[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH.]

THE HYDROLYSIS OF THE SILICATES OF SODIUM.[1]

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Introduction.

An investigation of the electrical conductivity of solutions of sodium silicates was made by Kohlrausch[3] in 1893. He studied especially compounds of the formulas Na_2SiO_3 and $Na_2O.3.4SiO_2$, and also a solution of sodium hydroxide to which was added increasing amounts of silicic acid. He found that in dilute solution the metasilicate conducted the current very readily while that same compound in concentrated solution was a very poor conductor. This was also true of the more acid silicate. Kohlrausch furthermore found that if a solution of silicic acid were added to one of equivalent concentration of sodium hydroxide, the conductivity decreased constantly until the ratio $Na_2O:2SiO_2$ was attained, beyond which point no further changes were observed. The conclusions which he draws from these experiments are that in concentrated solutions the extent of hydrolytic or of ionic dissociation is very slight, while in dilute solutions hydrolysis has taken place to a very great extent. He also infers that, except in very dilute solutions, a compound of the formula $Na_2Si_2O_5$ is present.

Kahlenberg and Lincoln[4] a few years later urged that while Kohlrausch was probably correct in his conclusions yet his procedure of experimentation did not prove that the increased conductivity obtained upon dilution was due to hydrolytic rather than to ionic dissociation, and that his results were not quantitative. They accordingly proceeded to examine compounds of the compositions Na_2SiO_3, $NaHSiO_3$ and $Na_2Si_5O_{11}$ (also the potassium, lithium, rubidium and cesium salts of the corresponding acids) from the data obtained by freezing-point determinations. Their conclusions confirm those of Kohlrausch, *e. g.*, that "in solutions of sodium silicates these salts are hydrolytically decomposed into sodium hydroxide and colloidal silicic acid." They further assert that "silicates of the general formulas M_2SiO_3 and $MHSiO_3$ are practically completely hydrolytically dissociated when one gram molecule is contained in 48 liters. Silicates of the general formula $M_2Si_5O_{11}$ are practically completely decomposed by water when one gram molecule is present in 128 liters."

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[1] Presented at the 60th General Meeting of the American Chemical Society, Chicago, Ill., September 6–10, 1920.

[2] Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

[3] Kohlrausch, *Z. physik. Chem.*, **12**, 773 (1893).

[4] Kahlenberg and Lincoln, *J. Phys. Chem.*, **2**, 77 (1898).

A year earlier Loomis[1] had also reported that the metasilicate Na_2SiO_3 gave a greater molecular depression in freezing-point determinations than would accord with the hypothesis of ionic dissociation alone.

In the course of an investigation upon hydrogen-ion concentrations by the author it seemed that such a method applied to a study of the hydrolysis of the silicates of sodium might throw further light upon this question.

Experimental.

The apparatus used in making the measurements of hydrogen-ion concentration was as follows.

Standard Half Cells.—The standard cells consisted of 0.1 *N* calomel cells made up with the utmost care. The mercury was washed in nitric acid and 3 times redistilled. The potassium chloride was several times recrystallized from conductivity water. Redistilled hydrochloric acid was allowed to act upon an excess of the purified mercury, and the precipitated calomel washed by decantation with conductivity water for a week, then several times with 0.1 *N* potassium chloride solution, and finally made up in the latter solution for the cells. These cells were tested against standard cells and solutions of known hydrogen-ion concentration and found to be accurate to about 0.1 millivolt.

Hydrogen Cell.—The hydrogen cell was of the type suggested by Clark.[2] The platinum electrode was platinized by the method described by Findlay.[3] Electrolytic contact was made through a saturated solution of potassium chloride. The hydrogen was supplied from a commercial tank, the gas being passed through, first, an alkaline solution of potassium permanganate, second, conc. sulfuric acid, and third, water containing a little barium chloride.

Thermostat.—All of the above apparatus was enclosed in an air thermostat which was set to a temperature of 30° and the average deviation during measurements was not greater than 0.02°.

Potentiometer.—Measurements were made upon a Leeds and Northrup Type K potentiometer, the current being supplied by a single accumulator cell which was set just before and after each reading against a Weston cell which had been recently calibrated by the U. S. Bureau of Standards. Rough adjustment of the current was made by a simple pointer galvanometer, and the final adjustment by a very sensitive Type R reflecting galvanometer.

