(2) Cubes of SbSn and crystals of a compound of tin and the third metal are found set in the eutectic of tin and the second (new) compound: copper and silver.

(3) A compound of antimony and the third metal is formed; the ground-mass consists of (*a*) crystals of the third metal in its eutectic with tin: aluminum. (*b*) Crystals of SbSn and a tin-rich solid solution: zinc and perhaps cadmium.

Arsenic probably belongs to a sub-group of (2) where SbSn and crystals of a compound of tin and the third metal occur in a ground-mass, which is a solid solution of tin.

It may be that most of the eutectics are not binary, but contain the three metals; however, only two constituents apparently are revealed by the microscope.

It remains to run cooling curves on each of the alloys and as far as possible to isolate and analyze their harder crystalline constituents by which means more light would be thrown on their constitution. It is intended to expand the work by making similar series with different percentages of tin and antimony, and different amounts of the added metal, from which, it is hoped, much more may be learned of the constitution of these ternary alloys.

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THE VISCOSITY OF SOLUTIONS IN RELATION TO THE CONSTITUTION OF THE DISSOLVED SUBSTANCE.

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Received July 28, 1904.

WORK upon this theme was first undertaken by Mr. M. A. Stewart in the laboratories of the New Hampshire College. The method herewith described was worked out by him and was presented in June, 1903, together with a considerable amount of experimental data as a thesis for the Bachelor's degree at the above-named college. A brief account of his work was given by the author at the June, 1903, meeting of the American Chemical Society at Cleveland.[1] Since then the work has been further carried on, partly at that college and partly at the Massachusetts Institute of Technology. The author wishes to acknowledge his

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[1] *Science*, **18**, 98 (July 24, 1903).

indebtedness to Prof. Charles L. Parsons, of the New Hampshire College, for many favors and for the interest shown by him in this work.

I. RELATION BETWEEN VISCOSITY AND MIGRATION VELOCITY IN SOLUTIONS OF ELECTROLYTES.

The theme of this article was first suggested by the striking relations between the migration velocities of various elementary ions and the viscosity of solutions of their salts. Wagner,[1] and notably Euler,[2] have shown that the viscosity effect of the individual ions increases regularly as the migration velocity decreases. Euler, indeed, has calculated so-called viscosity constants for a large number of ions and finds the relation between these and the migration velocities expressed by the following formula, to hold:

$$(A - 0.68) \cdot U = \text{konst},$$
$$\text{or } (K - 0.68) \cdot V = \text{konst},$$

where A and K are the viscosity constants and U and V are the rates of migration of the anion and cation respectively.

The value of *konst* for a series of fourteen different ions ranges between 18.7 and 22.4. The only ions studied which form exceptions to this rule are *H*- and *OH*-ions with values of *konst* 126.7 and 78.5 respectively.

The internal friction in a liquid undoubtedly depends, among other things, upon the mass of the rubbing particles. One would expect that the larger the mass of the ion the greater would be its friction to motion through a liquid, and hence, the smaller its rate of migration. Just the opposite, however, would appear to be actually the case if one compared the behavior of the ions in individual groups of the periodic system. Most markedly is this so in the group of the alkali metals, for which are copied the values from Euler's article.

Ion.	Migration velocity.	Viscosity constant.
Li	39.8	1.150
Na	49.2	1.091
K	70.6	0.962
Rb	73.5	0.958
Cs	73.6	0.949
NH_4	70.4	0.963

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[1] *Ztschr. phys. Chem.*, **5**, 31 (1890).

[2] *Ibid.*, **25**, 539.

II. POSSIBLE EXPLANATION OF PECULIARITIES IN THESE PHENOMENA BY THE HYDRATE THEORY.

The possibility that *ions* may be not merely electrically charged atoms or atom groups, but rather these in combination with a greater or lesser number of solvent molcules, has often been suggested. Indeed, it is held by some, notably Werner, that electrolytic dissociation is to be accounted for largely upon this ground. If this then be true, it is not hard to suppose that the elementary atoms lowest in each group have the greatest power of holding solvent molecules in combination, so that, as a matter of fact, the hydrated *Li*-ion might have a greater mass than the other alkali metal ions.

III. NEGATIVE VISCOSITY AND THE HYDRATE THEORY.

It seems to us that this *Hydrate Theory* of the constitution of the ions offers an explanation of the remarkable phenomenon of *negative viscosity*, and that, by this phenomenon, the theory is, therefore, given more probability. The ions NH_4, K, Rb, Cs, Tl, and NO_3, when dissolved in water, tend to lessen the time of flow of a given volume of liquid under the same pressure through a capillary tube. Thus the solution of any salt of one of these ions will have a lesser viscosity than pure water, provided that the other ion of the salt have not a positive viscosity great enough to counterbalance the effect of the first ion.

Negative viscosity has been accounted for upon the ground of Electrostriction,[1] according to which a charged ion is surrounded by a strong electrical field which causes a compression of the liquid in this field. This accords well with the fact that a salt solution occupies a lesser volume than the dry salt plus pure water. According to Röntgen,[2] and Warburg and Sachs,[3] the viscosity of water is slightly decreased by pressures up to 150 atmospheres. Cohen[4] found that at 1° the viscosity is decreased to the extent of 6.28 per cent. by a pressure of 600 atmospheres. At 15° this decrease is but 2.33 per cent., while at 23° it is but 1.01 per cent. Hauser[5] found that at about 32° pressure ceases to affect the viscosity of water, while above 32° it causes an increase of vis-

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[1] Drude and Nernst : *Ztschr. phys. Chem.*, **15**, 79 (1894).

[2] *Wied. Ann.*, **22**, 510 (1884).

[3] *Ibid.*, **22**, 514 (1884).

[4] *Ibid.*, **45**, 666 (1892).

[5] Drude's *Annalen*, **5**, 597 (1901).

cosity. Likewise the effect of salts with negative viscosity was found by Sprung[1] to become zero in the neighborhood of 32°, while above that temperature these salts caused an increase of viscosity. If there are not other objections to the Electrostriction hypothesis of negative viscosity, these facts afford it a strong confirmation.

If portions of solvent between charged ions are subjected to great pressure, due to the electric field, it seems quite as probable that the solvent so enmeshed between the ions would be mechanically dragged along with them, thus increasing the viscosity, as that the compression would decrease the viscosity.

From surface tension phenomena it seems probable that water consists of polymerized H_2O-molecules. If now ions exist as hydrates instead of simply as electrically charged atoms or radicals they must be built up at the expense of the polymerized water molecules. Now it would seem highly probable that some of the hydrated ions, $M.nH_2O$, might have a smaller mass, or, at least, a more symmetrical structure than the $(H_2O)_m$ molecules of pure water. In such a case there might well be less friction to their motion than to that of the molecules of pure water. It is important to note that complexes between undissociated molecules of solute and molecules of solvent may be formed, as well as the *solvates*[2] of ions.

