Thesis for the degree of
Doctor of Science, in Chemistry.

"On the action of solutions of Bleaching Powder and of Hypochlorous acid on metals."

Alice Dingwall White.
April 1902

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Edinburgh
It had frequently come under my observation, while connected with the linen bleaching industry in the North of Ireland, that if particles of metallic iron, clean and free from oxide, were allowed to come into contact with linen in presence of hypochlorite solution, a vigorous reaction took place, and in a very short space of time complete "tendering" of the linen — with production of holes — took place at the spots where there had been contact with the iron.

Experiments, in which strips of polished iron wrapped round with as pure cellulose as could be obtained — thoroughly bleached linen being used in some cases and pure filter paper in others — were immersed in Bleaching Powder Solution of 1:0 (by vol.), showed that, in addition to the disintegration of the fabric, ferric hydrate was produced and a gas evolved.

The gas was examined and found to be oxygen; the cellulose was thoroughly washed, treated with sodium bichlorate solution, washed again, in order to
remove all traces of hypochlorite, and then digested in solution of methylene blue (1/1000 in the cold) [Williams Bull. Sci. Ind. Res. [10].5. and [11].2]. The characteristic colour reaction around the holes and at the 'tendered' spots showed that the 'tendering' was due to the local production of celloulose.

Celloulose is then produced by the action of celloulose of vanescent copper arising from the interaction of hypochlorite solution and iron.

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Action of Bleaching Powder Solution on Iron.

Experiments were made to determine the nature of the reaction which takes place when solution of a hypochlorite comes into contact with iron.
holders were used; into each of them three strips of powdered iron, free from oxide, each measuring 100 m. long, 10 m. wide, and 1 m. thick, were intro-
duced; the vessels were then completely filled with freshly prepared solution of Bleaching Powder of 1.040 sp. gr. and the stop-cocks of each closed. From the lower opening of each gas holder a bent glass tube was led into more of the solution con-
tained in a beaker, and at its outer extremity where it dipped into this solution the tube had been drawn out almost to a capillary, in order to prevent as far as possible, diffusion backwards, into the gas holder, of solution richer in dissolved air or in hypochlorous acid than the liquid in contact with the metal. The vessels, on being filled, were immediately transferred to a perfectly dark room, of which the temp-
erature ranged from 10°C to 15°C. Bunsen reaction began at once, with production of a copious brown precipi-
tate and evolution of a gas. In each vessel about 500 cc. of gas
collected in 45 hours.

The brown precipitate is ferric hydrate; analysis of the gas shows it to be oxygen mixed with a small amount of nitrogen due to air which had been dissolved in the hydrochloric solution and had been swept out by the evolution of oxygen.

Analysis of gas:

<table>
<thead>
<tr>
<th></th>
<th>a.</th>
<th>b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. taken.</td>
<td>55.0 cc.</td>
<td>53.9 cc.</td>
</tr>
<tr>
<td>Vol. after shaking with KCl.</td>
<td>55.0 cc.</td>
<td>53.9 cc.</td>
</tr>
<tr>
<td>Vol. &quot; &quot; &quot; chlorine-propylol.</td>
<td>1.1 cc.</td>
<td>1.0 cc.</td>
</tr>
<tr>
<td>Vol. of air added.</td>
<td>5.9 cc.</td>
<td>3.0 cc.</td>
</tr>
<tr>
<td></td>
<td>7.0 cc.</td>
<td>4.0 cc.</td>
</tr>
<tr>
<td>Vol. after Borkh had been passed.</td>
<td>6.9 cc.</td>
<td>4.0 cc.</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
V_2 &= 95.0 \% \quad 95.1 \% \\
V_2 &= 2.0 \% \quad 1.9 \% \\
\hline
100.0 & 100.0
\end{align*}
\]

Ferric hydrate and oxygen are therefore the products of the action. No ferric salt is found in solution nor is any chlorine set free. Existence
iron was used in each experiment and parts of the strips were still bright
and marked on them when 5-10 c.c. of gas had collected.

The following equation represents the reaction taking place:

\[ 4Fe + 6Ca(OCl)_2 + 6H_2O = 4FeCl_3 + 6CaCl_2 + 3O_2 \]

A search for literature on the subject showed that nothing had been done before or since the times of

Sondeiran and Belard.

