TAYLOR AND BOSTOCK: RESEARCHES ON

LIV.—Researches on Bleaching Powder. Part II.

The Action of Dilute Acids on Bleaching Powder.

By ROBERT LLEWELLYN TAYLOR and CLIFFORD BOSTOCK.

MUCH discussion has taken place from time to time as to the action of dilute acids on bleaching powder. Long ago, Gay Lussac stated that a colourless solution of pure hypochlorous acid could be obtained by acidulating a solution of bleaching powder with dilute nitric acid, and then distilling it (Ann. Chim. Phys., 1849, [iii], 26, 163). On the other hand, Goepner (Dingl. Polyt. J., 1873, 209, 204) asserted that on decomposition with acids bleaching powder simply decomposes into its constituents (chlorine and lime), yielding chlorine and no hypochlorous acid. In 1874 Schorlemmer took part in the discussion (Journ. Chem. Soc., 27, 335), confirming Gay Lussac's observation, and pointing out that the students in Owens College prepared hypochlorous acid by Gay Lussac's method as part of their regular course.

This uncertainty was doubtless mainly due to the fact that no satisfactory method of distinguishing between free chlorine and hypochlorous acid was known at the time, most trust apparently being placed in the reaction with mercury, with which hypochlorous acid was said to produce an oxychloride, whereas chlorine did not.

Kopfer (Journ. Chem. Soc., 1875, 28, 713), trying to decide between these contradictory statements, investigated the action of dilute nitric, sulphuric, and hydrochloric acids on bleaching powder. He prepared the bleaching powder himself, but according to his analysis it was a very different substance from the ordinary commercial article, as it contained more than 50 per cent. of free lime.

Kopfer summarised his results as follows:

"If to a solution of bleaching powder, or to the same substance in the dry state, a dilute mineral acid, such as nitric, hydrochloric, or sulphuric be added in such quantity as to saturate the caustic lime and to decompose the hypochlorite supposed to be present according to Gay-Lussac's hypothesis, then, on distillation, an aqueous solution of almost chemically pure chlorine monoxide is obtained, which amounts in the most favourable case to about 92 per cent. of the chlorine monoxide as corresponding with the theoretical hypochlorite."

Recently one of us (Taylor, Trans., 1910, 97, 2541) described a method of distinguishing between hypochlorous acid and free chlorine, and of determining the proportions of each in a mixture of the two. The method depends on the fact that, for the same amount of chlorine present, the oxidising action of hypochlorous acid is twice as great as that of free chlorine. To a mixture of the two substances an excess of sodium arsenite is added. The liquid is then divided into two equal parts; in one part the amount of arsenite oxidised is determined, and in the other the amount of chloride produced. The proportions of the two substances in the mixture can then easily be calculated.

In the present investigation the above very simple and yet fairly accurate method has been applied to a repetition of some of Kopfer's experiments, extending it also to the action of acids other than those described by him. In all these experiments the chloride present in the second half of the arsenite solution was determined by Volhard's method, which is certainly more rapid and apparently quite as trustworthy as the one described in the former paper.

The bleaching powder used for most of the experiments was a fair average sample, analysis of which gave the following figures:

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Total chlorine = 39.05 per cent.

Available chlorine = 34.63 ,,

Total lime (CaO) = 44.9 ,,

Free lime = 13.1 ,,
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Assuming the bleaching powder to consist of calcium chloride and calcium hypochlorite, then 100 grams of it would contain 34.4 grams of the latter. Also 10 grams of it (the amount taken in practically all the experiments) would require 46.8 c.c. of N-acid to neutralise the whole of the free lime, and 48.8 c.c. more to decompose the whole of the calcium hypochlorite present, a total of 95.6 c.c.

In each experiment 10 grams of bleaching powder were rubbed with water, and then the desired volume of acid was added slowly from a burette, the mixture being continually shaken, in order to avoid, so far as possible, local excess of acid. (It is difficult to do this entirely, however, and this doubtless accounts, to some extent, for some of the irregularities in the results.) The whole was then distilled from a flask of about 1 litre capacity, the vapours being

passed through a small condenser. A few drops of the distillate were allowed to escape, and then 20 c.c. were collected. For determining the amounts of hypochlorous acid and chlorine, 10 c.c. only of this were used.

