XLII.—*Distillation of Chlorine Water.*

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THE composition of chlorine water and its hydrate has from time to time occupied the attention of chemists ever since the discovery of hypochlorous acid by Ballard in 1833. Following on this discovery, we find the statement, "apparently due to Schönbein in the first instance, that the chlorine in chlorine hydrate is present as hypochlorous and hydrochloric acids, and that its composition is represented by the formula $\text{HCl}, \text{HClO}, 9\text{H}_2\text{O}$. It does not appear, however, that this statement was based on any direct experimental evidence, although indirectly it received some support from an observation of Millon made in 1849, who found that a mixture of the two acids was stable in very dilute solutions at the ordinary temperature. The abnormal solubility of chlorine in water observed by Roscoe (this *Journal*, 1856, **8**, 15) at temperatures near that at which the hydrate is formed led him to suspect the formation of the oxy- and hydr-acids of chlorine in the solution. To determine whether they were present or not, he passed a stream of carbon dioxide through chlorine water, and led the escaping gas into a large volume of pure water, for since the oxy-acids are volatile it was to be expected that, if present, they would distil more or less completely from the first solution into the second, leaving excess of the less volatile hydrochloric acid behind. Analysis showed, however, that no such separation had taken place, but that the whole of the chlorine removed by the inert gas was present in the free state. Roscoe

therefore concluded that the oxy- and hydr-acids were absent from chlorine water. Copner (*Ber.*, 1875, 8, 287), commenting on the absence of confirmation for Schönbein's statement, assumed that the presence of hypochlorous and hydrochloric acids in chlorine hydrate was proved by the fact that mercuric chloride was formed on treating the hydrate with mercury (Waltner's reaction). Schiff (*Ber.*, 1875, 8, 419), on the other hand, showed that the same result was obtained when free chlorine was treated with the metal, this test failing to prove the presence of the two acids in the hydrate. Jakowkin (*Ber.*, 1897, 30, 515; *Zeit. physikal. Chem.*, 1899, 29, 613), from a study of the electrical conductivity of chlorine water, was led to the conclusion that very dilute solutions undergo dissociation into hydrochloric and hypochlorous acids, $\text{Cl}_2, \text{aq} \rightleftharpoons (\text{HCl} + \text{HClO}) \text{aq}$. He found the conductivity at 0° to be equal to that of hydrochloric acid containing the same amount of hydrogen chloride, and concluded that the oxy-acid is a non-electrolyte; the conductivity of the solution was much diminished with increased concentration. The recent photochemical researches of Mellor (*Trans.*, 1901, 79, 216; 1902, 81, 1280; Mellor and Anderson, *ibid.*, 1902, 81, 414; and Mellor and Russell, *ibid.*, 1902, 81, 1272), serve to emphasise the fact that chlorine gas, whether alone or in presence of hydrogen, is sensitive to light only when water is present; indeed, the new facts recorded and the exhaustive bibliography contained in these papers, whilst forming a valuable contribution to our knowledge of the subject, show also the need of further information regarding the composition of chlorine water, whether in the liquid or "gaseous" state, in order that the more complicated reactions brought about by light may be satisfactorily explained.

Closely connected with the present work is the observation, made many years ago by Pickering (*Trans.*, 1880, 37, 139), that when chlorine water was heated in an evaporating basin, an aqueous solution of hydrochloric acid remained after all the active chlorine had been expelled. This result, since confirmed by my own experiments, led me to inquire whether the formation of hydrochloric acid in the residue was accompanied by the separation of hypochlorous or other volatile oxy-acid, or whether the active chlorine escapes only in the free state. To test this, advantage was taken of the fact that when even very dilute aqueous solutions of hypochlorous acid are distilled, the oxy-acid, together with water, passes over below 100° . It seems probable, therefore, that by slowly distilling chlorine water, any oxy-acid present would be found together with free chlorine in the distillate.

