CCLX.—*Researches on Bleaching Powder.*

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For the purpose of this investigation, it was first of all necessary to devise a method for distinguishing between pure chlorine and hypochlorous acid, and, in a mixture of the two, finding their proportions.

The method used was to pass the gases through a known volume of *N*/10-sodium arsenite. The action of chlorine and of hypochlorous acid on sodium arsenite may be represented thus:

It is plain that, for the same amount of arsenite oxidised, twice as much hydrochloric acid (or chloride) is produced in the case of chlorine as in the case of hypochlorous acid. The arsenite (which must always be in excess, so that it is not completely oxidised) is then divided into two equal parts. In one-half, the amount of arsenite remaining unoxidised is determined by means of *N*/10-iodine solution, and from this the amount oxidised is ascertained. In the other half, the amount of chlorine is determined by means of *N*/10-silver nitrate. In the latter determination the use of an indicator was very soon discarded, although, if a considerable proportion of the arsenite has been oxidised, the arsenate produced acts fairly well as an indicator, and may be used instead of adding a chromate to the solution. Much more trustworthy results, however, are obtained by acidifying the solution with nitric acid, adding a little of the silver solution, boiling for a minute or two, and then filtering a portion of the liquid. A little more of the silver solution is added, drop by drop, to the filtered portion, which

is then returned to the bulk, and this boiled and filtered again. This is continued until the filtered portion gives no further precipitate with the silver solution. As described, the process seems tedious, but in practice it works very well, and the determination of the chlorine can be made fairly rapidly. In this process, as the solutions used are all decinormal, and therefore equal to each other, when the oxidising agent is pure chlorine, the amount of silver nitrate used (=amount of chloride present) is the same as the amount of arsenite oxidised. When hypochlorous acid is the oxidising agent, the chloride produced is only half the amount of arsenite oxidised.

The Action of Carbon Dioxide on Bleaching Powder.

It is very frequently stated, and probably usually considered, that carbon dioxide simply liberates hypochlorous acid from bleaching powder. A considerable number of observers, however, have pointed out that chlorine is produced when pure carbon dioxide acts on bleaching powder.

Thus, Richards and Juncker (*Dingl. Polyt. J.*, 1874, **211**, 31) state that dry bleaching powder is almost undecomposed by carbon dioxide. If about 10 per cent. of water is present, both chlorine and hypochlorous acid are produced.

Wolters (*J. pr. Chem.*, 1874, [ii], **10**, 128) refers to the liberation of chlorine by the action of carbon dioxide on bleaching powder, and Lunge and Schäppi (*Dingl. Polyt. J.*, 1889, **273**, 63) state that carbon dioxide expels nearly the whole of the chlorine from bleaching powder.

Dreyfus (*Bull. Soc. chim.*, 1884, [ii], **41**, 600) found that carbon dioxide has no action on calcium chloride, but, in the presence of chlorine monoxide, either dry or in aqueous solution, it liberates chlorine.

More recently this question, with others relating to bleaching powder, has been investigated by von Tiesenholt (*J. pr. Chem.*, 1901, [ii], **63**, 30; 1902, [ii], 512; 1906, [ii], **73**, 301). Some of his conclusions will be referred to later.

In my first experiments, carbon dioxide, in its ordinary moist condition, after being well washed with water, was passed through a U-tube containing bleaching powder and a sufficient amount of glass wool to give a free passage for the gas. Carbon dioxide, as ordinarily prepared by the action of hydrochloric acid on marble, invariably carries with it a little hydrochloric acid, and, in some of the experiments, this was removed by passing the gas through glass wool wetted with a solution of silver nitrate, which acts quite effectually. When, however, the gas is well washed with water, the

amount of hydrochloric acid accompanying it is not sufficient seriously to affect the results. After passing through the bleaching powder, the gas was passed through a Bunsen U-tube containing *N*/10-sodium arsenite.

