

# SOLUTIONS OF SILICATES OF THE ALKALIES

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## INTRODUCTION

The electrical conductivity of solutions of sodium silicates has been investigated by F. Kohlrausch,<sup>1</sup> who worked mainly with the compounds corresponding to the formulæ  $\text{Na}_2\text{SiO}_3$  and  $\text{Na}_2\text{O} \cdot 3.4\text{SiO}_2$ , although he also tested the conductivity of solutions containing sodium hydroxide and silicic acid in other proportions varying from pure  $\text{NaOH}$  to the acid silicate just mentioned. Kohlrausch obtained the solution of the normal silicate by dissolving the crystallized salt ( $\text{Na}_2\text{SiO}_3 + 9\text{H}_2\text{O}$ ) in water while that of the acid silicate was prepared by boiling the solution of the normal salt with excess of silicic acid. By mixing sodium hydroxide with various quantities of the acid silicate, the other solutions mentioned were obtained. Kohlrausch found that a dilute solution of sodium silicate conducts electricity better than that of any other salt of equivalent concentration and concludes that this is due to the fact that in solution this salt suffers hydrolytic decomposition into sodium hydroxide and silicic acid. In concentrated solutions  $\text{Na}_2\text{SiO}_3$  was found to be a rather poor conductor. Dilute solutions of the acid silicate were also found to conduct well, while strong solutions showed an abnormally low conductivity. This behavior is also explained by the hydrolytic decomposition of the salt. Kohlrausch<sup>2</sup> appears to give this explanation in rather a tentative way, for, besides the fact that silicate solutions have an alkaline reaction and that the alkali they contain can be estimated by titrating with a normal acid, he had simply the results of conductivity determinations upon which to base his argument. No

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<sup>1</sup> Zeit. phys. Chem., **12**, 773 (1893).

<sup>2</sup> See paragraph 2, p. 773; also p. 778, loc. cit.

doubt the high conductivity of a solution of  $\text{Na}_2\text{SiO}_3$ , which, if the salt were supposed to dissociate into the ions  $2\text{Na}$  and  $\text{SiO}_3$ , would necessitate the assumption that the latter ion has a mobility exceeding that of the chlorine ion by about 70 percent, is an excellent reason for believing that the silicate is decomposed into  $\text{NaOH}$  and silicic acid and that the great conductivity of the solution is due to the presence of the mobile ion  $\text{OH}$ ; nevertheless a determination of the freezing-points of solutions of silicates together with conductivity investigations, would more definitely answer the question as to whether these compounds are hydrolytically decomposed, and would furthermore enable one to make a quantitative estimate of the extent of such decomposition. To determine the extent of the hydrolytic decomposition of the silicate from the electrical conductivity of its solution, is not possible, for the silicic acid split off exercises an unknown retarding influence on the movements of the ions. It is possible only to state as Kohlrausch does that in very dilute solutions the decomposition is very great and that probably even in strong solutions it is still appreciable. Colloidal silicic acid has but very little effect on the freezing-point, as is well known; indeed, in the case of a solution of sodium silicate the lowering of the freezing-point caused by the colloidal silicic acid present, is generally so small that for most purposes it may be left out of consideration. From this it is evident that from the lowering of the freezing-point of a silicate solution the extent of the hydrolytic decomposition of the salt may be calculated very approximately. The present investigation was undertaken in order to throw more light on the nature of silicates in solution; for this purpose the freezing-points and the electrical conductivity of solutions of various silicates were determined.

#### EXPERIMENTAL PART

The solutions that were investigated are those of the silicates of sodium, potassium, lithium, rubidium, and caesium. These solutions were in all cases prepared by adding to a solution of silicic acid, obtained by dialysis according to the well-known method of Graham,<sup>1</sup> the required amount of a standard solu-

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<sup>1</sup> Phil. Trans. Roy. Soc. London, 1861.

tion of the pure hydroxide of the alkali metal. That a solution of sodium silicate thus prepared is the same as that obtained by dissolving the salt, will be shown below. It is a well established fact that a solution of NaCl is the same as that obtained by mixing equivalent quantities of NaOH and HCl<sup>1</sup> and consequently it seemed at first unnecessary to prove that a solution of Na<sub>2</sub>SiO<sub>3</sub> is the same as a solution of equivalent amounts of silicic acid and caustic soda; but because in the case of silicate solutions equilibrium is established only after a measurable period of time<sup>2</sup> and because objections might possibly arise to using a colloidal solution of silicic acid in the preparation of silicate solutions and then finding that the latter contain colloidal silicic acid, it was thought best not to omit the experimental proof.

