ART. XI.—*The Action of Carbon Dioxide on the Borates of Barium*; by LOUIS CLEVELAND JONES.

[Contributions from the Kent Chemical Laboratory of Yale University—CVIII.]

IN 1888 Morse and Burton described "A Method for the Separation and Determination of Boric Acid."* I published an article in 1898 entitled "The Action of Carbon Dioxide on Soluble Borates,"† an account of certain results not in accord with those of Morse and Burton. More recently‡ Morse and Horn record at some length "preliminary experiments" made in an effort to substantiate the original analytical results of Morse and Burton.

I have waited for some time for the promised resumption of these experiments, and lest further silence be misunderstood, will show that the action of carbon dioxide and boric acid, in the presence of the one base—barium hydrate—both in the dry state and in solution, is that which I pointed out in my original paper, and, further, that these later experiments of Morse and Horn, correctly interpreted, completely substantiate this position.

The question is concerning the action of carbon dioxide gas upon a mixture containing boric acid and an excess of barium hydrate, viz: what part of the total barium is converted into carbonate and, upon evaporation and ignition, how much, if any, of this barium carbonate is reconverted into borate? Indirectly, and stated differently, it is: Can boric acid, when once separated, be brought into definite and weighable condition by the method recommended by Morse and Burton? (Loc. cit.) Despite the title of the contribution of Morse and Burton, Morse and Horn now regard the separation of the boric acid "as the most, and in fact the only, important feature of their contribution."

The following is the entire description of that part of the process relating to the determination of the boric acid as originally given by Morse and Burton: "The quantity of the dilute barium hydroxide solution" (about 25^{cc}) "which is equivalent to 25^{cc} of the standard sulphuric acid" ($N/10$) "is run into the flask, and the apparatus attached to a filter-pump." This is done preparatory to receiving the alcoholic solution of boric acid—a little over 75^{cc}. "*Finally, the excess of the barium hydroxide is precipitated by passing into it a current of carbon dioxide: the contents of the flask are transferred to*

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* Am. Chem. Jour., March, 1888, vol. x, pp. 154–158.
† This Journal, vol. v, pp. 442–446, June, 1898.
‡ Am. Chem. Jour., August, 1900, vol. xxiv.

a platinum dish, evaporated to dryness, and heated to a constant weight over a triple burner."*

In my original article I made three claims: 1st, that the metaborate of barium may be decomposed by gaseous carbon dioxide; 2d, that the boric acid thus "liberated" may be lost by volatilization; 3d, that the metaborate of barium and the carbonate may interact at high temperatures with the loss of carbon dioxide. These facts preclude the use of the method described by Morse and Burton for the determination of boric acid. The more recent experiments of Morse and Horn not only substantiate these facts but disclose a fourth objection to the use of this method for its original purpose, viz: the difficult dehydration of the metaborate of barium, concerning a mixture of which with barium carbonate, Morse and Burton originally said that it "being neither markedly hygroscopic nor capable of absorbing carbon dioxide, can be brought to a constant weight more readily than one containing oxide of calcium or magnesium."

The decomposition of barium metaborate.—That barium metaborate may be decomposed by carbon dioxide in aqueous solution, is proved by my original experiments; and now is corroborated by those of Morse and Horn. These authors, however, urge that, in alcoholic solutions—78 per cent—the boric acid would be in the form of metaborate of barium only and this should be unattacked to the extent of its insolubility. To test this point directly, carbon dioxide was passed into equivalent parts of barium hydrate and boric acid in 78 per cent alcoholic solution. The precipitate gave abundant evidence of the presence of carbonate, showing decomposition of the metaborate. The extent of this decomposition was determined quantitatively by determining the carbon dioxide in another similar precipitate. Barium hydrate and an excess of boric acid in a mixture consisting of 73 per cent alcohol, were treated in the cold for three hours with carbon dioxide. The precipitate was filtered, washed, and analyzed for carbon dioxide with the following result:

$Ba(OH)_2$ taken, 0·7883 grm.; B_2O_3 taken, 0·3576 grm.; excess B_2O_3, 0·0357 grm.; CO_2 found, 0·2042 grm.; CO_2 in total barium carbonate, 0·2024 grm.