The silicates[4] which were studied consisted of 7 of various compositions, as follows:

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[1] Loomis, *Ann. Phys. Chem.*, **60**, 523 (1897).

[2] Clark, *J. Biol. Chem.*, **23**, 475 (1915).

[3] Findlay, "Practical Physical Chemistry," 1911, p. 150.

[4] The author is indebted to the Philadelphia Quartz Company for the silicates experimented upon. The analyses of these samples were furnished by William Stericker, of the Mellon Institute of Industrial Research.

Number.	Na_2O. %.	SiO_2. %.	H_2O. %.	Approximate molecular structure. Na_2O.	SiO_2.	H_2O.
1	7.0	26.9	66.1	1	4	33
2	8.98	30.3	60.72	1	$3^1/_2$	23
3	11.0	31.2	57.8	1	3	18
4	13.7	32.9	53.4	1	$2^1/_2$	13
5	17.83	36.45	45.72	1	2	9
6	24.2	38.3	37.5	1	$1^1/_2$	5
7	26.95	28.85	44.2	1	1	6

Number 7, the metasilicate, was in the form of clear well-defined crystals, and was unquestionably the pure compound Na_2SiO_3. The others were all in the form of liquid glasses. These glasses, according to Stericker,[1] probably contain various amounts of compounds of the formulas Na_2SiO_3, $NaHSiO_3$, $Na_2Si_2O_5$, in addition to colloidal silica, and sodium hydroxide. Foreign impurities are, however, practically absent.

The 7 silicates were each made up in 5 different concentrations, the number of liters containing one gram molecule of the several silicates being 3.3, 10, 20, 50 and 100 respectively. These were each examined in the hydrogen gas cell previously described, and their P_H value calculated according to the well-known formula of Nernst: $E = E_0 + RT/nF \log_e C$ where E is the electrode potential corresponding to ionic concentration C, E_0 is the electrolytic potential (electrode potential at molar concentration), R is the gas constant (8.32 joules per degree), T is the absolute temperature, n is the valence of the ion, F is the faraday constant (96,500 coulombs), and C is the ionic concentration of the solution. Using the value 0.337, obtained by Auerbach,[2] as the electromotive force of a normal hydrogen electrode against a 0.1 N potassium chloride-calomel electrode, and calculating for a temperature of 30°, the working formula becomes $P_H = E - 0.337/0.0601$. The corresponding values for hydroxyl-ion concentration were taken from the tables of Schmidt and Hoagland.[3]

Assuming that, first, if there were no hydrolytic dissociation whatever, the hydroxyl-ion concentration would be identical with that of pure water at the same temperature (according to Michaelis[4] 1.37×10^{-7} at 30°), and second, if the silicate had suffered complete hydrolysis the hydroxyl-ion concentration would be identical with that of an equivalent solution of sodium hydroxide at the same temperature, and if we may assume further that the hydroxyl-ion concentration is a straight-line function of the degree of hydrolysis, then it becomes an easy matter to calculate the degree of hydrolytic dissociation which the several silicates at their sev-

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[1] Stericker, personal communication.

[2] Auerbach, *Z. Elektrochem.*, **18**, 13 (1912).

[3] Schmidt and Hoagland, University of California, *Pub. Physiology*, **5**, No. 4, 23–69 (1919).

[4] Michaelis, "Die Wasserstoffionenkonzentration," **1914**, p. 8.

eral dilutions have undergone. In doing this the degree of ionization of the sodium hydroxide at the several concentrations was taken directly, or extrapolated, from A. A. Noyes' publications[1] as follows:

Concentration, M.	Ionization, %.	(OH)$^-$ion concentration.
0.66	77	5080×10^{-4}
0.2	85	1700×10^{-4}
0.1	88	880×10^{-4}
0.04	93	372×10^{-4}
0.02	95	190×10^{-4}

If $n \times 10^{-7}$ = observed hydroxyl-ion concentration of the silicate solution, $m \times 10^{-7}$ = calculated hydroxyl-ion concentration of sodium hydroxide at the same equivalent concentration, and 1.37×10^{-7} is the hydroxyl-ion concentration of water, then $n - 1.37/m - 1.37$ = degree of hydrolysis (h). The values of both n and m are so great in comparison with the corresponding value for water that the latter may be eliminated from the equation without error and the equation becomes $n/m = h$. This equation was accordingly used in calculating h.

