cold. Its specific gravity at 17.5°, referred to water of the same temperature, was 1.1502.

Next a solution of cane sugar of the same density was prepared by dissolving 98.496 grams (calculated by Arrhenius' formula) of sugar in water and diluting to 250 cc. at 17.5°. A specific gravity determination at that temperature gave 1.1501.

The quantities of water in the two solutions differed by less than 1 per cent. When equal samples of the two were mixed together, neither contraction nor expansion took place: the specific gravity of the mixture at 17.5° was found to be 1.1501.

It was thus possible, by mixing the two solutions in several different proportions, and observing the rotations of the mixtures, to determin whether the partial rotations of the fructose solution were proportional to the quantities of that solution in the mixture, and hence whether the specific rotation of fructose remained constant.

If the partial rotation of the fructose solution is proportional to its percentage in the mixture, then the total rotation (α) must be a linear function of that percentage (p). As a matter of fact, Table XI shows that the observed rotations are almost perfectly reproduced by the equation

$$\alpha = 24.54 - 0.5830p,$$

and hence, that the specific rotation of fructose in our mixtures was independent of its concentration. But this matter will be subjected here to further study.

TABLE XI.

p.	α obs.	α calc.	Diff.
0.00	+24.54°	+24.54°	±0.00°
10.41	+18.53	+18.47	—0.06
20.12	+12.78	+12.81	+0.03
30.04	+ 7.03	+ 7.03	±0.00
40.23	+ 1.09	+ 1.09	±0.00
60.03	—10.55	—10.46	+0.09
69.76	—16.17	—16.12	+0.05
89.69	—27.72	—27.75	—0.03

WORCESTER, MASS., June, 1911.

STUDIES IN CONDUCTIVITY. I. THE CONDUCTIVITY OF AMMONIA IN (ANHYDROUS) FORMIC ACID. I. "FORMIC ACID HYDROLYSIS."

BY H. I. SCHLESINGER AND R. P. CALVERT.

Received October 24, 1911.

In recent years, a great deal of attention has been given to the study of non-aqueous solutions, especially from the point of view of the theory of ionization. While this work has covered a wide range of solvents, the solutions investigated are, with but few exceptions,[1] solutions of salts. It is therefore very desirable that a similar, systematic study of acids and bases in solvents other than water should be made. The importance of such an investigation has been emphasized by a recent paper by Walden,[2] in which he suggests that in solvents of acid character bases should be highly ionized, and *vice versa*, provided that the other properties of the solvents tend to make them ionizing agents. In view of the special interest thus attached to solutions of acids and bases in solvents of varying chemical character, a study of the conductivity of such solutions has been undertaken. Although the work is as yet in the initial stages, some of the results have proved of sufficient interest in themselves to warrant their publication.

Formic acid, on account of its decidedly acid character in aqueous solution and its high dielectric constant, is a particularly favorable solvent for this investigation. The results of Zanninovich–Tessarin[3] indicate that, in agreement with Walden's postulate, acidic substances are but little ionized when dissolved in formic acid. In fact, the results for hydrogen chloride show an association rather than a dissociation. On account of the rather high initial conductivity of the formic acid employed in the investigations referred to, it is impossible to decide from them whether the latter reaction does not take place to a slight extent; for this reason this work is to be repeated in this laboratory. In order to test the other phase of the postulate mentioned, the conductivity of ammonia in the same solvent was studied.

The acid was prepared from Kahlbaum's 95 per cent. formic acid by repeated distillation from phosphorus pentoxide, at about 35° and a pressure of about 35 mm. of mercury.[4] After about nine distillations, the specific conductivity of the acid at 25° averaged 6.82×10^{-5}, and its freezing point was 8.60°. The latter constant was determined with all of the necessary precautions and a thermometer, compared with a standardized platinum resistance thermometer, was employed.[5] The freezing point obtained is slightly higher than the highest found in the previous literature, namely 8.50°.[6] The specific conductivity does not compare quite so favorably with other values, the lowest actually at-

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[1] See, for example, Kablukov, *Z. physik. Chem.*, 4, 429. Zelinskii and Krapivin, *Ibid.*, 21, 35. Walden, *Ibid.*, 54, 129 and 43, 400, where other references may be found. Franklin, *Am. Chem. J.*, 23, 277, and THIS JOURNAL, 27, 191. Röhler, *Z. Elektrochem.*, 16, 419. See also below.

