ART. XVIII.—*Waterglass;* by JOHN M. ORDWAY. Part V.

[Continued from vol. xxxv, p. 196.]

Its Reaction with Stannates.

THE statement made in Part II,[1] that stannate of soda produces no alteration in a solution of waterglass, is found, by more rigid experiments, to require some limitation. What is true of the stannate prepared, as it commonly is, with such an excess of alkali as is needed to make it dissolve perfectly and keep well, does not necessarily hold good with regard to the pure normal salt. In fact the behavior of neutral stannates with acid silicates, is peculiar, and worthy of something more than a passing notice. The conditions, character, and results of the mutual reaction, may be best shown by giving a condensed account of some few of the many trials which I have made. But it will be proper in the first place to describe, somewhat in detail, the methods adopted for securing materials suitable for such experiments—methods which may lay some claim to novelty as well as convenience.

Stannate of Soda.—Time alters the crystallized salt, and dissolved stannate of soda having just one equivalent of alkali to one of acid, soon begins to change and deposit an insoluble metastannate, leaving an excess of soda in the liquid. Hence, whenever the really normal combination is wanted, it is best to make use of the freshly prepared crystals.

The commercial "preparing salt," when it is free from arsenic, may be advantageously used to produce the pure stannate.

1. A refined product, of English manufacture, was found to contain 47 p. c. $NaO.SnO_2$, 20 p. c. NaO, 11·3. p. c. $NaO.SO_3$, and 2·6 p. c. Na Cl. Some of it was purified thus:

400 grams of the white "preparing salt" and 84 grams of acetate of baryta were dissolved together in 1600 cub. cent. of water; and, as the solution was too caustic for a paper filter, it was passed through thick cotton cloth, the first portions of the liquor being poured back till the filtrate came no longer turbid. The clear liquid treated with about its own bulk of alcohol of sp. gr. 0·850, soon gave an abundant deposit of fine, indistinct crystals, which were gathered into a stout cotton cloth and submitted to very strong pressure. The damp product, weighing 181 grams, was dissolved in twice its weight of water, and the filtered solution was mixed with somewhat more than its own bulk of alcohol. The crystals of this second precipitation, after undergoing very hard pressure, were spread out on paper and left in a cold place over night, to exhale the alcohol. They now weighed 143 grams and contained 76 p. c. of $NaO.SnO_2$. They were free from carbonate, hydrate, sulphate, and

[1] This Journal, [2], xxxii, 339.

chlorid of sodium, but made a slightly opaline solution with water, thus showing the presence of a trace of metastannate.

Crystals fresh from the press give a clear and complete solution; and as a trifling amount of adhering alcohol is seldom of any consequence, it is best to expose the pressed cake to the air as little as possible.

When the product is freed from mother liquor by absorption and careful drying it appears to have the composition $NaO, SnO_2, 3HO$.

To get pure and clean crystals for an exact determination of the water a strong solution of the preparing salt was treated with acetate of baryta, and as much alcohol was added to the filtrate as it would bear without turning milky. In two days there gathered around the sides and bottom of the bottle a thin, hard coating of transparent crystals, which were detached and pressed in absorbent paper till they appeared dry, but not at all effloresced. The average of two analyses showed 55·695 p. c. of SnO_2 and 22·921 p. c. of NaO. This would make $\dot{N}a\,\ddot{S}n\,\dot{H}_{3\cdot2}$.

But it is worthy of notice that when the precipitated crystals are rapidly dissolved in water, heat is produced instead of cold; and it might be inferred from this fact, that stannate of soda is capable of entering into intimate combination with more water than is contained in the trihydrate. Thus, by the solution of a quantity of the pressed crystals, still damp, in a little more than twice their weight of water the thermometer was raised 5° C.

Stannate of Potash.—Stannate of Potash is more soluble in water than the soda salt,[2] and cannot be, by any means, so neatly and easily precipitated in the solid state.

[2] Storer, in his Dictionary of Solubilities, under the heads "Stannate of Potash" and "Stannate of Soda," has collected nearly all that is known respecting these salts. We are there told that, according to Fremy, stannate of soda is *much* more soluble in cold than in warm water. To test this matter, and to reduce indefinite terms to exact numbers, I have made the following experiments:

I. A saturated solution was prepared by frequently agitating water with an excess of the fine, freshly prepared crystals, in a flask surrounded with snow. It was filtered in a funnel also kept at 0° C. The clear liquor warmed to 15·5° C. had the sp. gr. 1·472. It contained 32·1 p. c. of dry stannate.

II. A saturated solution made in a room kept at 10°C. had the sp. gr. 1·448, and contained 31 p. c. of the dry salt, or 39 p. c. of $\dot{N}a\,\ddot{S}n\,\dot{H}_3$.

III. A saturated solution was made in a flask kept in water at 20° C. Cooled to 15·5° C. it had the sp. gr. 1·438. It contained 30·3 p. c. of $\dot{N}a\,\ddot{S}n$. So 100 parts of water dissolve 67·4 parts of the crystals, $\dot{N}a\,\ddot{S}n\,\dot{H}_3$, at 0° C.; and at 20° C., only 61·3 parts, or nine-tenths as much.

Stannate of potash shows no such anomaly, but its solubility is somewhat increased by heat.

IV. At 10° C. a saturated solution was made with crystals of $\dot{K}\,\ddot{S}n\dot{H}_3$ formed by spontaneous evaporation *in vacuo*. It had the sp. gr. 1·618 and contained 42·3 p. c. of $\dot{K}\,\ddot{S}n$.

V. A saturated solution made at 20° C. had the sp. gr. 1·627 and contained 43 p. c. of dry stannate of potash.

By using many successive portions of strong alcohol, we may withdraw the dissolving water and compel hasty and pretty complete crystallization; and as all the precipitates subside with great rapidity, the whole round of operations may be carried out in a few hours. But while stannate of soda can be readily procured coarse grained, white, and of normal composition, the precipitated potash salt is very fine, and besides obstinately retaining much of whatever organic coloring matter may have been present in the original solution, it is liable to come out at last with somewhat too much or too little alkali.