As one would anticipate, the amount of water, and thus the extent of dilution of the acid, makes a considerable difference in the results, and, in order to ascertain what was the best amount of water to use, some experiments were made, using 10 grams of bleaching powder and 50 c.c. of N-sulphuric acid for each experiment, but varying the amount of water. It was found that with quantities of water varying from 50 c.c. to 200 c.c. considerably more free chlorine was produced than with larger amounts, and in all the subsequent experiments 300 c.c. of water were always used.

In the following tables, where two or more sets of figures are given they relate to separate experiments.

Table I.

Distillation with Sulphuric Acid.

| | | | Hypo- | |
|---------------------------------|--------------------|-----------------------|-----------------------------|------------------------|
| Volume of $N-H_2SO_4$, in c.c. | Arsenite oxidised. | Chloride produced. | chlorous acid, per cent. | Chlorine, per cent. |
| 80 | 0.4 | 0.2 | 100.0 | 0.0 |
| 40 | 6.8 | 3 · 45 | 97.0 | 3.0 |
| 50 | 8·65 | 4·5 | 92·2 | 7·8 |
| | 9·15 | 4·75 | 92·6 | 7·4 |
| 60 | 16·3 | 8·85 | 84·2 | 15·8 |
| | 16·05 | 8·8 | 82·4 | 17·6 |
| 70 | 24·55 | 14·4 | 70·5 | 29·5 |
| | 24·6 | 14·15 | 73·8 | 26·2 |
| 80 | 30.65 | 17·55 | 74·6 | 25·4 |
| | 31.05 | 17·9 | 73·5 | 26·5 |
| 90 | 34·1 | 19·35 | 76·0 | 24·0 |
| | 33·4 | 18·8 | 77·7 | 22·3 |
| 100 | 24·0 | 14·0 | 71·4 | 28·6 |
| | 28·55 | 17·1 | 67·0 | 33·0 |
| 150 | 10·15 | 8·3 | 22·3 | 77·7 |
| | 10·75 | 8·75 | 22·9 | 77·1 |
| 200 | 7·05 | 7·25 | 0.0 | 100·0 |
| | 9·1 | 9·35 | 0.0 | 100·0 |
| | | | | |

It may be pointed out that in the above table the figures in the column headed "arsenite oxidised" afford an indication of the amount of hypochlorous acid (or hypochlorous acid and chlorine) in the distillate. As 10 c.c. of the distillate were used in each determination, and as the solution of arsenite was N/10, and, further, as the "arsenite oxidised" represents the amount in half of the solution, it is plain that, using 50 c.c. of N-sulphuric acid, a

distillate is obtained which is $N/10\times1.7$ or 1.8. A decinormal solution of hypochlorous acid would contain 2.62 grams of HOCl per litre, or 0.262 per cent., so that the distillate referred to would contain about 4.5 grams of HOCl per litre. It will be observed that with 80 or 90 c.c. of acid the distillate is much stronger, but it contains a greater proportion of chlorine.

The figures representing the proportion of hypochlorous acid and chlorine in the distillate are not of much value beyond the point where 70 c.c. of acid were used, because, as the amount of free chlorine increases, the whole of it is not condensed in the distillate. It begins to escape about the point referred to, and, as the amount of acid is further increased, more and more, and finally most of it, escapes.* Therefore, in the accompanying curve, the progress of the alteration in the reaction is indicated by the gradual diminution of the amount of hypochlorous acid. These remarks apply to the cases of the other mineral acids as well.

Table II.

Distillation with Hydrochloric Acid.