A considerable number of experiments were made, and the following is an example of the results invariably obtained. Twenty c.c. of the *N*/10-arsenite were used:

I.

Amount of arsenite oxidised	8.35 c.c.
Amount of <i>N</i> /10-silver nitrate used	8.4 c.c.

It is plain from this that the sole product of the action of carbon dioxide on bleaching powder is chlorine. The escaping gas has a strong odour of chlorine, and none at all of hypochlorous acid. The action proceeds very rapidly if the carbon dioxide is quite moist.

In some further experiments, the carbon dioxide was dried by passing it over calcium chloride. The effect of drying the gas is that the action becomes much slower, and, as the moisture usually present in the bleaching powder is gradually carried away by the dry carbon dioxide, it soon becomes extremely slow. When this point has been reached, the instantaneous acceleration of the action when the drying tube is removed is very striking. The following three experiments show that the product is the same with the dry as with the moist gas, namely, nothing but chlorine:

II.

	Arsenite oxidised.	Chloride produced.
1.	3.4	3.5
2.	1.9	1.95
3.	6.55	6.65

The slight excess of silver nitrate used may have been due to a little hydrochloric acid carried over, although the actual amounts are not beyond the limits of accuracy of the method.

When carbon dioxide is passed through a solution of bleaching powder in water, the action is very rapid, but the result is exactly the same, as the following experiments show:

III.

	Arsenite oxidised.	Chloride produced.
1.	5.6	5.58
2.	3.1	3.1

The issuing gas again had a strong odour of chlorine, and none at all of hypochlorous acid.

Action of Carbon Dioxide on a Mixture of Sodium Chloride and Hypochlorite, and on a Mixture of Bromide and Hypobromite.

The mixture of sodium chloride and hypochlorite was prepared by passing chlorine into a moderately concentrated cold solution of sodium hydroxide. The following experiments show that the action is exactly the same as with a solution of bleaching powder :

IV.

	Arsenite oxidised.	Chloride produced.
1.	4·1	4·12
2.	6·1	6·13

When carbon dioxide is passed through a solution containing a mixture of a bromide and a hypobromite there is, as one would naturally expect, an immediate and copious liberation of bromine.

It is well known that carbon dioxide acts in a similar way on a mixture of iodide and hypoiodite.

It appears, from the foregoing experiments, that the action of carbonic acid on bleaching powder and similar substances is exactly like that of any other acid. There has been much discussion as to the actual constitution of dry bleaching powder, but, whatever that constitution may be, it may be taken that, in solution or in presence of water, it is, to all intents and purposes, a mixture of chloride and hypochlorite. The usual explanation of the action of, say, sulphuric acid (when used in considerable quantity) on bleaching powder is that the chloride and hypochlorite are both decomposed, with the simultaneous production of hydrochloric and hypochlorous acids, and that these decompose each other, with the liberation of chlorine. The question is whether or not we must seek for some other explanation of the action of carbonic acid. There would seem to be no doubt that the action of carbonic acid is exactly like that of other acids. Of course, this involves the conclusion that calcium chloride (or sodium chloride, for example) is decomposed, when in solution, by carbonic acid, with the liberation of hydrochloric acid, and that, therefore, the action of hydrochloric acid on carbonates is a reversible one :

I have tried to obtain some experimental evidence that this is the case, and not altogether without success.

Many years ago Müller (*Journ. Chem. Soc.*, 1870, **23**, 36) stated that a solution of lead chloride is decomposed when carbon dioxide is passed through it, with liberation of hydrochloric acid and precipitation of a chlorocarbonate, and that some of the liberated acid could actually be distilled off. He also stated that carbon dioxide,

under considerable pressure, would decompose sodium and calcium chlorides, when in solution in water, with liberation of hydrochloric acid. He used ultramarine as an indicator, and stated that, whilst carbon dioxide alone does not decompose ultramarine suspended in water, even under considerable pressure, if the water contains common salt dissolved in it the colour of the ultramarine is destroyed.