2. A crude stannate prepared by heating strongly a mixture of tin, caustic potash, and nitrate of potash, was dissolved in twice its weight of cold water. 400 c. c. of the clear, decanted liquor, were thoroughly agitated with 400 c. c. of alcohol of sp. gr. 0·840, and gave a dense liquid deposit measuring 275 c. c. This being in turn treated with 400 c. c. of alcohol, yielded 175 c. c. of still denser liquor. A third precipitation with 400 c. c. of alcohol gave a deposit with some solid matter beginning to appear in it.

So far a weaker spirit had been used so as to allow the impurities to remain in solution while the stannate was thrown down.

400 c. c. of alcohol of sp. gr. 0·820 now changed the precipitate into a pasty mass, which became crumbly on being stirred up again with 400 c. c. of strong alcohol. The stannate was then gathered in stout canvass and subjected to great pressure. The resulting cake still contained about one-eleventh of an equivalent of alkali in excess, there being originally two equivalents of potash to one of stannic acid; it was therefore dissolved in a little more than its weight of water and submitted to another round of treatment with alcohol. The hard pressed final product contained 73 p. c. of dry stannate. Being spread out and exposed to the air for some hours, it lost all smell of spirit, and was then pure and almost exactly normal.

When greater nicety is required, such a product should be dissolved in a little less than its weight of water and recrystallized by spontaneous evaporation *in vacuo*.

A careful analysis was made of some pure, hard, colorless, transparent, oblique rhombic crystals produced by this last method and dried by pressure in absorbent paper. It showed

VI. A saturated solution made at about 45° C. had the sp. gr. 1·658 and contained 44 p. c. of $\dot{K}\,\tilde{S}n$.

Therefore, at 20° C., 100 parts of water take up 110·5 parts of $\dot{K}\,\tilde{S}n\dot{H}_3$, or nearly twice as much as of stannate of soda crystals.

When there is present an excess either of alkali or of stannic oxyd, a saturated solution contains less of the net normal stannate.

VII. A solution of $\dot{K}\,\tilde{S}n_{0\cdot9}$ saturated at 0° C. had the sp. gr. 1·64 and contained 40·4 p. c. of $\dot{K}\,\tilde{S}n$.

VIII. A solution of $\dot{K}\,\tilde{S}n_{1\cdot2}$ saturated at 0° C. had the sp. gr. 1·74 and contained 41·5 p. c. $\dot{K}\,\tilde{S}n$ and 5·3 p. c. of $Sn\,O_2$ in excess.

Or speaking with special reference to the oxyd of tin, we may say that its solubility increases as the amount of alkali present is diminished.

49·430 p. c. of stannic acid, and 30·704 p. c. of potash. If we call the equivalent weight of tin 59, these proportions would make $\dot{K}\,\dot{S}n\,\dot{H}_{3\cdot3}$. The true formula must therefore be KO.Sn O_2.3HO.

The specific gravity of these crystals was found to be 3·197.

Metastannate of Potash.—When a dilute acid is slowly, and with constant stirring, dropped into a cold solution of normal stannate of potash, there is no permanent precipitation till more than three-fourths of the alkali is abstracted. The stannate thus robbed of its base, remains perfectly dissolved, but has acquired different properties. Alcohol now gives with it not a liquid or crystalline deposit, but a light flocculent precipitate which, when it is well drained and exposed to the air for a day or two, dries to heavy, transparent, gum-like lumps. There is thus opened up a neat way to procure, in a state of purity, metastannates containing various proportions of alkali.

3. A nine per cent solution of $KOSnO_2$ was treated with enough five per cent nitric acid to take up two-fifths of the potash. When the liquor had recovered its clearness, somewhat more than twice its bulk of alcohol of sp. gr. 0·830 was stirred in. The precipitate, after being washed once with alcohol, was drained on a filter and left on absorbent paper till it became a transparent, exceedingly shrunken mass containing 79 p. c. of $\dot{K}\,\dot{S}n_{4\cdot6}$. This easily dissolved in twice its weight of water.

4. In a similarly conducted experiment, the same quantity of stannate with twice as much acid as before, gave nearly twice as much metastannate containing 59 p. c. of $\dot{K}\,\dot{S}n_{5\cdot6}$. This dissolved in four times its own weight of water to a faintly-opaline liquid.

5. Some of the solution of 3 was diluted and cautiously treated with sufficient nitric acid to neutralize one-third of the remaining potash. The despoiled metastannate was then precipitated with alcohol. The final product consisted of $\dot{K}\,\dot{S}n_{10\cdot6}\,\dot{H}_4$ and was readily soluble in water.

It is well to dissolve the rough metastannate and reprecipitate, in order to get rid of the last traces of nitrate and obtain a substance which will give a clear and mobile solution. And the product of the second precipitation can be advantageously freed from the adhering liquor by pressing it very strongly in stout closely woven cotton cloth. Even the first precipitate may be pressed, but it is much softer and the pressure must be applied very gradually indeed; otherwise the pulp itself will pass through the pores of the cloth.

Waterglass with Stannates.—As in some preliminary experiments sulphates were not perceived to exert any influence on the reaction of stannates with silicates, sulphates were afterward purposely added, to serve as indicators of the amount of mother liquor retained by the precipitates. The liquid stannate of soda was made to contain about five per cent of sulphate of soda, and stannate of potash was dissolved in a weak solution

of potash sulphate. The waterglass was such as had been well purified by precipitation with alcohol.

While treating this part of our subject we will take the formula adopted in planning the experiments, and consider silicic acid as $\dot{S}i\,O_2$.

6. 80 g. of a solution containing 14 p. c. of $NaO\,SnO_2$, were mixed with 32 g. of a 29 p. c. solution of $NaO.2SiO_2$, so as to have in the united liquors $\dot{N}a_2\,\dot{S}n\,\dot{S}i_2$.

There was no apparent change at first, but, in the course of two days, it became an opaque, consistent jelly from which no liquor could be decanted.