[2] *Trans. Far. Soc.*, 6, 71 (1910).

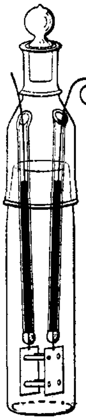
[3] *Z. physik. Chem.*, 19, 251 (1896).

[4] The acid is partially decomposed by this treatment.

[5] We are indebted to the kindness of Prof. Menzies for this calibration.

[6] Walden, *Loc. cit.* But Novak (*Phil. Mag.*, [5] 44, 828) arrives at the value 8.52° by extrapolation, from the freezing points of the aqueous acid.

tained being about 3.7 × 10^{-5} at 18°.[1] Novak,[2] by an extrapolation based on the change of conductivity of the acid on the addition of water, derives the value 1.4 × 10^{-5} at 8.52° which corresponds to about 2–3 × 10^{-5} at 25°, judging roughly from analogous calculations by Novak. That this acid of high freezing point is not the monohydrate as has been suggested by others, is shown by the results of titration of the acid against standard alkali. The mean of a large number of determinations gave 99.96 per cent. as the degree of purity. Owing to an apparent action of the acid upon the indicators, the results agreed to only 0.5 per cent., but this error can not affect the conclusion, since the monohydrate ($2HCOOH.H_2O$)[3] contains only 83.7 per cent. of acid.


One-third actual size.

Ammonia carefully dried over soda-lime and freshly cut sodium was passed into the acid. The strength of the resulting solution was determined by a modification of the Kjeldahl method. The conductivity was determined between platinized electrodes in the cell which is shown in the accompanying sketch. Resistances were measured by the usual Wheatstone-Kohlrausch method, with standardized resistances and a calibrated bridge. Constant temperature was maintained by placing the cell into a Freas thermostat adjusted at 25° ± 0.01 (hydrogen scale). The cell constant was determined by the use of both *N*/50 potassium chloride and *N*/64 sodium chloride.

In making the solutions of varying concentration, the method of employing two calibrated pipets, as it is described in the manuals, was used. The delivery pipet was calibrated first with water and then with formic acid but no appreciable difference in the volume delivered was found. The two pipets differed, for content and delivery, by less than 0.02 cc. in the total volume of 10 cc. This method of making up the solutions has the disadvantage that changes in density, as the solutions become more dilute, are not accounted for; but owing to the expense of the solvent and the relatively large amount of time required in purifying it, we considered it inadvizable to attempt to make up each dilution separately. In making the dilutions in this way there was also considerable chance of allowing the acid to absorb moisture: by having all materials in vessels with carefully ground stoppers and by the use of a pump and calcium chloride tubes in drawing the liquids into the pipets the danger from this source was decreased. In order to determin roughly

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[1] Sapozhnikov, *J. Russ. Phys. Chem. Soc.*, **25**, 629. The data are given in Siemens units in the original. The same is true of Novak's data.

[2] *Loc. cit.*

[3] Colles, *J. Chem. Soc.*, **89**, 1251. The results of Kremann, *Monatsh.*, **28**, 893, 900, make the existence of hydrates seem doubtful.

how great the effect of absorbed moisture might be, pure formic acid was pipetted in and out of the cell exactly as was done in a conductivity determination. In a number of operations corresponding to five dilutions, the conductivity of the acid[1] changed from 11.96×10^{-5} to 12.09×10^{-5}, a change of 1 per cent., which is but little greater than the experimental error in the measurement of these small conductivities. For more accurate work, in which moisture must be more effectively excluded, a special cell has been constructed, which will be described in a later paper.

In Table I are given the experimental results for the conductivity of the ammonia solutions and a few calculations based upon them. The first column gives the concentration (c) in gram molecules per liter, the second the specific conductivities (κ) in reciprocal ohms,[2] the third the molecular conductivities (μ_v) calculated in the usual way. The figures in the remaining columns will be discussed below.