I am unable to confirm the latter observation. Carbon dioxide, when bubbled through water in which a little ultramarine is suspended, has no effect on it, whether the water contains salt or not. Under a pressure of a few atmospheres, however, ultramarine is decomposed and decolorised by carbonic acid alone, and I have been unable to observe any difference in the action when the water contained salt as well. The experiments I made were performed in an ordinary sparklet apparatus, in which the pressure attains five or six atmospheres. If distilled water with a little ultramarine suspended in it is placed in such an apparatus, and then the liquid charged with carbon dioxide in the usual way, there is no immediate effect, but, in the course of a day or two, the colour of the ultramarine gradually disappears. As stated above, the presence of salt (or of calcium chloride) in the water makes no apparent difference in the result.

Methyl-orange is, however, a much more delicate indicator for acids than ultramarine. It is usually assumed that the former is not affected by carbonic acid, but this is not quite correct. If well washed carbon dioxide is bubbled through distilled water containing a little methyl-orange, there is a distinct alteration of the colour, although it does not turn pink. If, however, the water contains also a little pure salt, or calcium chloride, or potassium chloride, the colour becomes distinctly pink when the carbon dioxide is bubbled through. The change of colour is most striking in the case of the common salt, but it is quite evident with the other chlorides. This may be taken as evidence that carbonic acid liberates a sensible amount of hydrochloric acid in solutions of chlorides, that is to say, the action of hydrochloric acid on carbonates is a reversible one. Of course, the amount of hydrochloric acid thus liberated must be extremely small, but it will be quite sufficient to explain the action of carbonic acid on bleaching powder and similar substances. The small amount of hydrochloric acid liberated will be at once decomposed by the hypochlorous acid liberated simultaneously from the hypochlorite; this will enable the action of the carbonic acid to proceed as before, and so there will be a continuous evolution of chlorine, and, if this is carried away as fast as it is formed, the bleaching powder will be almost completely decomposed.

It may here be noted that if carbon dioxide is bubbled through water containing potassium bromide or ammonium chloride and coloured with methyl-orange, the change of colour is not so striking as in the case of the three chlorides mentioned above. Pure water coloured with methyl-orange becomes quite pink when charged with carbon dioxide in a sparklet apparatus.

Von Tiesenholt (*loc. cit.*) explains the production of chlorine when carbon dioxide acts on bleaching powder by supposing that hypochlorous acid is first formed by the action of the carbon dioxide on the hypochlorite present, and that this acts on the calcium chloride, liberating chlorine:

He finds, in confirmation of this view, that chlorine is liberated when a solution of hypochlorous acid is added to calcium chloride or to common salt. The experiments here described, however, show that nothing but chlorine is produced by the action of carbonic acid on bleaching powder, so that all the hypochlorous acid which is liberated must be decomposed. Apparently, if von Tiesenholt's view is right, hypochlorous acid cannot exist in the presence of a sufficient amount of a chloride, so that it would be impossible to expel any hypochlorous acid from a solution which contains chlorides. As will be seen later, however, mixtures of chlorine and hypochlorous acid containing a considerable proportion of the latter can be expelled from solutions of bleaching powder. Consequently, whilst it is possible that the action of hypochlorous acid on chlorides may account for some of the chlorine which is produced in the case of concentrated solutions or the merely moist bleaching powder for example, von Tiesenholt's explanation would not appear to be preferable to the one offered above.

The Action of Air on Bleaching Powder.

Although this was not the order in which the experiments were actually tried, it will be best to describe first the effect of air from which all the carbon dioxide has been removed. This was done by passing the air through washing cylinders containing coke wet with a concentrated solution of sodium hydroxide. It was then bubbled through a milky solution of bleaching powder (about 5 to 10 per cent.), and afterwards through the solution of sodium arsenite.

In all the experiments with air, it was passed through at a rate of about 10 to 15 litres per hour.

