XXXIX.—*The Action of Chlorine on Water in the Light, and the Action of Light on Certain Chlorine Acids.*

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THAT a solution of chlorine in water when exposed to the action of light gradually changes in composition is, perhaps, one of the best known facts in chemistry. The explanation of the change, as given in most modern text-books on chemistry, is that oxygen is evolved by the direct action of the chlorine with the formation of hydrogen chloride, according to the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$. The statement is also made that when chlorine-water is placed in direct sunlight, the *whole* of the free chlorine may thus combine with the hydrogen of the water, evolving its equivalent volume of oxygen. A proposal has indeed been made (Wolters, *Pogg.*, **94**, 579; *Ann. Chem. Pharm.*, Suppl., **4**, 63) to employ this reaction in measuring the chemical action of light. In direct tropical sunlight the decomposition of chlorine-water is so rapid that it can be used as a lecture experiment, and a strong solution of chlorine in water in the full blaze of the sun in the hot season in Calcutta, is actually seen to effervesce very decidedly. It is also stated in connection with this

decomposition that "the rate of the decomposition of the water (by the chlorine) is influenced by the quantity of hydrogen chloride which has previously been formed, and the presence of this substance is said to greatly retard the action, according to a complicated law" (Roscoe and Schorlemmer, "Treatise of Chemistry," **1**, 124).

Berthelot (*Ann. Chim. Phys.* [5], **22**, 459) has, however, shown that the solubility of chlorine in water varies for the same temperature with the time of contact and the intensity of light, the variations being due to a slow decomposition of water with the formation of oxy-acids of chlorine, thus indicating that the equation given above, in some cases, at all events, is not strictly true.

Popper (*Annalen*, **227**, 161; also Abstr., 1883, **48**, 631) has subsequently made experiments proving that chlorine-water, on exposure to sunlight, is probably converted into hydrogen chloride and chloric acid, whilst oxygen is given off; perchloric acid is not formed, and the question as to the formation of hypochlorous acid was left unsettled. In a subsequent paper, the same author (*Annalen*, **231**, 137; also Abstr., 1886, **50**, 301), describing his further work on the subject, gives the following equation as representing the decomposition of chlorine-water by sunlight:—

In the course of a long series of experiments made on the action of light on various substances and on different chemical reactions, certain facts have been discovered which prove that neither of the statements made above really represents the whole facts of the case, and that neither equation is wholly right, or wholly wrong.

The action, indeed, of chlorine on water, in the first place, requires certain conditions before it will take place at all; and secondly, it has been found that more than one action is possible when the conditions of exposure of light vary.

In the first experiments which will be described, the following was the plan of procedure. Pure moist chlorine was passed through glass tubes of known capacity, provided either with stopcocks at each end, or which could be easily hermetically sealed, until all the air was swept out; when this was effected, definite volumes of distilled water were run into the tubes, displacing the corresponding volume of chlorine, and the tubes were then sealed or the stopcocks closed, and the tubes exposed to the direct rays of the sun for certain periods. At the conclusion of the exposure, the tubes were opened, first under water, and any water which entered was measured, so as to note the contraction; next, the amount of any free chlorine left was estimated; and third, the volume of the oxygen produced was measured. It will be noticed that in the first equation given above, for every ten volumes

of chlorine which act on the water, five volumes of oxygen should appear, and by Popper's equation ten volumes of chlorine would only yield two volumes of oxygen.

Experiment 1.—83.5 c.c. of chlorine were taken with 4 c.c. of water in a tube. As for both the equations, 1 mol. of chlorine requires 1 mol. of water, the quantities here used represent roughly 64 mols. of water to 1 mol. of chlorine. The tube was exposed for a month to strong diffused daylight, and for another month to the direct action of tropical sunlight in Calcutta, where all these experiments were made. The tube throughout remained strongly coloured, from the presence of free chlorine, and no change whatever in the intensity of the colour could be detected. On opening, it was found that no appreciable change had taken place; there was no diminution in volume of the gases in the tube, and it was still practically filled with chlorine.