| Volume of N-HCl, in c.c. | Arsenite oxidised. | Chloride produced. 2.0 | Hypo- chlorous acid, per cent. 100.0 | Chlorine, per cent. 0.0 |
|--------------------------|--------------------|------------------------------|---|-------------------------------|
| 50 | 11.25 | 5·8 | 94·0 | 6·0 |
| | 11.2 | 5·75 | 94·8 | 5·2 |
| 60 | 17·4 | 9·5 | 83·2 | 16.8 |
| | 17·0 | 9·45 | 80·0 | 20.0 |
| 70 | 24·2 | 14·1 | 71·6 | 28·4 |
| | 24·4 | 14·05 | 73·7 | 26·3 |
| 80 | 29·25 | 17·0 | 72·1 | 27·9 |
| | 29·3 | 17·0 | 72·4 | 27·6 |
| 90 | 27·6 | 16.5 | 67·3 | 32·7 |
| | 29·1 | 17.25 | 68·7 | 31·3 |
| 100 | 21 ·65 | 13·05 | 65·9 | 34·1 |
| | 21 ·3 | 13·0 | 63·8 | 36·2 |
| 120 | 9·5 | 8·15 | 16.6 | 83·4 |
| | 8·75 | 7·8 | 12.2 | 87·8 |
| 130 | 6.9 | 6.9 | 0.0 | 100.0 |

^{*} The irregular way in which the free chlorine escapes is probably one of the causes of the observed irregularities in the results.

TABLE III.

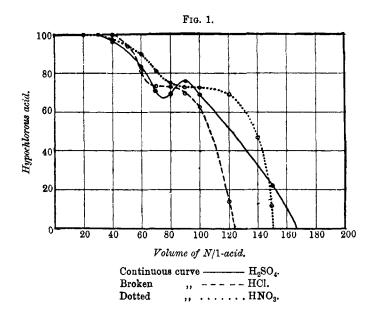
Distillation with Nitric Acid.

| 40 4·45 2·25 9 50 11·8 6·1 9 11·1 5·65 9 60 17·55 9·25 8 13·5 7·05 9 70 20·6 11·35 8 | ous acid, Chlorine cent. per cent |
|--|-----------------------------------|
| 50 11.8 6.1 9 11.1 5.65 9 60 17.55 9.25 8 13.5 7.05 9 70 20.6 11.35 8 | 0.0 |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 8.0 2.0 |
| 13·5 7·05 9 70 20·6 11·35 8 | 93·4 6·6 96·5 3·5 |
| | 9·7 10·3 91·5 8·5 |
| | 1.5 18.5 1.5 18.5 |
| | 5·2 24·8 7·5 22·5 |
| 36.4 20.65 7 | 0.6 29.4 6.2 23.8 3.8 26.4 |
| | 2·2 27·8 4·7 25·3 |
| | 8·1 31·9 3·0 27·0 |
| | 9·5 50·5 3·3 56·7 |
| 8.2 7.3 1 | 2·7 97·3 2·3 87·7 2·1 87·9 |
| | 0·7 99·3 0·0 100·0 |

It will be observed that the above results do not altogether agree with those of Kopfer. It is plain that, with an amount of acid just a little more than what is required to neutralise all the free lime, a distillate is obtained which is a moderately concentrated solution of almost pure hypochlorous acid, and in this respect there is very little difference between the three acids employed; but (and here is the principal difference between our results and those of Kopfer) long before the amount of acid is sufficient to decompose the whole of the calcium hypochlorite theoretically present in the solution (see p. 445), the proportion of hypochlorous acid has fallen to about three-quarters of its original amount, and considerable quantities of chlorine have begun to be evolved. After the point at which all the hypochlorite theoretically present is decomposed, there is, as would be expected, a rapid drop in the amount of the hypochlorous acid produced, and this drop is more rapid in the

case of the hydrochloric acid than with the other acids, because immediately there is an excess of hydrochloric acid it decomposes some of the hypochlorous acid, whereas the other acids have first to liberate some hydrochloric acid from the calcium chloride present.

The curves in Fig. 1 represent the action of the three acids already described. The point where two of them are almost horizontal, and in the other an actual rise in the proportion of hypochlorous acid is shown, is very near where the amount of acid



is just sufficient to neutralise all the free lime and to decompose all the hypochlorite present.

TABLE IV.

Distillation with Acetic Acid.

| Volume of N-acid, in c.c. | Arsenite oxidised. | Chloride produced. | Hypo- chlorous acid, per cent. | Chlorine, per cent. |
|---------------------------|--------------------|-----------------------|--------------------------------------|------------------------|
| 20 | 0.0 | 0.0 | _ | - |
| 30 | 0.0 | 0.0 | - | _ |
| 40 | 0.8 | 0.35 | 100.0 | 0.0 |
| 50 | 8.35 | 4.15 | 100.0 | 0.0 |
| 60 | 11.5 11.5 | 5·95 5·9 | 93·3 94·9 | 6·7 5·1 |

TABLE IV (continued).

