will be mentioned; namely, that mixtures of sodium and potassium salts may be rapidly analyzed with an accuracy equaling or even exceeding that of the most careful gravimetric analyses. For instance, suppose we wish to determine the amounts of soda and potash in a mixture of their sulfates, which need not weigh more than 50 mg. altogether. We dissolve this mixture in exactly 200 times its weight of water and compare it on the interferometer with a standard solution containing pure, dry K_2SO_4 dissolved in 200 times its weight of water; the reading will range from 430 to 0 as the composition of the mixture ranges from pure $NaSO_4$ to pure K_2SO_4. In this way any mixture can, with the aid of a calibration curve previously determined once for all, be analyzed in a few minutes with an accuracy of 0.1 mg. of either constituent (on a 50 mg. sample).

Summary.

The foregoing pages present a brief description of the principle and mode of operation of the interferometer, a form of instrument which enables one to determine the single varying constituent in a mixture or solution, with ease, rapidity, and very great accuracy. The only important source of error arises from differences in optical dispersion; it can readily be obviated by use of the methods discussed in the text.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY.]

THE VISCOSITIES OF BINARY MIXTURES OF THE ASSOCIATED LIQUIDS, WATER, FORMIC ACID AND ACETIC ACID.[1]

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Jones and Murray[2] showed in 1903 that when two associated liquids are mixed, each diminishes the association of the other. They determined the molecular weight of water in formic acid on the one hand, and in acetic acid on the other. Also the molecular weight of formic acid in water, and in acetic acid, and finally the molecular weight of acetic acid in water and in formic acid.

They found that the molecular weight of water in formic acid varied from 19.7 at dilution 0.93 *N* to 21.9 at 6.18 *N*, showing that the formic acid diminished slightly the association of the water.

The molecular weight of water in acetic acid varied from 21.7 at 0.64 *N* to 38.8 at 12.65 *N*. This showed that the acetic acid diminished greatly the association of the water.

[1] This work was done in connection with an investigation which is being carried out with the aid of a Grant from the Carnegie Institution of Washington, to H. C. Jones.

[2] *Am. Chem. J.*, 30, 193 (1903).

The molecular weight of acetic acid in water varied from 55.4 at 0.17 *N* to 72.1 at 7.06 *N*, showing that water diminished very appreciably the association of acetic acid.

The molecular weight of acetic acid in formic acid varied from 61.9 at 0.18 *N* to 83.8 at 9.17 *N*. The association of the acetic acid was thus diminished considerably by the formic acid.

The molecular weight of formic acid in water varied from 45.2 at 0.38 *N* to 51.0 at 6.16 *N*, showing that water had very little effect on the association of the formic acid; and, finally, the molecular weight of formic acid in acetic acid varied from 50.4 at 0.82 *N* to 65.7 at 8.26 *N*.

If we take into account the dissociating action of the water on the formic and acetic acids, we are justified in concluding that water and formic acid affect each other's association very little; acetic acid and formic acid affect each other's association considerably, while both water and acetic acid have a marked effect each on the association of the other.

These facts were used by Jones and Veazey[1] to explain the increase in viscosity which takes place when water and alcohol are mixed. These are both strongly associated solvents, and each, therefore, very probably diminishes appreciably the association of the other. From a smaller number of larger molecules of each solvent, we have a larger number of smaller molecules of each solvent produced. The surfaces of the molecules present are therefore increased, and, consequently, the friction of these molecules as they move over one another. Viscosity is a function of the surface friction of the molecules.

In the same manner Jones and Veazey[2] were able to explain why it is that salts of potassium, rubidium and caesium lower the viscosity of water and other solvents[3] in which they are dissolved. The large atomic volumes of these cations when mixed with the molecules of water, diminish the frictional surfaces which come in contact, and, consequently diminish the viscosity.

Having found the above action of water, formic acid and acetic acid, each on the association of the other, the question arose, what would be the effect of each on the viscosity of the other? If the above explanations offered by Jones and Veazey were correct, then two liquids, like water and acetic acid, which diminished each others association, ought to increase the viscosity of one another—the viscosity of the mixture should be greater than that of either pure liquid separately.

The viscosities of binary mixtures of the above-named three liquids were measured at 15° and 25°. Water was regarded as the solvent for

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[1] *Z. physik. Chem.*, **61**, 641; **62**, 44 (1908); Carnegie Institution of Washington, Publication No. **80**, 170 (1907).