Sondeiran [Annales de Chimie et de Physique [45] 1836] investigated the action of hypo-
chlorites on Silver, Mercury, Iron, Tin, Zinc, Antimony, Arsenic and Copper.

Concerning the action on iron he says (page 125): "The iron is transformed almost immediately into a red powder. The
other disappears, the liquor retains hardly any traces of iron, while the
precipitate itself is only oxide of iron free from chlorine.

Belard [Annales de Chimie et de Physique [57] 1834] investigated the action of
Hypochlorites and of hypochlorous acid on gold, platinum, silver, lead, mercury, copper, iron, tin, arsenic and antimony. Concerning the action of hypochlorite solution on iron, he only says (loc. cit. p. 301) “iron is very readily reduced.”

As apparatus for accurate gas analyses was not much in use at the time at which the work of Sontheim and of Belard was done and as neither of these men makes any mention of having obtained the evolution of oxygen during the action of a hypochlorite on iron, work already done by them with tin. Copper and arsenic was repeated by the writer; and experiments were also made with each of four metals, nickel, cobalt, aluminium and magnesium, of which in the metallic state nickel and cobalt were probably little more than chemical curiosities, and aluminium and magnesium unknown at the time of Sontheim and Belard.
in each case the apparatus
used was exactly similar to that used
in the experiment with iron, dealt with
above, and as soon as the Bleaching
Powder Solution and the respective
metal had been introduced, each
vessel was placed in the dark room,
and kept there, at a temperature which
never rose above 15°C, until sufficient
gas for analysis had collected.

Action of Bleaching Powder Solution
on Tin.

According to Souleiman (loc. cit.
p. 156) hypochlorite of tin is produced
and oxygen evolved, but the amount
produced is so small that I would not
have hesitated to attribute it to some
unaccounted decomposition of the hypochlorite.

Had the same phenomenon not shown
perfectly sharp in operating with copper.

Balard (loc. cit. p. 301) says
"as to tin, it becomes promptly enough oxy-chloride, while giving rise to a slight solution of chlorine mixed with oxygen."

In a number of experiments made now it is found that tin is slowly attacked and that stannic acid and oxygen are the only products of the action. No oxy-
chloride of tin is produced nor is any chlorine liberated.

The reaction goes on slowly and in 96 hours only 40 cc. of gas had collected.

Analysis of gas:

<table>
<thead>
<tr>
<th>Vol.</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td></td>
<td>after shaking with KOH</td>
</tr>
<tr>
<td></td>
<td>alkaline Hydroxide</td>
</tr>
<tr>
<td>Vol.</td>
<td>air added</td>
</tr>
<tr>
<td></td>
<td>after spark has been</td>
</tr>
<tr>
<td></td>
<td>passed</td>
</tr>
</tbody>
</table>

O₂ = 96.47 %

H₂ = 3.53 %
In order to reduce if possible the percentage of nitrogen present in the gas from air which had been in solution in the hypochlorite solution, all the gas was withdrawn from the jar holder and the solution which had already been used in the experiment was used to refill the jar holder. The reaction was then allowed to go on for 72 hours, in which time 65 c.c. gas had collected; in it the percentage of nitrogen had been reduced to 2.4%.

Analysis of gas:

<table>
<thead>
<tr>
<th>Description</th>
<th>Volume (c.c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. taken</td>
<td>57.4</td>
</tr>
<tr>
<td>Vol. after shaking with KOH</td>
<td>54.4</td>
</tr>
<tr>
<td>Vol. &quot;</td>
<td>Alkaline solution.</td>
</tr>
<tr>
<td>Vol. of air added</td>
<td>5.3</td>
</tr>
<tr>
<td>Vol. after spark had been passed</td>
<td>5.3</td>
</tr>
</tbody>
</table>

\[ O_2 = 97.6\% \]
\[ N_2 = 2.4\% \]

\[ 100 \times 0.8 \]

The gas was again all withdrawn and the same solution used to
refill the gas holder. After 48 hours action 55 c.c. of gas had collected. On analysis it was found to contain 95.17% of oxygen.

