XLVII.—*Observations on the Properties of some Highly Purified Substances.*

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INTRODUCTION.

THE interesting observations made during the last few years by Prof. H. B. Dixon, Mr. H. Brereton Baker, and others have shown that many chemical changes only take place in the presence of some substance, presumably the vapour of water, which can be readily removed by phosphoric anhydride. The number of well established cases of the kind, moreover, is sufficiently great to give rise to the question—may not the occurring of all chemical changes depend on the presence of the vapour of water among the acting substances?

On the other hand, a good many of the changes which have been examined have not hitherto been prevented by the withdrawal of water vapour from the sphere of action,* and it seems to me that a stage has been reached at which it is more important to re-examine

* For a list of most of the changes hitherto examined, see Baker, Trans., 1894, 65, p. 611.

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as carefully as possible the changes comprised in the latter and smaller class, than to search for fresh examples of conformity to what I may, for convenience, term the general rule. I have, therefore, spent a good deal of time during the past two or three years in further investigating several of these so-called exceptions.

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I.

INFLUENCE OF MOISTURE ON THE PRODUCTION OF OZONE FROM OXYGEN BY ELECTRIC DISCHARGE, AND ON THE STABILITY OF OZONE.

In their classical memoirs on ozone, both Andrews and Tait, and also Brodie, distinctly indicate their opinion that the oxygen employed for the production of ozone should be carefully dried. In the description of his process, Brodie says: "The gas is thus submitted to the electric action in a very dry condition, which is an essential point for the production of a considerable percentage of ozone" (*Phil. Trans.*, 1872, p. 438), whilst Andrews and Tait state that their experiments could not be carried on in the presence of water, as ozone is rapidly destroyed by contact with that substance (*Phil. Trans.*, 1860, p. 114). I am inclined to suppose that these statements were founded on the fact that when ozonised oxygen is mixed with steam at the boiling temperature, the ozone is rapidly destroyed (see Andrews, *Phil. Trans.*, 1856, p. 11).

In 1887, shortly before the publication of Brereton Baker's interesting memoir on combustion in dry oxygen (*Phil. Trans.*, 1888, A, p. 571), Mr. Cundall and I showed that carefully dried oxygen is readily converted into ozone and, incidentally, that dry ozone has no oxidising action on mercury. These observations have recently been confirmed by Baker (*Trans.*, 1894, 65, *loc. cit.*). In 1887, however, the effect of

the electric discharge on oxygen had to be observed with the aid of manometers containing strong sulphuric acid, so that quantitative experiments of a suitable kind were then impossible; and therefore when Mr. Priest and I overcame, in 1893, the difficulties which for long prevented the use of a mercury manometer in experiments with ozone, I thought it desirable to repeat my former experiments. After a good deal of unavoidable delay, I have now succeeded in doing this, and the results show, quite unmistakably, that all previous statements on this subject are wrong.

I commenced the work with the expectation that a numerous series of observations would be required, but owing to the great risk of accident, and indeed of the spontaneous breaking of the apparatus, I found as I proceeded that I must content myself with the three experiments described in this paper. Fortunately, these have proved sufficient for my purpose.

Method of Experimenting, and Results Obtained.

For the sake of brevity, I shall omit all details so far as they have already been described in a former paper (Shenstone and Priest, *Trans.*, 1893, **63**, p. 938). All the details of the manipulations, necessary precautions, and sources of error not mentioned here will be found in that earlier paper.

The apparatus employed is shown in Fig. 1 (p. 474). It was entirely built up before the blow-pipe except that a cup-joint sealed with mercury was employed at X. It was filled as described below.