Evidently the metaborate of barium in alcohol was completely decomposed by carbon dioxide and the boric acid *liberated.*

Another experiment was made as above, except that equivalents were taken and the treatment with carbon dioxide was discontinued after thirty minutes. After stopping the flow of carbon dioxide, the mixture was boiled for three minutes, to remove any excess of gas. The precipitate was filtered, washed

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* The italics, as in other quotations to follow, are mine.—L. C. J.

with 150^{cc} of hot water and analyzed for carbon dioxide. The result was as follows:

$Ba(OH)_2$ taken, 0·4379 grm.; B_2O_3 taken, 0·1788 grm.; alcohol, 76 per cent; CO_2 found, 0·1135 grm.; CO_2 in total barium carbonate, 0·1124 grm.

Upon evaporating to small volume the filtrate from this experiment, boric acid in abundance crystallized from the solution. Under these conditions, then, well within the limits of the recommendations of the Morse and Burton process, it is clear that barium metaborate is completely converted into carbonate with consequent *liberation* of boric acid, and that alcoholic solutions in no way prevent the action.

It might be argued that, in an evaporating mixture containing barium carbonate and boric acid in 78 per cent solution, the reaction would be reversed after the volatilization of the alcohol and the solutions became more concentrated. Indeed, Morse and Horn use this explanation (p. 110). To test this hypothesis, equivalent parts of barium hydrate and boric acid in alcohol were treated with carbon dioxide for two hours, the mixture evaporated to dryness and the carbon dioxide remaining in the dry residue determined. The following results were obtained:

$Ba(OH)_2$ taken, 0·4554 grm.; B_2O_3 taken, 0·1860 grm.; alcohol, 82 per cent; CO_2 found, 0·1018 grm.; CO_2 in total barium carbonate, 0·1169 grm. This shows that even with the very strong alcoholic solution, which was used by mistake, about 90 per cent of the metaborate was converted into carbonate and remained as carbonate after bringing to dryness.

To demonstrate, in another way, the presence of boric acid after the treatment recommended by Morse and Burton, I have used the methyl alcohol flame-test. Equivalents of barium hydrate and boric acid (I have used the word equivalents repeatedly, meaning quantities to form exactly the most important salt under discussion, viz: metaborate) were evaporated to dryness, methyl alcohol added and burned without getting the slightest indication of free boric acid. Again, equivalents of barium hydrate and boric acid were treated in alcoholic solution with carbon dioxide, the ethyl alcohol and water removed by evaporation, and methyl alcohol applied and burned with unmistakable indications of free boric acid—burning with a solid green flame.

Since free boric acid does not decompose barium carbonate upon evaporation, the question arises as to what is the temperature required to bring about this decomposition. The following experiment throws some light upon this point: finely divided anhydrous boric acid (0·1925 grm.) and barium carbonate (0·5177 grm.) were mixed in a platinum crucible, moistened with water and allowed to stand sixty hours. The contents of the crucible were then dried on a steam bath and afterwards heated for thirty minutes in an air bath at 350° C. The carbon dioxide remaining in the mixture was determined and found to be 0·0844 grm. Total CO_2 in $BaCO_3$ taken, 0·1154 grm.; CO_2 liberated by B_2O_3, 0·0310 grm.; CO_2 displaceable with formation of $Ba_2OB_2O_2$ by B_2O_3 taken, 0·1210 grm. Therefore, 74·38 per cent of the boric acid taken, if still unvolatilized, remains uncombined—at 350° C.

From the foregoing experiments, then, it is obvious that carbon dioxide decomposes the metaborate of barium in either aqueous or alcoholic solutions, and a portion, at least, of this boric acid liberated not only remains uncombined after evaporating to dryness but even upon heating to a high temperature.

Loss of boric acid by volatilization.—It is scarcely conceivable that a mixture of boric acid and barium carbonate in water should not lose an appreciable amount of boric acid on evaporation. Morse and Horn have found a detectable loss of boric acid from treating aqueous mixtures of barium hydrate and boric acid with carbon dioxide and evaporating. The carbon dioxide was stopped shortly after the alkaline coloration with phenolphthalein was destroyed. The quantity found by them is given, and varies from 0·0001 grm. to 0·00016 grm.; in one instance exactly 0·00012 on 0·0633 grm. of total boric acid present: $\left\{ \frac{0{\cdot}00636 + 0{\cdot}02538}{2} \times 13{\cdot}77 \right\} \div 3{\cdot}448 = 0{\cdot}0633$ grm. The decrease in weight should be even more noticeable in the presence of alcohol, though Morse and Horn did not detect more than 0·0040 grm. B_2O_3 $[(1/14200) \times 50 = 0{\cdot}0040]$ and this only when the concentration of alcohol arose above 92 per cent. Amounts below one part in 14,200 they were not able to discover.