Air free from carbon dioxide is practically inert so far as bleaching powder is concerned, and naturally all that it can do is to sweep out any chlorine or hypochlorous acid which may happen to be present. Consequently, the action is very slow, and the experi-

ments had to be carried on for a long time (from seventy-two to ninety-six hours) in order to obtain sufficient oxidising action in the solution of arsenite to be able to judge what was being carried over. The following results were obtained in three separate experiments:

V.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	1.08	0.57	90	10
2.	1.0	0.45	100	0
3.	0.8	0.38	100	0

The amount of oxidation in these experiments was very little, but they appear to show that a small amount of free hypochlorous acid exists in a solution of bleaching powder, which is simply swept out by the passage of air free from carbon dioxide through it. Probably the free hypochlorous acid is due to the calcium hypochlorite in a dilute solution being slightly hydrolysed, thus:

This possibly accounts for the fact that solutions of bleaching powder have an odour of hypochlorous acid.

One similar experiment to the above was made in which the solution of bleaching powder was kept at a temperature of about 40° the whole of the time. In this experiment, also, practically nothing but hypochlorous acid was swept out, the only difference being that, as one would expect, the time required was rather less.

Action of Ordinary Air on Bleaching Powder.

A considerable number of experiments were made with ordinary air, passing it through a tube containing dry bleaching powder, and then through the solution of arsenite. At first the action is rather slow, but, as the bleaching powder gradually becomes wet, the action proceeds more and more rapidly. In some of the experiments the moisture of the air was purposely increased by passing it through a tube containing wet glass wool. In each of the two following series of experiments the same tube of bleaching powder was used throughout. The time occupied by each experiment varied from about twenty-four hours at the beginning to six hours when the bleaching powder had become wet:

VI.

Series 1.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	4.45	4.0	11	89
2.	2.9	2.56	13	87
3.	2.55	2.3	10	90
4.	7.0	6.95	0	100
5.	7.9	7.95	0	100

Series 2.

1.	2.1	1.83	15	85
2.	3.35	3.1	8	92
3.	6.0	6.05	0	100

The above experiments are selected from a considerable number, and they all tend to show that, at the outset, ordinary air sweeps out from bleaching powder a mixture containing from 80 to 90 per cent. of chlorine, and from 10 to 20 per cent. of hypochlorous acid, but that, as the action proceeds, the amount of hypochlorous acid gradually diminishes, and at last nothing but chlorine appears. The gradation of the experiments is not the same in the two series, but that is partly due to the fact that some intermediate experiments in both series were spoiled by going on too long.

When ordinary air is passed through a solution of bleaching powder (not filtered, and containing about 5 to 10 per cent. of the powder), the proportion of hypochlorous acid swept out is considerably greater, as indeed one would expect if we accept the suggestion that the hypochlorous acid is due to hydrolysis of the calcium hypochlorite. As in the case of the dry powder, however, the amount of hypochlorous acid gradually diminishes as the experiment proceeds, although it does not disappear altogether. The following experiments were made with the same solution of bleaching powder, in the order in which they are given. In experiment No. 4, the proportion of hypochlorous acid appears to have risen slightly, but the method of determining it is not accurate enough to enable one to say that the amounts in experiments 3 and 4 were not substantially the same. The action was very slow in the first experiment, but much more rapid afterwards:

VII.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	4.48	2.94	52	48
2.	9.15	7.27	25	75
3.	3.18	2.88	10	90
4.	3.34	2.87	16	84

It must be pointed out that the above numbers, showing the relative amounts of hypochlorous acid and chlorine swept out of the liquid by the air, do not necessarily represent the actual proportions present at any moment in the liquid itself. There is no doubt that chlorine, being less soluble in water than hypochlorous acid, will be swept out more readily, so that the proportion of hypochlorous acid actually present in the liquid is certainly greater than the above numbers indicate.