Experiment 2.—A sealed tube, containing 47.5 c.c. of chlorine and 3 c.c. of water, giving roughly 88 mols. of water for 1 mol. of chlorine, was exposed to direct sunlight from January 29th, 1890, to February 11th, 1890. During the experiment the amount of sunshine was estimated by a Jordan's sunshine recorder, and there were 132 hours of bright sunshine out of a possible amount of 156.3 hours during this period. No perceptible diminution in the intensity of the colour of the chlorine could be detected throughout the exposure. On opening, 33.5 c.c. of chlorine out of the original 47.5 c.c. of chlorine were found to be unacted on, or that only 14.0 c.c., or 29 per cent. of the original amount of the chlorine, had acted on the water, while only 6.5 c.c. of oxygen had been formed, theory, according to the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$, requiring 7 c.c. of oxygen to be produced. So there must clearly have been a *very small* portion of the chlorine undergoing another reaction, possibly that suggested by Popper, that is, $5\text{H}_2\text{O} + 5\text{Cl}_2 = \text{HClO}_3 + 9\text{HCl} + \text{O}_2$, or some reaction similar to this.

Experiment 3.—51 c.c. of chlorine and 5 c.c. of water were exposed in a sealed tube to direct tropical sunlight for 14 days, during which there were, by the sunshine recorder, 137.1 hours of bright sunshine out of the possible amount of 165.3 hours. The above quantities represent a little more than 130 mols. of water to 1 mol. of chlorine. A slight diminution in the intensity of the colour of the chlorine could be detected during the experiment, but even after the 14 days, the colour of the chlorine was very strongly marked. On opening the tube, 27.6 c.c. of chlorine were still unacted on, and 11 c.c. of oxygen had been formed; 23.4 c.c. of chlorine, or about 46 per cent. of the original volume, had thus acted on the water, but instead of 11.7 c.c. of oxygen being produced, as is required by the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = \text{O}_2 + 4\text{HCl}$, only 11 c.c. were produced. Again,

therefore, a *very small* amount of the oxygen had disappeared in the formation of one of the oxidised acids of chlorine.

Experiment 4.—79·5 c.c. of chlorine and 8 c.c. of water, representing roughly about 1 mol. of chlorine to nearly 140 mols. of water, were exposed to tropical sunlight from January 20th, 1890, to February 3rd, 1890, during which period there were 137·1 hours of bright sunshine out of the possible amount of 165·3 hours. Again, during the exposure the intensity of the colour of the chlorine scarcely changed, and at the close the tube had still a deep colour. On opening, 56·4 c.c. of free chlorine were found to be present, and there were only 6·2 c.c. of oxygen formed. Thus in this case only 23·1 c.c. of chlorine, or 29 per cent. of the gas originally present, had acted on the water, and instead of the formation of 11·5 c.c. of oxygen required by the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$, only 6·2 c.c. of oxygen were formed. There had in this case, therefore, been considerable combination of the oxygen to form an oxidised acid of chlorine.

Experiment 5.—37 c.c. of chlorine, and 10 c.c. of water, representing about 1 mol. of chlorine to 412 mols. of water, were exposed to tropical sunlight for 14 days, during which there were 137·1 hours of bright sunshine, as indicated by the sunshine recorder, out of the possible amount of 165·3 hours. Even after two days, there was a perceptible diminution in the intensity of the colour of the chlorine, showing that action was taking place, but the diminution of colour subsequently continued extremely slowly (if at all), and even after the 14 days, there was a distinct amount of free chlorine in the tube, as indicated by the colour. On opening it, 8·5 c.c. of free chlorine only were found, and there were 10 c.c. of oxygen formed. Thus, 28·5 c.c. of chlorine, or about 78 per cent. of the total amount used, had acted on the water, and instead of the 14·25 c.c. of oxygen which should have been formed according to the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$, only 10 c.c. of oxygen were formed, proving, again, that a certain amount of the oxygen had been utilised in forming one of the oxidised acids of chlorine.