Such were also the products in most other cases; and at first these jellies proved rather intractable, for when they were subjected to quick pressure in common cotton cloth, such as had been used in former experiments, both liquor and coagulum passed through. Farther experience showed it best to let the mixtures stand several days to get fully gelatinized, and then proceed to press very gradually in thick, closely woven canvass. The cloth was folded over the drained precipitate and placed between two bits of pine board. To insure moderation at first, the boards were put under a small hand screw which was very slowly turned till the greater part of the clear liquor was forced out and the substantial portion of the coagulum was reduced to small bulk. The boards with their contents were then transferred to a large press urged by the full strength of two men and theoretically capable of multiplying the power nearly 1200 times. The pressed products were hard and brittle, and could be rubbed in a mortar to a damp powder without caking much under the pestle. The powder was generally soluble in chlorhydric acid. On being ignited the cake contracted greatly and became opaque, but showed no sign of fusion.

To make an analysis a weighed portion of the powder was treated with chlorhydric acid in excess and dried down at a moderate heat. The residue digested for twenty-four hours with chlorhydric acid and then well washed with water containing a little of the same acid, left the silica pure and in full quantity.

Another portion of the powder was treated with nitric acid in excess and dried down. By washing the dry mass with water and igniting and weighing the undissolved matter, the sum of the silica and oxyd of tin was ascertained; and a comparison of this with the former determination showed the per centage of oxyd alone. The solution being evaporated to dryness the resulting saline matter was fused and weighed. The amount of sulphate in the mixed salts was found by means of chlorid of barium; and then the quantity of nitrate and the corresponding amount of alkali were easily calculated.

The composition of the mother liquor was ascertained by the same method. Then the percentage of sulphate in the pressed cake, divided by the percentage of sulphate in the mother liquor, showed the quantity of mother liquor retained in one part of the cake. And finally the net composition of the curd was found by deducting from the gross amounts of silica, stannic acid, and alkali in the pressed cake, the quantities of the same substances due to adhering mother liquor.

In the present instance the hard pressed curd weighing 24 grams, contained 40 p. c. of mother liquor, and 38·6 p. c. net of $\dot{N}a_3\,\bar{S}n\,\bar{S}i_5$.

7. 75 g. of a 14 p. c. solution of $\dot{N}a\,\bar{S}n$ were mixed with 20 g. of a 20 p. c. solution of $\dot{N}a\,\bar{S}i_3$, so as to have a mixture of $\dot{N}a_4\,\bar{S}n_3\,\bar{S}i_3$. In a few hours it became a firm opaque jelly. After standing six days it was pressed and left 24·3 g. of cake containing 34 p. c. of mother liquor and 38 p. c. net of $\dot{N}a_5\,\bar{S}n_4\,\bar{S}i_8$.

8, *a*. 60 g. of a 14 p. c. $\dot{N}a\,\bar{S}n$ solution were mixed with 40 g. of a 20 p. c. solution of $\dot{N}a\,\bar{S}i_3$; so that the quantities of $Sn\,O_2$ and $Si\,O_2$ should be equal. It soon began to get opaline, and, in the course of two hours, made an opaque jelly, so stiff that it was not disturbed by inverting the dish. The hard pressed cake weighed 36·3 g. and contained 45 p. c. of mother liquor and 36 p. c. of $\dot{N}a_4\,\bar{S}n_3\,\bar{S}i_6$.

8, *b*. 240 g. of a 3·5 p. c. $\dot{N}a\,\bar{S}n$ solution were stirred into 200 g. of a 4 p. c. $\dot{N}a\,\bar{S}i_3$. In the course of two hours it formed a thin opaque jelly. After two days this was thrown on a cloth and much clear mother liquor drained out without pressure. The remainder was very gradually squeezed and finally hard pressed, and gave a cake weighing 31 g., which showed 17 p. c. of mother liquor and 36 p. c. of $\dot{N}a_4\,\bar{S}n_3\,\bar{S}i_9$.

8, *c*. 480 g. of a 1·75 p. c. solution of $\dot{N}a\,\bar{S}n$ were mixed with 400 g. of a 2 p. c. $\dot{N}a\,\bar{S}i_3$ solution. There was no change at first, but in the course of two days it formed a thin jelly. After standing six days it was drained, squeezed, and hard pressed, and the cake weighed 26·7 g. This product contained 21 p. c. of mother liquor and 36 p. c. of $\dot{N}a_4\,\bar{S}n_4\,\bar{S}i_{10}$.

These three trials show something of the influence of dilution, though in the case of *c* longer standing had also modified the composition of the coagulum by increasing the amount of stannic oxyd rendered insoluble.

9, *a*. A 120 g. mixture was compounded so as to contain 18 g. of $\dot{N}a_3\,\bar{S}n_2\,\bar{S}i$. There was no change at first, but in the course of two days it became a thin opaline jelly. After seven days being hard pressed it yielded a translucent cake weighing 8·6 g. and containing 37 p. c. net of $\dot{N}a_9\,\bar{S}n_7\,\bar{S}i_{13}$.

9, *b*. A similar mixture was made by adding a saturated solution of stannate to fused crystals of silicate and evaporating till it contained 40 p. c. of solid matter. It remained clear, and when exposed to severe cold showed no sign of crystallization.

10. A mixture was made containing somewhat over 16 p. c. of $\dot{N}a_3\,\bar{S}n\,\bar{S}i_2$. There was no change for six weeks.

11, *a*. A mixture was made so as to contain about 16 p. c. of $\dot{N}a_2\,\bar{S}n\,\bar{S}i$. There was no change for some days, but in the course of a month it gelatinized.

11, *b*. A saturated solution of stannate was put with as much melted $\dot{N}a\,\tilde{S}i\,\dot{H}_8$ as would make $\dot{N}a_2\,\tilde{S}n\,\tilde{S}i$, and the mixture was evaporated at a gentle heat till it contained 47·5 p. c. of solid matter. It remained clear and would not crystallize though set out in the open air during several of the coldest days of winter. The strong liquor bore boiling without apparent change, but when much diluted was coagulated by heat.

Stannate of Potash with Silicate of Potash.

12. A mixture made so as to contain 21 p. c. of $\dot{K}_2\,\tilde{S}n\,\tilde{S}i$, underwent no visible change in a month.

A mixture containing 19 p. c. of $\dot{K}_3\,\tilde{S}n\,\tilde{S}i_2$ also remained unchanged for a month.