The actual amount of boric acid volatilized on evaporating such mixtures to dryness is, of course, small, but certainly appreciable. Furthermore, under the analytical conditions described by Morse and Burton, the greater loss of boric acid doubtless occurs with the escape of water of combination between the temperature 100° C. and that at which the boric acid completely replaces its equivalent of carbon dioxide in barium carbonate. This temperature I have shown by experiment to be at least above 350° C. On the other hand, as was shown in my original paper, under extreme conditions, by the use of methyl alcohol and a continuous current of carbon dioxide, it is possible to volatilize all the boric acid from a mixture of barium hydrate and barium metaborate.

The interaction at high temperatures of the carbonates and borates of barium.—I have shown that the treatment recommended by Morse and Burton may result in a mixture containing barium carbonate and barium metaborate, or barium carbonate, barium metaborate and boric acid, or, indeed, barium carbonate and *free* boric acid. Of these compounds, both the barium metaborate and boric acid retain water considerably beyond 100° C.

Morse and Burton assumed that they had, after evaporation, a mixture containing only barium carbonate and barium metaborate. Morse and Horn explain it as follows: "It may be urged that even if Morse and Burton had the metaborate in insoluble condition, and it had been sensibly attacked during the treatment with carbon dioxide, nevertheless, in the subsequent attempt to heat the dried residue to constant weight, the metaborate must have attacked the carbonate. It has *since* then come to light that *some caution* must be exercised in this part of the manipulation. In the original description of the method, it was simply stated that the residue was heated to constant weight over a triple burner. The practice then, and on the few occasions when the process has since been used, was to hold the burner in the hand and rapidly play the flame over the platinum dish in order to secure as uniform a temperature of the contents as possible. The object in using a triple burner was not to obtain a *very high temperature*, which is not necessary, but, rather, to employ a flame large enough to keep the whole dish hot. No difficulty was experienced, when the heating was conducted in this manner, in *quickly* obtaining *constant and correct weights*. Nevertheless, it must be admitted, the authors of the method did not at that time suppose that the temperature at which the meta salt will attack the carbonate is so low as it has since been found to be. The temperatures employed by Jones were evidently *far* above those to which Morse and Burton heated their mixtures of metaborate and carbonate."

The use of a triple burner to secure gentle and uniform heating is unusual. Indeed, Morse and Horn use it in experiment XIV for a quite different purpose, i. e., to secure a temperature which decomposed the carbonate and borate mixture present. That the temperatures employed by me in my original experiments were *not* "*far* above those" used by Morse and Burton, can be answered best by the words of Morse and Horn: "At a *full red heat* the meta salt attacks the carbonate with expulsion of carbon dioxide" (page 130). "The temperature at which a mixture of the metaborate and the carbonate of barium is stable and which is still sufficiently high to insure the dehydration of the former, *appears* to be *just* under a red heat" (page 130). Morse and Horn do not, however, produce any evidence to show that the meta salt is dehydrated below red heat. In fact, their experimental evidence points the other way: "The experiment of heating the material, after treatment with carbon dioxide, until the weight fell below that calculated for a mixture of metaborate and carbonate, and then of exposing it in the air until the weight became very nearly constant, and finally, of removing the slight excess of weight by placing the material over calcium chloride or sulphuric acid, was many times repeated and always with a satisfactory degree of success except in two cases. In these it was *suspected* that, *while some portions of the material had been heated high enough to decompose the carbonate, other portions had not reached the temperature required for the complete dehydration of the metaborate;* for it was observed that the weights gained in the air on these occasions far exceeded the calculated deficits." Evidently, the temperatures at which decomposition of the carbonate and dehydration of the metaborate of barium takes place, cannot be *far* apart when both processes are going on in the same crucible.