The principal facts detailed in the above five experiments are summarised in the table (p. 617).

The general result of these experiments, therefore, is to show that chlorine and water, when placed in very strong tropical sunlight, have comparatively little action on each other, even when the number of molecules of water is as much as a hundred times as great as that required by theory; the action is larger, ranging up to, perhaps, nearly 50 per cent. of the possible amount, when the number of molecules of water is about 150 for every molecule of chlorine. When the number of molecules of water is more than 400 for every single molecule of

No. of Expt.	Vol. of Cl taken.	Vol. of H ₂ O used.	No. of molecules of H ₂ O for every 1 molecule of Cl.	Period of exposure to sunlight.	Percentage of Cl which had acted on the H ₂ O.	Vol. of O liberated for every 2 vols. of Cl which had disappeared.
1	83·4 c.c.	4 c.c.	64	2 months	No perceptible action	
2	47·5 „	3 „	88	132 hours*	29	0·93
3	51·0 „	5 „	130	137·1 „	46	0·94
4	79·5 „	8 „	140	137·1 „	29	0·54
5	37·0 „	10 „	412	137·1 „	78	0·70

chlorine, the reaction becomes much more rapid, but even then reaction only proceeds to the extent of about four-fifths of the possible amount.

Further, it would appear that with the smaller ratios of water and chlorine, the reaction becomes nearly that required by the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$, but that as the amount of water is increased, a certain amount of oxidised chlorine acids is formed, and that in addition to the simple action usually represented to occur, other actions represented by some such equation as that suggested by Popper ($5\text{H}_2\text{O} + 5\text{Cl}_2 = 9\text{HCl} + \text{HClO}_3 + \text{O}_2$) may take place.

In the case of ordinary chlorine water, supposing the water to be saturated, say, at 30° to 32° , which is about the average working temperature in a laboratory at Calcutta, the weight of chlorine in 100 c.c. of water would be about 0·5566 gram. In other words, the ratio of chlorine to water in such a sample would be 1 mol. of chlorine to about 708 mols. of water, and hence the results of the above experiments would show that with ordinary chlorine water the decomposition may be expected to be both more rapid and more complete than in the above cases, and that also the reaction may perhaps yield oxidised chlorine acids, and hence the quantity of oxygen evolved in the reaction will be comparatively small.

A very large series of experiments on the action of light on chlorine water has been made, and in these experiments three degrees of intensity of light were used. In some experiments the direct rays of the tropical sun in the hottest season of the Indian year were allowed to fall on the chlorine-water; in others, the experiments were carried on in very strong diffused daylight, by putting the apparatus in an open verandah facing the south, but so that the direct rays of the sun could not reach the apparatus; and, third, the experiments were made opposite the window, in a room with a north light only, so that only

* Actual hours of full tropical sunlight as indicated by sunshine recorder.

Chlorine Water Exposed to full Tropical Sunlight.

No. of Expt.	Before exposure.	Period of exposure to sunlight.	After exposure to light.				Remarks.
	Amount of free chlorine in 10 c.c. chlorine-water.		Whether oxygen evolved.	Total amount of free acid found, calculated to equivalent weight of chlorine.	Amount of hydrochloric acid.	Amount of chlorine as determined by reduction with Zn-Cu couple, &c.	
1	gram 0·0305	10 days	large quantity	gram 0·0300	gram 0·0313	trace only	Solution colourless, no smell, no bleaching power in cold, but faint bleaching action when boiled with strong hydrochloric acid.
2	0·0296	several days	do.	0·0288	0·0301	"	Do.
3	0·0304	do.	do.	0·0292	0·0296	"	No bleaching action in cold, faint bleaching action on boiling with strong acids.
4	0·0299	do.	do.	0·0295	0·0284	—	Solution had distinct odour of hypochlorous acid, and very feeble bleaching action in cold.
5	0·0296	do.	do.	0·0288	0·0294	trace only	Solution colourless, no odour of chlorine or hypochlorous acid, no bleaching action in cold, but feeble bleaching action when heated with strong acid.
6	0·0372	17 days*	do.	0·0356	0·0348	0·0024 gram	Solution colourless, no odour, no bleaching action in cold, slight bleaching action on heating with acid.
7	0·0372	18 days†	do.	0·0338	0·0341	0·0031 "	Solution quite colourless, no free chlorine, but exceedingly faint smell of hypochlorous acid, no practical bleaching action in cold, but distinct bleaching action on heating with acid.