Distillation with Acetic Acid.

| Volume of N-acid, in c.c. | Arsenite oxidised. 15.3 14.75 | Chloride produced. 8·1 7·8 | Hypo- chlorous acid, per cent. 88 9 89 1 | Chlorine per cent. 11.1 10.9 |
|---------------------------|-------------------------------|-------------------------------------|--|---------------------------------------|
| 80 | 18·8 | 10.45 | 79·9 | 20·1 |
| | 18·1 | 10.0 | 81·0 | 19·0 |
| 90 | 21·1 | 12·35 | 70·8 | 29·2 |
| | 20·45 | 11·95 | 71·1 | 28·9 |
| 100 | 22·9 | 13·4 | 70·9 | 29·1 |
| | 23·9 | 14·0 | 70·7 | 29·3 |
| 120 | 25·35 | 14·45 | 75·4 | 24 6 |
| | 25·45 | 15·15 | 68·0 | 32 0 |
| | 26·0 | 15·1 | 72·2 | 27 8 |
| 140 | 25·6 | 15·9 | 61.0 | 39·0 |
| | 25·6 | 15·7 | 63.0 | 37·0 |
| 150 | 25·4 | 15·8 | 60.8 | 39·2 |
| | 25·8 | 15·8 | 63.3 | 36·7 |
| 170 | 25·0 | 15·7 | 59·2 | 40·8 |
| | 25·55 | 15·5 | 64·8 | 35·2 |
| 200 | 24·5 | 15·3 | 60 ·1 | 89·9 |
| | 24·5 | 15·5 | 58 ·1 | 41·9 |
| 250 | 22·5 | 15·05 | 49·5 | 50·5 |
| | 23·1 | 15·25 | 51·5 | 48·5 |
| | 20·8 | 13·55 | 53·5 | 46·5 |

Table V.

Distillation with Phosphoric Acid.

| Volume of N-acid, in c.c. | Arsenite oxidised. 3.4 | Chloride produced. 1.65 | Hypo- chlorous acid, per cent. 100.0 | Chlorine per cent. 0.0 |
|---------------------------|------------------------------|---|---|------------------------------|
| 50 | 11 [.] 35 | 5·85 | 94·0 | 6·0 |
| | 9·4 | 4·9 | 91·8 | 8·2 |
| 60 | 15·8 | 8·8 | 79·5 | 20·5 |
| | 15·55 | 8·55 | 81·9 | 19·1 |
| 70 | 21·0 21·0 | $\begin{array}{c} 12.25 \\ 12.25 \end{array}$ | 71·4 71·4 | 28.6 28.6 |
| 80 | 24·85 26·45 | 14.65 15.6 | 69·6 | 30·4 30·4 |
| 90 | 32·7 | 19·1 | 71 · 2 | 28·8 |
| | 30·5 | 17·75 | 71 · 3 | 28·7 |
| 100 | 32·85 | 19·4 | 69·3 | 30·7 |
| | 34·05 | 20·2 | 68·6 | 31·4 |
| 120 | 33·25 | 20·3 | 63·8 | 36·2 |
| | 32·0 | 19·75 | 62·0 | 38·0 |
| 140 | 29·15 | 18.5 | 57·6 | 42·4 |
| | 30 · 15 | 19.0 | 58 7 | 41·3 |

Table V (continued).

Distillation with Phosphoric Acid.

| Volume of N-acid, in c.c. | Arsenite oxidised. 29.4 30.0 | Chloride produced. 18.75 19.2 | Hypo- chlorous acid, per cent. 56.8 56.2 | Chlorine per cent. 43.2 43.8 |
|---------------------------|------------------------------|--|--|---------------------------------------|
| 170 | 24·45 | 15·95 | 53·3 | 46·7 |
| | 27·2 | 17·2 | 58·1 | 41·9 |
| 200 | 24.95 | 16.35 | 52.6 | 47.4 |
| 250 | 21 ·6 | 14·2 | 52·1 | 47·9 |
| | 21 ·9 | 14·9 | 47·0 | 53·0 |