13, *a*. 72 g. of a 10 p. c. solution of $\dot{K}\,\tilde{S}n$ were mixed with 60 g. of 12 p. c. $\dot{K}\,\tilde{S}i_3$, so as to bring together about equal weights of SnO_2 and SiO_2. There was no perceptible alteration for a day, but in three days it became a thin transparent jelly. After standing a week it was squeezed gradually and then hard pressed. The transparent product weighed 28 g. and contained 39 p. c. net of $\dot{K}_6\,\tilde{S}n_4\,\tilde{S}i_{13}$.

13. *b*. 288 g. of a 2·5 p. c. $\dot{K}\,\tilde{S}n$ solution were mixed with 240 g. of 3 p. c. $\dot{K}\,\tilde{S}i_3$. It remained apparently unchanged for a week. In the course of the second week it became gelatinous, but no liquor could be pressed out. At the end of three weeks it had fully coagulated, and being now hard pressed it gave a translucent cake weighing 23 g. This contained 17 p. c. of mother liquor and 40 p. c. of $\dot{K}_6\,\tilde{S}n_6\,\tilde{S}i_{14}$.

14. 77 g. of a solution containing 15 p. c. of $\dot{K}\,\tilde{S}n$, were mixed with 33 g. of a 20 p. c. solution of $\dot{K}\,\tilde{S}i_3$, so as to make in all $\dot{K}_3\,\tilde{S}n_2\,\tilde{S}i_3$. It underwent no noticeable modification for some time, but in two days it formed a firm, slightly opaline jelly. After standing a week, it was hard pressed and yielded a mass weighing 28 g. and containing 38 p. c. net of $\dot{K}_4\,\tilde{S}n_2\,\tilde{S}i_7$.

Metastannate of Potash with Potash Waterglass.

15. 20 g. of a 10 p. c. $\dot{K}\,\tilde{S}i_3$ liquor were mixed with 20 g. of a solution containing 10 p. c. $\dot{K}\,\tilde{S}n_{4\cdot4}$. There was no change for some time, but in the course of 17 days it thickened. The hard pressed solid part weighed 5·5 g.

16. 10 g. of a 30 p. c. solution of $\dot{K}\,\tilde{S}i_3$ were stirred into 10 g. of a 24 p. c. solution of $\dot{K}\,\tilde{S}n_{5\cdot3}$. It soon got a little thicker but did not gelatinize at all.

Weaker solutions of the same metastannate and silicate, were mixed with similar results.

17. 10 g. of a 10 p. c. $\dot{K}\,\tilde{S}i_3$ solution were put with 10 g. of a 10 p. c. $\dot{K}\,\tilde{S}n_{7\cdot5}$; no immediate change. In the course of 10 days it gelatinized, and when hard pressed it gave a cake weighing 4 g.

18. 20 g. of a 15 p. c. solution of $\dot{K}\,\tilde{S}i_3$ were mixed with 20 g. of 16 p. c. $\dot{K}\,\tilde{S}n_{10\cdot6}$. It continued unchanged a month, but at length gelatinized.

A comparison of all the experiments from which this selection has been made, brings to light nothing definite or uniform in

the products of the reaction of stannates with silicates. The strange looking *quasi* formulas here used to show their composition by equivalents instead of per centages—like the similar expressions employed for the precipitates described in Parts III and IV,—would be altogether preposterous, were they intended for anything more than compact and readily collatable expressions of the results of analyses. In vain do we search for any principle that will enable us to assign a rational constitution to substances which derive their unlimited variety of composition from mere accidents of dilution, purity, temperature, and of time allowed for segregation. Many picked instances, like 7, 8 *a*, and 9, might countenance the supposition of a tendency to the formation of an exact silicate of tin $SnO_2\ 2SiO_2$, united with different proportions of alkali. But such hasty generalization is checked by an enlarged view and more particularly by the special test experiments, 8 *a, b, c.* All that seems to be predicable of the reactions is that mixtures containing as many equivalents of alkali as the sum of the equivalents of SnO_2 and SiO_2, are likely to undergo little or no change at the common temperature of the air; but when the mixture contains less alkali, gelatinization will occur in a few hours or days; and the curd will be greater in amount according as the strength of the liquors put together is greater, and as the total proportion of alkali is less.

The segregated matter retains the alkali with no little force, for when the air-dried precipitate is washed with water a part indeed of the alkali is removed, but the greater portion remains obstinately in combination.

19. Some of the cake of 13 *a*, was reduced to powder and kept over lumps of caustic soda eighteen days. The dry powder was well washed with cold water. The air-dried residue amounted to 42 p. c. of the quantity of fresh cake taken, and contained 78·6 p. c. of $4KO.4SnO^2.13SiO^2$. Only one-third of the potash had been washed out.

It is difficult to ascertain whether the fresh undried cake may undergo dissociation in any greater degree; for if we attempt to wash it, though a part settles, the supernatant liquor remains milky a very long time, and the suspended matter cannot be separated by filtration, as it readily goes through the pores of the paper.

After seeing how a deficiency of alkali facilitates the coagulation of a mixture of stannate and silicate, we should hardly expect to find metastannates so slow in producing any effect on waterglass. But metastannates are evidently not mere polyacid stannates, and a higher degree of compatibility is the less surprising when we consider the many points of resemblance between metastannate of potash and waterglass itself. Both are uncrystallizable and dry to transparent gum-like masses, indefi-

nitely soluble in water. Both are precipitated by alcohol with partial decomposition, and indeed in both the acid and base seem to be in a state of association rather than of strict chemical combination. The following experiments, illustrating this point, may be compared with the similar trials of silicates mentioned in Part III:

20. 350 g. of a solution containing 6 p. c. of $\dot{K}\ddot{S}n_{4\cdot4}$, were mixed with 850 c. c. of alcohol of sp. gr. 0·840. After two washings with alcohol, the flocculent precipitate was collected in a cloth and hard pressed. The thin translucent, brittle cake, after twelve hours exposure to the air, weighed 24 g. and contained 82 p. c. of $\dot{K}\ddot{S}n_{7\cdot4}$. It was dissolved in 9 parts of water and treated with alcohol as before. The second precipitate when pressed and aired contained 81 p. c. of $\dot{K}\ddot{S}n_{8\cdot5}$. The third precipitate contained 80 p. c. of $\dot{K}\ddot{S}n_{9\cdot3}$. The product of a fourth precipitation showed 81 p. c. of $\dot{K}\ddot{S}n_{9\cdot3}$. The fifth precipitate contained 82 p. c. of $\dot{K}\ddot{S}n_{10\cdot5}$. And the sixth product was readily soluble in water and showed 72 p. c. of $\dot{K}\ddot{S}n_{11\cdot4}$.