TABLE I.—CONDUCTIVITY OF NH_3 IN HCOOH AT 25°.

c.	κ.	μ_v.	μ'_∞. (Kohlrausch).	μ_∞. (Ostwald).	α.[4]	k.
			First Series.			
0.135	0.008717	64.57	...	...	0.899	1.09
0.0675	0.004572	67.73	79.92	71.86	0.943	1.05
0.03375	0.002351	69.66	78.28	71.75	0.970	1.05
0.01687	0.001196	70.90	77.24	72.02	0.987	1.24
0.00844	0.000591	70.02	73.53	[70.42]	...	..
0.00422	0.000274	64.93	65.09	[51.58]	...	..
0.00211	0.000122	57.82	...	...	...	..
0.00105	0.00005	47.39	...	...	...	..
.....	....	...	Mean[3]	71.87	...	1.11
			Second Series.			
0.55	0.02918	53.05	...	...	0.738	1.15
0.275	0.01647	59.89	86.18	71.90	0.834	1.15
0.1375	0.008850	64.37	83.64	(70.98)	0.896	1.05
0.06875	0.004675	68.00	82.95	71.86	0.946	1.15
0.03437	0.002399	69.80	80.87	71.84	0.972	1.14
0.01719	0.001216	70.73	79.22	71.77	0.984	1.07
0.00859	0.000603	70.16	75.86	[70.46]	...	..
0.00430	0.000283	65.86	69.03	[66.03]	...	..
0.00215	0.000123	57.30	...	...	...	..
0.00107	0.000052	48.72	...	...	...	..
...	....	...	Mean	71.84	...	1.12

In most aqueous solutions, the molecular conductivities rize continuously with increasing dilution or approach a constant maximum

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[1] The best acid was not used in this test.

[2] Obtained from the observed conductivities by subtracting the specific conductivity of the acid used.

[3] Figures in parentheses or brackets were not included in the mean value.

[4] The value $\mu_\infty = 71.85$ was used in calculating α.

value. It will be seen from the data in column 3 that for the solutions under discussion this is not the case: the values rize to a maximum and then decrease. Similar phenomena have been observed by others[1] in non-aqueous solutions and several explanations have been suggested. While this is therefore not an isolated case, the nature of the solutions makes a specific interpretation of the divergence from the normal behavior of aqueous solutions seem probable here. From the values of the specific conductivities it appears likely that the drop in molecular conductivity in the solutions for which the specific conductivity is comparatively low, is associated with the relatively high conductivity of the solvent. That this is not in itself sufficient to explain the character of the curve is shown by the values obtained for ammonium chloride solutions. These are appended, for the purpose of comparison in Table II (see p. 1931); although the specific conductivities of the greater dilutions given in this table are fully as small as those for the ammonia solutions, no decrease in the molecular conductivities is observed. In the ammonia solutions, however, there is reason to believe that the specific conductivity of the solvent cannot be considered to remain constant nor to have the value found by measuring the conductivity of the acid directly; for the ammonia solutions undoubtedly contain highly ionized ammonium formate, which, on account of the large concentration of formate ion which it yields, would tend to repress the ionization of the formic acid almost completely. It is nevertheless not permissible to assume that in the solutions the conductivity of the acid is entirely destroyed, because the acid used was probably not absolutely pure[2] and part of its conductivity must be ascribed to these impurities. A second factor may also prove to be a matter of importance: both the conductivity of the acid itself and that of the impurities may possibly be increased by a "salt effect." The latter would in the more concentrated solutions tend to counterbalance the "common ion" effect, so that the more concentrated solutions would give us the more reliable data. This must be true also because variations in the specific conductivity of the solvent would have a much smaller influence upon the value for concentrated solutions, since, for these the specific conductivity is sufficiently high to render the *percentage* error introduced by the conductivity of the solvent very small. The only data available for deciding upon a minimum value for the specific conductivity of the pure acid are those of Novak;[3] but since they refer to a much lower temperature than that of our experiments, it is not

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[1] See, for example, Archibald, THIS JOURNAL, **29**, 674, where other instances are cited. Plotnikov, *J. Russ. Phys. Chem. Soc.*, 40, 1243. Walden, *Z. physik. Chem.*, **54**, 133, suggests an explanation similar to the one given in this paper, for a different case.

[2] Pure acid should have a conductivity of 2–3 × 10^{-6} (Novak, *Loc. cit.*); ours had a conductivity of 6.86 × 10^{-5}.