Analysis of gas:

Vol. taken: 54.4 c.c.
Vol. after shaking with alkali: 54.4 c.c.
Vol. of alkali hydroxyl: 1.0 c.c.
Vol. of air added: 2.5 c.c.
Vol. after spark had been passed: 3.5 c.c.

\[ \frac{2}{2} = 95.17\%
\]
\[ \frac{2}{2} = 1.97\%
\]
\[ \frac{1}{1} = 100.0\%
\]

The action which takes place may be represented by the following equation:

\[ \text{Sn} + 2\text{Ca(OCl)}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SnO}_4 + 2\text{CaCl}_2 + \text{O}_2 \]
Action of Bleaching Powder Solution on Copper.

According to Sombirain (loc. cit. p. 126) oxy-chloride of copper is produced, with evolution of oxygen with extreme slowness. A sheet of copper being plunged into a solution of bleaching powder, it has formed little by little on its surface a blue layer of oxy-chloride. At the same time as it is produced one sees small bubbles of oxygen evolved. The action proceeds slowly and in order to hasten the production of the gas, I have had recourse to finely divided copper, which has made the experiment less long but has modified the result, making the precipitate become green. The wanting oxygen which is produced in these circumstances is a remarkable fact which I had thought at first of being able to attribute to the spontaneous decomposition of the hypochlorite, but I have recognised that it belongs to the particular circumstances of the experiment.
According to Belard (loc. cit. p. 30) "as to copper, it becomes promptly enough our chloride, while giving rise to a slight solution of chlorine mixed with oxygen."

Copper turnings were used in the present experiments. The action goes on slowly and a green very chloride of copper, and oxygen are produced. Chlorine, mentioned by Belard, was not liberated in any of the experiments made.

On 12 hours 60 cc. of gas containing 94.3% by oxygen were evolved.

Analysis of gas:

<table>
<thead>
<tr>
<th>Description</th>
<th>Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. taken</td>
<td>52.8 cc.</td>
</tr>
<tr>
<td>Vol. after heating with test</td>
<td>52.5 cc.</td>
</tr>
<tr>
<td>Vol. alkaline Pyrargyline</td>
<td>2.9 cc.</td>
</tr>
<tr>
<td>Vol. of air added</td>
<td>7.5 cc.</td>
</tr>
<tr>
<td>Vol. after spark had been passed</td>
<td>10.4 cc.</td>
</tr>
</tbody>
</table>
\[\begin{align*}
D_1 & = 94.3\% \\
D_2 & = 5.7\% \\
\text{Total} & = 100.0
\end{align*}\]

The high percentage of nitrogen here is to be attributed to the slowness of the reaction and the small quantity of gas produced. In a second experiment in which the already used solution of hypochlorite was used for refilling the apparatus, 70 cc. of gas had collected in the next 12 hours. The gas was now found to contain 96.56% N. Oxygen analysis showed:

- Vol. taken: 57.8 cc.
- Vol. after shaking with KOH: 57.3 cc.
- Alkaline permanganate: 1.5 cc.
- Vol. of air added: 4.5 cc.
- Vol. after spark had been passed: 6.3 cc.

\[\begin{align*}
D_1 & = 96.86\% \\
D_2 & = 3.14\% \\
\text{Total} & = 100.00
\end{align*}\]
All the gas from this experiment was in turn withdrawn and the apparatus again filled with the same hypochlorite solution. In 12 hours more 55 c.c. of gas had collected, containing now 98.85% of oxygen.

Analysis of gas:

Vol. taken: 52.4 c.c.
Vol. after shaking with K.OH: 51.4 c.c.
Vol. ... alkaline pyrogallic: 0.6 c.c.
Vol. air added: 1.5 c.c.
Vol. after spark had been passed: 2.1 c.c.

\[ O_2 = 98.85\% \]
\[ N_2 = 1.15\% \]
\[ 100.00 \]
Action of Bleaching Powder Solution on Arsenic

Sondeiran (loc. cit. p. 124) states that calcium arsenate is produced and there is evolution of chlorine which disappears in contact with the matter decomposed as in acids.

