Art. III.—*Waterglass;* by John M. Ordway.

[Continued from p. 354, vol. xxxii.]

Part III.

Its Precipitation by Alcohol.

Among the few chemists who have made experiments on the precipitation of waterglass by alcohol, no one seems to have distinctly apprehended the fact that the spirit always effects a partial decomposition of the silicate. Fuchs says, in his first me-

[* The authority for the Newfoundland habitat is mentioned in vol. xxxii, p. 290, of this Journal. That *Calluna* also inhabits Nova Scotia is stated by Loudon, in his Arboretum, we know not upon what authority, but should be glad to be informed. If the claim for *Calluna* to be regarded as an American plant rested wholly or mainly upon this Tewkesbury locality, it would not gain acceptance. But its existence in Newfoundland, and still more in Nova Scotia (if verified) does away with all antecedent improbability of its indigenous occurrence in New England.—Eds.]

moir, that alcohol throws down potash waterglass unchanged.* In his later work he mentions that the supernatant liquor retains the undecomposed carbonate of potash, together with traces of sulphid of potassium, chlorid of potassium, and chlorid of sodium, but evidently looks upon the silicate deposited as having been merely stripped of these foreign salts and of the greater part of its water.

Forchhammer did indeed observe that, in one or two instances, "alcohol by precipitation and subsequent washing, removes from waterglass a part of its potash."† But in several other experiments detailed by him, he fails to notice the possible intervention of the same decomposing power, and seems to consider the precipitates as salts of precise and unvarying constitution. He accordingly enumerates the known silicates of potash as follows: "1. The salt formed by H. Rose, by melting together silica and carbonate of potash,—$\dot{K}_3 \ddot{S}i_2$. 2. The salt precipitated by alcohol from a solution containing an excess of potash,—$\dot{K}_3 \ddot{S}i_4$. 3. The waterglass discovered by Fuchs,—$\dot{K}_3 \ddot{S}i_8$. 4. The salt precipitated" [from Fuchs's waterglass] "with spirit of wine and washed with alcohol," [till the spirit no longer showed a decided alkaline reaction]—"$\dot{K}_3 \ddot{S}i_{16}$. 5. The salt separated from the former by washing" [with boiling water, which dissolved out $\dot{K}_3 \ddot{S}i_6$]—"$\dot{K} \ddot{S}i_{12}$. 6. The salt which separates by the cooling of a concentrated solution of silica and carbonate of potash,—$\dot{K} \ddot{S}i_{16}$."

He also determined the formula of soda silicate to be $\dot{N}a \ddot{S}i_2$,—as though there could be but one soda waterglass,—and found the precipitate from a cooling solution of silica in carbonate of soda, to consist of $\dot{N}a \ddot{S}i_{24}$.

Perhaps none of the substances in the list thus given, can properly claim anything more than an accidental existence. As to the products of fusion, it is well known that silica and carbonate of potash may, within certain limits, be melted together in any proportion. And we shall proceed to show by examples selected from a large number of trials, that the variety of combinations which may be thrown down by alcohol, is also unlimited.

There are two obvious methods of prosecuting the subject. The first is to make fractional precipitations from one and the same given silicate solution. The other is to redissolve and reprecipitate *ad libitum*, the successive products of integral precipitation. Sometimes one mode has been followed, sometimes the other, and sometimes both plans have been united.

* "Der Weingeist präcipitirt und scheidet es unverändert aus einer Anflösung ab." "Dieses Mittels kann man sich bedienen, um reines Wasserglas aus einer unreinen Auflösung darzustellen."—*Ueber ein neues nutzbares Produkt aus Kieselerde und Kali.*"—pp. 15, 16.

† *Poggendorff's Annalen*, xxxv, p. 340.

After having made many preliminary experiments on precipitation, I found that all the samples of commercial alcohol to be had, contained traces of acid. This possible source of infinitesimal error had therefore to be removed, and for the trials subsequently made, the spirit was purified by agitating it with caustic soda and redistilling.

In examining the various precipitates obtained, extreme accuracy would have involved an unwarranted waste of time; and there being scores of analyses to make, it was necessary to adopt modes which should be expeditious and without pretending to give figures absolutely exact, might still afford close approximations to the truth. The alkali was generally determined by saturation with a standard sulphuric acid. The neutralized liquor being then dried down in an oven, the silica was washed, ignited and weighed. For a partial control, in most instances, the whole amount of solid matter was ascertained by dissolving some of the silicate in a little water, adding freshly ignited sulphate of lime, and drying the coagulated mass by a heat gradually raised to dull redness. This method of expelling the water is, however, inapplicable when the silicate is excessively alkaline, as in such cases carbonic acid is absorbed from the hot gases of the flame rising round the crucible.