At the beginning of the experiments, after the air traps, I I', had been filled with mercury, the apparatus was exhausted until the tension of the residual air was less than 0.02 mm., then the whole apparatus, except A, was heated with a naked flame while the pumping was continued, and oxygen was afterwards slowly generated in one of the hard glass tubes, G G' G'', from a mixture of the chlorates of sodium and potassium, to which a little solid potash had been added, as recommended by Scott (*Phil. Trans.*, 1893, A, p. 544). The tube, G, was then removed. The apparatus, now filled with oxygen, was again heated throughout, while the ozoniser A, which could not then be safely heated, was sparked for one hour, and the drying material, highly purified phosphoric anhydride (*Trans.*, 1893, **63**, p. 475), was heated in D until a good deal of it had sublimed, in order to remove any gas that might be condensed upon its surface.* During the latter

* It has lately been stated (Baly and Ramsay, *Phil. Mag.*, Sept., 1894, 320) that phosphoric anhydride evolves a considerable quantity of carbon dioxide when strongly heated, and as the presence of the latter would be very objectionable, the anhydride used was carefully sublimed in a current of oxygen, and preserved from the air as much as possible afterwards.

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thoroughly exhausted, and then strongly heated for a long time while vacuous, pumping continuously. Afterwards, it was rinsed out thrice with oxygen, and again exhausted. Water vapour, free from air, was now admitted into the exhausted apparatus from a bulb M, kept at 0° in the chamber K, by ice and water in N. This was effected by dropping the weight, L, upon M, by fusing the two fine platinum wires previously employed to support it. Finally, the apparatus was filled with oxygen to a suitable pressure, mercury was admitted to the manometer B, the contents of the drying chamber D were isolated by admitting mercury into the U-tube O O, and the tube C C was sealed before the blow-pipe at Q. I satisfied myself by measurements made subsequently that little or no loss of water occurred during these operations, and that the oxygen thus confined in the ozone generator A, and the tube C C, contained sufficient water to saturate it at 0° .

It will be noticed that there were two passages from the rest of the apparatus to the pump. One of these, S, consisted of a tube packed with solid potash to prevent water vapour from reaching the pump at the earlier stages of the experiment, the other, H, was used for adjusting the final pressure of the moist oxygen, with which operation the potash in S would have interfered.

Influence of the Electric Discharge on Moist Oxygen at 0° .

It should be mentioned that the ozone generator A, the drying chamber D, and the tubes C C and E, had been calibrated before the apparatus was put together; and that whenever an experiment was made the whole was screened from the body of the operator by two sheets of glass. When making an experiment, the contents of the apparatus were carefully divided between the ozoniser A, and the drying chamber D (both previously cooled to 0°), by simultaneously bringing the mercury in the manometer to a reference mark, and closing the bend of O, which had been previously *slightly* opened. The mercury in E was then brought to a reference mark F, that in the manometer to a mark at B, the pressure required for this, the height of the barometer, and the temperature of the air were noted, and the volume of gas in A and C C under standard conditions was calculated from the data thus obtained.

The known volume of oxygen in A and C C was then submitted to the electric discharge, and when fully ozonised its volume under standard conditions was again determined; from the observed contraction, the amount of ozone formed could be calculated.

As the volume, temperature, and pressure of the unozonised oxygen in C C were known, it was simple to calculate what proportion of the oxygen actually submitted to the discharge in A had been converted into ozone.

The oxygen, saturated with water vapour at 0° , was ozonised several

times on different days, the lowest proportion of ozone formed corresponded with 13.3 per cent. of the oxygen submitted to the discharge, whilst the largest proportion was 13.6 per cent. The lower yield was undoubtedly due to slightly imperfect cooling of the ozone generator, but even the lowest percentage of ozone produced is at least as great as that which I have usually obtained from moderately *dry* oxygen under corresponding conditions.*

The slow rate at which the ozone disappeared in the intervals between the experiments showed that ozone is certainly not destroyed quickly by contact with water vapour at moderately low temperatures.

Influence of the Electric Discharge on Moderately Dried Oxygen.

