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TRANSACTIONS.

I.—*The Inertness of Quicklime.* Part II.

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INTRODUCTORY.

IN a former communication (Trans., 1893, **63**, 821—833), it has been shown that quicklime does not combine to any appreciable degree with carbon dioxide or sulphur dioxide at temperatures below 300°; it was further proposed to continue the investigation on these lines, and to examine the reactions of other gases, such as chlorine, which, under ordinary conditions, are readily absorbed by slaked lime.

HISTORICAL.

The well-known researches of Wanklyn (*Chem. News*, **20**, 271) and Couper (Trans., 1883, **43**, 153—155) have established the fact that certain metals, such as sodium, Dutch metal, &c., do not burn in carefully dried chlorine. Further, it has been shown by Pringsheim (*Wiedemann's Annalen*, 1887, **32**, 421), as also by Dixon (Bakerian Lecture, 1893, *Phil. Trans.*, A, 100), that a mixture of hydrogen and chlorine gases, when dried, are far less sensitive to the action of sunlight than when moist.

It was pointed out by Morin (*Ann. Chim. Phys.*, **37**, 139), that when bleaching powder is heated, chlorine, and, subsequently, oxygen, is given off. Mendeléeff (*Principles of Chemistry*, Eng. trans., **1**, 471) mentions the fact, without, however, quoting the authority, that "quicklime does not absorb chlorine when cold, but at a red heat in a current of chlorine it forms calcium chloride with evolution of oxygen." And also that "slaked lime, when dry, does not absorb chlorine at 100°."

Mr. Francis Jones has informed me, in a private communication, that he found "some years ago that there was no action between chlorine and lime at ordinary temperatures, or up to a red heat," and, under these circumstances, "a decomposition took place, with evolution of oxygen." In the present communication, these statements will be confirmed and amplified, except that it will be shown that the reaction, under the conditions of experiment, commences at about 300°.

Lunge (*Sulphuric acid and Alkali*, 3, 106—109) conducted a series of experiments, in which quicklime, containing variable proportions of water, was exposed to a continuously changing atmosphere of chlorine in a bell-jar, sealed by a hydraulic lute of sulphuric acid of specific gravity 1.4. The only results of special importance to this enquiry show that, if the amount of water present is 6.5 per cent., the amount of so-called available chlorine is as low as 9.6—12.49 per cent., instead of 40 per cent., or thereabouts. I have also been informed that, in samples of bleaching powder sent into the market, and deficient in available chlorine, lumps of quicklime are found, which, doubtless, have escaped hydration before being placed in the chambers.

It is not, of course, proposed to deal in any way with the composition or constitutional formula of bleaching powder; it will not, therefore, be necessary to allude to the literature upon this subject.

EXPERIMENTAL.

The method of experiment was mainly identical with that described in the former communication, but a few variations, by way of improvement, were introduced; I am indebted to Mr. H. B. Baker for kind suggestions upon these points.

The lime, after ignition in a platinum crucible, was placed in a piece of hard combustion tubing, sealed at the lower end, and with a constriction at the upper end; the latter was partially closed with asbestos fibre, beyond which a plug of phosphorus pentoxide was placed. The tube up to the constriction was heated for some hours in a combustion furnace, then allowed to cool slightly, and cut off at the constriction. The lime, still quite hot, was then poured into the U-tube, which had been kept heated for some time in a bath of nitre. It was hoped that, by this method, all traces of water were eliminated, not only from the lime, but also from the walls of the U-tube; for, though glass may, for all practical purposes, be dried in a water bath, yet, undoubtedly, even at the temperature of 100°, slight traces of water are persistently retained.

The only exposure to the air, and the operator who is, unfortunately, himself producing the two substances capable of reacting with the

lime, was during the pouring out of the lime from the combustion tube into the U-tube.

The chlorine gas, generated from lump manganese peroxide and hydrochloric acid, was purified by passing through a wash-bottle containing water, and surrounded with black paper, to prevent the decomposition of the chlorine solution into hydrochloric acid and oxygen, the former of which might pass through the apparatus.

Before any experiments were made, the chlorine was passed for some hours through the whole system of water and sulphuric acid bottles and phosphorus pentoxide tubes, set up as described in the former communication, so as to diminish the risk of any reaction between the last-named substance, or impurities contained therein, whereby hydrochloric acid might be generated, and thus vitiate the results.

The lime used was free from iron oxides, alumina, and silica, except minute traces; the proportion of chlorine, as chloride, found was 0.067 per cent., a value which would not materially affect the results obtained.

In this investigation, the amount of chemical change must necessarily be estimated, not only by synthetical, but also by analytical, methods, since one, or both, of two reactions may take place, namely, the direct addition of chlorine and the substitution of this element for the oxygen.