To facilitate comparison, the respective amounts of acid and base are expressed in equivalents instead of unmeaning percentages.

Sesquisilicate of Potash,—with Alcohol of sp. gr. 0·842.

1.—100 parts by weight, of a liquid containing 48 per cent of $\dot{K}_{100}\bar{S}i_{150}$,—with 38 parts by weight, of alcohol,—gave 81·25 parts of a liquid precipitate differing little from the original solution.

2.—100 pts. of a 25 p. c. solution,—with 41 of alcohol,—gave 44·8 pts. of a liquid precipitate containing 49 p. c. of $\dot{K}_{100}\bar{S}i_{162}$.

3.—100 pts. of a 17·3 p. c. solution,—with 40 of alcohol,—gave 23·2 pts. of a liquid precipitate containing 49·6 p. c. of $\dot{K}_{100}\bar{S}i_{163}$.

4.—100 pts. of a 9·3 p. c. solution,—with 39 of alcohol,—gave 4·2 pts. of a solid precipitate not entirely soluble in boiling water, and containing, besides alumina and oxyd of iron, 39 p. c. of $\dot{K}_{100}\bar{S}i_{125}$.

5, *a*.—100 pts. of a 4·8 p. c. solution,—with 40 of alcohol,—gave 0·9 pts. of an insoluble, pulverulent precipitate containing some alumina and oxyd of iron and 70 p. c. of $\dot{K}_{100}\bar{S}i_{226}$.

5, *b*.—The supernatant liquor of *a*,—with a further portion of alcohol,—gave 3·6 pts. of a hard, coherent precipitate soluble in water and containing 54 p. c. of $\dot{K}_{100}\bar{S}i_{185}$.

Bisilicate of Potash,—with Alcohol of sp. gr. 0·824.

6, *a*.—100 pts. of a crude solution containing 10 p. c. of $\dot{K}_{100}\bar{S}i_{188}$,—with 10 of alcohol,—gave 2·13 pts. of a hard precipitate which was not analyzed.

6, *b*.—94 pts. of the supernatant liquor of *a*,—with 19 of alcohol,—gave 10·3 pts. of a hard, soluble precipitate containing 52 p. c. of $\dot{K}_{100}\,\ddot{S}i_{210}$.

6, *c*.—100 pts. of the supernatant liquor of *b*,—with 20 of alcohol,—gave 2·13 pts. of a soft precipitate containing 54 p. c. of $\dot{K}_{100}\,\ddot{S}i_{180}$.

7, *a*.—100 pts. of a solution made from the product of 6, *b*, and containing 10 p. c. of $\dot{K}_{100}\,\ddot{S}i_{210}$,—with 10 pts. of alcohol,—gave 0·6 pts. of a solid precipitate which was not analyzed.

7, *b*.—102 pts. of the supernatant liquor of *a*,—with 20 of alcohol,—gave 12·8 pts. of a hard, soluble precipitate containing 53 p. c. of $\dot{K}_{100}\,\ddot{S}i_{239}$.

8, *a*.—100 pts. of a solution made from the product of 7, *b*,—and containing 10 p. c. of $\dot{K}_{100}\,\ddot{S}i_{239}$,—with 8 of alcohol,—gave 0·55 parts of a precipitate which was not analyzed.

8, *b*.—97 pts. of the supernatant liquor of *a*,—with 17 of alcohol,—gave 12·2 pts. of a hard, soluble precipitate—containing 53 p. c. of $\dot{K}_{100}\,\ddot{S}i_{270}$.

9.—100 pts. of a solution made from the product of 8, *b*, so as to contain 10 p. c. of $\dot{K}_{100}\,\ddot{S}i_{270}$,—with 25 of alcohol,—gave a very hard precipitate containing 49 p. c. of $\dot{K}_{100}\,\ddot{S}i_{313}$.

This substance, while new, dissolved completely in cold water, yielding a perfectly clear solution; but exposure to the air for several days, rendered the superficial portions insoluble.

Sesquisilicate of Soda mixed with Caustic Soda,—with Alcohol af sp. gr. 0·825.