In order to dry the oxygen for my next experiment, convection currents were started and maintained in A, and the gas was then gradually pumped from A into D, and *vice versa*, by alternately raising and lowering the reservoir, R', at regular intervals, about ten times in a day of nine hours. By measuring the effect of a given number of such pumping operations, I found that fifty of them were sufficient to reduce the tension of the water vapour present from, say, 1 mm. to 0.1 mm.; and I have used this observation as the basis for calculating the hygrometric state of the gas at subsequent stages; this method of calculating is, of course, open to criticism, but it is the best that presents itself for the present, and the statements based upon it will be more helpful to any one who may repeat my experiments than a mere enumeration of the number of times the mercury was introduced into and removed from O O. The probability is, of course, that the gas was less dry than my figures suggest.

When I concluded that the tension of the water vapour present had been reduced to *about* 0.0001 mm. (probably, however, there was a certain amount of condensed moisture on the glass), the contents of the apparatus were again carefully divided, and submitted to the electric discharge. The oxygen was now, of course, at a slightly lower pressure than before, but as it has been shown that small differences of pressure are without appreciable influence on the proportion of ozone produced (Hautefeuille and Chappius, *Compt. rend.*, 91), this was unimportant.

The results obtained were decidedly interesting. In the first place, the highest proportion of ozone I could obtain corresponded to 11.1 per cent. only of the oxygen submitted to the discharge. Secondly, the ozone now appeared to be singularly instable. When ozonising wet oxygen, I have always found it most convenient to submit the gas first to a rapid succession of discharges, and afterwards, when the rate of

* I was not, however, using the same ozone generator as before, and different instruments do not give strictly concordant results.

contraction has become very slow, to allow the ozone generator to cool (as a rapid discharge usually warms the gas a little), and to finish off with a slower discharge of about 60 to 80 sparks per minute.

When, however, oxygen, dried as described above, was treated in this way, it was found that the proportion of ozone in the gas diminished, during the action of the slow discharge, instead of increasing. This circumstance, together with the fact that the ozonised gas now visibly expanded whenever the discharge was stopped, seems to imply that the partial drying of the contents of the ozone generator had diminished the stability of the ozone.

Fortunately, as I had commenced my experiments with the intention of examining the influence of water vapour on the stability of ozone, I had already studied the rate at which ozonised oxygen loses ozone in the presence of moisture, and I was therefore able to follow up these unexpected observations.

Influence of Moisture on the Stability of Ozone.

1. Moist oxygen well charged with ozone loses ozone so slowly at 0° , that satisfactory measurements cannot be made within a reasonable time; it is therefore necessary to study the behaviour of the damp gas at a higher temperature.*

Moist oxygen, well ozonised, was maintained at 26.4° for 9 hours; during that time the proportion of ozone present was only reduced by 2 per cent., and during the last 4 hours only 0.4 per cent. disappeared, although, at the beginning of the latter period, nearly 12 per cent. must still have been present.

2. On the other hand, after the gas has been dried, as described above, it is impossible to study its behaviour at so high a temperature as before, as even at 0° , on stopping the discharge, the ozone decomposes so quickly that it is difficult to measure the exact proportion present.

The following observations were made with moderately dried oxygen.

a. The oxygen charged as strongly as possible with ozone (11.1 per cent.), was kept at 0° for 33 minutes, and then remeasured. The proportion of ozone was found to have fallen to 9.5 per cent., that is, a loss of 1.6 per cent. had occurred.

b. A similar experiment was made, except that the proportion of ozone at starting was only 11 per cent. In 30 minutes a loss of 1.4 per cent. took place.

From these observations, it seems certain that water vapour, at the ordinary temperature, retards the reverting of ozone to oxygen in a very remarkable degree.

*In a former research, *loc. cit.*, Mr. Priest and I made a similar observation.

The circumstance that it is necessary to study the behaviour of the moist and dried gas at different temperatures, renders it difficult to institute an exact comparison, but I may point out that the experiments make it clear that the dried ozone at 0° underwent decomposition about 30 times as rapidly as the damp gas at 26.4° , and this in spite of the fact that the damp gas was a trifle more highly charged with ozone at starting than that which had been dried. I think there can be no doubt but that, under the same conditions of temperature, the contrast would be much more striking.