[3] *Loc. cit.*

possible to make use of them for approximating the corrections suggested above. Consequently we are forced to leave out of consideration the values for the more dilute solutions, at least for the present, and to confine our attention to the more normal values of the more concentrated solutions. The following discussion is limited therefore to the concentrations for which rizing values for the molecular conductivities are obtained, *i. e.*, from 0.55 N to 0.01687 N.

For the interpretation of conductivity data several formulas are generally considered: the Ostwald dilution law; or, where this does not give satisfactory results, the equations of Kohlrausch, of Rudolphi, of van't Hoff or modifications of the last two. The use of any of these formulas in the usual way involves the knowledge of the value of the molecular conductivity at infinit dilution. For the reasons given this could not be determined experimentally. The formulas can however be used to calculate this value; if any one of them gives a constant for the conductivity at infinit dilution, the formula may be considered to apply to the case in question. In this way the first two of the equations mentioned were tried. The dilution law may be written as follows:

$$\frac{(\mu_1/\mu_\infty)^2 c_1}{1-\mu_1/\mu_\infty} = K_0; \qquad \frac{(\mu_2/\mu_\infty)^2 c_2}{(1-\mu_2/\mu_\infty)} = K_0;$$

in which c_1, c_2...... represent successive values for the concentration, μ_1, μ_2...... successive values for the molecular conductivity, μ_∞ the molecular conductivity at infinit dilution, and K_0 is a constant. By eliminating K_0 and solving for μ_∞, we get

$$\mu_\infty = \frac{\mu_1\mu_2^{\,2}.c_2/c_1 - \mu_1^{\,2}\mu_2}{\mu_2^{\,2}.c_2/c_1 - \mu_1^{\,2}}. \qquad \text{I.}$$

The equation of Kohlrausch may be transformed in like manner to read

$$\mu'_\infty = \frac{\mu_1 - \mu_2\sqrt[3]{c_1/c_2}}{1-\sqrt[3]{c_1/c_2}}. \qquad \text{II.}^1$$

By substituting different pairs of data for the concentration and the conductivity a series of values for μ_∞ can be calculated. The figures in the fourth column of the table are obtained in this way from equation II, those in the fifth column, from equation I.

It is clear that only the figures in the fifth column represent constant values. This is best shown in the second series where there are more data for comparison. In the two series there is but one value, of those under consideration, which differs from the mean by more than 0.3 per cent., an excellent agreement. From the average of the values of μ_∞ so obtained the degree of dissociation, $\alpha (= \mu_v/\mu_\infty)$, and K_0 can be calculated. These are given in columns 6 and 7 of the table. Although

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[1] The Kohlrausch equation is usually stated in terms of equivalent conductivities. In the present instance this value is identical with the molecular conductivity.

the values for K_0 calculated in this way show greater variation from the mean than do the values for μ_∞, they show no decided trend either to rize or to fall and may therefore be looked upon as constant. No such closeness of agreement is to be looked for in the values of K_0, since all of the errors in the calculation of μ_∞ are duplicated in that of K_0. Thus an error of 0.1 per cent. in the value for μ_v can result in one of 3 per cent. in K_0.

From the constancy of the values for μ_∞ calculated according to the dilution law, we may therefore conclude[1] that the dissociation of the substance in these solutions *obeys the law of mass action, although the electrolyte in question is as highly ionized as are the strong acids, bases and salts in aqueous solutions.* Whether this very unusual result is characteristic of the behavior of bases in acid solvents, or whether those substances which obey the law in one solvent obey it in all, irrespective of the degree of ionization, is a matter for further study. To decide this question, solutions of both strong and weak bases in formic acid will be investigated.