Dialyzed solutions of silicic acid were prepared using crystallized Na<sub>2</sub>SiO<sub>3</sub> · 9H<sub>2</sub>O and also commercial solutions of water-glass from different manufacturers. In each case the dialysis was carried on until no more chlorides were present in the solutions. No difference was found in the behavior of the solutions of the silicates prepared from the various colloidal silicic acid solutions thus obtained. The strength of the silicic acid solutions was determined by evaporating a measured quantity to dryness, igniting and weighing the SiO<sub>2</sub>; the purity of the latter was always established by finally volatilizing the same with hydrofluoric acid—no residue remained.

The solutions of the hydroxides of sodium and potassium were obtained by allowing the metals to act upon water freed from carbon dioxide. The hydroxides of lithium, rubidium and caesium were prepared by treating the sulphates of these metals with equivalent amounts of barium hydroxide. The strength of the solutions of these alkaline hydroxides was determined by comparison with a carefully standardized solution of hydrochloric acid.

The freezing-point determinations were made with the apparatus of Beckmann. The thermometer was graduated to hundredths of a degree and admitted of judging the thousandths

<sup>1</sup> Ostwald. *Zeit. phys. Chem.*, **2**, 80 (1888).

<sup>2</sup> Kohlrausch. *loc. cit.*, p. 783.

by use of a lens. The usual precautions<sup>1</sup> in making the freezing-point determinations were carefully observed.

The electrical conductivity was measured according to the method of Kohlrausch. In preparing the various solutions, water carefully freed from carbon dioxide and ammonium salts, was used. The water was first distilled from potassium bichromate plus sulphuric acid and then redistilled from barium hydroxide. A condenser of block tin was used; this was found to yield satisfactory results. The water thus obtained was carefully protected from the carbon dioxide of the air, and special precautions were taken in carrying out all the experiments to exclude the influence of carbon dioxide.

In preparing the silicate solutions the aim was to get fairly strong solutions with which to begin. In attempting this by the method of mixing caustic alkali with colloidal silicic acid some difficulty was encountered. The advantage of using this method of getting the solutions of the various silicates, is clearly that, by means of it, it is possible to more conveniently get the alkali and the silicic acid into solution in any desired proportions. The disadvantage is that very strong solutions cannot be thus prepared for the reason, that, when strong solutions of caustic alkali and silicic acid are mixed, the latter gelatinizes. Various attempts to get a solution of the normal silicates of sodium or potassium stronger than one-eighth of a gram-molecule per liter failed because the solutions gelatinized before the proper amount of alkali had been added. Still more difficulty was encountered in preparing the solution of the normal silicate of lithium. In this case a solution containing one thirty-second of a gram-molecule per liter was the strongest that could readily be obtained. In mixing the alkali with the silicic acid solution, it was found best to add the former to the latter gradually, always shaking the mixture and waiting until the precipitate that forms temporarily is completely dissolved before adding more alkali. It is best also to heat the silicic acid solution while the alkali is being added. The colloidal solution of silicic

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<sup>1</sup> See Ostwald's *Hand. u. Hilfsbuch*.

acid was slightly opalescent in appearance; the solutions of the silicates, however, were invariably perfectly clear.

Tables 1 to 9 give the results of the cryoscopic determinations. In the first column under  $v$  is given the volume in liters in which one gram-molecule of the salt expressed by the formula is contained. The second column gives the observed lowering of the freezing-point. In the third column are the molecular weights calculated on the supposition that the salt when in solution has the composition indicated by the formula. The fourth column gives the molecular weights calculated on the supposition that there is in the solution only the alkaline hydroxide; that is to say, in this calculation no account was taken of the silicic acid present. The solution of silicic acid that was used in preparing the silicate solutions according to the method above described contained 12.2180 grams  $\text{SiO}_2$  per liter and had a freezing-point of  $-0.018^\circ$ , which corresponds to the molecular weight 1019.