These results, showing the action of ordinary air on bleaching powder, are very remarkable. The difference between the action of ordinary air and air from which the carbon dioxide has been removed is, at first sight, almost incredible. Whereas the latter simply sweeps out from a solution of bleaching powder (although very slowly) practically pure hypochlorous acid, the presence of the really very small amount of carbon dioxide which usually exists in ordinary air causes the action to proceed much more rapidly (although not with anything like the rapidity with which pure carbon dioxide acts), and, after a time, has almost the same effect, so far as the product is concerned, as passing pure carbon dioxide through it.

I have already expressed the opinion that the action of pure moist carbon dioxide on bleaching powder is the same as that of other acids—it is a mass action, and the carbonic acid decomposes both the chloride and the hypochlorite. Whilst one may accept this explanation in the case of pure carbon dioxide used in comparatively large quantities, and always locally in large excess, it is impossible to believe that the small amount of carbon dioxide present in ordinary air can act in the same way. We must therefore look for some other explanation.

The Action of Chlorine on Alkalis a Reversible Action.

In former papers (*Mem. Manchester Phil. Soc.*, 1897, **41**, No. VIII; *Trans.*, 1900, **77**, 725) I have pointed out that the action of iodine on alkalis is a reversible one. If an alkali is added to a solution of iodine in water or in potassium iodide until the colour just disappears, the addition of potassium iodide to the solution causes the liberation of some of the iodine:

The addition of the extra amount of potassium iodide causes the reaction to proceed from right to left in the above expression. Also, and this, too, follows from the fact that the action is reversible, the amount of alkali needed to complete the reaction from left to right and to remove the colour of the iodine is considerably more

than is required by the equation, so that the almost colourless solution of iodide and hypiodite always contains some free alkali.

When these experiments were made, similar ones were also performed with bromine and alkalis, but analogous results were not obtained. The reason of this must have been that too strong a solution of bromine was used, because I find that the reversibility of the action of bromine on alkalis is quite as striking as that of iodine if a very dilute solution of bromine is employed. The action is not nearly so easy to see with ordinary bromine water, but if this is diluted with ten to twenty times its bulk of water, and then sodium or potassium hydroxide added drop by drop until the colour of the bromine has disappeared, the addition of a little concentrated solution of potassium bromide causes a manifest liberation of bromine. The liberation of bromine is seen still more plainly if, instead of the solution of potassium bromide, a considerable amount of the powdered salt is added. The addition of the extra potassium bromide causes the action to proceed from right to left:

It is perfectly reasonable to suppose, then, that the action of chlorine on alkalis is also a reversible action. This has already been suggested by von Tiesenholt (*loc. cit.*), who describes a number of experiments which point to this conclusion. I have been able to demonstrate, by experiments which are described later, that this conclusion is correct, and it will be seen that it supplies a perfectly satisfactory explanation of the action of ordinary air on bleaching powder, and that it also explains some well-known facts with regard to some bleaching solutions which have been hitherto apparently inexplicable.

If we represent the action of chlorine on sodium hydroxide and on slaked lime thus:

and

it is plain that the chlorides produced by the action are continually tending to reverse the reaction, so that, to carry it to a finish from left to right, there must always be a considerable amount of free sodium hydroxide or lime present. It is a well-known fact that bleaching powder always contains a considerable amount of free lime, and that it is impossible to prepare it otherwise. If this free lime, or a portion of it, is removed, then the reaction will proceed

* It is not suggested that this equation represents what actually occurs in the manufacture of bleaching powder, but simply the condition of equilibrium in which it exists when wet or in solution.

in the opposite direction to a greater or less extent, and chlorine will be liberated.

