass Action. Thorpe and Rodger[1] in studying mixtures of ether and chloroform, noted that there is a considerable heat evolution and contraction on mixing. So far as we can learn from their measurements, the maximum contraction occurs in a mixture con-

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[1] *Loc. ci'.*

taining less than 40 per cent. of ether by weight and perhaps less than 39 per cent. The maximum deviation of the fluidity-volume-concentration curve from the linear curve occurs in the 58 volume per cent. mixture ± 3 per cent. This corresponds to about 39.8 per cent. by weight. A mixture corresponding to the composition $C_4H_{10}O.CHCl_3$ contains 38.30 per cent. of ether by weight. Guthrie[1] has noted that the greatest heat evolution occurs in the mixture of equimolecular proportions and that the vapor-pressure curve of the mixtures gives confirmatory evidence of the formation of a compound with the formula corresponding to $C_4H_{10}O.CHCl_3$.

Since the evidence afforded by the different properties of mixtures of ether and chloroform was formerly conflicting, it is a source of great satisfaction and confidence that so many lines of evidence are absolutely in agreement in pointing to the formation of a definite compound. The reluctance which chemists have toward recognizing this class of compounds has no doubt been due partly to the fact that the compounds themselves cannot usually be isolated, and furthermore the mixture does not act like a chemical compound in that it maintains the properties of all of the original components. This however is doubtless due to there being a dynamic equilibrium between the compound and the original components. Nevertheless recognition will not be given to this large class of compounds, until their presence and properties can be quantitatively established. Fortunately in the case of ether and chloroform, this information seems available.

In the mixture containing 56.26 per cent. by volume of ether corresponding to one molecule of ether to one molecule of chloroform we may calculate the percentage combined as follows. From the atomic constants we find that the compound $C_4H_{10}O.CHCl_3$ should have a fluidity of 200 at the absolute temperature of 538.6°. But actually we find that a mixture of this composition has a fluidity of 200 at 282.9° absolute. Pure ether and pure chloroform have fluidities of 200 at 216.5° and 305.3° respectively, so that if the mixture were wholly uncombined, the absolute temperature necessary for a fluidity of 200 would be $216.5 \times 0.5626 + 305.6 \times 0.4374 = 255.4$. Letting x represent the fraction of the volume of the mixture which is combined, we obtain the equation

$$538.6x + 255.4(1 - x) = 282.9,$$

$x = 0.0971$. Since less than ten per cent. of the volume of the mixture is actually in combination, it seems reasonable to assume that a dynamic equilibrium exists between the combined and the uncombined portions. If the Mass Law holds, we have

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[1] Phil. Mag., *18* (5), 495 (1884).

$$\frac{[C_4H_{10}O]\,[CHCl_3]}{[C_4H_{10}O.CHCl_3]} = K,$$

where the concentrations are no longer volume but molecular concentrations.

In the above equimolecular mixture, if we let y represent the number of cubic centimeters of ether which are combined in every one hundred cubic centimeters of mixture, the volume of the chloroform combined will be $0.7366 \times 193.4y/74.08 \times 1.526$ where the specific gravities of ether and chloroform are taken as 0.7366 and 1.526 respectively and their molecular weights 74.08 and 193.4. Since the sum of the two volumes is 9.71 we find that the volume of the ether combined is 4.30 and of the chloroform 5.41 c.c. Substituting the molecular concentrations in the above formula we obtain for the value of the constant K

$$K = \frac{\left[\frac{(56.26 - 4.30)0.7366}{74.08}\right]\left[\frac{(43.74 - 5.41)1.526}{193.4}\right]}{\left[\frac{9.71 \times 1.1016}{277.52}\right]} = 4.0633.$$

With thsi value of K it becomes possible to calculate the absolute temperature corresponding to a fluidity of 200 for any mixture on the assumption that only one compound is formed and that the Law of Mass Action is obeyed. Thus for a mixture containing 28.21 per cent. by volume of ether, we have, if z is taken to represent the fraction of the volume of the ether which is combined,

$$\frac{\left[\frac{28.21 \times 0.7366}{74.08}(1 - z)\right]\left[\frac{71.79 \times 1.526}{193.4} - \frac{28.21 \times 0.7366}{74.08} \cdot z\right]}{\left[\frac{28.21 \times 0.7366}{74.08} \cdot z\right]} = 4.0633,$$

$z = 0.1162$. The volume of ether combined in 100 c.c. is therefore $28.21 \times 0.1162 = 3.278$ and the volume of the chloroform is $3.27 \times 0.7366 \times 193.4 \div 74.08 \times 1.526 = 4.131$ and the total volume in combination is 7.409 c.c. The volume of the uncombined ether is 24.94 c.c., and of chloroform 68.52 c.c. Hence the calculated absolute temperature corresponding to a fluidity of 200 is $0.2493 \times 216.5 + 0.6766 \times 305.3 + 0.07409 \times 538.6 = 300.4°$. The value read from the curve is 297.4°. Similar remarkable agreement is obtained for other mixtures whose fluidity was measured by Thorpe and Rodger.