The hydrolytic-dissociation constant was calculated according to the equation $h^2/(1-h)v = K_H$, where v = the number of liters in which one gram molecule is dissolved. The ionization constants for the hypothetical silicic acids were calculated from the equation: $K_A = K_W/K_H$, K_W being the water constant which according to Michaelis[2] is 1.89×10^{-14} at 30°.

The following tables present the data obtained.

Discussion.

An examination of the data brings out several points which are of interest. Most important, perhaps, is the relatively small values obtained for the percentage of hydrolytic dissociation, when contrasted with the high values obtained by the conductivity and freezing-point methods of Kohlrausch and of Kahlenberg and Lincoln.[2] This discrepancy leads one to look more closely to the several methods employed, to the assumptions made, and to an explanation for the differences observed.

A questionable assumption in the work of Kohlrausch was that his increased conductivity was due entirely to hydrolytic rather than to ionic dissociation. But in order to account for this increased conductivity on the ground of ionic dissociation would, as Kahlenberg and Lincoln emphasized, necessitate the assumption that the ion $SiO_3^{=}$ possessed a mobility exceeding that of the chlorine ion by about 70%. This reasoning has indeed led most of the older investigators to a rejection of the ionic theory in favor of the hydrolytic dissociation hypothesis as an explanation

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[1] A. A. Noyes, *Carnegie Inst. Pub.*, 63, 177, 340 (1908).

[2] *Loc. cit.*

TABLE I.—VALUES OBTAINED FOR EACH SILICATE AT VARIOUS DILUTIONS.

v.	E.	P_H.	$C_{OH} \times 10^{-4}$.	$100h$.	$K_H = \frac{h^2}{(1-h)v}$.	$K_A = \frac{K_W}{K_H}$.
Silicate No. 1. $Na_2O.4SiO_2$.						
3.3	0.9980	11.01	10.2	0.20	1.38×10^{-6}	13.70×10^{-9}
10	0.9859	10.80	6.4	0.38	1.45×10^{-6}	13.00×10^{-9}
20	0.9837	10.77	6.0	0.68	2.33×10^{-6}	8.12×10^{-9}
50	0.9748	10.61	4.13	1.11	2.51×10^{-6}	7.52×10^{-9}
100	0.9669	10.48	3.00	1.58	2.54×10^{-6}	7.44×10^{-9}
Silicate No. 2. $Na_2O.3.5SiO_2$.						
3.3	1.0020	11.08	12.1	0.24	1.93×10^{-6}	9.80×10^{-9}
10	0.9921	10.90	8.2	0.49	2.41×10^{-6}	7.84×10^{-9}
20	0.9877	10.82	6.6	0.75	2.83×10^{-6}	6.67×10^{-9}
50	0.9773	10.67	4.76	1.28	3.32×10^{-6}	5.70×10^{-9}
100	0.9692	10.52	3.36	1.77	3.20×10^{-6}	5.90×10^{-9}
Silicate No. 3. $Na_2O.3SiO_2$.						
3.3	1.0120	11.23	17.6	0.35	4.07×10^{-6}	4.64×10^{-9}
10	1.0019	11.08	12.0	0.71	5.21×10^{-6}	3.63×10^{-9}
20	0.9930	10.92	8.4	0.95	4.55×10^{-6}	4.15×10^{-9}
50	0.9831	10.77	5.95	1.60	4.32×10^{-6}	4.37×10^{-9}
100	0.9715	10.57	3.72	1.96	3.92×10^{-6}	4.82×10^{-9}
Silicate No. 4. $Na_2O.2.5SiO_2$.						
3.3	1.0191	11.36	23.4	0.46	7.10×10^{-6}	2.68×10^{-9}
10	1.0070	11.16	14.5	0.85	7.28×10^{-6}	2.60×10^{-9}
20	0.9996	11.02	10.8	1.23	7.69×10^{-6}	2.46×10^{-9}
50	0.9892	10.84	6.95	1.87	7.15×10^{-6}	2.65×10^{-9}
100	0.9791	10.69	4.94	2.60	6.96×10^{-6}	2.71×10^{-9}
Silicate No. 5. $Na_2O.2SiO_2$.						
3.3	1.0421	11.74	54.8	1.08	3.91×10^{-5}	4.83×10^{-10}
10	1.0279	11.50	32.0	1.88	3.62×10^{-5}	5.22×10^{-10}
20	1.0029	11.25	18.0	2.04	2.12×10^{-5}	8.91×10^{-10}
50	0.9937	10.93	8.8	2.37	1.15×10^{-5}	16.40×10^{-10}
100	0.9828	10.77	6.0	3.15	1.03×10^{-5}	18.30×10^{-10}
Silicate No. 6. $Na_2O.1.5SiO_2$.						
3.3	1.0678	12.18	155.0	3.05	3.20×10^{-4}	5.90×10^{-11}
10	1.0552	11.95	90.0	5.29	2.98×10^{-4}	6.34×10^{-11}
20	1.0361	11.63	53.5	6.08	1.97×10^{-4}	5.59×10^{-11}
50	1.0230	11.42	26.8	7.21	1.12×10^{-4}	16.90×10^{-11}
100	1.0121	11.24	17.6	9.27	0.95×10^{-4}	19.90×10^{-11}
Silicate No. 7. $Na_2O.SiO_2$.						
3.3	1.0992	12.69	504.0	9.92	3.64×10^{-3}	5.20×10^{-12}
10	1.0944	12.43	275.0	16.18	3.12×10^{-3}	6.05×10^{-12}
20	1.0710	12.21	162.0	18.40	2.08×10^{-3}	9.08×10^{-12}
50	1.0533	11.93	85.0	22.81	1.35×10^{-3}	14.00×10^{-12}
100	1.0422	11.73	54.0	28.43	1.13×10^{-3}	16.70×10^{-12}