[2] *Loc. cit.*

[3] Jones and Davis, *Z. physik. Chem.*, **81**, 68 (1912); Carnegie Institution of Washington, Publication No. **180**, 179 (1913).

formic acid and acetic acid, and solutions of these acids in water were prepared containing by volume 10, 20, 30, 40, 50, 60, 70, 80, 90%. The acids themselves contained somewhat less than 1% of water. The viscosity and the fluidity (reciprocal of viscosity) data are given in the following tables:

TABLE I.—VISCOSITIES AND FLUIDITIES OF FORMIC ACID IN WATER AT 15° AND 25°.

Per cent. HCOOH.	η 15°.	φ 15°.	η 25°.	φ 25°.
(H_2O)	0.01134	88.18	0.00891	112.23
10	0.01215	82.31	0.00932	107.3
20	0.01282	78.00	0.01014	98.62
30	0.01339	74.68	0.01072	93.28
40	0.01408	71.02	0.01135	88.11
50	0.01469	68.07	0.01202	83.20
60	0.01591	62.85	0.01287	77.70
70	0.01693	59.07	0.01371	72.94
80	0.01803	55.46	0.01452	68.87
90	0.01914	52.25	0.01546	64.68
(HCOOH)	0.01963	50.94	0.01571	63.65

TABLE II.—VISCOSITIES AND FLUIDITIES OF ACETIC ACID IN WATER AT 15° AND 25°.

Per cent. CH_3COOH.	η 15°.	φ 15°.	η 25°.	φ 25°.
(H_2O)[1]	0.01134	88.18	0.00891	112.23
10	0.01368	73.10	0.01059	94.43
20	0.01626	61.50	0.01244	80.39
30	0.01897	52.72	0.01446	69.16
40	0.02143	46.66	0.01624	61.58
50	0.02416	41.39	0.01818	55.01
60	0.02682	37.29	0.02015	49.63
70	0.02935	34.07	0.02219	45.07
80	0.03068	32.60	0.02318	43.14
85	0.03033	32.90	0.02292	43.63
90	0.02786	35.89	0.02115	47.28
95	0.02243	44.58	0.01775	56.34
CH_3COOH	0.01410	70.92	0.01174	85.18

TABLE III.—VISCOSITIES AND FLUIDITIES OF FORMIC ACID IN ACETIC ACID AT 15° AND 25°.

Percent. HCOOH.	η 15°.	φ 15°.	η 25°.	φ 25°.
(CH_3COOH)	0.01410	70.92	0.01174	85.18
10	0.01558	64.19	0.01286	77.76
20	0.01701	58.79	0.01391	71.89
30	0.01792	55.80	0.01463	68.35
40	0.01883	53.11	0.01506	66.40
50	0.01942	51.49	0.01564	63.94
60	0.01984	50.40	0.01587	63.01
70	0.02012	49.70	0.01607	62.23
80	0.02002	49.95	0.01607	62.23
90	0.01967	50.84	0.01582	63.21
(HCOOH)	0.01963	50.94	0.01571	63.65

[1] Values for water taken from Thorpe & Roger, *Phil. Trans.*, **185A**, 449 (1894).

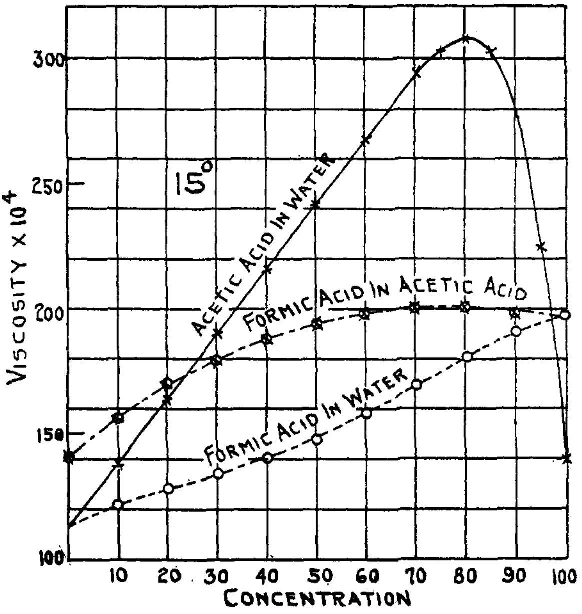

Fig. 1.