Table 1			
$\text{Na}_2\text{SiO}_3$	Mol. Wt. = 121.58		
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (NaOH)
8	0.695	41.3	27.0
12	0.498	38.4	25.2
16	0.385	37.3	24.4
24	0.280	34.2	23.9
32	0.210	34.0	22.4
48	0.150	31.9	20.9
64	0.110	32.6	21.4

( $\frac{1}{2}$  of 121.58 = 30.39)

( $\frac{1}{2}$  Mol. Wt. NaOH = 19.88)

$\text{Na}_2\text{SiO}_3$  (Obtained by fusion)

$v$	Freezing-point	Mol. Wt.
32	0.200	36.5
48	0.140	34.8
64	0.108	33.8
96	0.077	31.6

Table 2			
$\text{NaHSiO}_3$	Mol. Wt. = 99.7		
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (NaOH)
8	0.332	70.9	31.0
12	0.263	59.7	26.1
16	0.202	58.3	25.5
24	0.146	53.7	23.5
32	0.110	53.5	23.4

( $\frac{1}{2}$  of 99.7 = 49.85)

Table 3			
$\text{Na}_2\text{Si}_2\text{O}_7$	Mol. Wt. = 361.34		
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (NaOH)
32	0.178	119.9	27.0
48	0.139	102.4	23.1
64	0.104	100.3	22.6
96	0.089	79.9	18.0
128	0.059	90.4	20.4

( $\frac{1}{4}$  of 361.34 = 90.33)

Table 4

$K_2SiO_3$ Mol. Wt. = 153.46			
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (KOH)
8	0.710	51.1	37.1
12	0.503	48.1	34.9
16	0.394	45.4	32.9
24	0.279	43.5	31.4
32	0.215	42.2	30.6
48	0.146	41.4	30.0
64	0.110	41.2	29.9
96	0.082	36.8	26.7

( $\frac{1}{4}$  of 153.46 = 38.36)

( $\frac{1}{2}$  Mol. Wt. KOH = 27.85)

Table 5

$KHSiO_3$ Mol. Wt. = 115.64			
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (KOH)
8	0.326	83.8	40.4
12	0.248	73.4	35.4
16	0.196	69.7	33.6
24	0.153	59.5	28.7
32	0.110	62.1	29.9
48	0.078	58.4	28.1

( $\frac{1}{2}$  of 115.64 = 57.82)

Table 6

$Li_2SiO_3$ Mol. Wt. = 89.76			
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (LiOH)
32	0.228	23.3	12.4
48	0.166	21.2	11.3
64	0.120	22.1	10.4
96	0.090	19.6	10.4
128	0.071	18.5	9.9

( $\frac{1}{4}$  of 89.76 = 22.88)

( $\frac{1}{2}$  Mol. Wt. LiOH = 11.92)

Table 7

$Li_2Si_3O_{11}$ Mol. Wt. = 329.52			
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (LiOH)
32	0.172	113.2	16.4
48	0.139	93.3	13.5
64	0.112	86.9	12.6
96	0.077	84.3	12.2
128	0.062	78.5	11.4

( $\frac{1}{4}$  of 329.52 = 82.38)

Table 8

$Rb_2SiO_3$ Mol. Wt. = 245.38			
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (RbOH)
64	0.139	52.1	43.2
96	0.098	49.3	40.9

( $\frac{1}{4}$  of 245.38 = 61.34)

( $\frac{1}{2}$  Mol. Wt. RbOH = 50.83)

Table 9

$Cs_2SiO_3$ Mol. Wt. = 339.60			
$v$	Freezing-point	Mol. Wt.	Mol. Wt. (CsOH)
64	0.102	98.3	86.1
96	0.068	98.3	86.0