of the case in hand. McBain and has collaborators[1] have, however, recently shown that in such solutions as sodium silicate[2] colloidal electrolytes are

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[1] See especially, McBain and Salmon, THIS JOURNAL, 42, 426 (1920).

[2] *Ibid.*, p. 427, line 7.

present which, in the words of the authors are "salts in which an ion has been replaced by a heavily hydrated polyvalent micelle that carries an equivalent sum-total of electrical charges and conducts electricity just as well or even better than the simple ion it replaces."[1] This new discovery renders valueless deductions which have been made upon the assumption of an especially low conductivity for solutions of sodium silicate, *per se*.

Kahlenberg and Lincoln considered that it was more probable that the mobile hydroxyl-ion was the dominating influence, and their work apparently confirms that probability. It is permissible to point out, however, that the data obtained by the above mentioned investigators do not provide conclusive evidence in favor of a high hydrolytic dissociation. To illustrate: in the compound Na_2SiO_3, if ionization only had taken place, the apparent molecular weight would be $^1/_3$ of 121.58 or 40.53. If hydrolysis only had taken place, and the resulting sodium hydroxide were completely dissociated, the apparent molecular weight would be $^1/_4$ of 121.58 or 30.39. Thus a degree of hydrolysis from 0 to 100% would be revealed by variations in the apparent molecular weight of only 10 points. As a matter of fact, the authors obtain values at dilutions from 8 to 64 ranging from 41.3 to 32.6. It is suggested that those data may not warrant the all-conclusiveness of the deductions which have been drawn from them by the authors. And the function of the micelle in freezing-point determinations of silicates is still an unknown factor.

In the present investigation 3 assumptions have been made, and 2 of these are open to question. The first, namely, that if no hydrolytic dissociation had occurred, the hydroxyl-ion concentration would be the same as that of water at the same temperature, is undoubtedly justified. The second, that if hydrolytic dissociation had proceeded to completion, the hydroxyl-ion concentration would be the same as in an equivalent solution of sodium hydroxide, at first seemed entirely warranted. The third, that the hydroxyl-ion concentration is a straight-line function of the degree of hydrolysis, also seems warranted, and has often been made in previous investigations upon hydrolysis. But if the work of previous investigators, which has long been accepted, is to be taken as authoritative it follows that one of the above assumptions is not well made. The second, only will be considered. If hydrolytic dissociation has proceeded to completion at finite dilution, will the hydroxyl-ion concentration be the same as in an equivalent solution of sodium hydroxide? In order that the question may be answered in the affirmative, it is necessary to admit, first, the non-existence of any ionizable silicic acid,[2] and second, the absence of any influence of the colloidal or otherwise dispersed silica upon

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[1] THIS JOURNAL, p. 426.