With decreasing temperature the polymerization of water increases. The formation at least of some of the possible polymers is attended by an expansion (which between 4° and 0° C. exceeds the normal contraction). Pressure thus will lessen the amount of polymerization and also lessen the viscosity—since polymerization obviously causes increased viscosity. At 32° C. the critical point is reached, where the polymerization of water is so slight that it is not decreased by pressure. The formation of solvates takes place to a lesser extent the higher the temperature. At higher temperatures there are also fewer molecules of polymerized water whose concentration will be diminished by the formation of hydrates. At 32° the effect of certain salts in lessening the

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[1] Pogg. *Ann.*, **159**, 1 (1876, Vol. 5).

[2] As complexes of solute with molecules of solvent are likely to occur with other solvents than water, and since the term hydrate could not, without confusion, be applied to these, it would seem desirable to have a special term by which they could be designated. The name solvate, suggested by Professor A. A. Noyes, seems to be very appropriate.

viscosity, as well as that of pressure, becomes zero. The facts then which seemed so strongly to support the explanation according to Electrostriction agree with equal closeness to the requirements of the Hydrate Theory.

IV. THE VARIATION OF VISCOSITY WITH CONCENTRATION.

The viscosity of liquids is customarily determined by flow through capillary tubes by the method of Poisseule and of Hagenbach. The absolute viscosity is given by Hagenbach's formula:[1]

$$\eta = \frac{\pi D r^4 t}{8 l V},$$

where η = the coefficient of viscosity, that is, the force in dynes necessary to maintain a liquid surface, of unit area, in motion, with unit velocity, past another equal and parallel surface at unit distance; D is the pressure necessary to overcome friction, that is, the actual pressure diminished by that pressure which would be necessary to give, to the liquid flowing through the tube, the kinetic energy which it possesses; r is the radius of the capillary; t is the time, and V the volume of liquid flowing in time t; l is the length of the capillary.

The viscosity of solutions is, however, commonly expressed in terms of the viscosity of pure water at zero, or at the same temperature, taken as unity. Of the several formulae proposed to express the viscosity of solutions in terms of the concentration, the *linear formula was the first suggested*, and is indeed the one which at first thought seems the most plausible:

$$\eta = l + \alpha n.$$

η = the viscosity (in terms of $\eta_{(\text{pure water})} = 1$);
α = constant for the solute in question; n = concentration.

This was found, however, to agree very poorly with the facts; and the so-called *exponential formula* was introduced by Arrhenius. This was found by its originator,[2] as well as by Rehyer,[3] and Wagner,[4] to hold approximately for solutions of electrolytes within rather narrow limits of concentration.

$$\eta = A^x,$$

where η is the viscosity as in the first formula, A is a constant depending on the particular solution, and x is the concentration.

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[1] Hagenbach: Pogg. *Ann.*, 19, 385 (1860).
[2] *Ztschr. phys. Chem.*, 1, 285 (1887).
[3] *Ibid.*, 2, 744 (1888).
[4] *Ibid.*, 4, 31 (1890).

Rudorf,[1] 1903, discusses both of these formulae. He finds that for acetic acid over a wide range of concentration the linear holds better than the exponential formula; and he concludes that the linear formula is the one to be *à priori* expected in case that no polymerization or association of solvent with solute occurs. Reasoning from this assumption, he, in a measure quantitatively, accounts for the deviation from the linear formula in the case of non-electrolytes. Neither of these formulae, however, have a theoretical foundation. Hagenbach,[2] in his deduction of the relation between the coëfficient of viscosity and the flow through capillary tubes, assumes the liquid in the tube to be made up of concentric hollow cylindrical layers, each flowing at a different speed than that next inside or outside, and none of these layers mixing.[3] The layer in contact with the glass wall has the velocity zero; and the core in the middle has the maximum velocity. The viscosity is due to the frictional resistance of these layers moving against each other. A formula derived from the number and kind of molecules in the liquid surface (assuming two given molecules always to offer the same resistance to flow past each other) is complicated and its application is difficult, even to the simplest cases. For a purely physical solution of a single solute, such a formula would contain two arbitrary constants. Polymerization, association of solvent with solute, and electrolytic dissociation influence the kind and number of molecules, and, therefore, the viscosity, in a solution. The extent to which these phenomena take place is, in most cases, not even approximately known. The application of such a theoretically derived formula is manifestly impossible to the solutions used in this research. It was, however, found that the linear formula represented approximately the behavior of all of our solutions used, except at points where definite molecular changes took place. To the viscosity as ordinarily expressed, however, was applied a correction which seems to possess certain advantages.

V. CORRECTION APPLIED TO THE VISCOSITY VALUE.

The viscosity of solutions is most commonly found from the time of flow of a definite volume through a capillary tube under

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[1] *Ztschr. phys. Chem.*, **34**, 257 (1903).

[2] Hagenbach: *Loc. cit.*

[3] That this assumption is justified for straight tubes of even bore and smooth interior, and for moderate velocities, see Bovey's "Hydraulics."

the pressure caused by the difference in level of the free surfaces of the bodies of the liquid which the capillary connects. The viscosity is then given by the ratio of the time of flow for the solution to the time of flow for the same volume of pure water, multiplied by the specific gravity of the solution. This leaves out of consideration, however, the amount of solvent displaced from a given volume by the dissolved substance. In the following tables the figure for the viscosity, as usually calculated, will be designated, in the usual manner, by the letter η. To obtain what we shall call the Corrected Viscosity, we have added to the time of flow of the volume of solution, the time of flow of the amount of pure solvent which has been displaced from the given volume by the dissolved substance. This value we shall designate by the character η'.

Figure 1 represents the bulb of the viscosity apparatus used. For all measurements, the time is found which is required for the volume of liquid between the marks *a* and *b* to flow through the capillary tube *c*, by starting the stopwatch when the surface of the liquid passes the mark *a*, and stopping it as the surface passes *b*. When *a b* is filled with a solution, there is a less amount of solvent in the bulb than were it filled with the pure solvent. Suppose we pour pure solvent upon the top of the solution until the portion of the tube *a d* were filled with it and the amount of pure solvent in the total space *b d* were just such as would, in the pure condition, fill the bulb *a b*. This volume *a d* may be readily calculated from the specific gravity of the liquids. The correction is applied by simply adding the value of the ratio of the volumes *a d*/*a b* to the viscosity as ordinarily calculated. In the case of other solvents than water we have still adhered to the viscosity of water at 25° as unity. Hence, in this case, the ratio *a d*/*a b* must be multiplied by the viscosity of the solvent before being applied as a correction.

Fig. 1.

VI. METHOD.

The experimental method used was exactly that described by Ostwald-Luther.[1] The method of expressing results is modified as explained in the preceding section of this article.

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[1] *Physiko-chemische Messungen*, II Auflage (Leipzig, 1902), pp. 259-262.