10.—100 pts. of a mixture made to contain 18 p. c. of $\dot{N}a'_{100}\,\ddot{S}i_{33}$.—with 32 of alcohol,—gave 61·3 pts. of a very thin precipitate containing 24 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{43}$.

This precipitate,—as well as the four following,—retained the coloring matter and a part of the foreign salts which were present in the crude solutions used.

11.—100 pts. of a mixture containing 20 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{40}$,—with 36 of alcohol,—gave 64·3 pts. of a thin precipitate containing 25 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{50}$.

A 22 p. c. caustic soda solution is itself thrown down by alcohol; but that no such complication could occur with the weaker liquors used in this experiment and the preceding, was proved by a special trial with the omission of the silicate. 100 pts. of a solution containing 14·5 p. c. of NaO, was mixed with 38 pts. of alcohol. There was no precipitate; and even 81 pts. of alcohol caused no change.

12, *a*.—100 pts. of a mixture containing 10 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{40}$,—with 30 of alcohol,—gave 11·8 pts. of a thin precipitate containing 32·6 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{89}$.

12, *b*.—The supernatant liquor of *a*,—with 20 pts. of alcohol,—gave 5·3 pts. of a precipitate containing 34 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{78}$.

13.—100 pts. of a mixture containing 9 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{70}$,—with 26 of alcohol,—gave 15·4 pts. of a liquid precipitate containing 37 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{110}$.

Monosilicate of Soda—with Alcohol of sp. gr. 0·840.

14.—100 pts. of a solution containing 4·2 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{105}$,—with 40 of alcohol,—gave 5 pts. of a liquid precipitate containing 42 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{150}$.

15, *a*.—100 pts. of a solution containing 5 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{105}$,—with 20 of alcohol,—gave 2·16 pts. of a flocculent, insoluble precipitate, containing, besides earthy matters, 18 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{241}$.

15, *b*.—108 pts. of the supernatant liquor of *a*,—with 21 of alcohol,—gave 6·3 pts. of a liquid precipitate containing 41·5 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{138}$.

Sesquisilicate of Soda,—with Alcohol of sp. gr. 0·840.

16.—100 pts. of a solution containing 23 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{153}$,—with 40 of alcohol,—gave 42·5 pts. of a liquid precipitate containing 46 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{160}$.

17.—100 pts. of a solution containing 4·6 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{153}$,—with 40 of alcohol,—gave 4·4 pts. of a soft precipitate containing 48 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{192}$.

Sesquisilicate of Soda,—with Alcohol of sp. gr. 0·870.

18, *a*.—100 pts. of a clear crude waterglass solution containing 14 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{148}$,—with 10 of alcohol,—gave a bluish gray precipitate in which there were 4 pts. of mother liquor and 0·5 pts. of $\dot{C}a\,\dot{F}e_3\,\ddot{A}l_4\,\dot{N}a_{28}\,\ddot{S}i_{42}$.

a'.—104 pts. of the filtrate of *a*,—with 25 of alcohol,—gave 28·2 pts. of a thin liquid precipitate containing 42·3 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{153}$.

b.—111 pts. of a solution made from the product of *a'*, and containing 10·5 p. c of $\dot{N}a_{100}\,\ddot{S}i_{153}$,—with 10 of alcohol,—gave a white precipitate in which there were 2·6 pts. of mother liquor and 0·45 pts. of $\ddot{A}l_4\,\dot{N}a_5\,\ddot{S}i_{22}$ with traces of lime and iron.

b'.—119 pts. of the filtrate of *b*,—with 33 of alcohol,—gave 19·4 pts. of a liquid product containing 45·4 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{165}$.

c.—75 pts. of a solution made from the product of *b'*, and containing 11·3 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{165}$,—with 9 of alcohol,—gave, after standing some hours, a very white precipitate in which there were 0·519 pts. of mother liquor and 0·11 pts. of $\ddot{A}l\,\dot{N}a_4\,\ddot{S}i_8$ with a trace of lime.

c'.—83 pts. of the filtrate of *c*,—with 20·5 of alcohol,—gave 12·75 pts. of a thick liquid product containing 51·4 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{178}$.

