XII.—*On the amount of Water displaced from the Hydrates of Potash, Soda, and Baryta by Boracic and Silicic Acids.*

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IN a communication which was printed in the Society's Journal of July, 1859, I described a series of experiments upon the action of boracic acid on the carbonates of the alkalies and alkaline earths at high temperatures, from which it appeared, that, at a bright-red heat, one equivalent (34.9) of that acid is capable of expelling from carbonate of potash, one equivalent (22) of carbonic acid, from carbonate of soda, two equivalents; from carbonate of lithia, two and a half equivalents; from carbonate of baryta, two and a half equivalents; and from carbonate of strontia, three equivalents of carbonic acid.

It would be inferred, from these results, that one equivalent of boracic acid is capable of combining with three equivalents (and perhaps even with more) of a basic oxide of the type MO , and that its capacity for bases could not be fully satisfied by its action upon the carbonates of the more powerful bases, on account of the energy with which they retained their carbonic acid.

It might be expected that since the water is more easily expelled from the hydrates, than the carbonic acid from the carbonates, the former would allow the boracic acid to satisfy its capacity for bases far more readily, and it might be hoped that a limit would be found to the displacing power of this acid for water.

In the experiments made to determine this question with the hydrates of potash and soda, fair specimens of the fused hydrates were heated to dull redness in a silver tray enclosed in a glass tube, through which a current of air was drawn by an aspirator, the air having traversed, before entering the tube, a wash-bottle with strong potash, a wash-bottle with oil of vitriol, a U-tube with fragments of fused potash, and a second U-tube with pumice and oil of vitriol. The composition of the hydrates fused under these circumstances until of constant weight, having been carefully determined, fresh quantities were fused in the tray and weighed in the corked tube, at intervals of ten or fifteen minutes, until their weight ceased to vary to any important extent. A weighed quantity of freshly fused boracic acid was then introduced as

rapidly as possible, the tube and its contents being again weighed, in case a little water or carbonic acid should have been absorbed from the air. Heat was then gradually applied to the tube, and the boracic acid fused with the hydrate, in the current of pure and dry air, until the weight of the (corked) tube and its contents ceased to vary to any extent capable of affecting the result of the experiment. At the conclusion, the temperature was always high enough to soften the hard glass tube, an Argand gas-lamp being employed, and a hood of sheet platinum being placed over the heated part of the tube.

Since, in this way, the boracic acid was allowed to act upon the same sample of hydrated alkali, which had already been subjected to the same conditions until it ceased to lose weight, any loss which was suffered during the fusion with the boracic acid must represent the amount of water displaced from the hydrate by that acid.

In many of the experiments, a weighed chloride of calcium tube was introduced between the fusion-tube and the aspirator, and after this had ceased to gain any water from the fused hydrate alone, the boracic acid was introduced and the experiment continued until the drying tube suffered no increase of weight.

The gain of the chloride of calcium tube was found to correspond almost exactly with the loss of the fusion-tube.

Action of Boracic Acid upon Hydrate of Potash at a red heat.

A somewhat unexpected difficulty arose in the course of these experiments, from the tendency of the fused hydrate of potash to absorb oxygen when heated in a current of air.

When 50 grains of the hydrate, which had been heated to fusion in the silver tray, and maintained in fusion for half an hour in the stream of dry and pure air, were allowed to cool, and dissolved in water, 0.4 cubic inch of oxygen escaped with rapid effervescence, and grey spangles of silver separated. The loss suffered by the silver tray in the course of the experiment amounted to 0.14 grn., and the corrosion of the tray was evident, soon after the commencement of the fusion, from the appearance of lustrous spangles of silver in the clear fused hydrate.

The fused masses obtained with hydrate of potash and boracic acid effervesced very rapidly with water, from the evolution of oxygen, and allowed inky black flakes to separate, which appeared to be simply silver in a finely divided state.

In order to ascertain to what extent this absorption of oxygen would interfere with the determination of the amount of water displaced by the boracic acid, the tube containing the fused mass was heated until its weight was very nearly constant, and a weighed drying tube was then attached to the fusion-tube; on continuing the application of heat for half an hour, in a current of dry and pure air, the fusion-tube with the hydrate had lost only 0.02 grn., whilst the drying tube had gained 0.17 grn. of water, showing that the absorption of oxygen by the fused hydrate was attended by a disengagement of water. On dissolving the fused mass in water, 0.5 cubic inch of oxygen was collected, the weight of which would be 0.17 grn., so that it would have exactly counterbalanced the loss of water. Doubtless the oxygen absorbed is not exactly equal to the water expelled; but it was proved by several experiments that the difference between the two weights was not sufficient to affect the result of the experiment.