Influence of more thorough Drying of the Oxygen on the Production of Ozone.

When the above experiments were completed, I proceeded to dry the gas more thoroughly; for this purpose, it was necessary to heat the whole of the apparatus strongly.

A and B are the tubes of the ozone generator, C is a closed tube of thin glass, D one of thick Jena glass, W W a platinum wire embedded in asbestos paper and coiled between C and D, W' W' wires in circuit with W and W; the latter are continued in a coil inside the inner tube A.

It would have been very dangerous, if not impossible, to have applied a naked flame to both the outer and inner tubes of the ozone generator, but I succeeded in heating it to a high temperature by means of the little furnace shown in Fig. 2.

This little furnace was heated by passing an alternating current through W and W'. A choking coil in circuit with W W' was used to regulate the temperature, and a blank experiment, made with an ozone generator, similar to that which I was using, enabled me to judge the temperature employed. With this furnace, the ozone generator was heated to between 300° and 400° four times for several hours, at intervals of 2 weeks, the final heating lasting 6 hours. Each time it was heated, its contents were diligently pumped into D, at short intervals, for a day of fourteen or fifteen hours, and the pumping was continued at longer intervals during the whole period of 2 months. Whenever A was heated, the tubes

C C, and the side B of the gauge were also heated.

When I reckoned that the tension of the water vapour had been reduced to, say, 0·000000001 mm.* (see p. 476), I subjected the oxygen to the electric discharge for the last time. No visible effect was produced (the barometer happened to be rising quickly when the experiment was made), but measurements showed that 0·2 per cent. of ozone had been formed, and a repetition of the experiment made on the following day gave a similar result. I tried the effect also of the discharge from Tesla's apparatus, but without any decisively different result. Well dried oxygen, therefore, ozonises exceedingly badly.

II.

THE BEHAVIOUR OF CAREFULLY DRIED CHLORINE, BROMINE, AND IODINE WITH CAREFULLY DRIED MERCURY.

In 1883, Cowper examined the action of several of the metals on dried chlorine, and found that several of them did not combine with the halogen, although mercury, tin, antimony, arsenic, and perhaps potassium did so readily. (Trans., 1883, 43, 153.) I myself, some time ago, made a number of similar experiments in conjunction with Mr. C. R. Beck, using well dried mercury, chlorine, and bromine, and in every experiment the mercury and the halogen combined readily. The ordinary methods of making chlorine are, however, so unsatisfactory, that I have always distrusted the results obtained in these early experiments, and I have made many attempts to discover a more satisfactory process for obtaining this gas. Some years ago, at the suggestion of Dr. Armstrong, and in connection with the work of a Committee appointed by the British Association to investigate the forming of haloids from pure materials, I tried to prepare chlorine by electrolysis of fused silver chloride. But I failed, as others had failed before me, baffled by the "silver tree" which forms at the negative electrode. I have, however, frequently renewed my efforts, and about a year ago I succeeded in overcoming the difficulty. As the new method may be found useful by others, I will describe it fully.

Preparation of Chlorine from Silver Chloride.

The apparatus employed, which is shown in Fig. 3 (p. 481), consists essentially of two sections. On the right of the tap T, is the generating apparatus, on the left is the receiving apparatus. Communication be-

* That is, assuming that the oxide of phosphorus absorbed the water completely, which of course may not have been the case. When calculating the above number, I excluded the effect of the rapid pumping during the four days when the ozone generator was being heated, as I could not then allow full time for diffusion. Obviously some moisture was removed at this time, however, and this would tend to counter-balance imperfect action of the anhydride.

tween these two is prevented by the end of D, which is closed, but communication could be established on crushing this by rotating T. The bye-pass O established temporary communication during the building up of the apparatus, and enabled me to test the joints as they were made. This arrangement permitted me to guard the receiving apparatus from injury in the event of an accident to the generating apparatus at the beginning of an experiment, which was an object of importance, as the apparatus in question took a long while to prepare. The tubes marked B contained small bulbs partly filled with mercury; these, and also A and C, will be referred to subsequently.