Separation of Free Chlorine from Hypochlorous Acid.—Before approaching this problem, it was first necessary to devise some simple means of separating free chlorine from hypochlorous acid, since the

tests for the oxy-acid in the presence of free halogen are far from satisfactory. The difference between the vapour pressures of the two solutions affords a ready means of doing this: thus on passing an air current through chlorine water the free chlorine is rapidly removed, whilst a similar aspiration has but little effect on the strength of dilute solutions of the oxy-acid. This is seen to be the case from the following results obtained on estimating the active chlorine in samples of freshly prepared chlorine water, and of dilute solutions of hypochlorous acid, in each case before and after aspiration with a current of air saturated with moisture for 4 hours.

TABLE I.

No.	Solution.	Before aspiration.	After aspiration.
1	100 c.c. chlorine water	Active chlorine = 44 c.c. $N/10$ $Na_2S_2O_3$	Active chlorine = trace
2	100 c.c. hypochlorous acid	Active chlorine = 20 c.c. $N/10$ $Na_2S_2O_3$	Active chlorine = 20 c.c. $N/10$ $Na_2S_2O_3$
3	100 c.c. hypochlorous acid	Active chlorine = 92 c.c. $N/10$ $Na_2S_2O_3$	Active chlorine = 90 c.c. $N/10$ $Na_2S_2O_3$
4	<div> 50 c.c. chlorine water* } 50 c.c. hypochlorous acid } </div>	<div> Active chlorine = 22 c.c. $N/10$ $Na_2S_2O_3$ } Active chlorine = 45 c.c. $N/10$ $Na_2S_2O_3$ } </div>	Active chlorine = 44 c.c. $N/10$ $Na_2S_2O_3$

Such a process would obviously not apply to strong solutions where the vapour pressure of the acid is considerable; in the present work, however, we are concerned only with solutions of the same order of strength as those just indicated. This method was therefore applied to the separation of free chlorine from the products of distillation of chlorine water in the experiments now to be described.

Chlorine water was first prepared with chlorine generated by the action of hydrochloric acid on potassium dichromate, the gas being passed through water, then through a solution of chromic acid contained in a tube 1 metre long placed in an oblique position, and finally through water in a washing bulb, the exit tube of which was sealed to a delivery tube dipping into the water to be saturated with the gas.

* Here it is seen that the free chlorine in chlorine water is completely removed by aspiration, whereas the strength of solutions of hypochlorous acid is only little altered by the process, whilst in a mixture of the free halogen and oxy-acid the former only is withdrawn by the air.

Distillation of Chlorine Water.

Experiment I.—When 500 c.c. of water, saturated with chlorine at the ordinary temperature and pressure, were gently heated in a retort, drops of distillate soon began to pass over together with free chlorine. In 2 hours, 48 c.c. were collected, although the contents of the retort had at no time been allowed to boil. After the lamp was removed, an additional 10 c.c. of liquor distilled over from the hot solution. In the first place, the excess of free chlorine was removed from the 58 c.c. of distillate collected by aspiration with a current of air. After 2 hours, the smell of chlorine had entirely disappeared, but the solution was still rich in active chlorine, for it liberated iodine freely from potassium iodide, immediately bleached indigo solution, and on shaking with mercury gave a brownish-yellow deposit resembling that obtained with hypochlorous acid, and in this respect differing entirely from the slaty-grey precipitate formed when ordinary chlorine water was treated with the metal.

The residual solution in the retort still smelt of free chlorine, and 100 c.c. were subjected to aspiration. After 2 hours, the solution failed to liberate a trace of iodine from potassium iodide, and reddened but did not bleach litmus; it gave a white precipitate of silver chloride with silver nitrate, thus proving the presence of hydrochloric acid.

In this experiment, the preparation and distillation of chlorine water was conducted in the diffused light of an Indian summer day; it seemed possible, therefore, that the results here obtained might be due to photo-chemical action, since Peddler (*Trans.*, 1890, 57, 613) has shown that the oxy-acids of chlorine are formed by the action of diffused light on chlorine water.

Experiment II.—Fresh chlorine water was therefore prepared and distilled in a dark room. In this, as in the former experiment, the distillate, after removal of free chlorine, bleached indigo, freely liberated iodine from potassium iodide, and gave the characteristic yellow precipitate with mercury. The residual solution contained hydrochloric acid, this result proving that the changes observed in the first experiment are not due to the action of light; to avoid complications, however, all the subsequent experiments were made in a dark room.