Balard (loc. cit. p. 301) simply states that calcium arsenate is the product of the action and repeats the observation of Sondeiran that "Surfaces of arsenic which had become blackened by contact with air rapidly regain a metallic lustre if dipped in hypochlorite solution."

A number of experiments now made show that arsenic is attacked somewhat slowly by the Bleaching Powder Solution, and that in addition to the production of calcium arsenate there is evolution of oxygen. Thus in 72 hours 55 c.c. 7 per cent. had been evolved. Ten small lamps of arsenic
about 1 c.c. in size were used, and the gas contained 93.6% of oxygen.

Analysis of gas:

<table>
<thead>
<tr>
<th>Vol. taken</th>
<th>50.0 c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. after shaking with koh.</td>
<td>50.0 c.c.</td>
</tr>
<tr>
<td>Vol. ... alkali hypochlorite</td>
<td>3.2 c.c.</td>
</tr>
<tr>
<td>Vol. air added.</td>
<td>3.0 c.c.</td>
</tr>
<tr>
<td>Vol. after spark had been passed.</td>
<td>11.2 c.c.</td>
</tr>
</tbody>
</table>

\[
O_2 = 93.6\% \\
\text{H}_2 = 6.4\% \\
100.0
\]

The gas was all withdrawn and the apparatus refilled with the same hypochlorite solution.

In 72 hours 60 c.c. gas had collected, and the gas now contained 99.5% of oxygen.

<table>
<thead>
<tr>
<th>Vol. taken</th>
<th>51.7 c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. after shaking with koh.</td>
<td>51.7 c.c.</td>
</tr>
<tr>
<td>Vol. ... alkali hypochlorite</td>
<td>1.3 c.c.</td>
</tr>
<tr>
<td>Vol. air added.</td>
<td>4.0 c.c.</td>
</tr>
<tr>
<td>Vol. after spark had been passed.</td>
<td>5.3 c.c.</td>
</tr>
</tbody>
</table>
\[ O_2 = 97.5\% \]
\[ N_2 = 2.5\% \]
\[ \text{total} = 100\% \]

In none of the experiments made was chlorine liberated under any circumstances. The only products of the action are calcium arsenate, oxygen and calcium chloride.

In the pages immediately following, an account is given of new experiments with addition of Bleaching Powder on Nickel, Cobalt, Aluminium and Magnesium.
Action of Bleaching Powder Solution on Nickel.

Cubes of nickel about 1 c.c. in size were used. These are rapidly attacked with brisk evolution of a gas and formation of a black precipitate. In 12 hours 160 c.c. of gas had collected. On examination it was found to contain 97.9% of oxygen. The black precipitate is nickelous hydrate.

Analysis of gas:

Vol. taken: 52.4 c.c.
Vol. after shaking with HgO: 52.4 c.c.
Vol. after shaking with Alkaline Hypo: 1.1 c.c.
Vol. air added: 5.0 c.c.
Vol. after spark had been passed: 4.1 c.c.

\[
O_2 = 97.9\% \\
2\% = 2.1\% \\
100\%
\]

This gas was all withdrawn and the apparatus refilled with the
same hypochlorite solution. At this stage after the action has gone on for some hours, the evolution of gas becomes much more rapid. In the next 12 hours over 6,000 c.c. of gas had collected. This increased evolution of gas is doubtless due to the decomposition of bleaching powder solution by nickelate hydrate produced during the reaction.

Analysis of gas:

Vol. taken. 66.3 c.c.
Vol. after shaking with Ca. 66.3 c.c.
Alkaline ZnCl₂ 0.7 c.c.
Vol. of air added. 2.7 c.c.

Vol. after part had been passed. 2.7 c.c.

\[ \begin{align*}
\text{O}_2 &= 98.94 \% \\
\text{N}_2 &= 1.06 \% \\
\text{Total} &= 100.00 \%
\end{align*} \]

Nickel, then, is acted on readily with production of nickelate hydrate and oxygen.

The following equation represents the action:

\[ \text{4Ni} + 6 \text{Ca(OCl)}_2 + 6 \text{H}_2 \text{O} = 4\text{Ni(OH)}_3 + 6 \text{CaCl}_2 + 3 \text{O}_2 \]
Action of Bleaching Powder Solution on Cobalt.