In order that the process might be carried out rapidly, a large Fleuss pump and also two five-fall Sprengels were employed for exhausting the apparatus. These were protected from chlorine by large chambers M N, filled with solid potash. The tap Q, as may be seen, is of a novel type. It can be flooded with mercury to SS from R through an air trap, which is not shown; it is a true safety tap, not only can no air enter from the outside, but none can leak from one side of the plug to the other. When using a well-made tap of this description, I was able to generate chlorine on one side of it while pumping a vacuum on the other, and although the action of the chlorine on the mercury gave some trouble, it did not prevent the tap from acting. I have found taps of this kind invaluable, and I think they are likely to be generally useful. At V is a small mercury manometer, which can be put out of communication with the rest of the apparatus by a three-way tap, T². At F is a set of sampling tubes. The chamber K, contained phosphoric anhydride. The chlorine generator, H, which was made of the most infusible Jena glass I could obtain, had a capacity of 140 c.c. I had great difficulty in obtaining suitable electrodes, but Messrs. Edison and Swan were kind enough to make me a number of carbon filaments such as are used for 250 c.p. incandescent lamps, which answered admirably; each electrode consisted of three of these. The negative electrode was surrounded by a glass tube, with a small hole at X, the lower end of the tube slightly overlapping the carbon. H was almost filled with specially prepared chloride of silver before it was placed in position.

The method of filling the apparatus with chlorine was as follows. It was first well exhausted, and all gases driven as far as possible from the glass and silver chloride by heating; the chloride of silver was then fused, and the current from one or two storage cells passed through it, this current being gradually strengthened as we proceeded. When a little chlorine had accumulated, Q was opened, in order that the gas should pass into M and carry with it such impurities as it might contain (these were very sensible at first), then Q was again closed, M was re-exhausted, and more chlorine was generated and removed as before, these operations being repeated as often as was necessary. From time

FIG. 3.

to time, samples of the gas were removed in the tubes marked F, and exposed to the action of carefully prepared mercury free from air. When the chlorine was found to be completely absorbed by mercury, the thin glass at D was broken, and A, B, and C were filled with the gas, and sealed before the blow-pipe.

The difficulty I have alluded to as being created by the formation of silver trees can be overcome, if the electrodes are constructed as described above, by simply reversing the current for an instant at short intervals; a sudden evolution of chlorine is thus set up at Z, and this blows the trees into pieces which soon subside. It is necessary to promote their subsidence, however, by occasionally stopping the current for a short time. Of course, after a while they fill up the lower part of the vessel as they are rather bulky, and if sufficiently pure lead could be obtained it would be an improvement to provide a bath of that metal at the bottom of H to receive the silver.

Thirteen cubic centimetres of chlorine prepared in this way (a portion of that employed in the experiments described below) left no visible residue in the drawn-out tip of an absorption tube, F, when it was exposed to the action of mercury, nor could any residue be detected with the aid of a good lens. In order to detect any small bubbles that might have collected on the sides of the tube, it was kept for some weeks, and was subjected to frequent shaking and bumping, but no gas appeared in the tip of the tube. If it be admitted that, with the aid of a lens, the tenth of a cubic millimetre of residue could be detected, it would follow that not so much as one volume of the gas remained unabsorbed out of one hundred and thirty thousand volumes.

The great advantage of preparing chlorine in this way lies in the fact that it is unlikely to contain hydrogen chloride, which, if accompanied by traces of oxygen, would be as objectionable for my purpose as water vapour, in fact, much more so.

Mode of Preparing Iodine and Bromine and of introducing them into the Experimental Apparatus.

The iodine used in these experiments was purified by the "Stas" process some years ago by Mr. J. T. Cundall and myself, and had been preserved in a vacuum in a small glass bulb.