21. 50 g. of pressed crystals of stannate of potash were dissolved in water, so as to make 600 c. c. 200 c. c. of 5·4 p. c. nitric acid were stirred in, and, when the liquor had recovered its transparency, 1700 c. c. of alcohol were added. After one washing with alcohol the pultaceous precipitate was very gradually squeezed and then hard pressed. After some hours exposure to the air, the cake weighed 27 g. and contained 79 p. c. of $\dot{K}\ddot{S}n_{5\cdot2}$. It was dissolved in 9 times its weight of water and treated with alcohol. The second flocculent deposit hard pressed and dried in the air, contained 80 p. c. of $\dot{K}\ddot{S}n_{6\cdot3}$. The precipitation was repeated many times, and finally the tenth product, weighing 5·5 g., was not entirely soluble in water. The soluble part contained $\dot{K}\ddot{S}n_{17\cdot4}$, and the small insoluble residue had nearly the same composition.

Metastannate of potash is also thrown down as such by many potash salts; and here too, as with waterglass, the acetate and the chlorid prove most efficient.

22. 25 g. of a solution containing 21 p. c. of $\dot{K}\ddot{S}n_{4\cdot4}$ were mixed with 25 g. of a 20 p. c. KCl solution. The very bulky deposit after being squeezed and subjected to hard pressure, weighed 6·4 g. It contained 28 p. c. of mother liquor and 64 p. c. of $\dot{K}\ddot{S}n_{7\cdot7}$, and was readily soluble in water.

23. 40 g. of a 9 p. c. solution of $\dot{K}\ddot{S}n_{7\cdot7}$ mixed with 40 g. of a 10 p. c. solution of acetate of potash gave a precipitate that compressed to 4 g. and contained 68 p. c. of $\dot{K}\ddot{S}n_{8\cdot1}$. This was wholly soluble in water.

Carbonate, sulphate, chromate, or nitrate of potash give a precipitate after a time when added in inconsiderable quantity to the metastannate; but neutral stannate, of whatever strength and in whatever quantity, has no effect upon a metastannate solution.

On account of the insolubility of metastannate of soda, soda salts soon disturb a solution of metastannate of potash. Thus a

liquid containing 10 p. c. of $\dot{K}\dot{S}n_{5\cdot6}$, became opaque with its own weight of a 2 p. c. solution of $\dot{N}a\dot{C}$. A much less quantity of sulphate of soda sufficed to produce the same effect. A soda salt therefore affords a test of the presence of metastannate in a stannate of potash solution, but the liquors must not be too concentrated.

Fremy says that stannate of potash is precipitated from its solution by almost all soluble salts, and even by salts of potash, soda, and ammonia. He must have operated with liquors that had been kept too long and had thereby become contaminated with metastannate; for my own experiments afford no confirmation of his statement as far as potash and soda salts are concerned. On the contrary I have not found these salts to have any effect at all on solutions of fresh and really normal stannates of potash and soda. Stannate of soda when mixed with a neutral salt, does indeed become turbid by standing some time, but so does the diluted stannate without any addition.

Indefiniteness of composition pertains to the metastannates in no less degree than to waterglass. Fremy once assigned the formula[3] $KO.2Sn_3O_6+5HO$, but afterward settled down on $KO.Sn_5O_{10}+4HO$, and thus gives his reasons for the change:[4]

"Je préparais autrefois les metastannates en faisant bouiller de l'acide metastannique avec des alcalis, et en précipitant ces dissolutions par l'alcool; j'ai reconnu recemment que pendant l'ebullition, une partie du metastannate se transforme en stannate; en traitant ensuite la liqueur par l'alcool, je précipitais un melange on peut-être une combinaison de stannate, et de metastannate, etc."

"C'est ainsi que j'avais été conduit á représenter l'acide metastannique par la formale Sn_3O_6. Mais je prepare actuellement des metastannates qui ne penvent contenir de traces de stannates; aussi leur analyse donne-t-elle toujours un equivalent d'acide metastannique représenté par la formule Sn_5O_{10}."

Fremy's later method of preparing a metastannate which should contain no stannate, was to dissolve metastannic acid in caustic potash and precipitate the combination by adding to the solution bits of solid caustic potash. The precipitate was dried by absorption on unglazed porcelain. But it can hardly be possible by mere absorption to get a soft, pulpy substance, entirely free from so thick and dense a mother-liquor as the caustic potash would make. Fremy made five analyses which came out very nearly alike, as might indeed well happen so long as the products analyzed were made in just one way and by one individual. But the tacit assumption that none of the 10·5 to 10·9 p. c. of potash found, was due to retained mother liquor, is manifestly gratuitous. Nor was there any good reason for suppos-

[3] Annales de Ch. et de Phys. [3], xii, 476.
[4] Id., xxiii, 395.

ing that cold caustic potash exerts no modifying action on metastannate; for time often brings about in part what heat effects rapidly and fully, and in fact I have seen an abundant precipitate, produced by moderately strong potash liquor, disappear in an hour or two with but a very slight elevation of temperature. Some idea of the difficulty of separating a mother liquor from a gum-like precipitate, may be gathered from the experiments on precipitated waterglass given in part IV. There we had a substance as capable as metastannate of potash of being reduced to a very compact form. There we had the advantage of a mother liquor much thinner and much more easily separable from the curd. There was also a powerful pressure effectually accomplishing in a few moments, and consequently without chance of modification by time, what the contractility of metastannate and the imbibing power of porcelain could do but slowly. Yet the precipitated silicates retained, on an average, about thirty per cent of mother liquor. Due allowance being made for the greater density of a stanniferous compound, it certainly would not be making a very high estimate to say that metastannate of potash thrown down by potash, after as complete a drainage as possible, must retain not less than ten per cent of strong caustic potash liquor or some three per cent of dry potash in excess. I see no chance of actually finding out how much of the potash is combined and how much is free in such a case; for if we add any *indicator*, it would alter the conditions of the experiment.