In no case of the fusion of boracic acid with hydrate of potash, was more than 0.5 cubic inch of oxygen disengaged when the mass was dissolved in water.

In order to ascertain the composition of the specimen of hydrate of potash employed, and to prove that when subjected to the conditions of the experiment, the potash remained in combination with a single equivalent of water, the following experiments were made.

1. 29.16 grns. of a good specimen of the fused hydrate were fused, in the silver tray, in a current of pure dry air, for fifteen minutes, till the hydrate began to volatilise slightly. The loss amounted to 3.56 grns. or 12.2 per cent., representing the extraneous water. On further heating for ten minutes, it gained 0.03 grn.

25.04 grns. of this fused mass, dissolved in water, and the carbonic acid determined in Fresenius and Will's apparatus, gave 0.8 grn. carbonic acid, or 3.19 per cent.

2. 27.96 grns. of the hydrate which had been fused till it ceased to lose weight, were dissolved in water, and the total amount of available alkali determined by neutralising with hydrochloric acid of known strength. The (alkaline) potash present amounted to 22.79 grns. or 81.5 per cent. Deducting from this the weight of potash required to combine with the carbonic acid, viz. 6.8 grns., there are left 74.7 grns. of potash present as hydrate, which would give 89.0 per cent. of hydrate of potash.

The solution neutralised with hydrochloric acid was evaporated to dryness, the residue ignited and weighed; it gave 36·64 grns., which contained 0·37 grn. of sulphate of potash, and 0·36 grn. of chloride of calcium, leaving 35·91 grns. of chloride of potassium, representing 22·65 grns. of potash, or 81·0 per cent. Deducting from 100 parts of the hydrate, the sum of the constituents thus determined (viz.: potash, carbonic acid, sulphate of potash, and lime), amounting to 85·24 grns., there are left 14·76 grns. to represent the water of hydration. The amount of water required by theory to combine with the 74·7 of potash present as hydrate, would be 14·3 grns.

Since the sample contained small quantities of alumina, silica, and chloride of potassium, it may fairly be concluded that one equivalent of potash was combined in the fused hydrate with one equivalent of water.

The hydrate of potash fused till it ceased to lose weight, contained therefore, in 100 parts,

Hydrate of potash	89·00
Carbonate of potash	9·99

with a little lime, alumina, sulphuric acid, silica, and chlorine.

Three experiments were made upon the action of boracic acid on the hydrate of potash, with the results exhibited in the sub-joined table.

	Actual weights in grains.			Number of equivalents.*		
	Boracic Acid.	Hydrate of Potash†.	Water expelled.	Boracic Acid.	Hydrate of Potash.	Water expelled.
I.	9·92	41·90	5·01	1	2·60	1·96
II.	9·28	41·69	4·75	1	2·70	1·98
III.	4·96	31·78	2·59	1	3·98	2·02

In the last experiment, the air, after leaving the tube in which the fusion was conducted, passed through a bottle containing lime-water, which gave not the least indication of the presence of carbonic acid.

The mean of the last two experiments would give exactly two equivalents (18) of water displaced by one equivalent (34·9) of boracic acid from an excess of hydrate of potash.

* Equivalent of boracic acid = 34·9; hydrate of potash = 47; water = 9.

† Calculated from the result of the preliminary analysis.

Action of Boracic Acid upon Hydrate of Soda at a red heat.

Hydrate of soda attacked the silver tray very slightly, its weight, in some experiments, not having perceptibly diminished; and the fused mass evolved hardly a trace of gas when dissolved in water.

The sample of hydrate of soda employed, when fused till its weight was constant, lost 1.27 per cent. of extraneous water.

The hydrate thus freed from water, was analysed, as in the case of hydrate of potash, and was found to contain, in 100 parts,

Hydrate of soda	90.41
Carbonate of soda	4.02

with a little alumina, silica, lime, chlorine, and sulphuric acid.

The subjoined table exhibits the results of three experiments upon the action of boracic acid on the hydrate of soda.

Actual weights in grains.			Number of equivalents*.			
	Boracic Acid.	Hydrate of Soda.†	Water expelled.	Boracic Acid.	Hydrate of Soda.	Water expelled.
I.	4.89	31.91	3.77	1	5.6	2.98
II.	4.46	35.78	3.43	1	7.0	2.98
III.‡	2.67	„	2.10	1	„	3.04

The mean of these experiments would give exactly three equivalents (27) of water displaced by one equivalent (34.9) of boracic acid from an excess of hydrate of soda.