The bromine was prepared by heating it for many days with a large excess of potassium bromide, from which it was subsequently distilled, and was collected in glass bulbs, from which the air was expelled by boiling the bromine before they were sealed.

The bulbs containing the bromine and iodine were placed in a chamber A, Fig. 4, which was connected with a set of tubes, B B B. Moisture, &c., were removed by pumping and heating as already described, the

contraction, C, was sealed, the bulb broken by rotating T, and the tubes thus charged with bromine, or iodine, were sealed before the blow-pipe. The iodine was, of course, driven from A by heat.

FIG. 4.

Preparation and Drying of the Mercury.

Three distinct preparations of mercury were used.

1. Mercurous nitrate was made from mercury which had been frequently redistilled in a vacuum, and nitric acid free from iron. From this, mercurous chloride was prepared, which, after being thoroughly washed, was converted into mercuric chloride

and repeatedly recrystallised. The mercuric chloride was then mixed with potassium carbonate and a little water, dried, and distilled.

2. Mercurous nitrate, made as before from carefully prepared mercury, was decomposed by electrolysis, and the mercury obtained was well washed and dried.

3. Mercury obtained by heating oxide of mercury was converted into nitrate, and then again into oxide by igniting the nitrate; this oxide was then slowly decomposed by igniting it.

Each of these specimens was prepared for use in the following manner. After being distilled slowly in a vacuum, almost without ebullition, it was placed in a glass tube, Fig. 5, provided with a thin glass bulb C, and a chamber B, containing phosphoric anhydride.

FIG. 5.

This tube was well exhausted, then strongly heated for a day, pumping simultaneously; during this period, the mercury was distilled at least twice, in order to thoroughly free it from gases held in solution or on its surface. The glass bulb was also strongly heated by means of a furnace of platinum wire made hot by a current of electricity. The

tube was then sealed, removed from the air pump and placed aside for 10 days.

I observed during the foregoing operations that the mercury left no residue whatever when it was distilled, and that, however finely it might be divided, it ran into globules most readily.

As I was satisfied that the mercury could not be properly dried by mere exposure to air previously dried by phosphoric anhydride, even if heated occasionally, it was further treated in the following manner. The glass of each tube was heated to near its melting point, and any moisture or gas that might have been given off was driven at once into the chamber, B, by boiling out the tube with a little of the mercury. This was done many times, and on each occasion the whole of the mercury was afterwards volatilised and a portion driven into the drying chamber. At the same time, C was heated and boiled out repeatedly with mercury. Finally, the remainder of the mercury was collected in C, about half of it was boiled away, and the rest was secured by melting off the bulb. These bulbs were then placed in strong glass tubes provided with chambers containing purified phosphoric anhydride, which were attached to the generating apparatus (see B, Figs. 3 and 4) and prepared for receiving chlorine, bromine, or iodine, as the case might be, by thoroughly exhausting them, and repeatedly heating the glass and the phosphoric anhydride strongly, with long continued pumping. At this stage, the surfaces of the tubes and of the bulbs containing the mercury were from time to time actually coated with phosphoric anhydride which was afterwards driven back into the drying chamber.

Method of drying the Chlorine, Bromine, and Iodine.

The tubes B, Fig. 3, containing chlorine were sealed in April, 1896, those which contained bromine and iodine, B, Fig. 4, were sealed in the following July. In every case, the contents of the tubes were exposed to the drying agent until after Christmas Day, 1896. I did not, however, depend on the moisture reaching the drying agent by diffusion alone. During five or six weeks the drying chambers were alternately heated and cooled many times daily in order to promote the mingling of the contents of the two chambers, and during this period the iodine was repeatedly volatilised.

Finally, the drying chamber of each of the tubes containing chlorine or bromine was placed in a mixture of carbon dioxide and ether; when the halogen had condensed within this chamber, the other parts of the tube, and also the sealed bulb containing the mercury, were at once heated strongly, and before they had become cold again were rinsed out by allowing the chlorine or bromine to evaporate, and then again condensing it.* This rinsing process was repeated daily for a week.