VII. ACCURACY OF THE LINEAR FORMULA.

The closeness with which the facts agree with this formula was tested for the following substances which were to be used in the investigation: ammonia in water, pyridine in water, water in alcohol. The results obtained by us, which are shown in Tables I, II and III, accord well with those of other observers, but are more extensive for the particular substances in question. In the first column are the concentrations of the solutions expressed in molecules per liter. In the next column is the specific gravity at 25°, referred to that of water at 25° as unity. This temperature is that of all the measurements. The third column contains the actual time of flow of the solution through the apparatus. In the fourth and fifth columns are the viscosity η and the corrected viscosity η'. In the last two columns are the ratios of the increase of the viscosity and of the corrected viscosity, respectively, to that of the concentrations. These ratios are designated by D and D', as follows:

$$D = \frac{\Delta\eta}{\Delta \text{ conc.}}\ ;\ D' = \frac{\Delta\eta'}{\Delta \text{ conc.}}.$$

TABLE I.—NH_3 IN WATER, 25°.

Conc.	Sp. gr. 25°/25°.	Time. (Water = 98.8.)	η	η'	D	D'
0.0	.....	....	....	.....	....	....
1.30	0.9900	102.2	1.024	1.0561	0.018	0.043
2.66	0.9797	106.5	1.056	1.1216	0.024	0.048
4.16	0.9688	111.4	1.092	1.1943	0.024	0.048
5.93	0.9559	117.4	1.136	1.2810	0.025	0.049
6.60	0.9515	119.6	1.152	1.3124	0.023	0.047
8.39	0.9393	125.0	1.188	1.3917	0.020	0.044

TABLE II.—PYRIDINE IN WATER, 25°.

0.0	1.0000	1.000	1.000	....	....
0.530	1.0008	1.104	1.145	0.197	0.274
1.060	1.0016	1.211	1.293	0.203	0.279
1.545	1.0023	1.308	1.428	0.200	0.279
2.538	1.0033	1.536	1.736	0.229	0.310
4.73	1.0046	2.015	2.385	0.219	0.296

TABLE III.—H_2O IN ALCOHOL, 25°.

0.0	0.7876	1.211	1.211	....	....
0.257	0.7891	1.236	1.241	0.099	0.118
0.507	0.7909	1.259	1.268	0.094	0.110
3.445	0.8095	1.509	1.571	0.085	0.103
14.33	0.8591	2.180	2.466	0.062	0.082

With solutions of ammonia up to eightfold molar, it is seen that the value of *D'* varies but little about a mean which may be taken as 0.047. Therefore the linear formula holds approximately for this substance. For solutions of pyridine in water up to the strength of 4.73-fold molar the rate of increase of viscosity is seen to vary not more than 6 per cent. from a mean value of 0.292 although it passes through a slight maximum. For water in ethyl alcohol, the *D'*-values diminish steadily and quite appreciably from the outset.

If instead of to a pure solvent, small amounts of ammonia, pyridine, water, etc., be added to *solutions*, there would be two possibilities: The added substances might have a strong affinity for the solute, thus combining with it, and displacing any possible molecules of solvent held in combination with it in the form of *solvate*.[1] Or the added substance might have no affinity for the solute. In the latter case we should expect the same increase in the viscosity of the solution as we have previously found in the case of pure solvent. In the former case the compound of the solute with the added substance would have a viscosity of its own, which would probably be entirely different from that of the sum of the viscosities of the solute and of the added substance in solution separately.

VIII. RESULTS WITH METAL-AMMONIA SALTS.

The condition of the metal-ammonia salts in aqueous solution has been considerably studied, so that much concerning their molecular constitution is known. Numerous investigations upon mixed solutions of silver salts and ammonia by means of freezing-point, pressure of ammonia vapor, partition of ammonia with chloroform, solubility, migration, and electrical potential measurements[2] have shown that for every mol of silver salt 2 mols of ammonia exist in the state of combination, while any surplus ammonia exists in the same form as in a simple aqueous solution. The combined ammonia exists as a part of the complex cation $Ag.2NH_3$.

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[1] See note 2, page 1318.

[2] Reychler: *Ber. d. chem. Ges.*, **28**, 555 (1895); Konawalow: *Chem. Centrbl.*, 11, 659 (1898); Gaus: *Ztschr. anorg. Chem.*, **25**, 236-64 (1900); Dawson and McCrae: *Ztschr. anorg. Chem.*, **26**, 94-103 (1901); Bodländer and Fittig: *Ztschr. phys. Chem.*, **39**, 597 (1901); Whitney and Melcher: This Journal, **25**, 69 (1903).

Similar measurements by Dawson and McCrae[1] on copper-ammonia salts by means of the partition of ammonia between chloroform and aqueous phases gave a molecular ratio of *salt: fixed* NH_3, which approached the value *4*.

Work of Bonnsdorf,[2] by the method of Bodländer and Fittig of potential measurements, gave the value of *salt: fixed* NH_3 for zinc salts as 3.01-3.13.

It seemed best on account of the definiteness of the constitution of these metal-ammonia salts, to first test upon them the method outlined in the last section.

To silver nitrate in solution was first added ammonia in 1 or 2 drops excess of the amount necessary to redissolve the precipitate of silver oxide which first formed. Thereupon the volume was increased with pure water to make the resulting concentration exactly molar as regards silver salt. The viscosity of this solution was determined, then of solutions varying from it only in the ammonia content. In Table IV are found the results, tabulated in the same manner as in the preceding tables. It is seen from the table that the addition of 2 mols of ammonia to 1 of silver salt produces a decrease in the viscosity. Additions of ammonia beyond 2 mols give almost the same values of *D* and *D'* as if added to pure water. This offers a confirmation of the conclusion that 2 molecules of NH_3 in solution are united with one of silver salt, forming a stable complex, and that any further amount of ammonia does not unite with the silver salt in solution.

TABLE IV.—NH_3 IN 1.0 MOLAR $AgNO_3$, 25°.

Conc. NH_3.	Sp. gr. 25°/25°.	Time. (Water = 98.8).	η	η'	D	D'
0.0	1.1390	91.8	1.058	1.089	......	......
2.04	1.1195	88.3	1.002	1.087	—0.027	—0.001
2.51	1.1157	90.0	1.016	1.113	+0.030	+0.055
3.56	1.1080	92.7	1.040	1.162	0.022	0.047
5.00	1.0967	96.9	1.076	1.234	0.025	0.050
7.03	1.0818	102.7	1.124	1.333	0.024	0.048

Similar series of experiments were made upon solutions of copper nitrate, copper sulphate (two concentrations), zinc sulphate, and zinc chloride (two concentrations), the results being given in Tables V, VI, VII and VIII.

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[1] *J. Chem. Soc.*, 1900, p. 1239.

[2] *Ber. d. chem. Ges.*, 1903, p. 2322.

TABLE V.—NH_3 IN 0.5 MOLAR $Cu(NO_3)_2$.