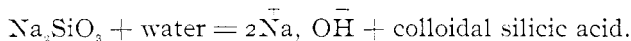
( $\frac{1}{4}$  of 339.60 = 84.9)

( $\frac{1}{2}$  Mol. Wt. CsOH = 74.38)

The first part of table 1 gives the results obtained from freezing solutions of  $Na_2SiO_3$  prepared by mixing solutions of silicic acid with caustic soda as above described; the second part gives the results obtained from freezing solutions of  $Na_2SiO_3$

prepared by dissolving the salt obtained by fusing the alkali and the acid together. It will be observed that the freezing-points of the corresponding dilutions agree fairly well and justify the conclusion that the solutions are identical. The fact that the depressions in the second series are not quite as large as those in the first, is very likely due to the slight formation of carbonates in case of the salt obtained by fusion, for in the process of fusing it is especially difficult to exclude the influence of carbon dioxide. Tests of the electrical conductivity of the solutions obtained in these two different ways also pointed to the fact that they are identical. The salt obtained by fusion of course had a slightly lower conductivity for the same reason that its solution possessed a slightly higher freezing-point.

Table I shows that the molecular weights calculated on the assumption that the substance in solution has the formula  $\text{Na}_2\text{SiO}_3$  approach as their limit the value of one-fourth the calculated molecular weight of  $\text{Na}_2\text{SiO}_3$ . There are then in the dilute solutions four part-molecules active in lowering the freezing-point. The action of water on the silicate may be expressed by the equation

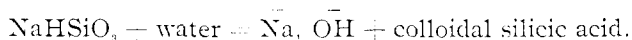


The four part-molecules that are active in lowering the freezing-points are thus two sodium ions and two hydroxyl ions. As stated above the effect of the colloidal silicic acid on the freezing-point can, at least for the more dilute solutions investigated, be considered too small to take into account. The results show that this hydrolytic decomposition is nearly complete for the concentration  $v = 48$ , and that it has progressed to the extent of 64.8 percent<sup>1</sup> even when  $v = 8$ . The last column of the table giving the molecular weights calculated on the assumption that there is only NaOH in the solution, confirms in a striking manner what has just been said. These results approach as their limiting value one-half the molecular weight of NaOH. This

<sup>1</sup> This calculation as well as the similar ones that follow has been made on the supposition that the caustic alkali present in the solution has suffered practically complete electrolytic dissociation.

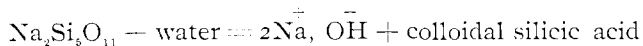
is what would be expected since this compound dissociates into the ions Na and OH.

The investigations of solutions containing  $\text{NaHSiO}_3$  yielded the results in table 2. Here the molecular weights calculated from the observed lowerings on the assumption that the dissolved substance is  $\text{NaHSiO}_3$  give values that approach as their limit one-half of the molecular weight of  $\text{NaHSiO}_3$ . This shows that in the dilute solutions there are two part-molecules active in lowering the freezing-point; these are sodium and hydroxyl ions as before. The equation expressing the action of water on  $\text{NaHSiO}_3$  may be written



This decomposition is nearly complete at the same concentration as that of  $\text{Na}_2\text{SiO}_3$ , and even when  $v = 8$  it has progressed to the extent of 40.7 percent. As in the case of table 1, the values in the last column (obtained on the supposition that the solution is simply one of NaOH) approach the limit of one-half the molecular weight of NaOH.

Table 3 gives the results obtained by freezing solutions of the more acid silicate  $\text{Na}_2\text{Si}_5\text{O}_{11}$ . This salt was selected because a lithium silicate of analogous formula occurs in nature. The molecular weights in the third column approach as a limit the value of one-fourth the molecular weight of  $\text{Na}_2\text{Si}_5\text{O}_{11}$ .<sup>1</sup> Here again then there are four part-molecules active in lowering the freezing-point. The equation



expresses the hydrolytic decomposition that takes place. This decomposition is practically complete at  $v = 128$  and has gone on to the extent of 67.3 percent even when  $v = 32$ . In the fourth column the molecular weights calculated on the basis that there is only NaOH in solution again approach as a limit the value of one-half of the molecular weight of NaOH. This salt then behaves very much like those of tables 1 and 2 except that the