A number of experiments were made to test this point. A filtered solution of bleaching powder was employed, having a specific gravity of 1·03 to 1·06 in different experiments. In order to remove some of the free lime, the solution was exposed to air for some hours in a shallow dish, with occasional shaking. The amount of free lime present in such a solution is considerable, and the latter becomes very milky on exposure to air. The liquid was filtered from the precipitated calcium carbonate, and air free from carbon dioxide was passed through it and into the arsenite solution in the usual way. The following are some of the results obtained :

VIII.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	4·0	3·16	26	74
2.	3·8	3·0	27	73
3.	2·6	1·8	44	56
4.	5·92	5·15	15	85
5.	4·35	4·04	8	92
6.	2·27	1·52	50	50

Most of the separate experiments were made with different portions of the solution, which had been exposed to air for different lengths of time, so that the extent to which the free lime was removed varied. Doubtless this accounts for the irregularity in the results. In all the above experiments the action was much more rapid than was the case with the solution from which none of the free lime had been removed, the rapidity evidently depending on the extent to which this removal had been carried. It will be noted that besides the large quantities of free chlorine produced, in most of the experiments the amount of hypochlorous acid swept out from the liquid was very much greater than was the case with the solution from which no free lime had been removed. This is quite what one would expect to occur. The hypochlorous acid, as before stated, is probably due to hydrolysis of the calcium hypochlorite in the solution. This also is a reversible action, and as one of the products of the hydrolysis is free lime, the removal of the lime naturally stimulates this action as well.

These experiments demonstrate quite sufficiently the reversibility of the reaction between chlorine and calcium hydroxide. As the free lime is more or less removed, the reaction proceeds in the opposite direction, and chlorine is liberated. In these experiments the free chlorine is swept out of the solution, but it is continually being reproduced, the steady removal of the chlorine allowing the

reverse action to take place continuously. If the free chlorine were removed from the solution in any other way, by bleaching, for example, it would in the same way be continually reproduced as long as any of the bleaching substance remained. It follows from this, of course, that the bleaching action of a solution of bleaching powder will be stimulated by the removal of free lime from the solution. This will be referred to again later.

The action of ordinary moist air on bleaching powder, both solid and in solution, described on p. 2548, is now perfectly intelligible. The carbon dioxide in the air combines with the free lime, and, as this gradually diminishes and finally practically disappears, the reverse action proceeds freely, and, of course, chlorine is produced.*

It is usually understood, and has been frequently stated, that a pure solution of hypochlorous acid bleaches more energetically and more rapidly than free chlorine. It may be doubted whether this is really the case. I have prepared practically pure solutions of hypochlorous acid, and compared its action with that of a solution of chlorine on various colouring matters, and I have failed to find any evidence of the greater activity of hypochlorous acid. Rather the contrary. With a solution of indigo-carmin, for example, the bleaching action of chlorine is much more rapid than that of hypochlorous acid—in the case of the latter the action is to be described as sluggish, rather than rapid. This is an important point, because I am strongly of opinion that in the use of solutions of bleaching powder and similar substances for bleaching purposes, most of the actions generally attributed to hypochlorous acid are really due to chlorine, and that, in practice, hypochlorous acid plays only a minor part in bleaching.

It is remarkable how the bleaching action of a solution of bleaching powder is stimulated by the mere removal of the free lime in it. If a strip of Turkey-red calico is placed in a clear solution of bleaching powder so that it is completely immersed in the liquid, and if the liquid is kept in a closed vessel so that air has no access to it, there is scarcely any bleaching action at all, even after several days. If, however, the solution is placed in a

* It may be asked if the removal of free lime by carbon dioxide is a satisfactory explanation of the fact that ordinary air expels chlorine from bleaching powder, would not this also explain the action of pure carbon dioxide on bleaching powder, so that there would be no need to assume, as is done in the first part of this paper, that carbonic acid decomposes chlorides with the liberation of hydrochloric acid? The author adheres to the latter explanation simply because the action of carbon dioxide is so much more rapid than that of air. A stream of carbon dioxide through a solution of bleaching powder liberates chlorine from ten to twenty times more rapidly than air at its quickest, and the action altogether suggests a rapid and complete decomposition, such as is effected by other acids, rather than the mere sweeping out of chlorine produced by the reversed action.

basin or a shallow dish, so that air has free access, and if a small portion of the red calico is left outside the liquid, so that it is reached by the solution and the air at the same time, the portion outside is bleached quite rapidly. Further, if the coloured calico is completely immersed in a little of the solution contained, say, in a deep test-tube, and the test-tube is breathed into about half a dozen times, shaking after each time, the calico is very soon bleached. Also, whilst, as stated above, a fresh solution of bleaching powder has very little, if any, bleaching action on a piece of red calico completely immersed in it, if the solution has been exposed to air in a shallow dish for a few hours, with occasional shaking, then a piece of red calico completely immersed in it is bleached rapidly.