There is a slight possibility that, on account of the uncertainty in regard to the value to be used for the specific conductivity of the solvent, these results may prove to be accidental. This is rendered highly improbable, however, by the excellent agreement between the value for μ_∞ calculated as described above and that calculated in another way. That a simple relationship exists between the conductivities, at infinit dilution, of the same substance in different solvents and the viscosities of the solvents has been pointed out by a number of writers. A number of different formulas have been suggested,[2] but for our purposes the one expressing a simple inverse relationship will be sufficiently accurate. The electrolyte in the solutions of ammonia in formic acid is undoubtedly ammonium formate. The value of μ_∞ for this substance in water at 25° is 128.8, as calculated from the mobilities of the ions. The viscosity of water at this temperature is 0.009,[3] that of the acid is 0.0162.[4] Then according to the relation suggested, μ_∞ in formic acid should be:

$$\begin{aligned}\mu_\infty &= 0.009/0.0162 \times 128.8 \\ &= 71.57\end{aligned}$$

This differs by only 0.4 per cent. from the value found from our conductivity measurements, namely 71.85. This excellent agreement is very strong evidence of the correctness of the interpretation given above

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[1] For the concentrations, $N/2$–$N/60$.

[2] See, for instance, Jones, Lindsay and Carrol, *Z. physik. Chem.*, 56, 170. Walden, *Ibid.*, 55, 207. Pisarzhevskii and Karp, *Ibid.*, 63, 257. Washburn, THIS JOURNAL, 33, 1461. The more accurate formulas must take into consideration the solvation in the respective solvents.

[3] Castell-Evans, "Physico-Chemical Tables," Vol. II, 598.

[4] *Ibid.*, 609. The last place of decimals is rounded off.

for the behavior of the ammonia solutions and discounts any doubts introduced by the large conductivity of the pure acid.

We see therefore that the basic substance, ammonia, forms a highly dissociated electrolyte in the acid solvent, formic acid. The degree of dissociation actually obtained is, as a matter of fact, extremely great; ammonium hydroxide in water is about 4 per cent. ionized in 0.01 normal solution; potassium hydroxide about 95 per cent. in the same solvent and at the same concentration; ammonia in formic acid is about 99 per cent. ionized at the same concentration.[1]

In order to determin whether the high conductivity of the formic acid used as solvent might be alone sufficient to account for the decrease in the molecular conductivity of the ammonia solutions, as described above, a similar series of measurements was carried out with ammonium chloride as the solute. Since the data served also to confirm some conclusions which were drawn from the results discussed in the previous pages, they are given below in Table II. The data in this table have the same significance as those in the first five columns of the first table. It will be seen that, although the specific conductivities observed in the case of the ammonium chloride solutions reach as low a value as the specific conductivities, which in the ammonia series correspond to falling values for the molecular conductivity, no such decrease is noticeable here. This may be taken as evidence in favor of the interpretation of the falling values given above.[2]

TABLE II.—CONDUCTIVITY OF NH_4Cl IN HCOOH AT 25°.

c.	κ.	μ.	μ'_∞. (Kohlrausch).	μ_∞. (Ostwald).
0.2500	0.00848	33.94	...	...
0.1250	0.00473	37.83	52.73	44.18
0.0625	0.00256	40.96	52.94	45.73
0.03125	0.001364	43.65	53.36	46.17
0.01562	0.000715	45.75	53.52	47.28
0.00781	0.000384	49.16	53.69	50.22
0.00391	0.000197	50.59	56.09	51.10

Although the measurements, the results of which are given in the first two columns of Table II, were not as accurate as those for the ammonia solutions and must therefore not be considered as final, a brief discussion will not be out of place. It will be seen that neither the dilution law nor

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[1] Although the electrolyte is ammonium formate, it must, in the acid solvent, be considered a base, as will be shown below.

[2] See p. 1928. The objection might be raised that in the ammonium chloride solutions a similar falling off in conductivity may be masked by a very great rise in the real molecular conductivities, *i. e.*, the conductivity of the acid may decrease what really is a much greater rise in these values than the one actually observed. This, however, is very improbable, since the rise in the molecular conductivity, as shown in the table, is very large for such dilute solutions and a more rapid increase would be most unusual.