<sup>1</sup> The small molecular weight found corresponding to the concentration  $v = 96$  is no doubt due to experimental error.

hydrolytic decomposition is not as far advanced at the same stage of dilution. This is to be expected from the law of mass action. For a like reason  $\text{NaHSiO}_3$  is not quite as far dissociated hydrolytically at the same degree of dilution as  $\text{Na}_2\text{SiO}_3$ , though here the difference is less since the amount of silicic acid present has only been doubled, while in the salt  $\text{Na}_2\text{Si}_5\text{O}_{11}$  there is five times as much acid (to the same amount of sodium) as is contained in the normal salt.

Tables 4 and 5 show the behavior of solutions of  $\text{K}_2\text{SiO}_3$  and  $\text{KHSiO}_3$  respectively. What has been said of the sodium compounds applies also to these salts. The action of water on these silicates may be expressed by analogous equations. At  $\tau = 8$  the normal salt is dissociated 66.9 percent and the acid salt 39 percent. In both cases the dissociation is practically complete at  $\tau = 48$ .

The lithium silicates investigated yielded the figures in tables 6 and 7. The normal salt is decomposed to the extent of 95.5 percent at  $\tau = 32$ , while at  $\tau = 48$  the decomposition is practically complete as in the case of the analogous sodium and potassium salts. The salt  $\text{Li}_2\text{Si}_5\text{O}_{11}$  is hydrolytically dissociated 67.7 percent and this decomposition is practically complete at  $\tau = 128$ . The behavior of the lithium salts then is perfectly analogous to that of the potassium and sodium salts.

The determinations made with rubidium and caesium silicates are given in tables 8 and 9. The quantities of these alkalies that were available were small and hence but few determinations were made. A glance at the results shows that these silicates behave like those of the other alkalies. The solutions investigated were quite dilute and in them, as the results show, the hydrolytic decomposition had gone on very far. The lowerings obtained with the rubidium salt are greater than they ought to be theoretically. This is probably due to the fact that the rubidium salt, from which the hydroxide of rubidium that was used was prepared, contained some sodium. As the quantity of rubidium salt available was small a special analysis to ascertain the amount of sodium present was not made.

The results of the determinations of the electrical con-

ductivity of the solutions are contained in tables 10 and 11. The former table contains the conductivity of solutions of the free alkalis at 25° C. It was necessary to make these determinations, for the conductivity of solutions of the alkaline hydroxides at 25° C. could not be found in the literature, and only by comparing the conductivity of solutions of the alkaline silicates with that of solutions of the free alkalis, can an idea of the extent of the retarding influence that the colloidal silicic acid has on the movements of the ions, be gained.

Kohlrausch<sup>1</sup> noticed that on diluting silicate solutions the conductivity changed for a time and finally became constant. The time of this variation and the degree of the latter depended of course on the conditions of experiment. Kohlrausch investigated this time factor as well as the variation of the conductivity of sodium silicate solutions with the temperature. He found that in some cases equilibrium was established in the solution in a few minutes, in others it took five hours or more. The time effects studied by Kohlrausch were also observed by us and on the whole we were able to confirm his experiments as far as we went. It was not the purpose of this investigation, however, to study this time effect further, and for this reason the conductivity of the solutions was determined only after equilibrium had become established in them. The strongest silicate solution was prepared as already described, then the various dilutions ( $v = 16$  to 1024) were prepared in thoroughly cleaned and steamed flasks, which were kept tightly corked. The dilutions were made by means of carefully calibrated pipettes. At the end of five to six hours (when equilibrium had practically become established) the contents of the various flasks were quickly transferred to the resistance cell and the conductivity determined.

In tables 10 and 11  $v$  denotes the volume in liters in which one gram-equivalent of the compound indicated by the formula is contained, and  $\lambda$  denotes the equivalent conductivity expressed as usual in mercury units.

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<sup>1</sup> Loc. cit.