This precipitate was free from chlorid and showed but a very faint trace of sulphate, while the original solution used in *a*, contained 0·7 p. c. of dry sulphate and 1·4 p. c. of chlorid of sodium.

d.—49 pts. of a solution made from the product of *c'*, and containing 12·85 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{178}$,—with 5 of alcohol,—gave at once a slight white precipitate in which there were 0·327 pts. of mother liquor and 0·038 pts. of $\ddot{A}l_2\,\dot{N}a_{11}\,\ddot{S}i_{33}$ with a slight trace of lime.

d'.—53 pts. of the filtrate of *d*,—with 16 of alcohol,—afforded 12 pts. of a soft solid product containing 43·6 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{185}$.

e.—46·5 pts. of a solution made from the product of *d'*, and containing 11 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{185}$,—with 16 of alcohol,—gave 9·5 pts. of a solid product containing 45·5 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{211}$.

Sesquisilicate of Soda and Nitric Acid,—with Alcohol of sp. gr. 0·849.

20.—59 pts. of a solution containing 19 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{148}$, were mixed with 41 pts. of 5 p. c. nitric acid so as to neutralize one third of the alkali. Before any farther change ensued, 23 pts. of alcohol were added. The hard, soluble deposit amounted to 20·4 pts.

This was subjected to three purifying fractional precipitations,—as in 19,—and two subsequent integral precipitations, and finally yielded three parts of a very hard product which afforded a clear solution with four times its weight of cold water,—all being taken up except a thin external film of silica. The clear liquor gave with chlorhydric acid 10·161 p. c. of silica and 4·504 p. c. of chlorid of sodium, indicating 62·2 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{302}$ in the final precipitate.

In rendering waterglass more silicious by a partial neutralization of the base, it is necessary to precipitate with alcohol very soon after the addition of the dilute acid; otherwise, under the influence of the neutral salt formed, the silicate gradually undergoes a change of state and finally gelatinizes. Nitric acid is peculiarly suitable for withdrawing the alkali, because the nitrates have less modifying power than most other salts.

7 : 4 *Silicate of Soda,—with Alcohol of sp. gr.* 0·842.

21, *a*.—100 pts. of a solution containing 9·3 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{175}$,—with 10 of alcohol,—gave 4·55 pts. of a flocculent soluble precipitate containing 45 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{263}$.

b.—99 parts of the supernatant liquor of *a*,—with 10 of alcohol,—gave 8 pts. of a hard precipitate containing 50·5 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{217}$.

c.—100 pts. of the supernatant liquor of *b*,—with 10 of alcohol,—gave 2·24 pts. of a soft precipitate containing 50 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{194}$.

d.—105 pts. of the supernatant liquor of *c*,—with 20 of alcohol,—gave 0·67 pts. of a very soft precipitate containing 57 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{160}$.

e.—123 pts. of the supernatant liquor of *d*,—with 24 of alcohol,—gave 0·76 pts. of a liquid precipitate containing 52 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{154}$.
The remaining alcoholic liquor contained 0·5 pts. of $\dot{N}a_{100}\,\ddot{S}i_{12}$.

Bisilicate of Soda,—with Alcohol of sp. gr. 0·824.

22, *a*.—100 pts. of a solution containing 10 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{191}$,—with 7 of alcohol,—gave 0·5 pts. of a hard precipitate insoluble in water.

b.—102 pts. of the supernatant liquor of *a*,—with 10 of alcohol,—gave 12·8 pts. of a hard, soluble precipitate containing 47·4 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{231}$.

c.—98 pts. of the supernatant liquor of *b*,—with 10 of alcohol,—gave 2·75 pts. of a soft precipitate containing 47·4 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{185}$.

23, *a*.—100 pts. of a solution made from 22 *b*, and containing 10 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{123}$,—with 7 of alcohol, gave 1·7 pts. of an insoluble precipitate containing, besides earthy matter, 73 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{279}$.

b.—95 pts. of the supernatant liquor of *a*,—with 9 of alcohol—gave 11·2 pts. of a hard, soluble precipitate containing 42 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{255}$.

c.—83 pts. of the supernatant liquor of *b*,—with 9 of alcohol,—gave 2·1 pts. of a soft precipitate containing 65 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{220}$.

d.—The supernatant liquor of *c*,—with 9 pts. of alcohol,—gave 0·7 pts. of a soft precipitate containing 48·5 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{200}$.

24.—100 pts. of a solution made from 23 *b*, and containing 10 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{235}$,—with 20 of alcohol,—gave 16·5 pts. of a soluble precipitate containing 44 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{290}$.

Bisilicate of Soda,—with Alcohol of sp. gr. 0·840.

25.—100 pts. of a solution containing 1 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{214}$,—with 50 of alcohol,—gave a slight, insoluble, pulverulent precipitate containing $\dot{N}a_{100}\,\ddot{S}i_{414}$.