We are not quite justified in stating that this proves that the mass law applies to all of those loose combinations which are believed to exist in solution, but it points the way toward a solution of this interesting question. In the case of highly associated liquids the problem is complicated by the breaking down of this association upon dilution. Other constants are thereby introduced, but it is believed that this difficulty may be overcome. Finally it may be pointed out that this method seems suited for the solution of various problems which have vexed the organic chemists such as the mechanism of esterification. Our experiments seem to indicate that there is a loose combination between the alcohol and acid before the ester is actually formed.

Fluidity Formulas.[1]—Since fluidities are normally additive, the formula expressing the change of fluidity with the temperature in its simplest form should be $\varphi = AT$ or $\varphi = \alpha + \beta T$. This latter form may be deduced from the empirical viscosity formula of Meyer and Rosencranz,[2] $\eta = c/(1 + at)$. But most liquids do not expand equally on heating and it may be that almost all liquids are associated to some extent. However that may be, mercury is the only liquid known which has a linear fluidity curve within the limits of experimental error, over a large range of temperature. The curves of other substances must not cut the temperature axis since we cannot conceive of negative fluidities, yet they must all approach the temperature axis at absolute zero. Therefore we conclude that the fluidity curves must be asymptotic to that axis. At high temperatures the association is broken down and the fluidity curves become more and more nearly linear as we observe to be the case in Fig. 17. A general fluidity equation must therefore incorporate the following properties.

1. It must reduce to a linear equation for the ideal substance.
2. One branch of the curve in its general form must be asymptotic to the temperature axis.
3. At high temperatures the curve must be linear, so that the other branch of the curve must be asymptotic to a line which forms an acute angle with the temperature axis. This will not be true to the critical temperature as indicated later.

These conditions are fulfilled by the equation.

$$t = A\varphi - \frac{B}{\varphi} + C, \tag{9}$$

where A, B, and C are constants. This is the equation of a hyperbola, $t_1 = A\varphi$ representing the equation of the ideal substance and $t_2 = C - B/\varphi$ representing the breaking down of association which is complete at the temperature C. An extended study has shown that the average

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[1] Cp. seventh paper.

[2] Wied. Ann., 2, 387 (1877).

percentage difference between the observed and calculated values for 85 substances with some 1,000 duplicate observations is 0.17. If the alcohols are omitted from the calculation, the percentage difference falls to 0.09 for 70 substances.

The best formula heretofore proposed is perhaps that of Slotte,[1]

$$\eta = \frac{c}{(a + t)^n},$$

or in the slightly simplified form of Poiseuille,[2]

$$\eta = \frac{c}{1 + \alpha t + \beta t^2}.$$

From this latter is derived the formula

$$\varphi = A + Bt + Ct^2, \tag{10}$$

which is the equation of a parabola, and hence may be debarred at once since it does not meet the conditions of a general equation that it must be asymptotic to the temperature axis and to a line at an acute angle to this axis As a matter of fact, it has been found that this equation does not apply at all to the alcohols where the fluidity curves depart most widely from linearity. The average percentage deviation between the observed and calculated values with Slotte's equation applied to 64 substances is 0.15. The alcohols were excluded because Slotte's formula breaks down entirely when applied to them.

By introducing a fourth constant into our equation a much better agreement may be obtained, while keeping the general properties of the equation the same. Thus with the equation

$$t = A\varphi - \frac{B}{\varphi + D} + C \qquad (11)^3$$

eight substances which gave an average percentage difference between the observed and calculated values of 0.77 with equation (9), with equation (11) give a percentage difference of only 0.07.

Fluidity and Volume.[4]—Evidence from several different quarters points to a relation between fluidity and volume in liquids.

1. We have seen that the association of liquids may be calculated from the fluidity, and Traube[5] has calculated the association from the volume. There is therefore a connection between the two and it is

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[1] Wied. Ann., *14*, 13 (1881).

[2] Pogg. Ann., *58*, 424 (1843).

[3] Cp. seventh and ninth papers.

[4] Cp. third, sixth, and ninth papers.

[5] *Loc. cit.*

evidently possible to calculate the volume of a compound from its fluidity and *vice versa*.

2. Again we have seen that in mixtures a contraction in volume is usually accompanied by a decrease in fluidity.

3. In pure liquids an increase in the temperature is usually accompanied by an increase in both the volume and the fluidity. Water and sulphur are exceptional.