Table 10

$\tau$	NaOH $\lambda$	KOH $\lambda$	LiOH $\lambda$	$\tau$	NaOH $\lambda$	KOH $\lambda$	LiOH $\lambda$
1	157.5	....	....	64	199.1	220.4	189.2
2	181.2	196.7	157.6	128	199.0	218.4	189.2
4	188.1	207.2	171.0	256	196.3	215.0	184.0
8	194.7	213.1	179.2	512	188.9	208.0	174.9
16	197.4	216.7	185.9	1024	181.8	201.4	170.0
32	199.0	219.1	189.3				

(The water used had a specific conductivity of  $1.7 \times 10^{-6}$ . This has not been deducted in the above table.)

Table 11

$\tau$	$\text{Na}_2\text{SiO}_3$ $\lambda$	$\text{NaHSiO}_3$ $\lambda$	$\text{Na}_2\text{Si}_3\text{O}_{11}$ $\lambda$	$\text{K}_2\text{SiO}_3$ $\lambda$	$\text{KHSiO}_3$ $\lambda$	$\text{Li}_2\text{SiO}_3$ $\lambda$	$\text{Li}_2\text{Si}_3\text{O}_{11}$ $\lambda$
8	105.3	72.4	....	....	87.3	....	....
16	112.0	78.8	....	130.9	110.3	....	....
32	117.8	84.9	73.0	176.4	117.6	125.0	55.4
64	115.0	90.1	79.9	182.6	126.2	126.0	61.6
128	119.5	103.7	87.3	185.5	133.4	129.2	67.5
256	95.7	114.2	93.1	187.1	141.7	130.2	72.6
512	91.8	133.1	101.1	191.8	155.9	138.5	78.9
1024	104.8	148.5	113.3	182.5	175.6	145.2	90.6

(The conductivity of the water which was  $1 \times 10^{-6}$  has been deducted in each case.)

It will be observed that in table 10 the values for  $\lambda$  increase as  $\tau$  increases until they reach a maximum after which they decrease. This behavior of the alkaline hydroxide is well known and is to be ascribed to impurities in the water. Table 11 shows that in case of the normal silicates of sodium and potassium the values for  $\lambda$  also pass through a maximum. In case of the acid silicates of sodium and potassium and those of lithium the values for  $\lambda$  do not pass through a maximum. It will be noted that the conductivity of the normal salts is uniformly greater than that of the acid salts of the same metal. The values of  $\lambda$  for  $\tau = 256$  to 1024 in the case of  $\text{Na}_2\text{SiO}_3$  are less than those for the acid silicates at the same concentrations; this, however, is undoubtedly due to experimental error. A redetermination of  $\lambda$

for these concentrations was contemplated, but was not carried out, as it is especially difficult to get a mixture of the silicic acid solution and caustic soda in the proportions required by the formula  $\text{Na}_2\text{SiO}_3$ , owing to the fact that the mixture gelatinizes just before the entire quantity of alkali has been added.

By comparing the values for  $\lambda$  in table 10 with those of the salt of the corresponding metal in table 11, the effect of the presence of the silicic acid on the conductivity may be seen. It will be observed that even in the most dilute solutions of the normal salts the values for  $\lambda$  still fall considerably short of equalling those of the hydroxides. The values of  $\lambda$  in table 10 pass through their maximum at about  $v = 32$  to  $64$ ; at this concentration then the hydroxides are practically completely dissociated. It will be recalled that from the cryoscopic determinations on the normal silicate solutions it was inferred that in the latter hydrolytic decomposition is practically complete at  $v = 48$ . Although the errors of measurement in the freezing-point determinations are greater than in the measurement of the electrical conductivity, yet it would appear safe to say that the increase in the value of  $\lambda$  for the silicate solutions beyond  $v = 64$ , is mainly due to a decrease of the retarding influence of the silicic acid on the movements of the ions.

The conductivity of solutions of caesium and rubidium silicates was also determined. Unfortunately the water used in making the dilutions had become contaminated, a fact which was later discovered, and hence the figures obtained are not given here. It may be stated, however, that the figures obtained showed beyond any reasonable doubt that the silicates of these alkalies behave in a manner entirely analogous to that of the silicates of the other alkalies.