The action of acetic and phosphoric acids is evidently very different from that of the stronger acids. As with those, when the amount of acid is only a little more than is required to neutralise the free lime, the distillate is almost pure hypochlorous acid, although in the case of acetic acid it is considerably weaker. As the amount of acid is increased, also, free chlorine begins to be evolved long before the acid is sufficient to decompose the whole of the hypochlorite present. The diminution in the amount of hypochlorous acid proceeds much more slowly than in the case of the stronger acids, and even with so large an amount of acid as 250 c.c. the amount of hypochlorous acid in the distillate does not fall much below 50 per cent.

The curves in Fig. 2 represent the action of acetic and phosphoric acids. As in Fig. 1, the point where the acid is just about sufficient to neutralise the free lime and to decompose all the hypochlorite present is plainly indicated.

The Action of Boric Acid on Bleaching Powder.

A Convenient Method of Preparing a Solution of Hypochlorous A cid.

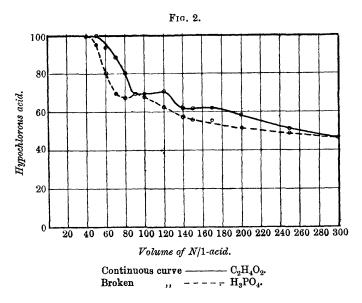
It is known that boric acid liberates hypochlorous acid from bleaching powder. Lauch (Ber., 1885, 18, 2287) took advantage of this for the preparation of some additive compounds of hypochlorous acid.

Of the two constituents of bleaching powder, boric acid appears to be only able to decompose to any considerable extent one of them—the calcium hypochlorite; so that, when bleaching powder is distilled with boric acid, there is never much free chlorine produced, and there is no difficulty in obtaining practically pure solutions of hypochlorous acid.

The best conditions for this purpose appear to be to distil the

bleaching powder with about thirty times its weight of water and twice its weight of boric acid. So long as this proportion of water is maintained, it makes very little difference as to the amount of boric acid employed; it may even be increased to three times the weight of the bleaching powder. If, however, much less water is used, more free chlorine is produced.

If 10 grams of bleaching powder are distilled with 300 c.c. of water and any amount from 15 to 20 grams of boric acid, from 50 to 100 c.c. may be distilled off, and this will be a practically pure solution of hypochlorous acid, giving only a slight immediate turbidity with silver nitrate. This appears to us to be the simplest



method of obtaining a solution of hypochlorous acid, as any ordinary variation in the proportions of acid and bleaching powder makes little difference in the result, so long as a sufficient amount of water is used, and there is not the difficulty of trying to avoid local excess of acid such as occurs when the stronger acids are employed.

The solution of hypochlorous acid so prepared is usually from 1.5 to 2N/10, and contains from 4 to 5 grams of pure hypochlorous acid per litre.*

* Investigations on the bleaching and other properties of a solution of hypochlorous acid are in progress, the results of which will be communicated later.

The Action of Carbonic Acid on Bleaching Powder.

In the former paper already referred to (loc. cit.) it was demonstrated that, as had been stated by other observers (Wolters, J. pr. Chem., 1874, [ii], 10, 128; Lunge and Schäppi, Dingl. Polyt. J., 1889, 273, 63; Dreyfus, Bull. Soc. chim., 1884, [ii], 41, 600; von Tiesenholt, J. pr. Chem., 1902, [ii], 65, 512, and 1906, [ii], 73, 301), when carbon dioxide is passed through a solution of bleaching powder, or over the moist solid substance, no hypochlorous acid is evolved, but only free chlorine. At first sight it appears remarkable that there should be such a wide difference between the action of two such weak acids as boric and carbonic acids as is indicated by the results described above. It must be borne in mind, however, that the conditions under which the two acids were experimented with were widely different, particularly as regards temperature, and we find that, under similar conditions, carbon dioxide acts practically in the same way as boric acid. If carbon dioxide is passed through a solution of bleaching powder which is kept boiling continuously, almost pure hypochlorous acid is given off. The experiment succeeds best if the carbon dioxide is bubbled fairly rapidly through the mixture of bleaching powder and water (in the same proportion as used in all the other experiments, namely, 10 grams of bleaching powder to 300 c.c. of water) from the beginning, whilst the liquid is being heated, and then the distillate collected as soon as the liquid boils vigorously. The yield of hypochlorous acid is not nearly so good if the liquid is heated first, and the carbon dioxide led in as soon as it boils. Doubtless the reason for this difference is that, when the carbon dioxide is bubbling through whilst the liquid is being heated, it is gradually removing the free lime, so that it is free to act on the calcium hypochlorite by the time the liquid is boiling.