the equation of Kohlrausch give constant values for the conductivity at infinit dilution; in other words neither of these equations represents the course of the dissociation of the salt in the solutions. This is in agreement with similar findings of Zanninovich-Tessarin.[1] It is furthermore exactly what is to be expected when the nature of the salt is considered. For, in formic acid solution, *ammonium chloride is the salt of a strong base, ammonia (ammonium formate), and the very weak acid hydrogen chloride.*[2] *Consequently it should be partly decomposed by the solvent into these two substances, exactly as similarly constituted salts are hydrolyzed*[3] *in aqueous solutions.* Since the extent of this decomposition must vary with the concentration of the solution, none of the "dilution laws" could be expected to apply. That this interpretation is correct can be shown qualitatively by a simple experiment. If dried air is passed through the solution and then into water, the latter in a few moments gives a heavy precipitate of silver chloride with silver nitrate, showing that free hydrochloric acid is present in the solution of ammonium chloride in formic acid.[4] Similar experiments were carried out with formic acid solutions of potassium and sodium chlorides, and with potassium bromide and iodide. Corresponding results were obtained.[5] In fact, if all acids are but slightly ionized in formic acid, we might expect a similar behavior of all true salts in this solvent. Further interesting confirmation of these conclusions might be found by a comparison of the temperature coefficient of salts in formic acid with that of bases.[6]

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[1] *Loc. cit.*

[2] See p. 1925.

[3] Similar analogies, for other solvents, have been pointed out by Franklin, THIS JOURNAL, 27, 820. Walden, *Z. physik. Chem.*, 54, 146. Ley, *Ibid.*, 30, 202. Bruni and Manuelli, *Z. Elektrochem.*, 11, 554.

[4] The addition of relatively small amounts of water, prevented the decomposition completely.

[5] Except that in the case of the iodide, hydrogen had to be used in place of air to prevent oxidation. The results were obtained most rapidly with the chloride and the least rapidly with the iodide. An attempt will be made to determin the equilibrium quantitatively by a modification of these experiments, or by some other method depending upon the partition principle, as may prove best. The conductivity of the salts, in the presence of an excess of the acids, will also be determined.

[6] In a recent article Prof. Garner has announced his intention of studying the conductivity, etc., of salts in formic acid solution (*Am. Chem. J.*, 46, 236 (1911)). The work described here was of course completed before the other appeared, and was begun long before Prof. Garner's intentions were known to the authors. Although our work is in no sense an infringement of the large field reserved by Prof. Garner, we shall make all efforts to avoid duplication of his work. We shall therefore not take up the study of temperature coefficients as suggested above, except for ammonium chloride to verify the conclusions which we drew from the main portion of our work (the study of bases in this solvent), nor shall we study the conductivity of salts, except of those which according to the views above presented, must, in formic acid solution, be considered as being analogous to bases in aqueous solutions, namely, the formates.

Summary.

It has been shown:

(1) That the solutions obtained by dissolving ammonia in (anhydrous), formic acid are excellent conductors.

(2) That the substance formed in these solutions (ammonium formate), although a very highly ionized electrolyte, obeys the law of mass action (in the more concentrated solutions).

(3) That, in accordance with the conception that the salts of the halogens are in formic acid solution really the salts of strong bases (the formates) and of weak acids, potassium chloride, bromide and iodide and sodium and ammonium chlorides are decomposed by "formic acid hydrolysis."

Further work along the lines suggested is in progress, using formic acid as well as other acidic and basic solvents.

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EQUILIBRIUM IN THE SYSTEM, POTASSIUM IODIDE, IODINE AND WATER.

BY CHARLES L. PARSONS AND C. F. WHITTEMORE.

Received October 12 1911.

The question of the existence of polyiodides of potassium has been for years one of deep interest to physical chemists, involving as it does so many theoretical questions. In July, 1910,[1] one of us in collaboration with H. P. Corliss, presented a paper at the San Francisco meeting of the American Chemical Society, attacking the problem through phase rule considerations in aqueous alcohol solutions. Experimental difficulties had previously made accurate work in aqueous solutions impossible in our hands, owing to the high specific gravity and great concentration. Aqueous alcohol was chosen in the expectation that more dilute solutions would result. Such, however, did not prove to be the case, but the experimental difficulties were overcome and the experience then gained seemed to make it desirable to study the mutual solubility of potassium iodide and iodine in pure water with special reference to that portion of the curve representing complete saturation, which had never before been plotted.

In describing the results it is unnecessary to refer again to the literature of the subject, which will be found in the article above mentioned, or indeed to describe methods of procedure or of analysis, for they were precisely the same as those previously used. The portion of the curve covered by dilute solutions was also not studied, as it has been carefully covered by Noyes and Seidensticker[2] and others.

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[1] THIS JOURNAL, 32, 1367.

[2] *Z. physik. Chem.*, 27, 357 (1898).