0.0	1.0727	107.5	1.167	1.188	....	....
2.02	1.0594	95.9	1.028	1.097	—0.069	—0.045
2.55	1.0550	97.4	1.040	1.122	+0.023	+0.047
3.09	1.0509	98.6	1.049	1.145	0.017	0.043
5.06	1.0353	104.4	1.094	1.239	0.023	0.048
7.08	1.0202	110.9	1.145	1.339	0.025	0.049

TABLE VI.—NH_3 IN 0.5 MOLAR $CuSO_4$.

0.0	1.0791	123.9	1.353	1.354	....	....
2.03	1.0677	110.0	1.189	1.236	—0.081	—0.058
3.04	1.0603	114.6	1.230	1.301	+0.040	+0.065
5.99	1.0379	126.6	1.330	1.472	0.034	0.058

NH_3 IN 1.0 MOLAR $CuSO_4$.

0.0	1.1553	158.9	1.858	1.862	....	....
4.08	1.1312	128.4	1.470	1.568	—0.095	—0.072
4.76	1.1271	131.0	1.494	1.608	+0.035	+0.059
5.53	1.1212	134.4	1.525	1.658	0.040	0.065

TABLE VII.—NH_3 IN 0.505 MOLAR $ZnSO_4$.

0.0	1.0808	124.6	1.363	1.362	....	....
2.47	1.0621	109.7	1.179	1.239	—0.075	—0.050
3.25	1.0562	112.6	1.204	1.283	+0.032	+0.056
6.80	1.0292	127.7	1.330	1.496	0.035	0.060

TABLE VIII.—NH_3 IN 0.5 MOLAR $ZnCl_2$.[1]

1[1]	0.0	1.0601	110.8	1.189	1.197	....	....
2	2.53	1.0412	98.2	1.035	1.105	—0.061	—0.036
3	2.86	1.0396	99.5	1.047	1.124	+0.040	+0.063
4	3.69	1.0323	102.8	1.074	1.173	0.031	0.057
5	4.67	1.0251	106.0	1.100	1.223	0.027	0.051
6	6.96	1.0077	115.1	1.174	1.353	0.032	0.057
7	8.35	0.9989	120.6	1.215	1.426	0.029	0.053

NH_3 IN 0.955 MOLAR $ZnCl_2$.[1]

8[1]	0.0	1.1174	122.3	1.383	1.403	....	....
9[1]	c.	1.1139	120.8	1.262	1.381	....	....
10	4.51	1.0820	99.9	1.094	1.219	....	....
11	6.68	1.0667	107.9	1.165	1.342	+0.033	0.057
12	10.98	1.0363	127.0	1.332	1.613	0.039	0.063

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[1] Solutions of $ZnCl_2$ can not be diluted with pure water without a precipitation of basic salt. To the stock solution for Nos. 1-7 inclusive has been added hydrochloric acid to make 0.024 molar on the final dilution. No. 1 contains a further addition to make 0.045 molar. In Nos. 8-12 inclusive sulphuric acid was used by mistake instead of hydrochloric acid in an amount to make 0.016 molar on dilution. Nos. 8 and 9 contain additional amounts to make 0.079— and 0.030 molar respectively.

The precipitate of basic copper salt redissolved in each case in somewhat less than 4 mols of ammonia to 1 of copper salt, but the first determinations were made on solutions containing fully 4 molecules. A copper-ammonia salt containing but 2 molecules of NH_3 is known to exist, but the more stable complex salt is that containing 4 molecules. In the case of copper nitrate, additions of ammonia in excess of four equivalents give the normal D' values. With copper sulphate, on the other hand, values of D' some little higher than, but still not far removed from, the normal are obtained. This would indicate that ammonia in excess of four equivalents still had some action upon copper sulphate, but that this action was very much more feeble than that of the first 4 mols. Copper ammonium nitrate crystallizes with the composition $Cu(NH_3)_4(NO_3)_2$, while copper ammonium sulphate crystallizes as $Cu(NH_3)_4SO_4.H_2O$. Of the ammonia-free salts, copper nitrate at a low temperature, crystallizes as $Cu(NO_3)_2.6H_2O$, while copper sulphate can, under certain conditions (when mixed with other vitriols), exist as $CuSO_4.7H_2O$.[1] The sulphates then seem to have the power in the solid state of combining with more molecules of H_2O than do the nitrates. This power is most probably due to the negative component, and is also possibly possessed by the SO_4-radical when in the dissolved state. In copper nitrate solution it is shown that only 4 molecules of NH_3 unite with an atom of Cu. In copper sulphate solution further action with ammonia is probably that of the (possibly hydrated) SO_4-radical.

To redissolve the basic zinc salt, which at first precipitates, ammonia considerably in excess of four equivalents is necessary at the dilutions used, although in very concentrated solutions a bare excess is sufficient. Zinc chloride itself forms a basic salt with pure water, so that to the stock solution, which was used for the dilutions, a small amount of acid, as indicated in the tables, was added. This solution, on further dilution with water, again precipitated basic salt, making necessary a slight further addition of acid before determining the viscosity of the non-ammoniacal solutions. The zinc-ammonia salts which crystallize from ammoniacal solutions are $Zn(NH_3)_4Cl_2.H_2O$ and $Zn(NH_3)_4SO_4.4H_2O$.

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[1] Dammer: "Anorganische Chemie," Band II, 2.

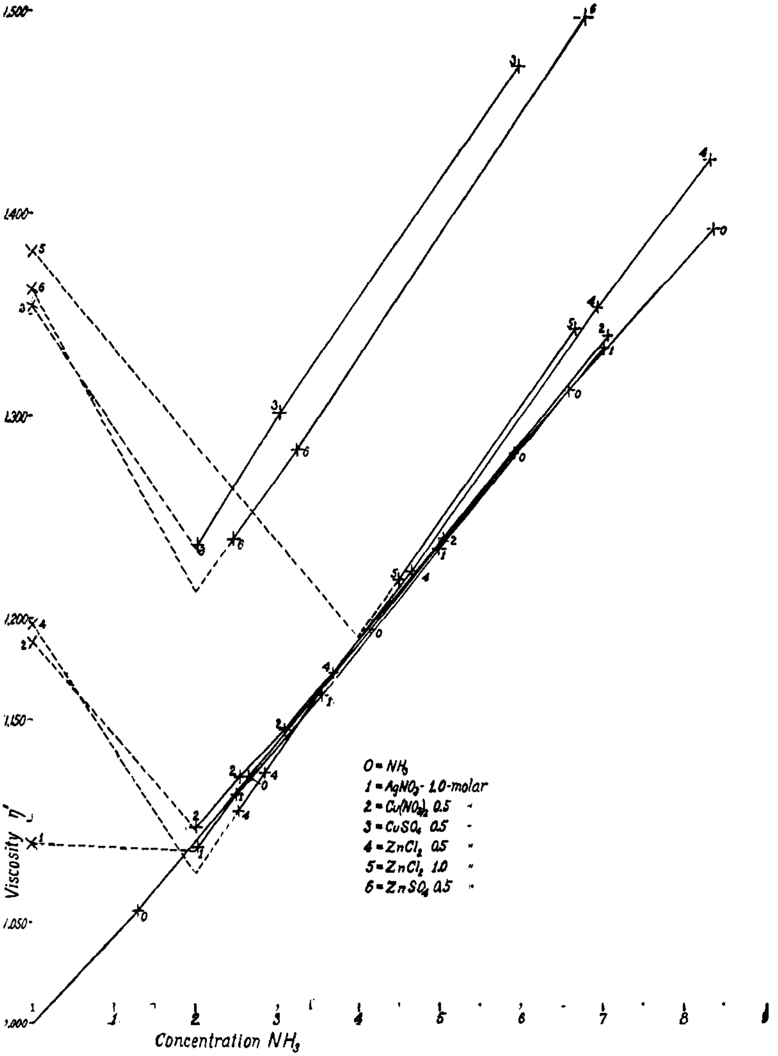

Diagram 1.