* In the 17 days (in May, 1889) there were 148·5 hours of bright sunshine (by the sunshine recorder) out of a possible 236·8 hours.

† " 18 " " 157·0 " " " " " 250·1 "

Chlorine Water in Strong Diffused Daylight.

No. of Expt.	Before exposure.		Period of exposure to diffused daylight.	Whether oxygen evolved or not.	After exposure.				Remarks.
	Amount of free chlorine in 10 c.c. of solution.				Total amount of free acid found, calculated to equivalent weight of chlorine.	Amount of chlorine as hydrogen chloride.	Amount of chlorine as hypochlorous acid.	Amount of chlorine as chloric acid (by reduction with Zn-Cu couple, &c.).	
1	gram 0·0358		25 days	moderate amounts	gram 0·0320	gram 0·0320	none	gram 0·0038	Solution colourless, no odour, no bleaching action in cold, but slight bleaching action on boiling with hydrochloric acid.
2	0·0369		23 days	do.	0·0355	0·0337	none detected	0·0032	Solution colourless, faint odour, very slight bleaching power in cold, no chlorous acid.
3	0·0149		14 days	exceedingly small amounts	0·0146	0·0149 gram		none detected	Solution entirely colourless, no free chlorine detected, solution made alkaline bleached rapidly, no chlorous acid.
4	0·0139		14 days	scarcely any	0·0128	0·0135	"	0·0004 (traces only)	Solution colourless, smell of hypochlorous acid, gave strong reaction for hypochlorous acid by forming soluble salt with mercury,* no chlorous acid present, no hydroxyl present.

* This reaction is used by Wolters (*J. pr. Chem.*, 7, 468) in detecting hypochlorous acid in presence of chlorine and other chlorine acids, and he has shown that the reaction can also be used for the quantitative estimation of hypochlorous acid.

feeble diffused daylight could act on the solutions. The usual method of experimenting was to place the chlorine water of known composition in flasks holding half a litre and upwards, almost filled with the liquid, and provided with tightly fitting corks and delivery tubes, the latter being placed under graduated tubes filled with water, and standing in pneumatic troughs. After exposure, the gas evolved was measured, and the contents of the flasks analysed. In the first set of experiments the effect of full tropical sunlight on chlorine water was determined, and the results are given in the table (p. 618).

In all these cases the volumes of oxygen evolved were determined, but in each experiment the gas collected fell considerably short of the theoretical amount. In the first place as shown above, small amounts of chloric acid were produced which would account for a diminution in the oxygen, and secondly, the oxygen evolved would probably first thoroughly saturate the liquid with the gas, and it was noticed in each case that on agitation of the liquid at the end of each experiment considerable effervescence took place. Thus the amounts of oxygen collected could not be used to indicate definitely the reaction which was going on.

The general result of the experiments with chlorine water exposed to direct tropical sunlight may, therefore, be said to be in favour of the simple equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$ as representing practically the reaction, for the amount of chloric acid formed in each case was exceedingly small.

Next, the influence of strong diffused daylight as obtained in an open south verandah was tried on chlorine water, the experiments being so arranged that no direct rays of the sun could fall on the apparatus, while it could receive the strongest diffused light possible. The general results of these experiments are contained in the table (p. 619).