Hence, Fremy's formula having no fixed basis must be looked upon as a rather uncertain approximation to the true composition of the metastannate made by his method.

According to Rose,[5] Weber found solid metastannate of potash to consist of $KO.7SnO_2+3HO$. But we are not told by what process it was made.

Berzelius says that one part of potash will dissolve sixteen parts of stannic acid, and these proportions would make about $KO.10SnO_2$.

As to matastannates obtained by precipitation with alcohol or with neutral potash salts, we have found that by varying the conditions the composition of the products may be made to range from less than five up to more than seventeen equivalents of binoxyd of tin to one equivalent of potash. And Graham[6] has shown that when the alkali is eliminated by neutralization and dialysis, metastannic acid is itself soluble in pure water. Hence there is probably no limit to the possible diminution of potash in the still soluble metastannate.

I have heretofore enunciated the general rule that soluble salts having as bases, ferric, chromic, stannic, or other oxyds contain-

[5] Poggendorff's Ann. lxxv, 15.
[6] Repertoire de Chimie, Sept., 1864, p. 184.

ing more than one equivalent of oxygen to one of metal, may have a large part of the acid withdrawn and still remain dissolved. And now it is interesting to find that when binoxyd of tin is brought into solution by an alkali, a similar principle holds good, and the greater portion of the base may be removed without any immediate permanent precipitation of the acid. Metastannate of soda, however, is but temporarily soluble, and is thrown down from solutions of the neutral stannate by long standing or by boiling. It is also soon deposited from a solution in which the alkali of normal stannate has been partly taken up by a stronger acid. These precipitates are, by no means, of the same composition, though they often approach very closely to the proportions required for $NaO.5SnO_2$.

24. Some purified stannate of soda that had been dried in the air and then kept in a well stopped bottle for two years, on being treated with ten times its weight of cold water, left undissolved one twenty-third of the tin, combined with soda enough to make $NaO.3{\cdot}7SnO_2$.

The clear liquor, by standing several weeks, let fall one-seventeenth of its tin as $NaO.4{\cdot}7SnO_2$.

25. A ten per cent solution of normal stannate being kept 34 days, deposited one-twelfth of the oxyd of tin in combination with enough alkali to make $NaO.5SnO_2$.

26. A ten per cent solution of $NaO.SnO_2$ was boiled a few moments and let fall one-sixteenth of its tin with some soda forming $NaO.5SnO_2$.

27. A solution containing five per cent of pure stannate, by boiling deposited one-seventh of the tin as $NaO.5{\cdot}7SnO_2$.

28. Boiling a two per cent solution of $NaO.SnO_2$ caused the precipitation of over one-third of the tin and enough soda to make $NaO.7SnO_2$.

29. A one per cent solution of pure stannate of soda required long boiling to make a decided precipitate and the clear liquor filtered out of the bulky product very slowly. The well drained gelatinous residue was soluble in water and consisted of $NaO.7{\cdot}5SnO_2$. It contained over one-half of the tin.

30. A solution containing 1·1 p. c. of $NaO.SnO_2$ and 3 p. c. of NaCl, being boiled five minutes, gave a dense, opaque precipitate very easy to collect, drain and press. It contained one-fourth of the tin and consisted of $NaO.6{\cdot}7SnO_2$.

The addition of chlorid of sodium and subsequent boiling causes a precipitation in a solution containing no more than 0·1 p. c. of normal stannate of soda.

So far as is known at present, there is nothing to show that any one of the metastannates more than another is entitled to rank as a definite chemical compound. None crystallizes; none is a product invariably coming the same by several different ways of formation; none exhibits a plain analogy to any undoubted exact chemical combination; nor is there any point up to which the variation gradually decreases, and beyond which it gradually increases. There being then nothing certain on

which a formula may be based, it seems hardly right to take any one chance product, and, rejecting the odd parts of equivalents, to set down that product with its analysis so amended, as the true metastannate of potash or of soda. The composition of substances can not always be squared with exact atomic proportions, for there is a class of indefinites in which one of the constituents may admit of a large increase or diminution without apparent alteration in the character of the compound. As the world was very slow to comprehend Wenzel's proposition that bodies must unite in fixed and invariable proportions, so has it since been quite as slow to learn that there are cases in which this great principle does not hold good. Wenzel says:[7] "Dass eine jede Verbindung der Körper, eine bestimmte und unveränderlich bleibende Abmessung haben muss, die ohne aüsserlich mitwürkende Ursachen weder grösser noch geringer werden kann, weil sonst auch nichts gewisses aus ihrer Vergleichung bestimmt werden könnte, ist schon an sich klar. Es folgt daher nothwendig, dass eine jede mögliche Verbindung zweyer Körper, mit jeder andern beständig in dem genauesten Verhaltnisse stehet, und dieses Verhältniss drücket den Grad der Verbindung aus." That the constitution of bodies is determinate and unalterable, is hardly self evident, and indeed it is a matter to be proved by the balance rather than by mere reasoning. It is true that the confirmatory instances have been found to be numberless. Still a great many do not necessarily make all, and a single negative example is sufficient to disprove absolute universality. Wenzel himself, while laying the sure foundations of chemical science, fell in with some of the indefinites and thus unwittingly furnished some negative instances. He proceeded to determine the equivalents by neutralizing the acids with different bases, and worked correctly so long as those bases were protoxyds. But such a method is as little applicable to alumina and similar peroxyds as it is to bone earth,—"Elfen beinerde,"—which he reckoned among the simple bases. So after attempting to saturate nitric acid with alumina, he concluded that[8] "Das Verhaltniss der Alaunerde zum stärksten Salpetersauern, ist also beynahe . . . . wie 349 : 240." Instead of forming the normal nitrate Wenzel in this case must have got the soluble basic $3Al_2O_3 . 2NO_5$, and stopped at a supposed but not real limit of solubility.