$ZnSO_4.5NH_3$ can be obtained by leading ammonia gas over dry $ZnSO_4$, but this complex is readily decomposed by water.[1] The D' values for ammonia with zinc chloride and zinc sulphate are a little above the normal, which indicates, as in the case of copper sulphate, that after the formation of the fairly stable metal-

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[1] Dammer: "Anorganische Chemie," Band II, 2.

ammonia complex ($Zn.4NH_3$), there is some slight further tendency for ammonia to react with the salt and indeed most probably with the negative component.

The foregoing results are represented graphically in Diagram 1, where abscissae represent concentrations of NH_3 and ordinates the values of η'. For the nitrates the values of η' fall off sharply to the points where ammonia, sufficient to give a clear solution, is present; from there on the curves for the nitrates coincide almost exactly with that for ammonia and pure water. For zinc chloride at two different dilutions the same is nearly true; but for the sulphates, although the addition of the first 4 molecules of ammonia causes a great decrease in the values of η', the entire curve is very much above, although its latter portion runs in about the same direction as, the curve for ammonia in pure water. If curves for the uncorrected viscosity, η, be drawn, much the same characteristics are shown in that the addition of 2 or 4 molecules, respectively, of ammonia causes a great drop, and that further additions of ammonia cause a steady rise. But with the uncorrected viscosity the curves for the nitrates and chlorides investigated are no longer nearly coincident with each other and with that for ammonia and pure water.

Some rather rough experiments with pyridine and copper nitrate were tried with the results in the following table:

PYRIDINE IN 0.4 MOLAR $Cu(NO_3)_2$, 25°.

Conc.	Pyridine.	Sp. gr.	η	η	D	D'
....	0.0	1.058	1.140	1.156	....	....
....	1.84	1.062	1.626	1.784	+0.26	+0.34
....	2.03	1.063	1.697	1.870	0.37	0.45

Apparently pyridine forms a complex with the copper salt in exactly the same manner as does ammonia, for the basic copper salt, precipitated by the first addition, dissolves when somewhat in excess of four equivalents of pyridine have been added, and the color of the resulting solution is identical with that of the copper-ammonia salts. The D values, however, show a large increase in viscosity from the simple salt to the pyridine complex salt. This is what would be expected, for addition of such large molecules as pyridine, even though they might displace water molecules, could hardly otherwise than greatly increase the viscosity of the copper salt molecules.

Dissolved molecules, if in a state of purely physical solution, may be supposed to offer friction according to their nature; and the relation between that friction and the molecular weight and constitution of the molecules is probably of the same order of magnitude whether we are dealing with the molecules of pure liquids or of dissolved substances. To place clearly before us the effect of molecular weight and constitution upon viscosity, the values for a number of typical liquids have been taken from Landolt and Börnstein's tables. The values are all for 20° (interpolated where necessary); they are expressed in the absolute measure, and in some cases they are the average of values by different observers.

TABLE IX.—VISCOSITY OF PURE LIQUIDS, 20°.

(Taken from Landolt and Börnstein's Tables.)

Substance.	Molecular weight.	Viscosity.
Ethyl ether	74	0.0026
Carbon bisulphide	76	0.0037
Propyl chloride	78	0.0036
Ethyl bromide	109	0.0038
Chloroform	120	0.0057
Propyl bromide	123	0.0055
Carbon tetrachloride	154	0.0102
Ethyl iodide	156	0.0059
Propyl iodide	170	0.0076
Ethylene bromide	186	0.017
Methyl propionate	88	0.0047
Ethyl acetate	88	0.0046
Propyl formate	88	0.0057
Isopropyl formate	88	0.0052
Methyl butyrate	102	0.0059
Ethyl propionate	102	0.0055
Propyl acetate	102	0.0061
Isopropyl acetate	102	0.0054
Butyl formate	102	0.0070
Benzene	78	0.0065
Toluene	92	0.0060
Xylene	106	0.0067
Water	18	0.0102
Methyl alcohol	32	0.0062
Ethyl "	46	0.012
Propyl "	60	0.023
Butyl "	74	0.013
Amyl "	88	0.037

TABLE IX.—(*Continued.*)

Substance.	Molecular weight.	Viscosity.
Formic acid	46	0.019
Acetic "	60	0.013
Propionic acid	74	0.011
Butyric acid	88	0.016
Valerianic acid	102	0.022

For the first group of liquids the general statement may be made that the viscosity is greater, the greater the molecular weight, although the two quantities are far from being exactly proportional.

In the next two groups is shown the effect of structure in series of isomeric compounds. As a general rule, it may be stated that the more symmetrical the structure the lower the viscosity.

In the last two groups in the table are some of the substances which, in the liquid form, we have good reason to believe do not exist as the simple molecules indicated by their chemical formulae, but as polymers of these. It is noticed, first, that the viscosities of bodies in the latter groups are much higher than of those of the same molecular weight in the first four groups; and second, that there is here much less regularity in increase of viscosity with the increase of the molecular weight corresponding to the simple formulae.

Let us try to interpret the behavior of the metal-ammonia salts in the light of our knowledge of pure liquids. Addition of 2 and 4 mols respectively of ammonia to solutions of silver, copper and zinc salts decreases very greatly the viscosity. Probably the degree of ionization of the metal-ammonia salts is slightly greater than that of the plain metal salts. This will, however, hardly account for the large decrease in viscosity, for Wagner[1] found, without taking ionization into account, that the viscosity of salts is, in general, very nearly equal to the sum of definite values assigned to each of the metallic and acidic atoms or radicals respectively; Rehyer[1] further found that the sodium salts (dissociated) of various weak organic acids possessed, in normal solutions, viscosities higher, by values ranging from 0.18 to 0.41 than those of the corresponding undissociated acids. Furthermore substitution of the dissociated *H*-ion by *Na*-ion in normal solu-