Synthesis.—For this purpose, the dried chlorine was passed into the lime contained in the U-tube and heated to the required temperature; to ensure, as far as possible, the complete reaction between the substances, that limb of the U-tube which served, in any experiment, for the entry of the gas was made, in the succeeding experiment, to serve for its exit. The chlorine, which escaped absorption by the lime, after passage through a guard-tube containing phosphorus pentoxide and pumice, was collected in a tared vessel, containing a concentrated solution of soda. At the conclusion of the synthetical experiments, a current of air, purified from carbon dioxide and dried by sulphuric acid and phosphorus pentoxide, was drawn through the U-tube, so as not only to remove the atmosphere of chlorine, but also to eliminate any gas which might mechanically adhere to the lime. The sample was then quickly taken out, rubbed up in a mortar, and introduced into a dry and warm weighing tube.

Methods of Analysis.—The total calcium was determined, in all cases, as the sulphate, by evaporating the substance with sulphuric acid, a method susceptible of great accuracy.

The available chlorine, if any, was determined by Bunsen's iodometric method, and half the amount found was taken as the chlorine present in the form of hypochlorite.

The *total chlorine* was determined, in those cases in which there was evidence of the production of oxygenated chlorine compounds, by destroying these by boiling with a solution of urea, purified from a slight impurity of chloride by allowing it to stand over crystals of silver nitrate, and drawing off the solution as occasion required. (It was found that better results were obtained, when dealing with such small quantities of oxygenated chlorine compounds, by using urea rather than a concentrated solution of ammonia, as recommended in most manuals.) The solution, with the partially undissolved lime, was then made up to a definite volume, the whole allowed to settle, and the amount of chlorine determined in an aliquot portion, after neutralisation of the dissolved lime with nitric acid, by a standard solution of silver nitrate of the strength commonly used in water analysis. If no appreciable quantity of oxygenated chlorine compounds was present, the preliminary treatment with urea was, of course, omitted.

The free, or *unaltered, lime* was determined by treatment with urea, evaporating the whole to dryness, extracting the calcium chloride with alcohol (recently dehydrated by distillation with lime), and then evaporating the solid residue with sulphuric acid. The method was much simplified in the absence of oxy-acids of chlorine; in this case, the substance was dissolved in an excess of a dilute standard solution of sulphuric acid, the excess being subsequently determined by a standard solution of ammonia.

The results obtained by the analytical and synthetical methods are compared, not only by way of a check, but also for the indirect determination of the amount of the oxygen eliminated by the chlorine.

Effect of Temperature.

Various series of experiments were conducted, in order to determine the temperature at which there are indications of a chemical change; the points selected were 20°, 40°, 100°, 200°, 300°, and 352° (temperature of melting nitre).

After passage of gas for 17½ hours, there was practically no absorption of the chlorine by the lime at a temperature of 20°, for, though the gas was passed at rates varying from 0.616 to 4.733 grams per hour, yet the total gain in weight, in terms of lime, was 1.1 per cent., and, in terms of chlorine passed, 0.5 per cent., the greater part of which was in the first experiment. The product contained

| | |
|--------------------------|--------|
| Chlorine available | 1.17 |
| Lime free | 98.87 |
| | <hr/> |
| | 100.04 |

The above results also confirm those obtained by synthesis, in showing that the lime is practically unaltered.

By way of comparison, the above experiment was repeated, under otherwise the same conditions, except that the hydrate was substituted for the anhydrous oxide. A recently ignited sample of the latter was hydrated, under conditions which precluded the access of carbon dioxide, and the superfluous water was removed by desiccation over sulphuric acid and then analysed.

| | Found. | Theory. |
|---------------------|--------|---------|
| Water per cent..... | 24.21 | 24.32 |

Under these conditions, about 95 per cent. of the gas was absorbed during the first periods of exposure, and, subsequently, about 10 per cent.; when the absorption was apparently completed, the product was taken out, and, on analysis, the following results were obtained.

| | Per cent. |
|-------------------------|-----------|
| Total chlorine | 43.33 |
| Available chlorine..... | 41.94 |
| Free lime | 9.30 |
| Total calcium..... | 30.71 |
| Water | 14.69 |

The results would point to the following composition.

| | |
|--|--------|
| Bleaching compound, $\text{CaCl} \cdot \text{OCl}$ | 74.85 |
| Calcium chloride. | 2.01 |
| Free lime | 9.30 |
| Water..... | 14.69 |
| | <hr/> |
| | 100.85 |

The experiments were then repeated with calcium oxide at various temperatures, the first point selected being 40° , namely, that at which the formation of calcium chloride and chlorate, instead of hypochlorite, commences.

Under these conditions, the gain in weight was only 0.1 per cent. after passage of the chlorine for $13\frac{1}{2}$ hours, even though the rate of the gas was purposely varied from 0.5 to 2 grams per hour. The analysis (I, table, p. 7) showed that a small quantity of chlorate was formed. The results given above would point to the composition given under I in table.

At a temperature of 103° , after passage of the chlorine for 12 hours, the total gain was less than 1 per cent., and the analysis showed that over 96 per cent. of the lime remained unaltered (II, p. 7). Neglecting the insignificant amount of available chlorine, which would

amount only to 0.015 per cent. of chlorine present as hypochlorite, the results point to the composition given under II.