26.—100 pts. of a solution containing 1·9 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{214}$,—with 40 of alcohol,—gave 1·1 pts. of a hard precipitate containing earthy matters and $\dot{N}a_{100}\,\ddot{S}i_{478}$. Out of this boiling water dissolved nearly all the soda and one fourth of the silica.

27.—100 pts. of a solution containing 3·45 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{214}$,—with 40 of alcohol,—gave 4·6 pts. of a hard precipitate, soluble in cold water, and containing 51 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{237}$.

28.—100 pts. of a solution containing 34·5 p. c. of $\dot{N}a_{103}\,\ddot{S}i_{214}$,—with 40 of alcohol,—gave 63·5 pts. of a hard precipitate containing 52 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{217}$.

Ferruginous Silicate of Soda,—with Alcohol of sp. gr. 0·824.

29, *a*.—Into 40 pts. of a solution containing 23·5 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{169}$ were stirred 60 pts. of a solution containing 1·1 p. c. of dry protosulphate of iron. The protoxyd of iron was almost entirely taken up. The filtered liquor was perfectly transparent and of a very deep blue black color.

98 pts. of this filtrate,—with 10 of alcohol,—gave 4·7 pts. of a blue gray precipitate containing, besides the silicate of the mother liquor soaked up, 41·7 p. c. of $\dot{F}e_4\,\dot{N}a_6\,\ddot{S}i_{15}$.

b.—80 pts. of the colorless supernatant liquor of *a*,—with 11 of alcohol,—gave 7 pts. of a soft, soluble precipitate containing 45 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{191}$.

c.—84 pts. of a supernatant liquor of *b*,—with 21 of alcohol,—gave 3·5 pts. of a very soft precipitate free from iron, and containing 47 p. c. of $\dot{N}a_{100}\,\ddot{S}i_{173}$.

In investigating the nature of alkaline silicates it is, for some purposes especially important to eliminate the last traces of foreign matters. For instance, a crude article which is already more or less charged with lime, alumina, or iron, has its power of dissolving metallic oxyds greatly impaired. And again, one may be easily deceived as to the highest possible relative proportion of silica capable of entering into complete solution. Thus Fuchs could not get much beyond $\dot{K}_2\,\ddot{S}i_5$, and even this he describes as being usually somewhat lacking in clearness—"gewöhnlich etwas trübe oder opalisirend."* And Forchhammer says:—"Silicate of potash in which the oxygen of the acid is eight times as great as that of the base, is still soluble; but the slightest additional quantity of silica is no longer dissolved."† They both evidently overlooked the disturbing influence of minute portions of earthy matter. For in reality, by operating

* Op. supra cit.—p. 15. † Poggendorff's Annalen,—xxxv, p. 341.

with a well purified silicate, it is possible to get at least as far as $\dot{K}\tilde{S}i_3$ or $\dot{N}a\tilde{S}i_3$, and have a solution perfectly transparent.

Crude waterglass, unless it is made in unalterable vessels and from absolutely pure materials, is sure to contain more or less saline and earthy impurities. But it appears from the foregoing experiments that these contaminations may be got rid of by several properly conducted precipitations,—the salts remaining in the alcoholic liquors while the earthy and metallic oxyds are withdrawn by the first small fractional deposits. We have therefore in this process a ready means of obtaining a waterglass of the utmost purity and of almost any required composition. And it is far easier thus to separate the extraneous substances from a roughly made silicate than to observe the many precautions required in preparing a pure product with pure ingredients. Considering the small proportion of alcohol needed, and the ease of recovering even this by distillation, the cost appears so moderate that the manufacturer might be warranted in resorting to a single precipitation when a nice waterglass is wanted for use in the arts. In such a case it will do to operate on a tolerably strong solution, say one containing twenty per cent of solid matter. But it should be observed that weaker liquors allow of a more intimate commingling of the alcohol and are more likely to retain the foreign salts. Therefore when the chemist would suit his own rigorous demands, he may advantageously take solutions containing not more than ten per cent of dry silicate. To ten parts of the liquor may be added, at first, one part by weight of strong alcohol, and before filtering, the mixture should be allowed to stand several hours in order to give the reluctant precipitate a chance to get fully segregated. Rejecting this first deposit which contains most of the earthy matters and very little of the alkaline silicate, add to the filtrate twenty parts of alcohol, and the larger part of the waterglass will be thrown down. When the product is rich in silica, it is quite voluminous at first but gradually contracts and becomes more or less coherent. After a rest of six hours or more, the alcoholic liquid being carefully decanted, the silicate, if solid, may be spread on absorbent paper and allowed to drain as long as it will remain without adhering to the paper. The mass thus deprived of mother liquor, can then be dissolved in four times its weight of water and carried through the same round of treatment as before. The result of this second series of operations will, in most cases, be found almost entirely free from impurities; but, if need be, a third or even a fourth course of fractionizing, may be resorted to.

