

the world; therefore the alchemists said that there is nothing which acts chemically but solutions. Solutions fill the oceans, solutions are running in our veins and solutions form the chief part of all organisms; life is bound to solutions, as well as chemical reactivity. In the broad sense of the word, the terrestrial and the celestial bodies chiefly consist of solutions, inasmuch as their chief parts are mixtures of different fluid bodies. Why should we not apply what we found regarding solutions to the different interesting problems regarding these bodies. By the application we already have cleared up fundamental chapters in different sciences, and especially in the field of physiology and biology. These applications have been of the greatest interest, and even in that line extremely good work is carried out here in America at the present time; and I have the greatest respect for and expectations from just that work, for it is clear that biology will be the chief science or the most practical science, I may say, of the coming time. It regards life, and we are living organisms, and that is our most special property; and therefore physiology, or the science regarding life, will have the greatest influence of all the sciences upon the principle of life and upon the development of humanity.

I have, perhaps, spoken too broadly regarding all of these questions which have lain so near to me, and I therefore will conclude my remarks. I only wish to say that if my dear friend, Mr. Mather, has said that I perhaps do not know that I am a member of the Society, he is very badly informed, for every month I receive four very valuable publications from here, which I read with the very greatest interest. Especially are they valuable for me because they record in a great number of cases the, for Americans characteristic, very practical treatment of the problems attacked. Mr. Mather said I am the first of the honorary members, and that is due to my great luck in having a name beginning with "A."

Now, in receiving this medal, struck in honor of our great master Willard Gibbs, I wish to express the hope that very many members of this Society, and colleagues of mine in this case, shall receive this medal in the coming years.

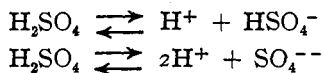
I thank you very heartily. [Great and prolonged applause.]

THE CONCENTRATION OF HYDROGEN ION IN SULFURIC ACID.

BY RICHARD C. TOLMAN AND LUCIEN H. GREATHOUSE.

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Sulfuric acid may dissociate according to either or both of the reactions:

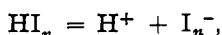


Since its method of dissociation is unknown, it is impossible to calculate,

from conductivity measurements alone, either the degree of dissociation of the acid or the concentration of any of the ionic substances produced.

It occurred to the authors that the concentration of hydrogen ion in sulfuric acid could be most easily determined by the use of an indicator. The method consists in finding a solution of hydrochloric acid which imparts the same color to a definite concentration of indicator as the sulfuric acid under consideration.¹

We may consider an indicator as a weak acid which ionizes according to the reaction



the undissociated acid and its ion differing in color.

The hydrogen ion concentration of the solution in which the indicator is present will determine the degree of ionization of the indicator, and hence indirectly its color. If we find a solution of hydrochloric acid which gives the same color with the same amount of indicator as the solution of sulfuric acid under consideration, the two presumably have the same concentration of hydrogen ion which can be calculated for the hydrochloric acid from conductivity data.

Experimental.

Four dyes were finally chosen for use as indicators and were made into stock solutions of the following suitable composition:

1. 0.05 g. malachite green, 5 cc. alcohol, 95 cc. water.
2. 0.0125 g. methyl violet, 2¹/₂ cc. alcohol, 97¹/₂ cc. water.
3. 0.0166 g. tropäolin 00 in 100 cc. 50% alcohol.
4. 0.05 g. methyl green, 100 cc. water.

Approximately 0.2 *N* solutions of sulfuric, hydrochloric and nitric acids and of barium hydroxide were prepared and standardized. The acids were all titrated against barium hydroxide, and this in turn titrated against succinic acid. Furthermore, independent determinations of the strength of the sulfuric and hydrochloric acids were made by precipitation of barium sulfate and silver chloride. The various standardizations were in satisfactory agreement.

Indicator was added to solutions of 0.2 *N*, 0.1 *N* and 0.05 *N* sulfuric acid and the color compared with that found in a series of differently concentrated solutions of hydrochloric and nitric acids, which were prepared by dilution from 0.2 *N* acid. The comparisons were made on a white background in Nessler tubes which had a depth of approximately 17 cm. to the 100 cc. mark. For the 0.2 *N* and 0.1 *N* acid, 50 cc. of the solutions were taken and 0.1 cc. of the indicator solution added. For the 0.05 *N* acid, 100 cc. of solutions were taken and 0.2 cc. of indicator solution added.

¹ Indicators were first systematically used for determining hydrogen ion concentration by Friedenthal, *Z. Elektrochem.*, 10, 119 (1904). See also Salm, *Z. physik. Chem.*, 57, 471 (1907).

Malachite green and methyl violet were found to be sensitive indicators in 0.2 *N* and 0.1 *N* solution, methyl green and tropäolin oo in 0.05 *N* solution.¹ The indicator was added from a buret provided with an automatic stopcock, which permitted the rapid delivery of 0.1 cc. portions. Since there is a tendency for the color of the solutions to fade, the solutions to be compared were all placed in the Nessler tubes and the indicator added to them in quick succession. The comparisons were made at room temperature, approximately 24°.