4. Pressure usually decreases both volume and fluidity. Water is again exceptional at certain temperatures.

5. If we regard the pressure as constant as is the case in ordinary viscosity measurements, then van der Waals' equation

$$\left(p - \frac{a}{v^2}\right)(v - b) = RT$$

may be written

$$T = \alpha v - \beta - \frac{\gamma}{v} + \frac{\delta}{v^2} \tag{12}$$

where α, β, γ, and δ are constants. This equation expressing the relation between the volume and temperature is the same in form as our equation (9) for expressing the relation between the fluidity and the temperature, except for the term δ/v^2, which is of minor importance. It follows therefore that fluidity and volume are either dependent upon some more fundamental property or upon each other, and that quite similar formulas may be used to represent the effects of the temperature upon both. Further work needs to be devoted to such relationships.

Nature of Viscous Resistance.[1]—As regards fluidity, gases and liquids afford a sharp contrast. In liquids the fluidity generally increases with the temperature, while in gases the fluidity decreases with the temperature, so that at the critical temperature the fluidity apparently passes through a maximum. In gases the fluidity is independent of the density, while in liquids the density, as we have already seen, is of prime consideration. This contrast suggests that the origin of these losses of energy must be different in the two cases.

In gases, the particles of one layer penetrate another layer with lower translational velocity and thus the uni-directional motion becomes changed into irregular molecular motion or heat. This loss increases with the temperature because the motion of the molecules is thereby increased. So long as the volume of the molecules themselves is negligible and the molecular free path is small in comparison with the dimensions of the containing vessel, it appears that as the density of the gas

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[1] Cp. tenth paper.

is increased, the increase in the loss of energy due to the greater number of molecules crossing a given plane surface in a unit of time, is exactly compensated by the decrease in the loss of energy due to the smaller depths from which the molecules have come, so that the viscosity is independent of the density.

In liquids the molecules themselves have such large volume in comparison with the spaces between them, that the excursions of the molecules are short and the cause of the loss of energy which is powerful in gases is of relatively small significance. On the other hand, as one layer of liquid moves over another, collisions will frequently be caused by the molecules of one layer overtaking and colliding with the molecules of the more slowly moving layer, and these collisions will cause a loss in translatory motion. Increasing the density either by lowering the temperature or increasing the external pressure will increase this effect.

It has been customary to ascribe the viscous resistance of liquids to the attraction between the molecules. In the opinion of the author, cohesion and fluidity are indeed related but not as cause and effect. Since the cohesive forces within the liquid are balanced, it is difficult to see how work can be done against them as one layer of liquid moves over another. Space will not now permit going further into this interesting and important subject.

The Fluidity of Solids.[1]—It has been assumed by some investigators that the damping of the vibrations of a wire, after allowing for the friction of the air and the loss of energy to the support, is a measure of the viscosity of the solid. To the present writer, it seems probable that while this loss of energy is a true viscous effect, the amount of the damping cannot for a moment be considered *directly* proportional to the viscosity of the substance. Such an assumption would lead us to the absurd conclusion that lead is less fluid than steel or quartz, since the damping in lead is very rapid. Moreover, since the rate of damping increases with the temperature, it would force us to conclude that solids are analogous to gases, in that the fluidity decreases as the temperature is raised, even though we recognize that amorphous solids are nothing but undercooled liquids. The truth is probably quite the opposite of this common assumption. Lead is of course more fluid than steel and the fluidity of both increases with the temperature, and the rate of damping is rather a measure of the *fluidity*. In bending a "perfectly elastic substance," the molecules do not move over one another, but merely move about in the spaces between the molecules, causing strains to be set up. Therefore as soon as the stress is removed the strain disappears without

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[1] Cp. tenth paper.

loss of energy by means of internal flow. But since these spaces are small, the elastic limit is soon reached, beyond which rupture or viscous flow must take place. In ordinary solids there is some flow of the molecules over each other as stress is applied, so that when the stress is removed the material does not fly back at once to its old position, but appears temporarily to be considerably distorted—the "elastic after-effect"—and *is* permanently distorted to a very much slighter extent. The rate of damping is then a measure of the viscous flow or fluidity. This conception may be used to explain many of the curious facts in connection with elasticity.

The Molecular Weight of Solids.[1]—Amorphous solids are to be regarded as liquids and hence there is no inherent reason why their molecular weights may not be obtained by the fluidity method as soon as sufficient data are accumulated for the purpose. When such undercooled liquids change to crystalline solids, the fluidity usually drops to but a small fraction of its former value. This indicates a great increase in apparent molecular weight which it seems possible to calculate by the method already given, but the viscosity data necessary for such calculation are lacking.

Conclusions.—Upon the relations between fluidity and physical and chemical properties we may add the following to the conclusions already given:

17. The fluidities of unassociated substances of a homologous series at their boiling-points are a linear function of their boiling temperatures.