Cubes of cobalt about 1 cc. in size were used. The action proceeds even more briskly from the start than in the case of nickel. A black precipitate is produced and a gas evolved in large quantity. In the first 2 hours 113 cc. of gas were evolved and 578 cc. in the first 12 hours. This gas contained 96.4% of oxygen.

Analysis of gas:

<table>
<thead>
<tr>
<th>Description</th>
<th>Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. taken</td>
<td>53.4 cc</td>
</tr>
<tr>
<td>Vol. after shaking w/ charcoal</td>
<td>53.4 cc</td>
</tr>
<tr>
<td>Vol. alkali pyrophosphate</td>
<td>2.0 cc</td>
</tr>
<tr>
<td>Vol. rain added</td>
<td>57.0 cc</td>
</tr>
<tr>
<td>Vol. after spark had been passed</td>
<td>2.0 cc</td>
</tr>
</tbody>
</table>

\[ \frac{O_2}{N_2} = \frac{96.4}{3.6} = \frac{100}{0.0} \]

The gas was all withdrawn and the bottle refilled with the same
hypochlorite solution. The gas was examined 4 hours after then 130 cc had
collected and was found to contain
99.1 % of oxygen.

Analysis of gas:

<table>
<thead>
<tr>
<th>Volume</th>
<th>cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taken</td>
<td>535.5</td>
</tr>
<tr>
<td>After shaking with KOH</td>
<td>53.5</td>
</tr>
<tr>
<td>After addition of alkaline pyrophosphate</td>
<td>0.5</td>
</tr>
<tr>
<td>After gas added</td>
<td>1.0</td>
</tr>
<tr>
<td>After spark has been passed</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
O_2 &= 99.1 \% \\
N_2 &= 0.9 \% \\
100.0
\end{align*}
\]

The black precipitate produced is cobaltic hydrate and the products
the action of hypochlorite on cobalt are thus cobaltic hydrate and oxygen.
The reaction which takes place may be represented in the following equation:

\[
4Co + 6 \text{ Ca} \left[ \text{O}_3 \right]^2 + 6H_2O = 4Co\left[ \text{OH} \right]_3 + 6\text{ Ca} \text{Cl}_2 + 3\text{O}_2
\]
Action of Bleaching Powder Solution on Aluminium.

Aluminium in the form of filings is rapidly attacked with brisk evolution of hydrogen and formation of unstable calcium aluminate. Owing to the relative lightness of aluminium, the filings were not suitable for the experiments in the apparatus used owing to the difficulty of completely filling the gas-holders with liquid and thoroughly excluding air: wire which had been flattened to a thin narrow ribbon was used in all the experiments, and with this the reaction proceeded very slowly, 5 or 6 days being always required (in a dark room at a temperature of 15°C) for the production of 40 to 50 cc. of gas. The gas evolved is hydrogen, and is always mixed with a small percentage of oxygen and nitrogen from air dissolved in the hypochlorite solution.

Analysis of gas
Vol. taken: | a. | b. | c. |
---|---|---|---|
| 26.9 | 25.9 | 32.3 c.c. |
Vol. after shaking with KOH: | a. | b. | c. |
| 26.9 | 25.9 | 32.3 c.c. |
Vol. ... alkali destilled: | a. | b. | c. |
| 26.3 | 28.6 | 31.6 c.c. |
Vol. air added: | a. | b. | c. |
| 65.6 | 65.7 | 74.2 c.c. |
| 91.9 | 91.3 | 110.5 c.c. |
Vol. after explosion: | a. | b. | c. |
| 53.9 | 54.4 | 64.6 c.c. |
Contraction: | a. | b. | c. |
| 38.0 | 36.9 | 46.2 c.c. |

<table>
<thead>
<tr>
<th>a.</th>
<th>b.</th>
<th>c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>94.05</td>
<td>95.7</td>
</tr>
</tbody>
</table>
O₂ | 2.2 | 1.1 | 2.1 |
H₂ | 3.75 | 3.2 | 2.6 |

\[ \text{Aluminium thus causes the evolution of hydrogen from solution of a hypochlorite. No aluminium salt is found in solution; all the aluminium acted on is precipitated as calcium aluminimite.} \]
Action of Bleaching Powder Solution on Magnesium.