Liquid precipitates are often milky at first, on account of the incomplete separation of the last portions of mother liquor, but they soon become clear by standing in a warm place. Solid products are commonly opaque and acquire their proper transparency only on being thoroughly drained.

The quantity of silicate which remains dissolved in the supernatant alcoholic liquid, is always exceedingly small but is somewhat increased by heat. For often a mother liquor which is quite milky when first decanted, becomes perfectly transparent by being warmed a few degrees, and the opacity reappears on cooling. Indeed a nicely balanced solution of this kind, is quite sensitive to changes of temperature in the room. The nearer we get to an entire precipitation of the silica, the more apt is the remaining liquid to exhibit such alternations of opacity and clearness.

The silicates containing less than 170 eq. of silica to 100 eq. of alkali, are usually thrown down in the liquid state; those more silicious yield solids of greater and greater firmness as the relative proportion of silica increases. But all these hard products belong to the same class of solids as pitch,—that is, heaped up fragments will, in the course of time, flatten themselves out and form one united cake.

It is obvious from the above examples that the more any given waterglass solution is diluted before adding alcohol, the greater will be the relative amount of silica in the precipitate. And thus by mere precipitation under varied conditions, we may get an unlimited number of differently constituted silicates. But while the ratio of acid and base admits of an infinite diversity, the quantity of water in the principal products appears to be nearly constant, generally amounting to not far from fifty per cent.

In this respect waterglass differs from the proper salts, many of which alcohol throws down combined or associated with an amount of water varying according to the proportion of spirit used. Thus 100 parts of a solution containing 10 p. c. of dry carbonate of potash, on being treated with alcohol of sp. gr. 0·820, gave with

60	of alcohol	no precipitate.					
70	"	a slight "					
100	"	17·8	p'ts	of a liquid	containing	26	p. c. $\dot{K}\dot{C}$
120	"	20·8	"	"	"	29	"
140	"	21·7	"	"	"	30	"
190	"	23·2	"	"	"	32	"
200	"	23·1	"	"	"	33	"
400	"	38·	"	"	"	38	"

Carbonate, sulphate, and stannate of soda afford liquid products with a certain amount of alcohol, but with a larger quantity they yield crystals.

Solutions containing even as much as ten per cent of any of the salts commonly occurring in the crude alkaline silicates, are not immediately affected by a moderate addition of alcohol. Hence it is not at all strange that the greater part of these salts

remains in the supernatant liquor while the waterglass is almost wholly precipitated.

I have not yet made a sufficient number of experiments to determine whether alcohol withdraws a part of the alkali from such weak combinations as the stannates, aluminates, and zincates; but so far as is known at present, the silicates are altogether peculiar in their susceptibility of partial decomposition. Their behavior with alcohol bears a remote resemblance to that of the bismuth salts with water. On the one side, however, amorphous substances give indefinite products; on the other crystallizable bodies yield definitely constituted precipitates.

Considering the large proportion of silica capable of being retained permanently in solution by a little alkali, the disturbing influence of foreign matters such as earths and neutral salts, and the gummy character of the silicates,—we find in the waterglasses a reverse parallelism to the soluble basic salts of the sesquioxyds and binoxyds;—the excess of base in the latter having the same effect as the excess of acid in the former. And instead of being regarded as real salts or mixtures of salts, they ought perhaps to be looked upon as combinations of active silica with some normal silicate,—like NaO, SiO_2, which one or two chemists have obtained distinctly crystallized.

As many of the supposed chromates of chrome, have vanished under the critical examination of Messrs. Eliot and Storer,* so it will doubtless be found that not a few other amorphous precipitates commonly laid down as definite substances, are mere chance combinations. And to avoid a needless multiplication of such encumbrances to the records of science, it would be best not to attribute a rational formula to any of the silicates of potash or soda till it can be shown to be crystallizable or to have a constant composition under varied influences.

Manchester, New Hampshire, Sept. 1861.