In order to further prove the existence of the hypochlorous acid in the last two cases, some of the solutions were divided into equal volumes, and one half neutralised with potassic hydrate, then mixed with the second half, and carefully distilled. In the distillate, considerable amounts of hypochlorous acid could be detected by the usual methods.*

It will be noticed in the case of these experiments in diffused daylight, that there were slight variations of the results, and that either hypochlorous acid or chloric acid, or both, were produced. The only variations in the circumstances of the experiments which could

* It may be desirable here to remark that considerable discussion has taken place between Göpner and Hugo Schiff as to the constitution of the so-called chlorine hydrate ($\text{Cl}_2 \cdot 10\text{H}_2\text{O}$), the former considering this compound to be HOCl , HCl , $9\text{H}_2\text{O}$, while the latter disputes this explanation of its constitution.

cause these differences were the possible variation in the intensity of the diffused light causing the reaction and the duration of the exposure. To test whether this was the cause of the variation in the results, some experiments were made inside a room, the apparatus being placed opposite a window with a north light, when only very moderate, diffused light could reach the chlorine water.

Experiment 1.—A sample of chlorine water, of which 10 c.c. contained 0.0195 gram of chlorine, was exposed to the action of the light from a north window for 37 days, and during the action, not a single bubble of oxygen gas escaped from the apparatus. At the end of the time, the liquid had a very faint yellow colour only, and had a smell of hypochlorous acid. With mercury, it gave a very decided reaction for the presence of hypochlorous acid, and the amount of this acid, as determined by this reaction, was 0.0089 gram in 10 c.c. The amount of chlorine in the hypochlorous acid as indicated by the liberation of iodine equalled 0.0077 gram.

Experiment 2.—In another experiment, chlorine water again yielded no gas after exposure for 38 days to the light from a north window, after which period the solution had become colourless, and it smelt strongly of hypochlorous acid. This acid was also proved to be present in considerable quantity by the reaction with mercury, &c. Chloric acid was also shown to be present in small amount in the exposed liquid.

Experiment 3.—In another experiment, an amount of chlorine water which, according to the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$, should have yielded about 74 c.c. of oxygen was exposed for 46 days in diffused daylight opposite the north window in a room, when only 5 c.c. of oxygen were evolved. The liquid became almost colourless, and was found to contain moderate amounts of hypochlorous and chloric acids, but no chlorous acid or hydrogen dioxide.

The most probable explanation of the general result of the above experiments on the action of strong and also more feeble diffused light appears to be that the first action of chlorine on water is to form hypochlorous acid and hydrochloric acid, according to the equation $\text{H}_2\text{O} + \text{Cl}_2 = \text{HCl} + \text{HClO}$, and that by the continued action of light, the hypochlorous acid itself changes into chloric acid.

That this is the most probable reaction is supported by such experiments as these. Chlorine water which contained 0.0355 gram of chlorine in 10 c.c., after standing for about 24 to 36 hours in rather feeble light, when tested by the usual mercury process of estimating hypochlorous acid, yielded in the same volume 0.0116 gram of this acid. After exposure to strong diffused daylight for 5 days, the amount was reduced to 0.0013 gram in 10 c.c. After 10 days' exposure, the acid could still be detected by the mercury process, but

the amount was very small, and after 32 days no hypochlorous acid could be detected, and the liquid had practically ceased to bleach in the cold. At the conclusion, by the zinc-copper couple process, the amount of chlorine as chloric acid in 10 c.c. of this liquid was found to equal 0.0030 gram, or to about a tenth of the original weight of the chlorine in the chlorine water.

The problem can also be approached by the study of the properties of dilute solutions of hypochlorous acid. The usual statement as to this acid is, that only dilute solutions are stable, and that concentrated solutions are readily decomposed by exposure to sunlight, partly yielding chlorine and oxygen, while another part undergoes oxidation, yielding chloric acid. In all the cases dealt with in the previous experiments, very dilute solutions of hypochlorous acid would be present. It was therefore thought desirable to make some experiments on the action of diffused light on dilute hypochlorous acid, and the following are some of the results.