Experiments were made with magnesium ribbon (free fromcontaining oxygen carbonate) and also with small blocks of magnesium. The metal is attacked with great rapidity, likely of presence of hydrogen being present. While magnesium hydroxide is precipitated. In 2 hours 500 cc. of gas had collected.

Analysis of gas:

<table>
<thead>
<tr>
<th></th>
<th>a.</th>
<th>b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. taken</td>
<td>45.0</td>
<td>24.9 cc</td>
</tr>
<tr>
<td>Vol. after heating w/ H₂</td>
<td>45.0</td>
<td>24.9 cc</td>
</tr>
<tr>
<td>Vol. Alkaline solution</td>
<td>44.5</td>
<td>24.5 cc</td>
</tr>
<tr>
<td>Vol. N₂ added</td>
<td>110.9</td>
<td>62.3 cc</td>
</tr>
<tr>
<td>157.7</td>
<td>87.1 cc</td>
<td></td>
</tr>
<tr>
<td>Vol. after explosion</td>
<td>55.5</td>
<td>53.3 cc</td>
</tr>
<tr>
<td>Contraction</td>
<td>66.9</td>
<td>36.5 cc</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>a.</th>
<th>b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>99.02</td>
<td>99.0 57.0</td>
</tr>
<tr>
<td>O₂</td>
<td>0.44</td>
<td>0.4 70.0</td>
</tr>
<tr>
<td>N₂</td>
<td>0.54</td>
<td>0.6 78.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Action of Sunlight on Bleaching Powder Solution.

It has already been noted that all the experiments recorded here were carried out in a dark room. This precaution was taken as it had been observed in the course of some preliminary experiments that if exposed to bright sunlight a solution of bleaching powder gives off bubbles of gas.


His details are given by Trouvaille, Morin, or Sonbeiran of any analyzing the gas. Longe and Landolt (Chem. Ind. 5, 337-346) have determined the wave strength of solutions of the hypochlorite of calcium.
Aluminium, zinc and magnesium on exposure to different daylight for periods up to 38 days, but make no mention of having observed actual evolution of gas.

To examine the effect of daylight the following experiment was made. A 500 c.c. Bunsen gas holder was completely filled with freshly prepared Bleaching Powder Solution of 1:000 sp. gr. The gas tube leading from the lower opening of the gas holder was drawn out almost to a capillary and allowed to drip into Bleaching Powder Solution in a beaker; the apparatus was then exposed to daylight where it would get the benefit of any sunshine that might come.

For the first seven days (it was in February) the weather was persistently dull and cloudy without sunshine, and no sign of evolution of gas took place.

On the 8th day there was bright sunshine and gas began to be slowly given off in very small quantities;
the solution almost entirely stopped at 4 p.m.

9th day was cloudy; gas was given off though extremely slowly.

10th day was wet and dull; the evolution of gas had stopped.

11th and 12th day were bright and sunny and gas was given off briskly; on the 13th day 40 c.c. of gas had collected; but the day being dull and cloudy the evolution of gas had almost stopped. On the 15th day over 50 c.c. of gas had collected and an analysis of it was made.

Analysis of gas:
Vol. Taken. 50.2 c.c.
Vol. after shaking with exc. 50.2 c.c.
Vol. after alkaline pyrogallic 4.5 c.c.
Vol. of nitrogen remaining 4.3 c.c.

\[ O_2 = 91.4 \% \]
\[ N_2 = 8.6 \% \]
\[ 100.0 \]

The oxygen given off by the decomposition of the hydrogen peroxide had probably swept out with it nearly all the air which had been dissolved
in the solution. The apparatus was refilled with the same solution and again exposed. During the next seven days which were bright with fairly good February sunshine the solution of gas went steadily on, and at the end of that time 50 c.c. of gas had collected. It now contained 96.3% of oxygen.

Analysis of gas:

| Vol. taken | 75.8 c.c. |
| Vol. after subtracting titration | 75.5 c.c. |
| Vol. after subtrating alkaline pyrogallol | 2.8 c.c. |
| Vol. of nitrogen remaining | 2.8 c.c. |

\[
\text{O}_2 = 96.3 \text{ %} \\
\text{N}_2 = 3.7 \text{ %} \\
\text{Total} = 100.0
\]
Action of Solution of Hypochlorous Acid on Metals.