The effect of passing carbon dioxide through a mixture of bleaching powder and water at different temperatures was tried, with the results given in table VI.

In each experiment the mixture of 10 grams of bleaching powder and 300 c.c. of water was heated in a flask to the desired temperature. The carbon dioxide was freed from hydrochloric acid by passing it over wet glass wool. It was not passed through from the commencement, but only when the desired temperature was reached. The resulting gases were passed through 25 c.c. of N/10-arsenite, and the proportions of hypochlorous acid and chlorine determined in the usual way.

VOL. CI. H H

TABLE VI.

| Temperature of mixture. | Arsenite oxidised. | Chloride produced. | Hypo- chlorous acid, per cent. | Chlorine, per cent. |
|-------------------------|--------------------|-----------------------|--------------------------------------|------------------------|
| 30° | 8.75 | 8.3 | 5.3 | 94.7 |
| 40 | 10.4 | 9.0 | 15.5 | 84 5 |
| 50 | 10.2 | 8.75 | 16.6 | 83.4 |
| 60 | 8.95 | 7.4 | 20.9 | 79.1 |
| 70 | 10.25 | 7.35 | 39.4 | 60.6 |
| 80 | 11.45 | 8.05 | $42 \cdot 2$ | 57 ·8 |
| 90 | 10.6 | 6.7 | 58·2 | 41.8 |
| 100 | 10.3 | 5.4 | 90.7 | 9.3 |

As will be seen from the table, hypochlorous acid (mixed with a large proportion of free chlorine) begins to come off as soon as the liquid becomes warm, and the proportion steadily increases as the temperature rises, until when the liquid is at 100° almost pure hypochlorous acid is evolved. (In the experiment at 100° the liquid was kept as nearly as possible at that temperature. Not being pure water it did not absolutely boil. As pointed out above, if the liquid is kept actively boiling all the time the carbon dioxide is passing through, practically pure hypochlorous acid is evolved.)

We venture to submit that this remarkable difference in the action of carbonic acid at different temperatures affords strong evidence in favour of Taylor's view that the action of carbonic acid on bleaching powder in the cold is the same as that of other acids, the carbonic acid decomposing both the calcium chloride and the hypochlorite, and the resulting hydrochloric and hypochlorous acids decomposing each other, with the liberation of chlorine. solubility of carbon dioxide in water diminishes as the temperature rises, and at the boiling point of water it is practically nil, so that at that temperature the amount of true carbonic acid (H₂CO₃) present must be almost infinitesimal. Consequently, at the higher temperature it, like boric acid, can only decompose the calcium hypochlorite in the bleaching powder, with the result that pure hypochlorous acid is evolved. Further (and this, of course, is of some importance), whilst the liquid is actually boiling, the hypochlorous acid is removed from it practically as fast as it is produced. The results of our experiments at different temperatures, as expressed in table VI, indicate the gradually diminishing amount of true carbonic acid which can exist in the water as the temperature rises, and the solubility of the carbon dioxide diminishes.

The removal of the hypochlorous acid from the solution as fast as it is produced is also an important factor in the action of boric acid on bleaching powder. As described above, when bleaching powder solution is boiled with boric acid, pure hypochlorous acid is driven off, but the action is very different at the ordinary temperature.