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[1] *Loc. cit.*

tions of strong mineral acids increased the viscosity only by the almost constant amount 0.035. This would show that weak acids would, if dissociated, possess specific vicosities greater by values from 0.15 to 0.38. This would indicate that the increased dissociation is not the cause of the decreased viscosity of the ammonia-metal salts. Also it furnishes another argument against the Electrostriction hypothesis of negative viscosity. The only way then open to account for the decreased viscosity seems to be a decrease in size or an increase in symmetry of the salt molecules, or more especially of the positive ions of the salts (since ammonia is shown by migration experiments to form a part of that ion). If the positive ion consists solely of a metallic atom bearing an electric charge, combination with ammonia molecules cannot de-

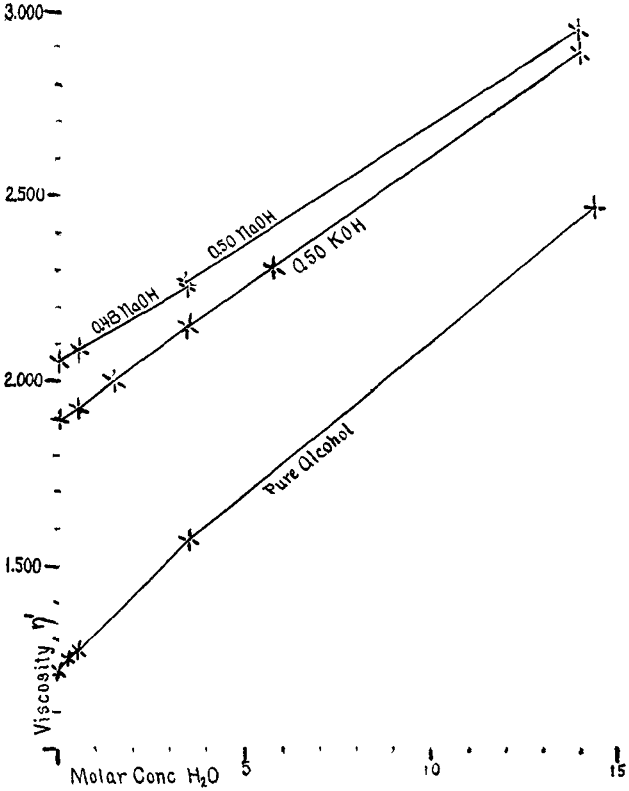

Diagram 2.

crease its mass and it is not easy to imagine that it can increase its symmetry. The only explanation then seems to be that metal ions in solution are hydrated; the hydrate-water is replaced by ammonia, which forms with the ion a more stable complex and one of lesser mass, or greater symmetry, or both. It will be seen that this explanation of the lowering of viscosity of a metal salt solution by addition of ammonia is similar to the one offered earlier in this paper, of negative viscosity.

This work has shown that where definite and fairly stable complexes are formed in solution their presence can, at least in certain cases, be clearly and quite conveniently demonstrated by means of viscosity measurements.

An attempt was now made, working in alcoholic solution, to show the existence of complexes of metal salt with water similar to those of metal salt with ammonia in aqueous solution. While the indications of these experiments are far less definite than of those just described, the data are nevertheless of some interest to present.

IX. THE EFFECT OF ADDITIONS OF WATER TO SOLUTIONS IN ABSOLUTE ETHYL ALCOHOL.

Series of viscosity measurements were made, similar, in every respect, to those with the metal-ammonia salts. In place of metal salts the hydroxides of lithium, sodium and potassium, and anhydrous cupric chloride were used. Instead of water absolute ethyl alcohol was the solvent, and instead of ammonia, water was the substance added in varying amounts.

The solutions were prepared by dissolving metallic sodium. metallic potassium, lithium hydroxide, and anhydrous cupric chloride respectively in absolute alcohol. For each experiment a definite amount of the proper solution was taken, the desired amount of water added, and the whole made up to a fixed volume with absolute alcohol.

The results for sodium and potassium hydroxides are found in Tables X and XI. For the first additions of water to pure alcohol the value of D' may be taken as approximately 0.11—it decreases with increasing concentrations, according to Table III. On addition of water to alcoholic sodium hydroxide this value is found to be only 0.06 and on addition of water to alcoholic potassium hydroxide 0.07. As the concentration of the water increases, the values of the ratio, particularly in the case of the potassium hydroxide solution, are more nearly the same as those for the same amount of water added to pure alcohol. These relations are shown graphically in Diagram 2. That the curves for the solutions do not run parallel with that for pure alcohol, in other words, that the *D'* value is altered by the dissolved hydroxide, shows that there has been some interaction of the added substances with the solute. That the curve for sodium hydroxide is inclined more than that for potassium hydroxide towards the curve of pure alcohol shows, as well as does the greater change in the *D'* value, that more of the added water is acted upon by the sodium hydroxide.

TABLE X.—H_2O TO 0.5 MOLAR NaOH IN ETHYL ALCOHOL.

	Concentration.	Sp. gr., 25°/25°.	η	η'	*D*	*D'*
1	$NaOC_2H_5$, 0.48, ...	0.8085	2.0419	2.060	....	....
2	NaOH, 0.48: H_2O, 0.020	0.8113	2.0565	2.050	0.029	....
3	NaOH, 0.48: H_2O, 0.510	0.8142	2.0777	2.081	0.043	0.063
4	NaOH, 0.48: H_2O, 3.435	0.8302	2.1911	2.252	0.039	0.058
5	$NaOC_2H_5$, 0.050, ...	0.8084	2.0467	2.068	....	....
	NaOH, 0.50: H_2O, 3.435	.....	2.1959	2.260	(extrapolated from 5, 4 and 1)	
6	NaOH, 0.50: H_2O, 13.92	0.8822	2.6726	2.944	0.045	0.065
7	NaOH, 0.50: H_2O, 20.19	0.9103	2.9465	3.348	0.044	0.064

TABLE XI.—H_2O TO 0.5 MOLAR KOH IN ETHYL ALCOHOL.

KOC_2H_5, 0.50, ...	0.8130	1.8677	1.893	....	....
KOH, 0.50: H_2O, 0.01	0.8159	1.8930	1.893	0.050	....
KOH, 0.50: H_2O, 0.50	0.8187	1.9182	1.927	0.051	0.069
KOH, 0.50: H_2O, 1.47	0.8245	1.9740	2.001	0.058	0.076
KOH, 0.50: H_2O, 3.44	0.8354	2.0837	2.149	0.056	0.075
KOH, 0.50: H_2O, 5.71	0.8473	2.1965	2.306	0.050	0.070
KOH, 0.50: H_2O, 13.93	0.8869	2.6060	2.883	0.050	0.070

TABLE XII.—H_2O TO 0.162 MOLAR LiOH IN ETHYL ALCOHOL.

LiOH, 0.162, ...	0.7961	1.5216	1.5145	....	....
LiOH, 0.162: H_2O, 0.358	0.7984	1.5543	1.5537	0.091	0.109
LiOH, 0.162: H_2O, 0.664	0.8002	1.5797	1.5848	0.083	0.102
LiOH, 0.162: H_2O, 1.32	0.8043	1.6330	1.6499	0.081	0.099

TABLE XIII.—H_2O TO 0.163 MOLAR NaOH IN ETHYL ALCOHOL.