Cases of indefinite combination are not unlike those of solution in which such things as gum or albumen are concerned. These may unite with water in all proportions, while most crystallizable substances dissolve, at any given temperature, until the liquid contains a certain percentage of solid matter,—a percentage which is exactly definable for each particular salt. In

[7] Lehre von der Verwandschaft der Körper. Dresden, 1782. p. 4.
[8] Idem, p. 113.

the phenomenon of fusion too, though almost all bodies liquefy at a temperature which is invariable and exact for each, yet there are a few substances that pass through an intermediate state of softening before fully melting. In fusion as well as in solution, abrupt transition from the solid to the fluid state is the general rule; and yet, as everybody allows, it is not the universal law. And why should we be over-reluctant to admit the possibility of some instances of chemical union in indefinite proportions?

Normal Silicate of Soda.—The only alkaline silicate certainly known to be crystallizable, contains two Berzelian equivalents of silicic acid, SiO_3, to three equivalents of soda. Respecting the amount of water in this salt, analysts do not agree; and as the several observers have examined crystals obtained by unlike methods, there may possibly be three or more hydrates producible under different conditions of temperature, concentration, and purity.

Fritzsche[9] produced a salt in the form of square prisms, by dissolving in caustic soda lye a quantity of silica equal to that of the dry soda present, and allowing the solution to rest several days. The bruised crystals freed from mother liquor by pressure between folds of absorbent paper, gave him amounts of silica and chlorid of sodium corresponding to $NaO.SiO_2.9HO$. These crystals melted at about 40° C. Kept over sulphuric acid they in time effloresced (verwittert) to the center.

Fritzsche says that he once chanced to obtain globular masses studded with minute crystals and having the composition $NaO.SiO_2.6HO$; but he had never succeeded in determining the conditions of their formation.

Yorke[10] fused 23 parts of sand with 54 parts of dry carbonate of soda, dissolved the resulting mass in water, and exposed the solution to slow evaporation *in vacuo*, over sulphuric acid. The rough salt was recrystallized *in vacuo*, to get rid of the excess of carbonate, and the pure product was found to have the composition $NaO.SiO_2.7HO$. He also obtained crystals of the same composition from a solution of silica in caustic soda.

Yorke found these crystals to part with all their water, except a fraction of one per cent, by exposure to a heat of 149° C.

Hausmann[11] says that in the purification of rough soda, the mother liquor has often yielded him, in large quantity (manchmal centnerweise), rhombohedral crystals of silicate, permanent in the air, and having the the composition $NaO.SiO_2.8HO$.

Ammon[12] also obtained the octohydrate in the form of monoclinic crystals, by dissolving silica in soda lye. They fused at 45° C.

[9] Pogg. Ann., xliii, 135.
[10] Phil. Trans., 1857, p. 533.
[11] Erdmann's Journal, xii, 294.
[12] Will and Kopp's Jahresbericht, 1862, p. 138.

I have found the same melting point, and have made several analyses which invariably go to confirm the formula given by Hausmann and by Ammon. Thus in one case the pure, carefully dried crystals, by suitable treatment with nitric acid, gave 22·74 p. c. of SiO_2, and nitrate corresponding to 23·66 p. c. of NaO. Another portion of the same sample being heated with fused bichromate of potash, lost 54·13 p. c.

The percentages answering to $NaO.SiO_2.8HO$, would be 22·55 of SiO_2, 23·31 of NaO, and 54·14 of HO.

The pure salt may be very easily made with the dense liquid which alcohol throws down from a cleansed solution of the commercial silicate,[13] $\dot{N}a\ddot{S}i_{2\cdot 25}$. When such a precipitate is stirred up with an equal weight of caustic soda liquor of sp. gr. 1·32 considerable heat is evolved, and if the mixture is set in a cold place, it begins to crystallize in a few hours. The first crop should be dissolved in a little water and recrystallized. We thus get a clear, hard salt permanent, except in presence of carbonic acid. And to avoid the action of this gas existing in the atmosphere, it is well to dry the broken up crystals in a closed space over lumps of caustic soda or lime, and keep them in a tightly stopped bottle. But as in cold weather both the formation of the rough salt and its recrystallization may be carried out in forty-eight hours or less, the absorption of carbonic acid by the dense solution, is too slight to affect the purity of the crystals deposited. Crystallization *in vacuo* is a needless refinement; and spontaneous evaporation is in any case unnecessary, for as long as the alkali is slightly in excess, a weak solution can just as well be rapidly concentrated by heat.

Ammon attempted in vain to crystallize the potash salt and to form a double silicate of potash and soda.

All my own efforts to produce crystals of potash silicate have thus far proved unavailing, though I have exposed very concentrated solutions, for many days, to the extreme cold of winter.

Berzelius fixed on SiO_3 as the constitution of silicic acid, principally on account of an assumed analogy between feldspar and alum; and there would be some show of reason for such an assumption, if feldspars contained twenty-four equivalents of water and were the only known combinations of protosilicates with sesquisilicates. But the numerous well characterized siliceous minerals are an intractable set of compounds, whatever theory we adopt, and any formula for silica which gives conformity to one class, makes other species altogether anomalous. Why should we slight the plain guidance of the simple silicates and selecting feldspar,—a complex, anhydrous combination,—presume on its resemblance to a double sulphate which

[13] See Part III, this Journal, xxxiii, p. 34. In the 18th line from the bottom of that page, it should read, "add to the filtrate two parts of alcohol," instead of "twenty parts."

crystallizes only as a hydrate? Why should we pay so little regard to analogy as to write $\dot{N}a_3\ddot{S}i_2\dot{H}_{2\,4}$ and $\dot{C}a_3\ddot{S}i_2$ for substances as definite as crystallization can make them, when soda and lime are not known to form any other unquestionable basic salts? If we attribute to silica a composition similar to that of carbonic acid, the monosilicates $\dot{C}a\ddot{S}i$, $\dot{M}g\ddot{S}i$, $\dot{M}n\ddot{S}i$, $\dot{C}u\ddot{S}i$, and the basic silicates $\dot{M}g_2\ddot{S}i$, $\dot{Z}n_2\ddot{S}i$, $\dot{M}n_2\ddot{S}i$, and $\dot{C}u_2\ddot{S}i$, will be no longer unparalleled; and though some minerals will show a composition unlike that of artificial salts, most of the double silicates will have far less strange looking formulas.