The hypochlorous acid used in the following experiments was prepared by saturating with chlorine gas, water with freshly precipitated mercuric oxide in suspension, then distilling the liquid (which had been filtered off) until one-fourth of its volume had passed over, then shaking this distillate with precipitated calcium carbonate (to remove all traces of chlorine and hydrochloric acid arising from decomposition of the hypochlorous acid) and distilling again in presence of calcium carbonate. The distillate—freed from chlorine and from hydrochloric acid—was freshly prepared for each experiment and used immediately.

All the experiments were carried out in a dark room of which the temperature ranged between 12°C and 15°C.
Action of Solution of Hypochlorous Acid

on Iron.

According to Balard (Ann. de Chim. et de Phys., 57, 1334, 267), ferric oxide, ferric chloride, and brick solution of chlorine are produced.

Analyses of the gas obtained in experiments made by the writer show that there is always hydrogen mixed with the chlorine, this hydrogen being produced by the action on iron of hydrochloric acid formed as reduction products of the hypochlorous acid. At first a simple oxidation of the iron takes place with formation of large quantities of ferric hydrate, and some hydrochloric acid. The hydrochloric acid as produced interacts with the ferric hydrate, iron, and hypochlorous acid, producing ferrichloride, hydrogen, and chlorine, which with ferric hydrate are the products of the action.
Action of Solution of Hypochlorous Acid on Tin.

According to Baland [loc. cit. p. 257]

'Tin filings may remain in presence of pure dilute hypochlorous acid for several days without making it undergo sensible decomposition and without losing its metallic lustre. But the presence of another acid makes the metal capable of going about decomposition. This acid must fulfil the condition of being able to form with the oxide of the metal a compound soluble in water. When one acts with hypochlorous and sulphuric acids on tin, the jar stained (carbon) contains a small quantity of hydrogen.'

Again [loc. cit. p. 263]

That if concentrated hypochlorous acid be used, action takes place after some time owing to formation of chloric acid from spontaneous decomposition of the hypochlorous acid. The action being the same as takes place if sulphuric acid be present.'
obtained in all the experiments made now. It is found that freshly prepared pure dilute hypochlorous acid acts at once, though slowly, on tin. A white precipitate, found to be stannic acid, made its appearance at once and went on increasing steadily, though slowly, in bulk. There was no evolution of gas noticed, but the liquid was found to contain free chlorine in solution, the slowness of the reaction enabling the water present to hold the chlorine dissolved.

The reaction is a simple oxidation of the tin with reduction of the hypochlorous acid to hydrochloric acid and consequent liberation of chlorine. So the salt is found in solution.

The following equation represents the action which takes place:

$$Sn + 2 HClO + 2 \times O = SnCl_2 + 2 HCl.$$
Action of Solution of Hypochlorous Acid on Copper.

Belard (loc. cit. p. 253) states that chloride and oxy-chloride of copper are formed, and chlorine, mixed with a very small proportion of copper, evolved.

The same products were obtained in the experiment made in the present examination.

Action of Solution of Hypochlorous Acid on Arsenic.

As stated by Belard (loc. cit. p. 253), arsenic is converted into arsenic acid, (a small quantity of arsenic chloride being also formed) and chlorine is evolved.
Experiments with solution of hypochlorous acid and nickel, cobalt, aluminum, and magnesium.

Action of solution of hypochlorous acid on nickel.

Nickel is quickly attacked with formation in the first instance of nickel chloride:

\[2\text{Ni} + 3\text{HClO} + 3\text{H}_2\text{O} = 2\text{NiCl}_3 + 3\text{H}_2\text{O}\]

The hydrochloric acid so produced, interacts with some of the nickel chloride forming nickel chlorite, and with the hypochlorous acid, forming chlorinating chlorine. Interaction also takes place between the nickel chloride and hypochlorous acid with formation of nickel chloride and liberation of oxygen. The reaction proceeds briskly and nickel chloride, nickel chloride hydrate, chlorine, and oxygen are the products obtained.