* This was possible because chlorine which has been exposed to phosphoric

The larger chamber was then again heated when vacuous, and rinsed with halogen as before. Five such series of operations were performed, so that the halogen was condensed on the drying material 30 times. A single operation such as I have described was probably more effective than 6 months of drying by diffusion would have been, for it must be remembered that, after each experiment, only the volatile halogen escaped from the drying chamber, moisture, if present, being left in it more or less in contact with the phosphoric anhydride, whilst its subsequent escape through the plug of glass wool at the contraction would be very slow in the presence of the large excess of chlorine or bromine.

The tubes containing iodine received corresponding, but of course not quite identical, treatment.

On December 30th, 1896, the contents of the tubes were again condensed in the drying chambers, and the bulbs containing the mercury were broken. In every case, there was immediate and rapid action in the cold, both the chlorine and the bromine being soon completely absorbed. The action of the iodine naturally proceeded at a slower rate, but it became manifest instantly.

One tube which contained iodine together with the mercury made by the first process was broken in liberating the quicksilver. Two others, both of which contained chlorine with mercury made from the oxide, did not escape without damage, for they showed minute cracks at their tips when the mercury struck them on escaping from the bulbs. But as these ends were sealed in advance by the mercury and as the cracks were too slight to admit air, except by diffusion, and showed no signs of leaking, whilst the interaction of the chlorine and mercury showed itself at once in all parts of the tubes, I believe that the observations made with these tubes may be trusted.

The other nine tubes,* namely, three containing bromine, two containing iodine, and four containing chlorine, were undamaged.

General Results and Conclusions.

From the above results, it may be concluded that, practically speaking, the action between mercury and chlorine, bromine, or iodine does not depend on the presence of water vapour.

It is more difficult to decide whether the presence of moisture is necessary for producing ozone from oxygen. The proportion of ozone obtained from the most highly dried oxygen was very small, and *perfect* drying might have reduced it, but a certain amount was produced, and it is by no means certain that the smallness of that amount may not anhydride attacks lead glass much less readily than before. I have even softened lead glass in contact with dried chlorine without diminishing its lustre.

* Two samples of each preparation of mercury were exposed to chlorine; only one to bromine and iodine, as the available supply of the latter substances was small.

have been due simply to the very remarkable instability of ozone in the absence of moisture. I hope to clear up this point on a subsequent occasion.

Finally, the remarkable fact that ozone changes into oxygen much more rapidly in the absence of water vapour than in its presence, seems to dispose of the idea that all chemical change may be impossible, except in the presence of water.

It remains to be seen, however, whether this is true of any particular class or classes of change.

III.

BEHAVIOUR OF CHLORINE UNDER THE INFLUENCE OF THE SILENT DISCHARGE AND IN SUNLIGHT.

I have long desired to examine the influence of the silent discharge of electricity on chlorine, as it seemed not at all unlikely that an allotropic form of this element might exist. But two difficulties stood in the way; first, I had no means of obtaining chlorine sufficiently free from impurities; secondly, no suitable liquid could be found for the manometer that must be employed, in order to observe the effect of the discharge. I have already explained how the former difficulty has been overcome, and I have lately learnt how to employ fused silver chloride in the manometer.

FIG. 6.

The apparatus shown in Fig. 6 having been filled with chlorine in the manner already described, the following experiment was made. The ozoniser, A, was placed in dilute acid at 0° , its inner tube was filled with acid at the same temperature, and the acid in A and that in the outer vessel were connected with the terminals of an induction coil. The manometer tube B, which had previously been charged with silver chloride, was then gradually heated by means of a small furnace closely resembling that shown in Fig. 2, and when the chloride was fused and the thermal conditions of the contents of the apparatus were in equilibrium, the narrow tube at C was sealed before the blow-pipe. At this moment, the manometer tube cracked at D, but, fortunately, the conditions of pressure were such that a good thread of fused chloride remained in E, and sealed the chlorine from the outer air.