The viscosity data at 15° are plotted in curves, Fig. 1; and the viscosity data at 25° in curves, Fig. 2. The viscosities of acetic acid in water pass through a well-defined maximum, which, before we carried out a single measurement of the viscosities of mixtures of these two solvents,[1] we predicted, would be the case from the molecular-weight determinations of this acid in water made by Jones and Murray.

The viscosities of formic acid in acetic acid pass through a slight maximum, as would be expected from the effect of each of these solvents on the molecular weight of the other.

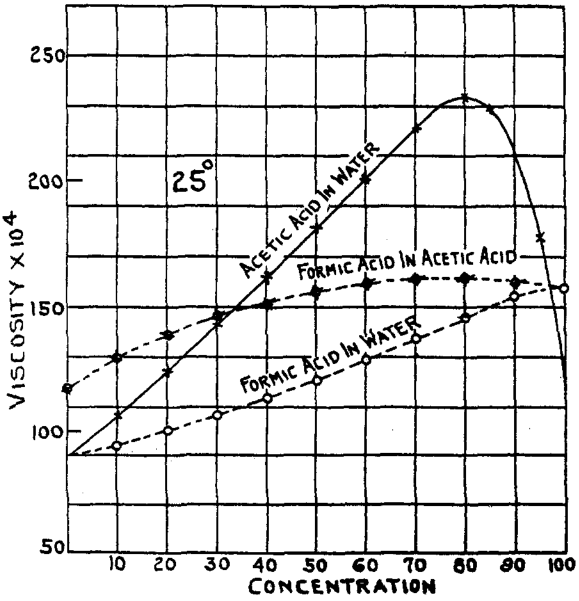

Fig. 2.

The viscosities of mixtures of water and formic acid, on the other hand, fall almost on a straight line. This again is just what would be expected, from the fact that neither solvent alters appreciably the molecular weight of the other.

These results are, then, all in keeping with

[1] Since completing our work, we find that a few measurements of the viscosities of mixtures of acetic acid in water had been made by Dunstan and Thole, *J. Chem. Soc.*, **85**, 825 (1904); **95**, 1560 (1909).

the suggestion made by Jones and Veazey, that the increase in viscosity which results when associated liquids which diminish each other's association are mixed, is due to the *larger number* of *smaller parts* that are present.

These results are also in perfect accord with their suggestion as to the cause of the diminution in the viscosity of water, produced by salts whose cations have very large ionic volumes, such as salts of potassium, rubidium and caesium.

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NOTES.

Some New Forms of Apparatus: I. A Substitute for the Twin-bulb Trap in Toluene–Mercury Thermoregulators.—Toluene, on account of its high coefficient of expansion, is to be preferred to all other liquids for use in thermoregulators. Since, however, it is practically a nonconductor and quite volatile, it is ordinarily used with mercury for the contact in all electrically operated thermostats.

In order to use these two liquids together, the common form of apparatus hitherto employed has been the twin-bulb device, which, however, has the following disadvantages:

1. It is very fragile and can only be made by an expert glass-blower.
2. When the mercury level in the capillary has been once adjusted for any given temperature and the toluene reservoir sealed, the regulator is practically useless for any higher temperatures without opening the reservoir and removing the excess of toluene in order to preserve the equilibrium in the two bulbs.
3. It is difficult to prevent the toluene from finally creeping around between the mercury and the glass walls into the capillary and fouling the contact surface of the mercury, since the same continuous tube contains both the toluene and mercury.

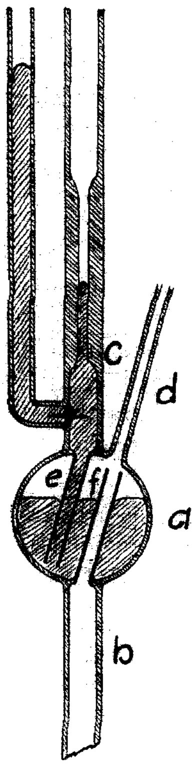

Fig. 1.

To overcome these difficulties as far as possible the apparatus illustrated in Fig. 1 has been devised. This consists of a bulb (*a*) attached at the bottom by the tube (*b*) to the toluene reservoir which may be of any desired form. Exactly opposite to (*b*) is a corresponding tube (*c*), which carries the capillary and sealed-in platinum contact.

The interior construction of (*a*) is as shown in the figure. The small tubes (*e*) and (*f*) are prolongations of (*c*) and (*b*), respectively, having a length nearly equal to