The reaction which take place may be
Summarised in the following equation:

\[
8 \text{Ni} + 24 \text{HClO}_4 = 4 \text{NiCl}_2 \cdot 6 \text{H}_2 \text{O} + 8 \text{Cl}_2 + 6 \text{H}_2 \text{O}
\]

Action of Solution of Hypochlorous acid on Cobalt.

Cobalt is readily attacked. The action is exactly similar to that of hypochlorous acid on nickel, cobaltic chloride and hydrate, chlorine and oxygen being produced.
Action of solution of hypochlorous acid on aluminium.

Aluminium is acted on somewhat slowly. Hydrogen and chlorine are noticed, aluminium chloride and hypochlorite are formed in solution, and aluminium hydride is precipitated.

Bubbles of hydrogen are given off as soon as the hypochlorous acid comes into contact with the aluminium and aluminium hypochlorite. The reaction is:

\[ 2\text{Al} + 6\text{HClO} = 2\text{Al(OCl)}_3 + 3\text{H}_2. \]

Aluminium is at the same time reduced with formation of aluminium hydroxide and hydrochloric acid:

\[ 2\text{Al} + 3\text{HClO} + 3\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 3\text{HCl}. \]

The hydrochloric acid dissolves some of the hydroxide forming aluminium chloride and interacts with the hypochlorous acid liberating chlorine.

An equation summarising the reactions taking place may be written:

\[ 3\text{Al} + 15\text{HClO} + 2\text{Al(OCl)}_3 + 2\text{AlCl}_3 + 4\text{Al(OH)}_3 + 3\text{H}_2 + 3\text{HCl} + 3\text{H}_2\text{O} \]
Mixed with the faces given off during the reaction there is always a small percentage of oxygen (up to 2%) arising from spontaneous decomposition of the aluminium hypochlorite in solution.

Action of Solution of hypochlorous acid on magnesium.

Magnesium dissolves with great readiness with evolution of hydrogen and formation of magnesium hypochlorite in solution.

\[ \text{Mg} + 2\text{HClO} = \text{Mg(ClO)}_2 + \text{H}_2 \]

Magnesium hypochlorite in solution is stable and the gas evolved is found to be pure hydrogen.
Action of Bleaching Powder solution on linen in presence of metals.

Experiments having shown that so far as is known if iron, tin, copper, nickel, or cobalt be treated with solution of bleaching powder, experiments were made to ascertain if with tin, copper, nickel, and cobalt, an effect could be produced on linen undergoing hypochlorite treatment — an effect similar to the one first observed with iron. Each of these metals was placed in contact with linen immersed in bleaching powder solution of a concentration such as is used in ordinary linen bleaching operations and allowed to remain in contact for a corresponding period of time.

In the case of nickel and cobalt, oxidation of the celllose and complete disintegration of the fabric took place at the parts where metal had been in contact; in a less degree the same results were obtained with copper; with tin, no evidence of the formation of any cellulose
was obtained, a result due, doubtless, to the presence of the interaction between tin and solution of bleaching powder.

Experiments with aluminium and magnesium showed that their presence in contact with chlorine in the hypochlorite bath did not at all affect the fabric, a result quite in accordance with the observations made in the experiments on the action of these metals on bleaching powder solution.

It has been shown in the experiments just recorded that the ordinary alkaline solution of bleaching powder at ordinary temperatures attacks iron, tin, copper, arsenic, nickel, cobalt, aluminium and magnesium; in the case of most of them with great readiness, in the case of all of them with evolution of a gas.

Schenkau and Belard independently investigated the actions in the case of iron, the copper and arsenic, but do not remark having obtained the evolution of oxygen in
the case of iron and arsenic; they also state that with tin, an oxy-chloride is produced. While in all the present experiments, the precipitate was stannic acid.

Of the four metals, the action on bleaching powder solutions was examined for the first time, nickel and cobalt in their behaviour resemble iron, forming a hydrate of the metal and causing rapid evolution of oxygen; while the action of aluminium and magnesium causes evolution of hydrogen from such a powerful oxidising agent as solution of bleaching powder is distinctive and noteworthy.

Equally distinct from the behaviour of other metals with solution of hypochlorous acid is that of aluminium and magnesium.