Action of Boracic Acid upon Hydrate of Baryta at a red heat.

Since it was proved by experiments described in a former communication‡ that hydrate of baryta when fused in a silver crucible till of constant weight is represented by the formula BaO.HO , the experiments upon the quantity of water displaced from it by boracic acid were made in a closed silver crucible.

Crystallised hydrate of baryta, the purity of which had been ascertained by a quantitative analysis, was effloresced in vacuo over oil of vitriol, until it was converted into the compound $\text{BaO.HO} + \text{Aq.}\S$. The proportion of water having been verified by direct

* Equivalent of soda = 31

† Calculated from the result of the preliminary analysis.

‡ A fresh quantity of boracic acid was added to the fused mass in II, and the experiment continued.

§ Quarterly Journal Chem. Soc. April, 1860.

experiment, a weighed quantity of the hydrate was rapidly and intimately mixed with a weighed quantity of pure boracic acid dried at 212° Fah., which had been previously shown to have the composition $\text{HO} \cdot \text{BO}_3$.

The crucible was then covered and heated until it ceased to lose weight. By subtracting from the loss of weight suffered by the contents of the crucible, the weight of water known to be expelled by heat from the effloresced hydrates of baryta and boracic acid, the amount of water really displaced from the hydrate of baryta by the boracic acid was inferred.

In the following table, the results of four experiments of this description are recorded.

Actual weight in grains.			Number of equivalents*.		
Boracic Acid ($\text{HO} \cdot \text{BO}_3$).	Hydrate of Baryta ($\text{BaO HO} + \text{Aq.}$)	Water expelled.	Boracic Acid.	Hydrate of Baryta.	Water expelled†.
I. 3.17	27.36	5.36	1	4.00	2.92
II. 3.00	22.93	4.86	1	3.55	3.12
III. 2.51	21.60	4.17	1	4.00	3.11
IV. 2.96	25.47	4.87	1	4.00	3.03

From the mean of these experiments, it appears that almost exactly three (3.045) equivalents (27) of water are displaced by one equivalent (34.9) of boracic acid from an excess of hydrate of baryta.

If the equivalent of boracic acid be taken as 34.9, it displaces, from hydrate of potash, two equivalents, and from the hydrates of soda and baryta, three equivalents of water. Now, it was found in the experiments cited above, that one equivalent of boracic acid displaced only two and a half equivalents of carbonic acid from the carbonate of baryta, though it displaced three equivalents from the carbonate of strontia, which stands in the same position with respect to the carbonates, as hydrate of baryta does to the hydrates, that is, the next in the series of carbonates (carbonate of lime) is decomposable by heat alone, just as hydrate of strontia (the next in the series of hydrates).

If it be granted that the water in hydrate of baryta is more easily displaced than that in hydrate of soda, it follows that since boracic acid displaces no more water from the former than from the latter, its capacity for bases must be satisfied by the three equivalents of soda or baryta with which it then combines, as by

* Equivalent of baryta = 76.5.

† After deducting that due to the materials.

the three equivalents of strontia with which it combined when heated with the carbonate.

If the number 34.9 be retained for the equivalent of boracic acid, it must therefore be regarded as a tribasic acid; a view which may be thought to receive some support from the following considerations.

Boracic ether is represented, upon the ethyl hypothesis, as $3C_4H_5O \cdot BO_3$, and its analogues in the methyl and amyl series have a similar composition. Crystallised boracic acid has the formula $3HO \cdot BO_3$. Borate of magnesia, obtained by Rammelsberg by boiling a solution of borax with sulphate of magnesia, had the composition $3MgO \cdot BO_3$. Octohedral borax, and common borax dried at $212^\circ F.$, have the composition $NaO \cdot 2BO_3 + 5HO$, which may be represented as a tribasic salt if the water be considered to play the part of a base.

The biborate of potash, according to Laurent, has a similar composition $KO \cdot 2BO_3 + 5HO$. A terborate of potash, obtained by Laurent, had the composition $KO \cdot 3BO_3 + 8HO$, which would also be a tribasic salt if the water were admitted into the formula.

The tendency of boracic acid to form acid salts and double salts, is not observed in acids which are undeniably monobasic.

Action of Silicic Acid upon Hydrate of Potash at a red heat.

The experiment was conducted in exactly the same manner as in the case of boracic acid. The fused mass of silicate of potash dissolved, in every case, entirely in water, with the exception of a few white lustrous flakes of silver, disengaging oxygen with rapid effervescence: The largest quantity of oxygen disengaged (from a mass containing 40 grains of hydrate of potash, which had been fused for about an hour, in all) was 0.9 cub. in., which would weigh 0.31 grn., and would be at least partly compensated for (as shown by the experiment previously cited) by a corresponding displacement of water from the fused hydrate.