Experiment 1.—A sample of hypochlorous acid was obtained by the action of chlorine on mercuric oxide suspended in water. It was then allowed to stand over mercuric oxide and distilled; no free chlorine was given off during the distillation. The liquid was very feebly acid, and a few drops of potassic hydrate solution made it alkaline, but the alkaline solution as well as the original solution bleached vigorously. Both by the mercury test ($2\text{Hg} + 2\text{HClO} = \text{HgCl}_2 + \text{HgO} + \text{H}_2\text{O}$), and as judged by the action with potassic iodide and titration of the iodine by sodic thiosulphate, 10 c.c. of distilled liquid contained an amount of chlorine in the acid equal to 0.0316 gram of chlorine. 10 c.c. of liquid were also reduced by the zinc-copper couple, and found to contain hypochlorous acid equivalent to 0.0306 gram of chlorine. Exposed to the action of strong diffused daylight, after 10 days, 60 c.c. yielded 9 c.c. of gas, and on continuing the exposure for 10 to 11 days, a total of 18 c.c. of oxygen was evolved, when by the mercury test no free hypochlorous acid could be detected. The liquid still bleached slowly, but not so vigorously as before. 10 c.c. when tested with standard potassic hydrate solution contained as much free acid as was equivalent to 0.0302 gram of chlorine, but when tested with standard silver nitrate solution, it yielded chloride corresponding with 0.0224 gram of chlorine only. 10 c.c. treated with the zinc-copper couple, and then the total chlorine as chloride estimated, contained 0.0292 gram of chlorine. These last two numbers are nearly in the ratio 3 : 4, for in that case the weights would be 0.0219 (instead of 0.0224) to 0.0292. Thus it is clear that about three-fourths of the acid present was in the form of hydrogen chloride, and one-fourth as an oxidised chlorine acid (that is chloric acid), and the slow bleaching action of the solution can be

accounted for by the presence of chloric acid. Now, it can be calculated that 60 c.c. of the acid of this strength would contain roughly about 60 c.c. of oxygen in the hypochlorous acid, but only 18 c.c. were evolved, which is a little more than a fourth of the total amount. By the action of concentrated hydrochloric acid and potassic iodide, distinct amounts of iodine were liberated, indicating again the existence of chloric acid in solution. The equation for the decomposition of hypochlorous acid which will therefore be most nearly in accordance with the above numbers is $4\text{HClO} = \text{HClO}_3 + 3\text{HCl} + \text{O}$. It is quite possible that the reaction representing the decomposition of hypochlorous acid by the action of strong diffused light is not very sharply defined, but for working purposes it may be taken that solutions of hypochlorous acid of the strength above indicated, when thus exposed, undergo the above decomposition. That this reaction partly depends on the strength of the acid which is being decomposed, is shown by the following experiment:—A dilute solution of distilled hypochlorous acid containing in 10 c.c. of solution 0.0293 gram of chlorine as hypochlorous acid, as judged both by reduction with the zinc-copper couple, and by the liberation of iodine from potassic iodide, that is, of practically the same strength as used in the previous experiment, was diluted with distilled water, 50 c.c. of the acid being taken to 30 c.c. of water, and the diluted acid exposed to strong tropical sunshine for seven days. Only a small amount of oxygen gas was evolved during the decomposition. At the end of seven days the solution had almost entirely lost its power of bleaching, and no trace of hypochlorous acid could be detected by the mercury reaction. A volume representing 10 c.c. of the original hypochlorous acid, after this exposure, required an amount of standard alkali solution equivalent to 0.0292 gram of chlorine, but by standard silver nitrate solution, the amount of chlorine present as chloride was found to be 0.0234 gram. The same volume of solution reduced by the zinc-copper couple, and tested with standard silver nitrate solution then contained 0.0289 gram of total chlorine as chloride, indicating also that there had been chloric acid present in this case. These figures stand nearly in the ratio of 4 to 5, and would indicate a probable decomposition according to the equation $5\text{HClO} = 4\text{HCl} + \text{HClO}_3 + \text{O}_2$. Further, the intensity of the light appears to exert a distinct influence on the character of the decomposition, for two samples of the same solution of hypochlorous acid were decomposed by the action of light, and while in one case 100 c.c. of the liquid exposed to the full blaze of tropical sunshine gave off 50.6 c.c. of oxygen, 100 c.c. of the same solution exposed merely to strong diffused daylight gave off only 20.0 c.c. of oxygen.