18 The above relation is true of other vapor-pressures than that of the ordinary boiling temperature, and it may be made evident in various ways. For example, the fluidities of the ethers are nearly identical at their boiling-points, so by plotting fluidities against vapor-pressures corresponding to the same temperatures, a single curve is obtained for the whole class of substances. Or by taking one substance as a standard and multiplying the fluidities of other substances by the ratio of the fluidity of the latter at their boiling-points to the fluidity of the standard at its boiling-point, "reduced fluidities" are obtained. Employing the fluidity-vapor-pressure curve of the standard substance, vapor-pressures may be calculated from the reduced fluidities. It is found that the calculated values of vapor-pressures of over 10 cm. for about 20 substances differ from the observed values by a little over 3 per cent.

19. There is shown to be a relation between fluidity and chemical composition. The fluidity-temperature curves of a given class of compounds consists of a family of nearly straight and nearly parallel lines.

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[1] Cp. tenth paper.

Hence the slope of the curves is characteristic of the class and their intercepts are indicative of the molecular weight, and of constitutive influences to a very much lesser degree. Evidence is given to show that absolute temperatures corresponding to a given fluidity form a proper basis of comparison. Constants obtained for a given fluidity enable us to calculate the absolute temperatures of many other substances at that fluidity. For 35 substances, the calculated values differ from the observed by less than 0.8 per cent.

20. Since fluidity gives a means for calculating the molecular weights of liquids it is evidently possible to use the method for calculating association, the association being the ratio between the observed absolute temperature corresponding to the fluidity used as a basis of comparison and the absolute temperature as calculated from the constants. A comparison of values of association by the fluidity method and the methods of Ramsay and Shields, Traube, and Longinescu for 27 substances shows as satisfactory an agreement as can well be expected.

21. Reasons are given why similar relations to those here given between fluidity and vapor-pressure, fluidity and chemical composition, and fluidity and association have not been and cannot readily be worked out by comparing viscosities instead of fluidities.

22. The fluidity method of calculating molecular weights may evidently be extended to the case of mixtures where the components unite in loose combinations as in hydration. The theory demands that the solutions be reckoned in terms of volume percentages and not in weight or molecular percentages, as is often done. It is proved furthermore that the occurrence of a maximum or minimum in a viscosity or fluidity curve does not necessarily indicate the composition of the solvate, and the shifting of a maximum or a minimum does not necessarily indicate a change in the composition of the solvate. Theory indicates that the point in the fluidity-concentration curve where the deviation of the fluidity curve from the linear curve, which would be expected were there no solution, is a maximum, may give us knowledge of the composition of the solvate. Evidence is given to show that solvation follows the law of mass-action, and the method is given of calculating the percentage of the mixture which is combined.

23. The properties of a general formula to represent the changes in the fluidity of a substance with the temperature are given, and the formula

$$t = A\varphi - \frac{B}{\varphi} + C$$

where t = temperature absolute, φ = fluidity, and A, B, and C are constants, is proposed, which has these general properties. This formula may be used to reproduce the observed values of 85 substances tested with an average percentage difference of 0.17. Another constant added to this equation reduces this already small percentage difference very much further.

24. Reasons are given for the belief that there is a close relation between the fluidity of a liquid and its volume:

(*a*) When liquids are mixed, a decrease in volume is generally accompanied by a decrease in fluidity, and the greatest decrease in both appears to coincide in the same mixture. The opposite seems to be true when liquids expand on mixing.

(*b*) Pressure generally decreases both volume and fluidity, and increase in temperature generally increases both.

(*c*) Association may be calculated from fluidity data, and Traube has also calculated association from volume.

(*d*) The above equation is almost exactly the relation between temperature and volume implied in van der Waals' well-known equation.

25. The nature of viscous resistance is discussed, and it is pointed out that while the kinetic theory explains the cause of viscosity in gases, it does not explain it in liquids. The usual assumption, that the viscosity of liquids is due to the attractions between the molecules, is insufficient. A theory is outlined which makes the volume of the molecules themselves the most important factor, the loss of energy arising from the collisions, due to their translatory motion, of the molecules of one layer with the molecules of adjacent but more slowly moving layers.

26. It is indicated that many of the phenomena of elasticity in solids may be explained on the basis of their fluidity. The rate of damping of a wire is probably directly proportional to the *fluidity* of the solid, and *not* to the viscosity, as has often been assumed. The "elastic after-effect" is, according to this view, caused by partial flows in the solid which cause a state of strain to remain after the deforming stress has been removed. This state of strain has been observed in the viscous flow of very viscous liquids like pitch.

27. A possible method for calculating the molecular weights of solids is suggested.

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