The annexed table contains the results of four experiments.

	Actual weights in grains.			Number of equivalents.*		
	Silicic Acid.	Hydrate of Potash†.	Water expelled.	Silicic Acid.	Hydrate of Potash.	Water expelled.
I.	4.65	31.46	2.15	1	3.6	1.54
II.	4.64	41.23	2.26	1	4.7	1.62
III.	5.20	32.17	2.44	1	3.3	1.45
IV.	4.97	31.24	2.29	1	3.3	1.53

* Equivalent of silicic acid (SiO_2) = 30.

† Calculated from the result of the preliminary analysis.

The silicic acid used in these experiments had been prepared by the fusion of sand with carbonate of soda, and carefully purified from all soluble ingredients by the usual processes.

It appears from these experiments that the proportion of water expelled increases, to a slight extent, with the proportion of hydrate of potash employed; but if the mean of experiments I, III, and IV be taken, we have almost exactly 1·5 eqs. (13·5) of water displaced by one equivalent (30) of silicic acid from an excess of hydrate of potash at a red heat*

Action of Silicic Acid upon Hydrate of Soda at a red heat.

The same specimen of silicic acid was used for these experiments, together with the hydrate of soda employed in the case of boracic acid.

	Actual weights in grains.			Number of equivalents.		
	Silicic Acid.	Hydrate of Soda†.	Water expelled.	Silicic Acid.	Hydrate of Soda.	Water expelled.
I.	4·83	35·75	2·94	1	5·5	2·02
II.	4·91	31·04	3·03	1	5·2	2·05

These results indicate that almost exactly two equivalents (18) of water are displaced by one equivalent (30) of silicic acid from an excess of hydrate of soda at a red heat.*

Action of Silicic Acid upon Hydrate of Baryta at a red heat.

The experiments with hydrate of baryta and silicic acid were attended, as might be expected, with more difficulty, partly from the want of fusibility of the silicate of baryta, and partly from the disparity in the equivalent numbers of these bodies.

The first three experiments in the table were made in a covered silver crucible, and the fourth in the silver tray, heated in a current of dry and pure air.

In experiments II and III, the silicic acid (in II, prepared from sand, in III pure rock-crystal) was mixed with effloresced hydrate of baryta, the extraneous water having been determined by preliminary analysis, and allowed for in the calculation.

In I and IV, the hydrate of baryta was fused till it ceased to

* Col. Yorke found that 30 parts of silicic acid expelled 8·76 of water (0·97 eqs.) from hydrate of potash, and 15·7 of water (1·74 eqs.) from hydrate of soda, the fusion being effected in a deep crucible.

† Calculated from the preliminary analysis.

lose weight, the silicic acid then added, and the fusion continued till no further loss was perceived.

The fused mass, in every case, gelatinised when treated with dilute hydrochloric acid.

	Actual weights in grains.			Number of equivalents.		
	Silicic Acid.	Hydrate of Baryta (BaO.HO).	Water expelled.	Silicic Acid.	Hydrate of Baryta.	Water expelled.
I.	1.97	21.30	1.09	1	3.8	1.84
II.	3.31	30.47	1.83	1	3.2	1.85
III.	3.61	30.49	1.97	1	3.0	1.82
IV.	2.85	31.78	1.61*	1	3.9	1.88

It may, I hope, be fairly inferred from these experiments, that one equivalent (30) of silicic acid does not displace more than two equivalents (18) of water from hydrate of baryta at a red heat.

Silicic acid then, like boracic, appears to have satisfied its capacity for bases in its action upon hydrate of soda, when it combines with two equivalents of that alkali, since it refuses to displace a larger proportion of water from the hydrate of baryta. If the formula SiO_2 (= 30) be accepted for silicic acid, it would be a bibasic acid, a conclusion to which the following considerations lend some support.

The disilicate of ethyl has the formula $2\text{C}_4\text{H}_5\text{O.SiO}_2$. The ordinary specimens of crystallised finery-cinder and of the slag from copper-smelting furnaces (melting for coarse metal), have the composition 2FeO.SiO_2 . It is also commonly asserted that the most fusible slag from the blast furnace is that in which the oxygen contained in the bases equals that in the silicic acid, which is the case in silicates of the bibasic type (2MO.SiO_2).

Berzelius obtained the salts—

which are obviously bibasic, since Al_2O_3 is equivalent to 3MO .