In the gum-like compounds of acid and base, crystallization can take place only when the colloid constituent is reduced to the normal quantity. Thus the sesquinitrates of glucina, iron, and chrome may form crystals when there is a full amount of acid present; but an excess of base utterly prevents crystallization. We have seen also that the stannates can remain stannates only while there is no lack of alkali. Now if we add caustic soda to waterglass, the mixture becomes capable of affording crystals just so soon as the quantity of soda very slightly exceeds that of silicic acid, and no sooner. Fair analogical reasoning would lead to the belief that then, and not till then, had we come to the proportions of the normal salt.

Thermic Relations of Waterglass.—Another argument for the formula SiO_2, though not of itself a perfectly conclusive one, may be drawn from the behavior of waterglass when mixed with caustic alkali. Taking a ten per cent solution of soda, which is too weak to become sensibly warm by mere dilution, if we add half an equivalent to an equivalent of $NaO\,2SiO_2$, the temperature immediately rises. Another half equivalent of alkali causes the evolution of somewhat less heat than before. A farther addition of soda, is not, indeed, entirely without effect,—as Thomsen[14] also observed with respect to silicic acid as well as phosphoric and boracic acids,—yet the elevation of temperature is now so very slight that we must consider the silicate as having already reached the composition of the normal salt. As $NaO\,SiO_3$ shows a capability of evolving much heat with soda, it must be an acid salt, and that cannot be its true constitution. Trials of mixture were made with two thermometers graduated to fifths of a degree Fahrenheit.

31. 110 g. of a solution containing 47 p. c. of $NaO.2{\cdot}37SiO_2$ at 64·4° F., were mixed with 212 g. of a 10 p. c. caustic soda liquor at 64·2°, so as to make $NaO.SiO_2$. The thermometer was raised to 71·4°, making a rise of 7·3° F.

32 *a*. 110 g. of 47 p. c. $NaO.2{\cdot}4SiO_2$ at 61·5° F. were mixed with 90 g. of 10 p. c. NaO at 61·7° to form $NaO.1{\cdot}5SiO_2$ or $NaO.SiO_3$. The thermometer rose to 71·4°, making an increase of 9·8° F.

b. The 200 g. of *a* at 65·2° F. were mixed with 122 g. of 10 p. c.

[14] Pogg. Annalen, xci, 90, 91.

NaO at 64·9°, so as to produce $NaO.Si_2$. The thermometer then stood at 67·3°, making a rise of 2·2° F.

c. Some of the neutral silicate of *b* at 64·6° F. was mixed with half its weight of a 10 p. c. soda solution at 64·9°. It rose to 65·4°, making an elevation of 0·7° F.

Reckoning the increase in each case as affecting only the original 110 g. of silicate, the rise in 30 would be 21·37° F. In 32 *a*, it would be 17·82°, and in *b* it would amount to 3·54°, or in both together 21·36°.

In 32 *c* it would be only 1·05°.

This heating by no means arises from simple condensation, for dilution of the same waterglass with mere water, causes even more contraction. Thus:

33 *a.* A narrow necked 100 c. c. bottle containing 50·616 g. of 47 p. c. $NaO.2{\cdot}4SiO_2$ of sp. gr. 1·558, was cautiously filled up with water. It was then closed and well agitated and there was a striking decrease of volume. Water was added once or twice with farther agitation till it stood at the right level at the normal temperature. 68·88 g. of water had been put in, and the sp. gr. was now 1·474. Calculation shows that instead of 100 c. c., it should have measured 101·36 c. c. So the contraction amounted to 1·34 p. c.

b. 110 g. of the 47 p. c. waterglass were mixed with 90 g. of caustic soda liquor of sp. gr. 1·164. The sp. gr. was now 1·363, and therefore the contraction amounted to 0·8 p. c.

c. The liquor of *b* being farther diluted with 125·2 g. of caustic soda liquor, the whole bulk was diminished 0·5 p. c.

The total contraction in both mixings amounted to 0·95 p. c. of what the aggregate volume should have been.

Though condensation results from the dilution of waterglass with water, it is a remarkable fact, and, as far as I can learn, one that has hitherto remained unnoticed, that there is at the same time a positive reduction of temperature.

34. 110 g. of 47 p. c. of $NaO.2{\cdot}4SiO_2$ at 63·6° F., were mixed with 90 g. of water at 63·4°. The temperature fell to 61·9°, making a fall of 1·6° F.

35 *a.* 100 g. of 47 p. c. $NaO.2{\cdot}4SiO_2$ at 66·2° F. were mixed with 50 g. of water at 66°. It got down to 65·1°, making a fall of 1° F.

b. These 150 g. cooled to 60·1° were mixed with 50 g. of water at 60°. The thermometer then stood at 59·2°, making a fall of 0·87° F.

c. The 200 g. of *b* at 61·3° were mixed with 50 g. of water at 61·4°. It fell to 60·85 making a fall of 0·45° F.

Bringing all to the same standard by reckoning the reduction of temperature as concentrated in 100 g., the fall in *a* would be 1·5°; in *b*, 1·74°; in *c*, 1·12°; and in 34 it would be 2·9° F.

It needs a more extensive examination than has yet been made, to show whether this unaccountable behavior is peculiar to waterglass. Metastannate of potash is neither heated nor cooled by dilution. Nor is the treatment of the metastannate with caustic potash liquor attended with any more elevation of temperature than might be due to the precipitation which results.

This latter fact, as well as the slight solubility of metastannate in caustic potash, shows that metastannate of potash is very slow to combine with more alkali. Still farther illustrations of this point will be given when we come to treat of the silicates of lime. The so-called metastannate is therefore rightly named, and is not an acid salt nor an unsaturated stannate. And, by contrast, the great avidity with which waterglass unites with more base, goes to prove that the silica in it is not a metacid, but is of the same kind as that in the normal, crystallized silicate of soda.

Manchester, N. H., April 29.