I quote further (page 133): "In general, it was found difficult, by heating in our bath, to bring the too great initial weight of the material down to that calculated for a mixture of metaborate and carbonate, though in one case (No. XXX) this was accomplished by heating in the bath for three hours over three burners. The temperature on this occasion, however, rose so high that the thermometer was removed." The thermometer used registered as high as 550° C.

The conditions described above can only be accounted for in two ways, viz: (1) The metaborate has been decomposed by carbonate dioxide, though this treatment was stopped five minutes after the disappearance of alkalinity with phenolphthalein—and the barium carbonate has not at this temperature been decomposed; or (2) the metaborate still contains water.

A combination of both these explanations, doubtless, more nearly expresses the truth. Morse and Horn, however (page 134), seem to prefer the latter explanation. "This," they say (i. e., the behavior of the ignited mixture in experiment XXX), "led us to *suspect* that the temperature at which complete dehydration occurs and that at which the metaborate begins to attack the carbonate cannot be very *far* apart."

The experiments made by Morse and Horn in an effort to show how these mixtures can be "quickly" brought to "constant and correct weights" are interesting, but not conclusive. They proposed (page 119) "to determine also the effect of exposing these mixtures, after heating, in an atmosphere containing carbon dioxide" with the object of finding "the temperature at which it was presumed a mixture of the metaborate and the carbonate of barium is stable, or rather the temperature at which it becomes stable." All these experiments, and those in which the mixtures were exposed to the air and dried in a dessicator, prove nothing; in fact, Morse and Horn only draw inferences from them (page 134): "From this it appears probable that the more basic borate which is formed at high temperatures, is decomposed at ordinary temperatures by the carbon dioxide of the air and reconverted into the borate and carbonate. A similar absorption of carbon dioxide takes place when material whose weight has been reduced below the normal amount, is reheated in the bath at temperatures under 500° C. From this it is *inferred* that normal weights could be *quickly* obtained by first heating to a high temperature and then at a lower one, but we have not yet tried the experiment."

Those final and satisfactory weights which are sometimes obtained may be due to the presence of an excess of carbon dioxide or water, or both, in an amount sufficient to replace any boric acid volatilized in evaporation and especially with the water of hydration. That Morse and Horn did have present in these experiments at the beginning of evaporation some free boric acid—or, if it is preferred, a more acid borate—and a corresponding increase in the amount of carbonate, is certain, because in all these experiments of which the results are recorded, carbon dioxide was passed for not less than fifteen minutes, or when phenolphthalein was used as an indicator, usually for five minutes after the disappearance of the alkaline reaction.

In my original paper I suggested the use of phenolphthalein to prevent too great an excess of carbon dioxide and corresponding decomposition of the metaborate. In a recent experiment I have tested the action of a metaborate in alcoholic solution upon this indicator, and find that exact equivalents of barium hydrate and boric acid in 78 per cent alcohol give a decided alkaline reaction, and that this alkaline coloration disappears only when about 36 per cent more boric acid is added. It is clear that phenolphthalein gives indication, not when the excess of barium hydrate is converted into carbonate, but at a point considerably beyond. Morse and Horn, then, were working with barium carbonate and an acid borate, and in many cases, most certainly, with barium carbonate and free boric acid.

If by accident—and I see no other way of doing it—the action of carbon dioxide is stopped just when the excess of barium hydrate has been converted into carbonate, still nothing is gained; for the experiments of Morse and Horn—if they show anything—make it clear that even these salts cannot be weighed with safety.

These experiments leave nothing more to be done to prove the impossibility of bringing to definite and constant weights the mixtures resulting from the method described by Morse and Burton. Furthermore, in the promised forthcoming continuation of this study by Morse and Horn, I see no possibility of any other deduction.

In conclusion, then, I reiterate:—First. Carbon dioxide decomposes the metaborate of barium in either aqueous or alcoholic solutions.

Second. The boric acid liberated may in part escape during evaporation to dryness and especially before reaching that temperature at which it has completely recombined with the barium, replacing carbon dioxide.

Third. A mixture, containing barium carbonate and hydrated boric acid, or barium carbonate with the hydrated metaborate and boric acid, or even barium carbonate and hydrated metaborate, cannot with safety be brought to definite composition for weighing.