In the following experiments 3 grams of bleaching powder were rubbed with 100 c.c. of water, and 6 grams of boric acid added. Through this mixture air, free from carbon dioxide, was bubbled, and the issuing gases were passed through N/10-arsenite, with the following results:

| | Arsenite oxidised. | Chloride produced. | chlorous acid, per cent. | Chlorine, per cent. |
|----|--------------------|-----------------------|-----------------------------|------------------------|
| 1. | 5.0 | 3.76 | 33 | 67 |
| 2. | 6.35 | 4.67 | 36 | 64 |

The experiments took about twenty-four hours to produce the observed amount of oxidation in the arsenite. This means that the action is very slow as compared with the action of carbon dioxide at the ordinary temperature. This, together with the fact that not pure chlorine, but a mixture of chlorine and hypochlorous acid, is evolved, leads us to the conclusion that boric acid at the ordinary temperature does not act on bleaching powder in the same way as carbonic acid and other acids. The slow evolution of chlorine we attribute to the fact that the boric acid simply unites with the free lime, and so enables the reverse action to proceed, as described in the former paper (loc. cit., p. 2550). The hypochlorous acid which accompanies the chlorine is doubtless due to the action of the boric acid on the calcium hypochlorite in the solution. must be borne in mind that, in all experiments where chlorine and hypochlorous acid are swept out by passing air through a liquid, the chlorine, being much less soluble in water, will be swept out more readily, so that the proportion of hypochlorous acid actually present in the liquid is certainly greater than the numbers indicate.)

The results of the above two experiments are somewhat similar to those in table VIII in the former paper (p. 2551), which were obtained by passing air, free from carbon dioxide, through a solution of bleaching powder which had been first exposed to air in order to remove the free lime. The addition of boric acid, even in considerable quantity, is simply equivalent to exposing the bleaching powder solution to air for some time; there is apparently no action of the boric acid on the calcium chloride in the solution.

It is hardly necessary to point out that if any other acid be added to bleaching powder solution in quantity just sufficient to unite with the free lime, the effect of afterwards passing air free from carbon dioxide through the solution will be similar to what is described above. Experiments were made with hydrochloric and nitric acid. With the former the air free from carbon dioxide swept

out a mixture of 85 per cent. of chlorine and 15 per cent. of hypochlorous acid, and with the latter 75 per cent. of chlorine and 25 per cent. of hypochlorous acid. One would expect the proportion of chlorine to be greater with hydrochloric acid than with nitric, because if in adding the acid to the bleaching powder solution there is at any time a local excess of acid, the former is more likely to produce free chlorine than the latter.

Summary.

- (1) When bleaching powder, mixed with thirty times its weight of water, is distilled with sulphuric, hydrochloric, or nitric acid in quantity slightly greater than is required to neutralise the free lime present, hypochlorous acid mixed with a small quantity of free chlorine is evolved. When the acid is in sufficient quantity to neutralise all the free lime and to decompose the whole of the hypochlorite theoretically present, the proportion of free chlorine is considerably greater. When the amount of acid is further increased, the hypochlorous acid produced rapidly diminishes, and very soon nothing but chlorine is evolved. There is not a great difference in the action of the three acids named.
- (2) Acetic and phosphoric acids behave much alike, but they differ considerably, as would be anticipated, from the three acids above mentioned. Even with comparatively large amounts of these acids the proportion of hypochlorous acid evolved does not fall much below 50 per cent.
- (3) When bleaching powder is distilled with boric acid and a sufficient amount of water, almost pure hypochlorous acid is produced, and there is very little difference in the result if the boric acid used is as much as three times the weight of the bleaching powder. This is recommended as a convenient method of preparing a solution of hypochlorous acid.
- (4) When carbon dioxide is bubbled through a mixture of bleaching powder and water at different temperatures, whilst at the ordinary temperature nothing but chlorine is evolved, as soon as the liquid becomes warm hypochlorous acid begins to come off. The proportion of hypochlorous acid increases as the temperature rises, and when the liquid boils it is practically pure, hardly any free chlorine being evolved. It is suggested that this is strong evidence in favour of Taylor's view that the action of carbonic acid on bleaching powder at the ordinary temperature is like that of other acids.
- (5) When boric acid is added to a solution of bleaching powder, and air free from carbon dioxide is passed through at the ordinary

temperature, a mixture of chlorine and hypochlorous acid is swept out, containing a considerable excess of the former. The boric acid simply unites with the free lime, and this allows the reverse action to proceed, free chlorine being produced. If any other acid is added to a solution of bleaching powder in quantity just sufficient to neutralise the free lime, the passing of air free from carbon dioxide through the solution gives a similar result.

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