Experimental Results.

The results of the experiments are given in Tables I-III. The first column in the tables states the concentration of comparison acid whose color

TABLE I.—COLOR COMPARISON WITH THAT IN 0.2 *N* ($\times 1.0174$) H_2SO_4 .

Concentration of comparison acid.		Color in comparison acid.			
HCl.	HNO ₃ .	Malachite green.		Methyl violet.	
HCl.	HNO ₃ .	HCl.	HNO ₃ .	HCl.	HNO ₃ .
0.150 \times (1.0033)	0.150 \times (1.0121)	Greater
0.140 \times (1.0033)	0.140 \times (1.0121)	Greater	Greater
0.130 \times (1.0033)	0.130 \times (1.0121)	Slightly greater	Greater	Greater	Greater
0.120 \times (1.0033)	0.120 \times (1.0121)	Less	Slightly less	Less	Slightly less
0.110 \times (1.0033)	0.110 \times (1.0121)	Less	Less	Less	Less
Conc. HCl (1.0033) or HNO ₃ (1.0121) equivalent to 0.2 <i>N</i> H_2SO_4 (1.0174)...		0.1275	0.1225	0.1250	0.1225
Concentration HCl or HNO ₃ equivalent to 0.2 <i>N</i> H_2SO_4		0.1257	0.1218	0.1233	0.1218
Concentration hydrogen ion.....		0.111	0.108	0.109	0.108

TABLE II.—COLOR COMPARISON WITH THAT IN 0.1 *N* ($\times 1.0174$) H_2SO_4 .

Concentration of comparison acid.		Color in comparison acid.			
HCl.	HNO ₃ .	Malachite green.		Methyl violet.	
HCl.	HNO ₃ .	HCl.	HNO ₃ .	HCl.	HNO ₃ .
0.080 \times (1.0033)	0.080 \times (1.0121)	Greater	Greater
0.075 \times (1.0033)	0.075 \times (1.0121)	Greater	Greater	Greater	Greater
0.070 \times (1.0033)	0.070 \times (1.0121)	Same	Slightly greater	Same	Slightly greater
0.065 \times (1.0033)	0.065 \times (1.0121)	Less	Same	Less	Slightly less
0.060 \times (1.0033)	0.060 \times (1.0121)	Less
Conc. HCl (1.0033) or HNO ₃ (1.0121) equivalent to 0.1 <i>N</i> H_2SO_4 (1.0174)...		0.0700	0.0662	0.0700	0.0675
Concentration HCl or HNO ₃ equivalent to 0.1 <i>N</i> H_2SO_4		0.0690	0.0659	0.0690	0.0672
Concentration hydrogen ion.....		0.0620	0.0597	0.0620	0.0609

¹ For solutions as dilute as 0.005 *N* dimethylamidoazobenzene was the most suitable indicator tried, but even that lacked great sensitiveness.

TABLE III.—COLOR COMPARISON WITH THAT IN 0.05 N (1.0174) H₂SO₄.

Concentration of comparison acid.		Color in comparison acid.			
HCl.	HNO ₃ .	Tropäolin oo.		Methyl green.	
HCl.	HNO ₃ .	HCl.	HNO ₃ .	HCl.	HNO ₃ .
0.0425 × (1.0033)	0.0425 × (1.0121)	Greater	Greater
0.0400 × (1.0033)	0.0400 × (1.0121)	Greater	Same	Slightly greater
0.0375 × (1.0033)	0.0375 × (1.0121)	Greater	Greater	Slightly less	Same
0.0350 × (1.0033)	0.0350 × (1.0121)	Same	Same	Less	Less
0.0325 × (1.0033)	0.0325 × (1.0121)	Less	Less	Less	Less
Conc. HCl (1.0033) or HNO ₃ (1.0121) equivalent to 0.05 N H ₂ SO ₄ (1.0174)...		0.0350	0.0350	0.0394	0.0381
Concentration HCl or HNO ₃ equivalent to 0.05 N H ₂ SO ₄		0.0345	0.0348	0.0389	0.0379
Concentration hydrogen ion.....		0.0315	0.0319	0.0356	0.0347

was contrasted with that of the solution of sulfuric acid in question and the other columns state whether the color of the comparison acid corresponded to a greater or a less hydrogen ion concentration than that of the sulfuric acid.

The results of the experiments are summarized in the lower part of each table. The first line states the concentration of comparison acid decided on as having the same color as the sulfuric acid used. The second line states the concentration of comparison acid having the same color as sulfuric acid of exact normality, and the third line states the hydrogen ion concentration of this strength of comparison acid.