Scheerer† has recently found that 30 parts of silicic acid fused with a large excess of carbonate of soda at a high temperature, expel 44 parts of carbonic acid. Col. Yorke had previously

* Increase of weight of the chloride of calcium tube. The loss of weight suffered by the fusion tube was 1.63, which would give 1.91 eqt. of water displaced by 1 eqt. of silicic acid. On the supposition that 1 eqt. of SiO_2 had displaced 2 eqs. HO, the actual weight of the water should be 1.71 grns.

† Ann. Ch. Pharm. cxvi. 129.

shown that 30 parts of silicic acid expelled 44 parts of carbonic acid from carbonate of lithia at a high temperature.

The disposition of silicic acid to form acid salts and double salts does not belong to a monobasic acid.

The formulæ of some of the chief natural silicates constituted upon a bibasic type are here given.

Villarsite	$2(2\text{MgO}.\text{SiO}_2) + \text{Aq.}$
Batrachite	$2\text{CaO}.\text{SiO}_2 + 2\text{MgO}.\text{SiO}_2^*$
Cerite	$2\text{CeO}.\text{SiO}_2 + 2\text{Aq.}$
Bucholzite	$2\text{Al}_2\text{O}_3.3\text{SiO}_2$
Pholerite	$2\text{Al}_2\text{O}_3.3\text{SiO}_2 + \text{Aq.}$
Vesuvian	$3\text{MO}.\text{M}_2\text{O}_3.3\text{SiO}_2^\dagger.$
Garnet	$3\text{MO}.\text{M}_2\text{O}_3.3\text{SiO}_2$
Scapolite } Anorthite }	$\text{CaO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$
Sodalite	$3(\text{NaO}.\text{SiO}_2 + \text{Al}_2\text{O}_3.\text{SiO}_2) + \text{NaCl.}$
Zircon	$2\text{ZrO}.\text{SiO}_2$
Phenakite	$2\text{GfO}.\text{SiO}_2$
Helvine	$\text{GfO}.\text{MnO}.\text{SiO}_2$
Hydrosilicate of manganese	$2\text{MnO}.\text{SiO}_2 + 2\text{Aq.}$
Kärfholite	$\text{MnO}.\text{Al}_2\text{O}_3.2\text{SiO}_2 + 2\text{Aq.}$
Electric Calamine	$2\text{ZnO}.\text{SiO}_2 + \text{Aq.}$
Hyalosiderite	$4\text{MgO}.2\text{FeO}.3\text{SiO}_2.$
Knebelite	$\text{MnO}.\text{FeO}.\text{SiO}_2$
Cyanite	$2\text{Al}_2\text{O}_3.3\text{SiO}_2$ (Klaproth).
Hisingerite	$\text{FeO}.\text{Fe}_2\text{O}_3.2\text{SiO}_2 + 6\text{Aq.}$
Olivine	$2(\text{MgFe})\text{O}.\text{SiO}_2$

Several points of resemblance between carbon, boron, and silicon, as well as between their acids, lead many chemists to associate them as a natural group. But the atomic weights (6, 10.9, and 14) do not exhibit any such simple numerical relation as is frequently to be traced in other groups of elements presenting similar analogies.

If the group BO_3 which appears by the above experiments, to

* According to Mitscherlich, many furnace slags, having the crystalline form of olivine have the same composition as batrachite (Gmelin).

† MO representing CaO , FeO , MnO , or MgO , and M_2O_3 , Fe_2O_3 or Al_2O_3 .

represent 3HO , be supposed really to contain 3 atoms of boracic acid, the atomic weight of the latter would be $\frac{34.2}{3}$ or 11.6 and that of boron, 3.6.

Again, if SiO_2 be supposed to represent 2 atoms of silicic acid, the atomic weight of the latter would be $\frac{30}{2}$ or 15, and that of silicon 7.

The atomic weights of the three elements would then be

Boron	.	.	.	.	.	3.6
Carbon	.	.	.	.	.	6
Silicon*	.	.	.	.	.	7

The atomic weight of boron added to twice that of silicon, would then give (17.6) nearly thrice that of carbon.

If boracic acid be regarded as BO_2 , the atomic weight of boron would be 7.3, or almost exactly half that assigned by Berzelius to silicon (14.8).

According to this view, the numbers would be

Carbon	.	.	.	.	.	6
Boron	.	.	.	.	.	7.3
Silicon	.	.	.	.	.	14.8

an arrangement more in accordance with our knowledge of the gradations observed in the properties of carbonic, boracic, and silicic acids, such as their displacing power over water, their physical states, solubility, acid character, &c.