[2] Stericker (*Loc. cit.*) and others have maintained the non-existence of silicic acids, *per se*.

the hydroxyl-ions. This latter assumption seems more open to question than any other. It seems indeed altogether possible that the particles of colloidal silica may either adsorb the ions upon their surface, or exert such a retarding influence upon their movements, that a numerical measurement of the latter would reveal an apparent ion concentration far below the actual or effective value. On the other hand, such a measurement might accurately represent the ionic condition of the *dispersed phase* of the solution. But if it be assumed that no such adsorption or other retarding influence is exerted upon the ions by the colloidal silica, then it would seem that the high values which have previously been obtained for the hydrolytic dissociation of the silicates of sodium have been erroneous. The several methods are in agreement in that the metasilicate, Na_2SiO_3, shows the greatest hydrolysis, while as the ratio of silica to soda increases, the degree of hydrolysis decreases.

The values for K_H and K_A have been inserted, as they are instructive. It is observed that the values for these constants at the several dilutions are not in all cases constant, but there is no great discrepancy in any instance. Indeed the values are in as close agreement as many that have been reported upon much better understood compounds. This can only mean, *if* the silica plays the role of an adsorbing or retarding agent upon the ions in solution, that the law governing the degree of adsorption or retardation is very similar to that which accounts for the hydrolytic dissociation constant, which is, in fact, the widely used "dilution law" of Ostwald.

Conclusions.

1. *If* the conclusions reached by earlier investigators to the effect that dilute solutions of sodium silicates are very highly dissociated hydrolytically may be accepted as authoritative, then it follows from data herein presented that the electrometric hydrogen-ion method is unsuitable as a means of measuring such dissociation. The reason for this appears to be in a possible ability of the colloidal silica to adsorb or retard or otherwise destroy the effect of a certain proportion of the hydroxyl-ions in the solution. The effect of the dilution upon this adsorptive or retarding influence follows closely the same laws as the effect of dilution upon hydrolytic dissociation. The hydroxyl-ion determination may serve, however, as a measure of the actual alkalinity of the dispersed phase.

2. The deductions put forward by earlier investigators are based upon data which, although expressive of a high degree of probability, are not, however, altogether conclusive evidence in favor of the much higher degree of hydrolysis which they report.

3. If the assumptions made in this report *are* found to be entirely justified, then it follows that the hydrolytic dissociation of the silicates

of sodium is much lower in dilute solutions than has been thought to be the case, ranging from 1.58 to 28.43% at a dilution of 100 liters per gram molecule in the silicates which vary respectively in their $Na_2O:SiO_2$ ratio of from 1:4 to 1:1.

4. The findings of earlier investigators, that the metasilicate, Na_2SiO_3, was most completely hydrolyzed, and that as more silica was added to the molecule the degree of hydrolysis decreased, have been confirmed.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION, OF WASHINGTON.]

THE SYSTEM CUPRIC OXIDE, CUPROUS OXIDE, OXYGEN.

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1. Previous Work on the System.

The system cupric oxide, cuprous oxide, oxygen has been studied by L. Wöhler.[1] The results of this investigation led to the conclusion that cupric and cuprous oxides form a continuous series of solid solutions. That is, if cupric oxide was heated *in vacuo* to a temperature such that it began to lose oxygen according to the reaction

$$4CuO(s) \rightleftarrows 2Cu_2O(s) + O_2,$$

this action was not accompanied by the formation of a second solid phase. The 2-component system remained in 2 phases, solid solution of the 2 oxides and gas, until all oxygen required by the reaction had been removed and pure cuprous oxide remained. If the temperature of the charge was held constant and successive quantities of oxygen were removed, the equilibrium pressure varied continuously from that of pure cupric oxide to that of pure cuprous oxide. The true dissociation pressure of cupric oxide was not determined directly by Wöhler, since some oxygen was always lost from the charge used, in order to fill the apparatus with oxygen at the pressure corresponding to the initial temperature of each experiment. The volume of the apparatus used is not given, nor are the successive quantities of oxygen removed in any experiment indicated and it is impossible to follow the composition of the solid phase. All the results are therefore qualitative. However, using the same apparatus, with varying charges and with removal of varying quantities of oxygen, different equilibrium pressures of oxygen were obtained at identical temperatures. There are given in Table I a few of the results, which are typical.

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[1] L. Wöhler. *Z. Eleckirochem.*, 12, 781 (1906).