$NaOC_2H_5$, 0.163, ...	0.7949	1.4614	1.4682	....	....
NaOH, 0.163: H_2O, 0.006	0.7961	1.4769	1.4740	0.091	....
NaOH, 0.163: H_2O, 0.210	0.7975	1.4926	1.4932	0.077	0.094
NaOH, 0.163: H_2O, 0.662	0.8006	1.5351	1.5434	0.094	0.111
NaOH, 0.163: H_2O, 1.33	0.8046	1.5857	1.6065	0.076	0.094

Owing to the small solubility of lithium hydroxide in alcohol only a 0.270 molar (almost saturated at 25°) solution could be prepared; 15 cc. of this were in each experiment diluted to 25 cc., thus giving an 0.162 molar solution. To compare with this series, a series of measurements was also made with the same strength of sodium hydroxide solution. From the results given in Tables XII and XIII it is seen that with these weak solutions there is but little change of the *D'* value. Thus, from a difference in the amount of the decrease it is not possible to say that either one or the other hydroxide has a greater action upon water. It is, however, seen that lithium hydroxide in alcohol has a higher viscosity than sodium hydroxide. The viscosities of the alkali hydroxides in alcohol increase from potassium to lithium, as well as do the viscosities of the salts of the alkalies in water.

In Table XIV and in Diagram 3 is shown the behavior of all mixtures of alcohol and water. My own values for these mixtures are given, since values at the concentrations and the temperature desired were not to be found. The form of the curve is, however, identical to that found by others. Small additions of water to alcohol or of alcohol to water cause a great increase of the viscosity. As shown in the curve, the maximum lies about at a point corresponding to a composition of $1C_2H_5OH + 3H_2O$. This might indicate, as has already been suggested by Graham,[1] by Thorpe and Rodgers,[2] and others, a definite though very unstable compound of the formula $C_2H_5OH.3H_2O$. It is otherwise hard to explain the great increase of the viscosity above the sum of the viscosities of the individual components. In cases where there is less probability of a compound being formed no such increase is observed. For example, the viscosity curves for mixtures of non-polymerizing liquids, such as benzene and toluene, benzene and carbon bisulphide, carbon tetrachloride and chloroform, etc.,[3] are either nearly straight lines or are convex downward.

Water added to alcoholic sodium hydroxide or potassium hydroxide can combine, first, with alcohol to form the hypothetical $(C_2H_5OH.3H_2O)$. If only this reaction took place, however, *D'* would equal 0.11. Secondly, it can combine with *ROH*, possibly displacing any alcohol which may exist in a compound of

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[1] *Phil. Mag.* (4), **24**, (1862).

[2] *J. Chem. Soc.*, 71, 360 (1897).

[3] Linebarger: *Am. J. Sci.*, IV., **2**, 331 (1896); also Thorpe and Rodgers: *Loc. cit.*

the form $ROH.nC_2H_5OH$. At all events if combination with water does increase the friction of the ROH-complex above that of the *ROH-alcohol*-complex, such increase, as is shown by the results, is less than that which would have been caused by the formation of the compound $C_2H_5OH.mH_2O$. Were a definite hydrate $ROH.lH_2O$ formed of a stability comparable to that of the metal-ammonia compounds, we should expect to get a curve like those for the latter, with a sudden change in direction at the point where just l water molecules have been added. We have, however, rather an equilibrium:

$$\mathrm{ROH}\cdot n\mathrm{C_2H_6OH} + \frac{l}{m}\,(\mathrm{C_2H_5OH}.m\mathrm{H_2O}) \rightleftarrows$$
$$\mathrm{ROH}\cdot l\mathrm{H_2O} + \left(n + \frac{l}{m}\right)\mathrm{C_2H_5OH},$$

in which the attraction of ROH for alcohol is so great (shown by its heat of solution in alcohol) that the reaction does not proceed by any means until one of the substances upon the left-hand side is exhausted. All we can expect then, upon successive additions of water, is to get a gradual displacement of the equilibrium towards the right which would result in giving a viscosity curve more or less inclined to that of water and pure alcohol.

Sodium hydroxide in alcohol has a greater viscosity than potassium hydroxide. If we account for this in the same way as in the case of aqueous solutions, we should conclude that the *Na-alcohol*-complex had a greater mass or was less symmetrically constituted than the *K-alcohol*-complex. Sodium hydroxide, from its greater effect upon the values of D', appears to have a greater tendency than has potassium hydroxide to combine with water. This is not at variance with the suggestion that the sodium ion, with its water of hydration, has a greater mass than the potassium ion.

It might be claimed that variations from the normal D value were caused by changes in the degree of electrolytic dissociation produced by the additions of water. Small amounts of water, however, do not materially change the nature of the solvent. Hence, if there are marked changes in the dissociation, it would seem that the dissociation itself must be caused by the chemical combination of electrically neutral molecules with the solute.

X. COPPER CHLORIDE IN MIXTURES OF ALCOHOL AND WATER.

The stock solution of copper chloride was prepared by dissolving dehydrated copper chloride in absolute alcohol. Here a very considerable evolution of heat was noticed with the first additions of alcohol, and there was formed a deep greenish brown solid mass. This dissolved in a further small addition of alcohol with no further evolution of heat. To this was added a small amount of an alcoholic solution of dry hydrochloric acid. The solution was now made up with absolute alcohol to give a concentration of 2 mols of copper chloride and 0.065 mol of hydrochloric acid.

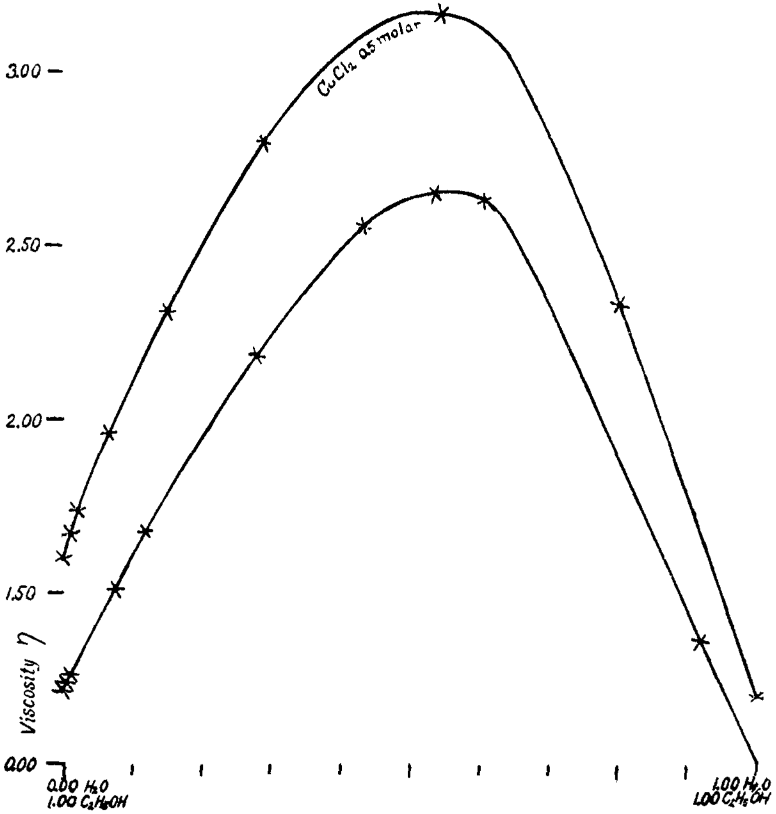

Diagram 3.