The following tabulation indicates the conventions made in deciding what concentration of comparison acid would have the same color as the sulfuric acid:

Color shown by successive samples of comparison acid, contrasted with color of H ₂ SO ₄ .	Equivalent concentration chosen as that which showed
Greater—same—less	Same color
Greater—less	Less color + 1/2 conc. interval
Slightly greater—less	Less color + 3/4 conc. interval
Slightly greater—same—less	Same color + 1/4 conc. interval

The concentration of comparison acid isohydric with sulfuric acid of exact normality was calculated by simple proportion from the normality factors of the two acids. The concentration of hydrogen ion in the comparison acid was calculated from the conductivity data of Kohlrausch at 18° using the values for λ₀ determined by Noyes and Sammet¹ and Noyes and Kato,² 396 for hydrochloric acid, 392 for nitric acid.

¹ THIS JOURNAL, 24, 944; 25, 165 (1902-3). *Z. physik. Chem.*, 43, 49-74 (1903).

² Carnegie Institution of Washington, Publication No. 63. THIS JOURNAL, 30, 318 (1908).

TABLE IV.—RATIO OF HYDROGEN ION CONCENTRATION TO FORMAL CONCENTRATION

Formal concentration.	H ₂ SO ₄ .		Picric acid expts., 25°.
	Indicator method, approx. 24°.	Conductance and transference, 25°.	
0.100	1.11	1.05-1.16	1.04
	1.08		
	1.09		
	1.08		
0.050	1.24	1.13-1.24	1.10
	1.19		
	1.24		
	1.22		
0.025	1.26	1.23-1.35	1.20
	1.28		
	1.42		
	1.39		

Conclusions.

From an examination of the last lines in Tables I-III, it will be seen that the different acids and the different indicators lead to approximately the same values for hydrogen ion concentration in sulfuric acid. Small differences between the values obtained using different indicators and different comparison acids are to be expected from the probability of slight but unknown action between indicator and the acid radical. Nevertheless, assuming that conductivity measurements for uni-univalent acids give a true measure of degree of dissociation¹ we may conclude that the values we have presented for the hydrogen ion concentration in sulfuric acid are approximately correct.

A comparison of our values of hydrogen ion concentration with those recently presented in an article by Noyes and Stewart² will be of interest. Their method consisted in determining the relative concentrations of hydrochloric acid and sulfuric acid which drive back the ionization of picric acid to the same extent. Table IV gives values for the ratio of hydrogen ion concentration to the formal concentration of sulfuric acid, as obtained by the indicator method, and by the picric acid experiments of Noyes and Stewart.³ It has furthermore been shown by Noyes and Stewart by combining transference and conductivity data that certain limits can be calculated between which the hydrogen ion concentration must lie. These limits are also presented in the table. It will be noticed that none of the values for hydrogen ion concentration obtained by the picric acid method by Noyes and Stewart lie within the necessary limits

¹ For a consideration of the possibility that conductivity measurements do not give true values of the degree of dissociation, see an article by Tolman and Ferguson, *THIS JOURNAL*, 34, 232 (1912).

² *THIS JOURNAL*, 32, 1133 (1910).

³ The data of Noyes and Stewart presented in the table is that obtained using the value $\lambda_0 = 365$ for hydrogen ion.

which they have calculated. This probably means that the degree of dissociation of picric acid in the presence of the acids is not merely dependent on the concentration of hydrogen ion. Of the twelve different values obtained by the indicator method using different indicators and different comparison acids, only two lie outside the limits, and these are the only ones in which methyl green was used as an indicator. The general conclusion may be drawn that a comparison of the results obtained with a number of different acids and different indicators will lead for simple solutions to values of the hydrogen ion concentration of reasonable reliability.

Using the same method, a determination of the hydroxide ion concentration in solutions of di-acid bases is now being carried out by one of the authors (L. H. G.).

The experimental work described in this article was done in the chemical laboratory of the University of Michigan.

CINCINNATI, OHIO, and ANN ARBOR, MICH.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF PLATINUM TETRAIODIDE AND OF IODINE IN ALCOHOL.

BY E. H. ARCHIBALD AND W. A. PATRICK.

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It is evident that the study of non-aqueous solutions must be greatly extended before the mystery surrounding the phenomenon of solution can be satisfactorily explained. Interesting examples of such solutions are those of the metallic iodides in ethyl alcohol. The following pages contain an account of some measurements of the electrical conductivity of solutions of platinum tetraiodide and of iodine in ethyl alcohol.

Materials Used.

Iodine.—Kahlbaum's resublimed iodine was ground with a little potassium iodide and again sublimed. This product, after being again carefully sublimed, gave the sample used in these experiments.

Platinum Tetraiodide.—Pure platinum was prepared by the repeated precipitation of ammonium chloroplatinate. From the pure platinum a solution of chloroplatinic acid was prepared and the platinum thrown down as the iodide with iodine and sodium iodide.

Ethyl Alcohol.—Kahlbaum's absolute alcohol was boiled for several hours with a large excess of pure calcium oxide and distilled. It was then allowed to stand for two days, with frequent shaking, over anhydrous copper sulfate. It was then distilled, reserving for the experiment only the middle portion of the distillate. This alcohol had a specific conductivity of 2.6×10^{-8} reciprocal ohms at 25°. If allowed to stand in contact with the air for only a few moments, its conductivity would increase tenfold.