### SUMMARY OF RESULTS AND GENERAL REMARKS

The results of the foregoing investigation may be briefly summarized as follows:—

1. The conclusion of F. Kohlrausch that in solutions of sodium silicates these salts are hydrolytically decomposed into

sodium hydroxide and colloidal silicic acid, has been confirmed by investigating the freezing-points of such solutions.

2. The freezing-points and the electrical conductivity of solutions of the silicates of potassium, lithium, rubidium, and caesium, show that these salts are also decomposed by water into the colloidal silicic acid and the hydroxide of the alkali metal. The silicates of the alkalies all show an analogous behavior when dissolved in water.

3. The same solution results whether a silicate is dissolved in water or whether solutions of caustic alkali and colloidal silicic acid in proper proportions are mixed.

4. Since colloidal silicic acid has but little effect on the freezing-point the degree of hydrolytic decomposition of the silicates can be calculated from the lowering of the freezing-point of their solutions.

5. Silicates of the general formulæ  $M_2SiO_3$  and  $MHSiO_3$  are practically completely hydrolytically dissociated when one gram-molecule is contained in 48 liters. Silicates of the general formula  $M_3Si_5O_{11}$  are practically completely decomposed by water when one gram-molecule is present in 128 liters.

6. A comparison of the electrical conductivity of silicate solutions with that of solutions of the alkaline hydroxides, shows that the values of the former approach the latter as the solutions become more dilute, the retarding influence that the silicic acid has on the mobility of the ions gradually becoming less.

The conclusions here arrived at are of general interest inasmuch as silicates occur in greater or less quantities in almost all natural waters. If the silicates of the alkalies are so easily decomposed by water, how much more readily would silicates of the alkaline earths and the heavier metals be hydrolytically decomposed, especially since solutions of these salts are always exceedingly dilute because the compounds are so difficultly soluble.

Of the waters of 859 springs in various parts of the United States<sup>1</sup> the one that contains the most silica is that of the Deep Rock Mineral Spring at Oswego, N. Y. According to an analy-

<sup>1</sup> See Bull. U. S. Geol. Survey, **32**, 35 (1886).

sis made in 1871 by S. H. Douglas it contains the molecular weight of  $\text{SiO}_2$  in grams in 48.84 liters.<sup>1</sup> Next to this is Opal Spring in Yellowstone National Park in the Gibson Geyser Basin, for according to an analysis made by Henry Leffmann in 1882, its water contains one gram-molecule  $\text{SiO}_2$  in 65.15 liters. The analyses of the other 857 springs show that the waters of but three of them contain over one gram-molecule  $\text{SiO}_2$  in 140 liters and only fourteen others contain more than a gram-molecule in 350 liters. The waters of the remaining 840 springs contain much smaller amounts of silica, usually less than one gram-molecule in 3500 liters.

Justus Roth's<sup>2</sup> compilation of the analyses of river waters from different parts of the globe (chiefly European, however) shows that the largest amount of silica was found in the water of the Rhine. A sample taken near Strassburg contained one gram-molecule  $\text{SiO}_2$  in 1250 liters. According to the same authority the Atlantic Ocean contains one gram-molecule  $\text{SiO}_2$  in 531 liters. Of the many analyses of the waters of springs of various kinds located in different parts of the globe that have been collected by Roth, none show a greater content of silica than one gram-molecule in 80 liters and of course most of them very much less.

In the face of these facts and the results of the above investigations it appears safe to say that in natural waters silicic acid always occurs in the colloidal state; only in very rare instances are the solutions of the silicates so concentrated that they are not practically completely hydrolytically decomposed. This conclusion will no doubt be of value to the mineralogist and geologist in explaining the formation of various siliceous deposits and the alterations produced in rocks by the action of water. It might also prove to be of value to the plant physiologist in explaining how plants take up various constituents from the soil.

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<sup>1</sup> It seems almost that the figures in the report must be a misprint.

<sup>2</sup> Allgemeine u. chemische Geologie, Vol. I.