I then submitted the gas to the action of the discharge for some time. At first, a *very* slight contraction occurred (the effect of the

discharge on an absolutely indifferent gas would result in a *slight* expansion, through rise of temperature), but this did not increase afterwards.

It appears, therefore, that highly purified chlorine remains almost unaffected by the ozonising discharge.

The Behaviour of Highly Purified Chlorine when Exposed to Sunlight.

In 1871, it was stated by Budde (*Phil. Mag.*, IV., 1871) that, when chlorine is exposed to sunlight, an expansion of the gas occurs which is independent of the direct heating effects due to the light. This statement has since been confirmed by Richardson (*Phil. Mag.*, Sept., 1891, p. 277), who, following a suggestion made by Budde, has applied this property of chlorine to the measurement of the actinic intensity of light.* As it is highly probable that the chlorine employed in the experiments of Budde and Richardson was not free from other substances, I thought it would be interesting to ascertain, if possible, whether chlorine prepared as I have described would act in a similar manner.

The apparatus I employed is shown in the accompanying figure. It is a copy of that constructed by Dr. Richardson, but modified with his kind assistance, to suit the altered conditions. Two chambers, A A', are respectively connected with the two ends of a narrow tube B B', which contains a thread of silver chloride at C. The contents of A and A' communicated at first through a bye-pass D, whilst E E served to connect this piece of apparatus to the pump and to the chlorine generator (see Fig. 3); when the apparatus was filled with chlorine, E E was sealed off at F. The apparatus was then plunged to the level, *d d*, into water contained in a tank. This was blackened internally, but one of its sides consisted of a sheet of glass which could be exposed or shaded at the will of the experimenter. When all was ready, the tube, B B', was heated by means of an electric furnace similar to that pre-

* I should say that the other coloured gases are said to exhibit similar phenomena.

viously described to a temperature sufficiently high to fuse the silver chloride. The tip of G was then broken; the bye-pass was sealed before the blow-pipe at D; the tip of F was opened, and air was gently aspirated into A' until the chlorine was replaced; G and F were then closed again, and the chlorine in A and the air in A' were exposed to the direct rays of the sun. At the moment of the exposure, the chloride of silver was sufficiently hot to be very fluent, and was already moving at a very slow rate towards B'. Its rate of movement was a little accelerated under the influence of the sunlight, but not much. On shading A and A', its rate of movement diminished, but its direction was not reversed. The effect of the sunlight was observed several times, and the results were similar. The movements observed by no means corresponded with those recorded by Richardson.

The liquid index having presently reached B', I opened G, attached an india-rubber tube, and endeavoured to force the index back to B. In doing this, the chloride was driven into the bulb provided at B, where it solidified on the sides, and a little air* entered A and mingled with the chlorine. The chloride of silver was fused with a spirit lamp, drawn back into B B', the india-rubber tube on G was securely closed, and the contents of A and A' were then again exposed to the sun. At each exposure, a much more marked movement towards B' now took place. This was at once arrested by shading the chamber. The effect was now so decided that my assistant remarked, "What a difference that little air has made!" Shading, however, had not even now the effect of reversing the movement of the index. The experiment was ultimately stopped, in consequence of the softening of the tube B B'. These results seem to make it certain that the abnormal expansion of chlorine in sunlight does not occur unless small quantities of other substances besides chlorine are present.

Before concluding, I should like to add that the experiments with chlorine were commenced in conjunction with Mr. C. R. Beck, and that, until his departure from Bristol prevented us from continuing the work jointly, I had his assistance in preparing a good deal of the material employed, and in making many preliminary studies, some of which have already been published. I wish also to express my thanks to my present assistant, Mr. W. T. Evans. Nothing could exceed the care and devotion he has shown in assisting me to perform many of the tedious mechanical operations required, or the skill he has exercised in preparing, under my supervision, the very complicated and delicate glass apparatus which it has been necessary to employ.

CLIFTON COLLEGE,
January, 1897.

* Moist air.