The analytical and synthetical results compare as follows.

| Weight of lime originally taken. | Weight of material after experiment. | |
|----------------------------------|--------------------------------------|---------------|
| | Found. | Calculated. |
| 12.707 grams | 12.8149 grams | 12.8722 grams |

In this case, also, both the synthetical experiment and analytical results show that there is no appreciable amount of chemical change between the reacting substances.

On repetition of the experiment at 203°, there was a total gain in weight of 3 per cent., and the product, on analysis, furnished the results given under III (p. 7). Neglecting the available chlorine, as before, these results point to the composition given under III.

The analytical and synthetical results compare as follows.

| Weight of lime originally taken. | Weight of material after experiment. | |
|----------------------------------|--------------------------------------|--------------|
| | Found. | Calculated. |
| 12.0285 grams | 12.3985 grams | 12.408 grams |

The above results show that, at this temperature, there is some evidence of the replacement of the oxygen by the chlorine, though the lime is, for the most part, as yet, unaltered.

Another experiment, conducted at the same temperature, led to a very similar result, and, on analysis, the following numbers, given under IV (p. 7), were obtained. These point to the composition IV.

The analytical and synthetical results compare as under.

| Weight of lime originally taken. | Weight of material after experiment. | |
|----------------------------------|--------------------------------------|---------------|
| | Found. | Calculated. |
| 12.8848 grams | 13.4638 grams | 13.5037 grams |

The composition of the material does not differ much from that

obtained in preceding experiments, though the mass of chlorine passed was nearly three times as much in the one case as in the other. Both series of experiments show that the amount of chemical change is very small, 93 per cent., or thereabouts, of the free lime being recovered unaltered.

When, however, the experiment was conducted at a temperature of 292° , there was, in the first period of four hours, a gain in weight in the lime of 8.3 per cent., or, to put the result in another form, the percentage gain was, to the amount of gas unabsorbed, in the ratio of 46.8 : 53.2; in a second period of four hours, there was a considerable gain in weight, but, in a third period, the alteration was inconsiderable. The analysis of the product is given under V (see below).

The analytical and synthetical results compare as under.

| Weight of lime taken. | Weight of material after experiment. | |
|-----------------------|--------------------------------------|---------------|
| | Found. | Calculated. |
| 12.897 grams. | 15.6578 grams | 15.4073 grams |

The material obtained at the conclusion of the synthetical experiment was a hard, caked-together mass, which was removed only with difficulty from the experimental U-tube. The results show that, at this temperature, there is a considerable amount of replacement of the oxygen of the lime by the chlorine, rather less than two-thirds of the lime taken being unaltered at the end of the process.

| Analyses.... | I. At 40° . | II. At 103° . | III. At 203° . | IV. At 203° . | V. At 292° . |
|-----------------------|-------------------------|---------------------------|----------------------------|---------------------------|--------------------------|
| Total chlorine..... | 3.14 | 2.52 | 4.15 | 5.28 | 24.93 |
| Available chlorine... | 1.78 | 0.03 | 0.004 | 0.003 | — |
| Free lime..... | 95.08 | 96.37 | 93.50 | 93.19 | 64.76 |
| Total calcium..... | 69.84 | 69.84 | 68.85 | 67.51 | 56.63 |

| Composition.... | I. | II. | III. | IV. | V. |
|----------------------|--------|--------|-------|-------|--------|
| Free lime..... | 95.08 | 96.37 | 93.50 | 93.19 | 64.76 |
| Calcium chloride.... | 2.58 | 3.97 | 6.41 | 6.57 | 35.32 |
| „ hypochlorite | 1.79 | — | — | — | — |
| „ chlorate.... | 0.66 | — | — | — | — |
| | 100.11 | 100.34 | 99.91 | 99.76 | 100.08 |

Lastly, a series of experiments was conducted at the temperature of melting nitre 352° , and the results obtained showed that a considerable reaction takes place at first, and, afterwards, the lime is slowly converted into calcium chloride; probably the latter cakes round the unaltered lime, and thus prevents a very intimate contact of the gas in its passage. The material obtained was detached from the tube with even greater difficulty than in the preceding series; during this manipulation, there was, doubtless, some absorption of moisture by the material, which contained such a large proportion of calcium chloride.

Results of Analysis.

| | Per cent. |
|-----------------------------|-----------|
| Free lime | 38.82 |
| Calcium chloride..... | 56.09 |
| Water (by difference) | 5.09 |

The results, however, suffice to show that a difference of 50° practically causes a reversal of the percentage proportions of the oxide and the chloride. It was not thought necessary to examine the chemical reaction at any higher temperature by the method described, owing to the manipulative difficulties involved in the process.

Conclusion.

I. Dry chlorine does not combine with dry lime, at ordinary temperatures, to form the so-called bleaching powder.

II. No appreciable chemical change is observable between these two substances below a temperature of 300° , when a partial replacement of oxygen by chlorine takes place; under these conditions, the reaction is analogous to that of baryta and chlorine, not specially dried, and at ordinary temperatures.

It is proposed to continue these investigations in the case of other anhydrous oxides and acidic gases.

I would express my thanks to Mr. G. B. Cronshaw, of Queen's College, for his care and attention in carrying out the analytical work of this investigation.

*The University Museum,
Oxford.*