A simple but very striking experiment which illustrates the same point is to immerse a strip of ordinary red litmus paper in a fresh solution of bleaching powder. The paper is turned blue, and in a short time it is bleached. If, however, immediately after it has been dipped in the solution, it is breathed upon, it is bleached almost instantly. A solution of bleaching powder which has been well exposed to air, as described above, bleaches litmus paper at once.

In all these cases the more rapid bleaching action is simply due to the removal of free lime, and I think it is plain, also, if reference is made to the experiments, series VIII, on p. 2551, that the principal bleaching agent is chlorine, and not hypochlorous acid. Certainly those experiments show that in some cases a considerable proportion of hypochlorous acid is swept out, but in all cases the rapidity of the bleaching action is roughly proportional to the extent to which the free lime is removed, and the more completely that is done the greater is the proportion of chlorine liberated.

It is a fact, well known in bleach-works, that an old vat is more active than a new one. The reason for this is obvious. Exposure to air, especially if the liquid is frequently stirred, gradually causes the removal of the free lime.

If the action of chlorine on lime is, as I think the above experiments sufficiently demonstrate, a reversible action, then the reverse action must be stimulated by the addition of calcium chloride to the solution. Experiments were made to see if this is the case. After experiment No. 2 (series VIII) on p. 2551 was finished, a considerable amount of crystallised calcium chloride was added to the same solution of bleaching powder and air free from carbon dioxide passed through it again. The action became considerably more rapid, and the effect of the calcium chloride is seen by a comparison

of the two experiments. No. 1 was before, No. 2 after, the addition of the calcium chloride.

IX.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	3.8	3.0	27	73
2.	4.75	4.73	0	100

The solution used in experiment No. 6 (series VIII) was treated in the same way with the following result:

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	2.27	1.52	50	50
2.	5.4	4.92	10	90

These experiments show plainly that, as anticipated, the reverse action is greatly increased by the addition of more calcium chloride.

Other chlorides, of course, ought to have a similar effect. The following experiments show the effect of adding common salt to the solution. As before, the greater part of the free lime in the solution was removed by exposing it to air. Experiments 1 and 2 were successive experiments before the addition of the salt, and No. 3 shows the effect of the salt. The salt was added in considerable quantity—almost sufficient to saturate the solution.

X.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	1.75	1.4	25	75
2.	5.25	4.1	28	72
3.	6.53	6.55	0	100*

The addition of the salt in the above experiment caused the action to proceed much more rapidly. Thus, whilst in experiment No. 2 it took twenty hours to oxidise 5.25 c.c. of the arsenite solution, in experiment No. 3, 6.53 c.c. were oxidised in four hours, the carbon dioxide-free air passing through at approximately the same rate in both experiments.

* The apparently complete disappearance of hypochlorous acid indicated in experiments 2 (IX) and 3 (X) is very remarkable, and seems difficult to explain. It is not claimed, however, that the method used for determining the relative amounts of chlorine and hypochlorous acid is perfectly accurate. It is doubtful whether it would be possible to determine very small proportions of hypochlorous acid by it. It must also be borne in mind (see p. 2549) that chlorine is more easily swept out from the solution than hypochlorous acid, so that it is possible that the latter does not altogether disappear. Possibly, also, von Tiesenholt's explanation (see p. 2546) may apply here, and the hypochlorous acid may be all decomposed by the large quantities of chlorides present in the solution.