It might perhaps be imagined that even chloric acid itself would

not be stable in the conditions worked under in these experiments, for it is stated that concentrated solution of chloric acid forms perchloric acid on being exposed to light. To test whether this was the case or not, some solutions of chloric acid of definite strengths were prepared and exposed to the action of strong tropical sunlight. Solutions of chloric acid containing a fifth of a mol. in grams, a tenth of a mol., a twentieth of a mol., and a thirtieth of a mol. in a litre of water, were prepared and placed in flasks, so that the solutions nearly filled them, the flasks being provided as usual with delivery tubes. They were then exposed to the action of sunlight. In no case was any oxygen evolved, proving that if any decomposition was occurring, it must be the entire conversion of the chloric into perchloric acid by such a reaction as $4\text{HClO}_3 = 3\text{HClO}_4 + \text{HCl}$. To estimate if any change of this kind had gone on, the amount of chlorine as chloride was determined in the solutions at different periods of the exposure. At first, all the solutions were entirely free from chloride, but after two days' exposure, that is, to about 16 hours' full sunshine, the N/5 and N/10 solutions showed distinct turbidity with silver nitrate solution, but N/20 and N/30 solutions showed little or no change. After six days' exposure, during which there were 48·4 hours of bright sunshine out of a possible duration of 68·4 hours, there was in all cases slight evidence of change, but it was found that less than a fiftieth of the chloric acid had been changed to hydrochloric acid. After 15 days' exposure, during which there were 134·2 hours of bright sunshine out of the possible amount of 184 hours, in the various solutions the proportions of chloride to the original chlorate were as follows:—

In the N/5 solution, 3·2 atoms of chlorine as chloride to 100 atoms of chlorine as chlorate.

In the N/10 solution, 2·1 atoms of chlorine as chloride to 100 atoms of chlorine as chlorate.

In the N/20 solution, 3·1 atoms of chlorine as chloride to 100 atoms of chlorine as chlorate.

In the N/30 solution, 2·3 atoms of chlorine as chloride to 100 atoms of chlorine as chlorate.

The decomposition of chloric acid in dilute solutions under the influence of sunlight is, therefore, so small that its change in the previous experiments with chlorine water may be practically neglected, and it may be considered that the change in the experiments made with chlorine water by the action of light ends with the production of chloric acid.

The results of the above experiments may be thus briefly summarised:—Chlorine has very little action on water, even in the direct

rays of a tropical sun, unless the water is in relatively enormous excess, the amount of water required being about 400 times as large as that indicated by theory, before even moderate action takes place. The main reaction which takes place between a large excess of water and small amounts of chlorine in the full blaze of an Indian sun in the hot season of the year is that expressed by the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$. On the other hand, in feeble diffused light, the first action which takes place between water and chlorine may be expressed by the equation $\text{H}_2\text{O} + \text{Cl}_2 = \text{HCl} + \text{HClO}$, but the hypochlorous acid formed is, in its turn, decomposed by light with the formation of chloric acid, so that in diffused light or in light less brilliant than tropical sunshine, the final reactions become such as put forward by Popper, or such as—

and

or, combining the two,

It will be therefore seen that, in the first stages at all events, the action of chlorine on water is quite similar to the action of chlorine on dilute and cold solutions of sodic hydrate or potassic hydrate, and also that the second reaction between chlorine and water is very similar to the action of chlorine on more concentrated and hot solutions of the two hydrates.