The small amount of acid was put in the solution for the purpose of preventing precipitation of any basic salt upon dilution. For three of the mixtures this was found to be not quite sufficient to prevent a slight visible turbidity. Measurements were, however, made in these cases without further addition of acid and with additions sufficient to entirely remove the turbidity. It was found that these small additions of hydrochloric acid did not greatly affect the viscosity.

TABLE XIV.—H_2O IN ETHYL ALCOHOL.

$\frac{\text{Parts water.}}{\text{Parts water + alcohol.}}$	Concentration water in molecules.	η
0.0	0.0	1.211
0.006	0.257	1.236
0.012	0.507	1.259
0.077	3.45	1.509
0.120	5.50	1.675
0.281 ($C_2H_5OH.H_2O$)	13.46	2.180
0.439 ($C_2H_5OH.2H_2O$)	21.8	2.551
0.540 ($C_2H_5OH.3H_2O$)	27.6	2.650
0.610 ($C_2H_5OH.4H_2O$)	31.6	2.628
0.920	50.4	1.352
1.000	55.4	1.000

TABLE XV.—H_2O AND 0.5 $CuCl_2$ IN ETHYL ALCOHOL.

	$\frac{\text{Parts water.}}{\text{Parts water + alcohol.}}$	Concentration water in molecules.	Concentration hydrochloric acid in molecules.	Sp. gr. 25°/25°.	η	*D*
1	0.00	0.0	0.016	0.8455	1.599	....
2	0.0115	0.50	0.016	0.8488	1.669	0.140
3	0.0229	1.00	0.016	0.8521	1.737	0.136
4	0.0665	2.94	0.016	0.8644	1.958	0.114
5	0.152	6.89	0.016	0.8857	2.308	0.089
6	0.291	13.8	0.016	0.9193	2.794	0.070
7	0.546	27.6	0.016	0.9793	3.163	0.027
7*b*	0.546	27.6	0.15	0.9813	3.168	....
8	0.804	42.8	0.016	1.0273	2.323	....
8*b*	0.804	42.8	0.24	1.0303	2.304	....
9	1.00	51.2	0.08	1.0582	1.193	....

The experimental results are given in Table XV, and in Diagram 3 are shown graphically the viscosities for mixtures of alcohol and water, alone, and with 0.5 molar copper chloride. Increasing from either pure solvent the curve mounts more steeply in presence of copper chloride, that is, presence of copper chloride causes an increase in the *D* value rather than a decrease, as in previous instances. The cause of this phenomenon is doubtless much the same as that of the phenomenon found by Jones and

Lindsay,[1] that the conductivity of certain salts in mixtures of water with methyl, ethyl and propyl alcohols usually shows a strong minimum. A maximum of viscosity corresponds closely to a minimum of conductivity and would seem to us to be caused by a maximum amount of polymerization or of association of solute and solvent, rather than by a mutual lessening of the polymerization of each simple solvent.

SUMMARY.

The relationship between migration velocity and the viscosity of ions in solution is discussed.

Negative viscosity is discussed and an attempt is made to account for it on the ground of the hydration of *solvation*[2] of the dissolved substance.

The viscosity of solutions as ordinarily represented takes into account only the given volume of liquid which contains the dissolved substance, applying thus to varying amounts of the solvent. A correction is used which, to a certain extent, fulfils the purpose of having the figure for each dilution always refer to the same amount of solvent.

Measurements are given for various additions of ammonia to some of the metal salts which give soluble metal-ammonia compounds. Sufficent ammonia to form the complex compounds in each case causes a large decrease in viscosity; further additions of ammonia cause nearly the same increase in viscosity as if made to pure water. The composition of the complex existing in solution can be inferred from the form of the viscosity curve. The conclusions from this method agree with the well-established facts regarding these solutions. An inspection of the curves of the corrected viscosities shows that beyond the point of re-solution of the basic salt the curves for silver nitrate, copper nitrate, zinc chloride and pure water almost coincide, while the curves of the sulphates of zinc and copper lie considerably above, but run roughly in the same direction as the former. If the curves are drawn for the uncorrected viscosity, the same conclusions regarding composition are made evident, but the latter striking peculiarity is not seen.

The decrease of viscosity with the addition of ammonia to metal salt solutions is compared with the negative viscosity of certain solutions and both seem to find a reasonable explanation in the *Hydrate* or *Solvate Theory* of solution.

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[1] *Am. Chem. J.*, **28**, 329 (1902).

[2] See note 2, page 1318

A few series of determinations with additions of water to solutions in ethyl alcohol were made. No very definite conclusions are drawn from them, yet they support, to a certain extent, the suggestion made that the slower rate of migration and the higher viscosities of the ions of the alkali metal, lowest in atomic weight, are due to a greater tendency to combine with molecules of solvent. A maximum of *increase* in viscosity for copper chloride in mixtures of ethyl alcohol and water corresponds with the minimum in conductivity, observed by Jones and Lindsay, in similar solutions, both perhaps being due to a maximum formation of highly associated molecules.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
July, 1904.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 4].

THE MIGRATION OF COLLOIDS.

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Received July 22, 1904.

I. PREPARATION AND DIALYSIS OF COLLOIDAL GOLD SOLUTIONS.

MOST of the work described in this paper was done with red colloidal gold, prepared by pouring an ethereal solution of gold chloride (dried at 160° to 170°) into water saturated with ether and acetylene gas.[1] The reduction was completed by the passage of more acetylene, but an excess of this reagent is to be avoided, since otherwise the presence of the supernatant layer of ether has a tendency to turn the red gold blue at the surface between the two liquids, thus often giving a purple or violet tint to the resulting solution. Such red, purple or violet solutions were then dialyzed in tubing of parchmentized paper, so as to remove the hydrochloric acid formed by the reaction. The progress of the purification was followed by measuring the conductivity of the liquid within the dialyzer. The dialysis was carried out by surrounding the parchment tube first with ten times its volume of ordinary distilled water, frequently renewing this until the electrolyte was mainly removed, and then replacing it by conductivity water (of conductivity 1.5×10^{-6} reciprocal ohms). The specific conductivities (κ) (in reciprocal ohms $\times 10^{-6}$) of the four gold

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[1] Blake: *Am. J. Sci.*, **16**, 381 (1903).