Experiments were also made to see the effect of the addition of calcium chloride and salt to an ordinary solution of bleaching powder, without removing any of the free lime. The free lime in the solution, of course, tends to stop the reverse action, so that the effect of adding calcium chloride or salt to the solution is not nearly so great as when the free lime is first removed. The following is the result of the two experiments tried.

To No. 1 calcium chloride was added, and to No. 2 common salt—both in large quantity. The action proceeded very slowly indeed in both experiments, but the results are sufficient to show that, even in ordinary bleaching powder solution, the addition of chlorides has a sensible effect in reversing the action:

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	2.24	2.22	0	100
2.	2.66	2.4	10	90

It follows from the above experiments that the addition of calcium chloride or salt to a solution of bleaching powder must exercise a stimulating effect on the bleaching action of the solution. This is actually the case. If some of the free lime has been removed from the solution, the effect of the addition of considerable amounts of calcium chloride or salt on the bleaching action is very striking. With bleaching powder solution in its ordinary state, containing the usual amount of free lime, the effect on its bleaching action of adding calcium chloride or salt is, for the reason pointed out above, not nearly so great, although it is quite sufficiently marked.

I understand that it has been found, in actual bleaching, that the addition of either calcium chloride or salt stimulates the action, but I am not aware that any satisfactory explanation of this stimulating effect has hitherto been given. It may perhaps be worth the while of practical bleachers to note that the addition of calcium chloride or salt has a much greater effect when some of the free lime has been removed—by exposing the solution to air, for example.

Bleaching solutions made by the electrolysis of a solution of salt have latterly come into considerable use, and I understand that the fact has been frequently noted that a solution of sodium hypochlorite thus prepared is more active than a solution of sodium hypochlorite, containing the same proportion of available chlorine, prepared by the addition of sodium carbonate to a solution of bleaching powder and allowing the precipitated calcium carbonate to settle. The explanation of this is obvious when it is understood that, in preparing the electrolytic bleaching solution, only a small fraction of the salt in the solution is usually decomposed. The

solution thus differs from that made by the other method by containing a large amount of salt, and the effect of this is to increase the reverse action and so to liberate chlorine in the solution. Also, in the electrolysis of the salt, chlorine and sodium hydroxide are produced in exactly equivalent proportions, so that there cannot be a sufficient amount of the latter to absorb the whole of the chlorine. Under these conditions, the reversing action of the excess of salt will naturally be very considerable. The greater bleaching activity of such a solution is therefore perfectly natural, and exactly what one would expect.

In addition to the experiments described in this paper, I have used my method for distinguishing between hypochlorous acid and free chlorine for investigating the action of various acids on bleaching powder and similar substances. This investigation is still proceeding.

Summary.

1. The action of carbon dioxide on bleaching powder and similar substances results in the liberation of chlorine only—no hypochlorous acid. The conclusion is drawn that the action is like that of any other acid, and that carbonic acid decomposes both the chloride and the hypochlorite in the bleaching powder. It follows from this that the action of hydrochloric acid on carbonates is a reversible one.

2. Ordinary moist air acts on solid bleaching powder, liberating at first both chlorine and hypochlorous acid, the former in much the larger amount. After a time nothing but chlorine is produced. When ordinary air is passed through a solution of bleaching powder, a mixture of hypochlorous acid and chlorine is swept out, at first in about equal amounts; but, as the experiment proceeds, the former diminishes, and the latter increases to about 90 per cent.

3. The action of chlorine on alkalis, like that of iodine and bromine, is a reversible one, as stated by von Tiesenholt. If the free lime in bleaching powder is removed, this causes the reverse action to proceed, and thus chlorine is liberated. This explains the action of ordinary air on bleaching powder. The reversibility of the action also explains the stimulating effect on bleaching which the addition of calcium chloride or of salt causes in a solution of bleaching powder.

4. In the ordinary processes of bleaching the active bleaching agent is probably free chlorine, hypochlorous acid playing only a minor part.