Experiment III.—The last experiment was next repeated with washed chlorine, further purified by conversion into the hydrate at 0°, the gas evolved from the melting crystals having been led into redistilled water. Distillation of the chlorine water so prepared gave a distillate similar in all respects to that obtained in the previous experiments; the residual solution contained hydrochloric acid, thus showing that further purification of the chlorine does not

influence the result obtained. From these qualitative experiments it is seen that, when chlorine water is heated, a mixture of free chlorine and an oxy-acid passes off, leaving hydrochloric acid in the solution.

In order to study this reaction, it was first necessary to further characterise the oxy-acid. For this purpose, the total chlorine and also the active form of this element were estimated in the distillate after removing the free chlorine by aspiration. Now it is obvious that a comparison of the values so obtained will serve as an indication of the condition of the active chlorine present; thus, if it is in the free state, the values found by the iodometric method will agree with those obtained for the total chlorine estimated as silver chloride after treatment with sulphurous acid:

If, on the other hand, the halogen is present as an oxy-acid, this agreement will no longer hold; thus in the case of hypochlorous acid the active chlorine will be represented by a value double that found for the total chlorine:

Analytical Method.—The active chlorine was estimated iodometrically with *N*/10 sodium thiosulphate after addition of potassium iodide and hydrochloric acid. The volumetric estimation of the total chlorine is, however, complicated by the excess of sulphurous acid, added in the first instance, which is precipitated as silver sulphite in neutral solutions. Roscoe (*loc. cit.*) overcame this difficulty by estimating the chloride gravimetrically in the solution acidified with nitric acid. The large number of estimations demanded by the present work, however, called for some simple means of removing the excess of sulphur dioxide in order that the chloride might be estimated volumetrically. In order to do this, the original solution containing excess of sulphurous acid was largely diluted, and then heated in an evaporating basin at a temperature just below the boiling point; by this means, the sulphur dioxide was rapidly expelled, so that on adding potassium chromate no trace of green chromic chloride was formed; the cold solution was then neutralised with sodium hydrogen carbonate and the titration with silver nitrate carried out in the usual way.

The accuracy of the method, on which the later results entirely depend, is seen on comparing the values obtained for the active and total chlorine found in dilute chlorine water, as estimated by *N*/10 thiosulphate and silver nitrate respectively, as follows:

TABLE II.

Sample.	Active chlorine.	Total chlorine.
No. 1 {	10 c.c. = 3.65 c.c. $N/10$ $Na_2S_2O_3$ 20 c.c. = 7.20 ,, ,,	10 c.c. = 3.7 c.c. $N/10$ $AgNO_3$ 20 c.c. = 7.25 ,, ,,
No. 2 {	10 c.c. = 4.60 ,, ,, 20 c.c. = 9.25 ,, ,,	10 c.c. = 4.60 ,, ,, 20 c.c. = 9.30 ,, ,,
No. 3 {	10 c.c. = 11.60 ,, ,, 10 c.c. = 11.50 ,, ,,	10 c.c. = 11.5 ,, ,, ,, ,, ,, ,,

Having decided these preliminary points, the active and total chlorine in the products of distillation of chlorine water were therefore estimated in this way.

Analytical Results.—Freshly prepared chlorine water (1000 c.c.), when distilled for 6 hours at a temperature just below the boiling point, yielded 77 c.c. of distillate. After 2 hours' aspiration, the active and total chlorine in one portion of the distillate was estimated with the following result, calculated for the total distillate: active chlorine = 26.1 c.c. $N/10$ $Na_2S_2O_3$; total chlorine = 14 c.c. $N/10$ $AgNO_3$.

Here the proportion of active to total chlorine found is not far removed from the ratio 2:1. The remainder of the distillate was again aspirated for 4 hours to remove any free chlorine still present. Analysis then gave: active chlorine = 22.3 c.c. $N/10$ $Na_2S_2O_3$; total chlorine = 11.0 c.c. $N/10$ $AgNO_3$.

The active chlorine is here represented by a value almost exactly double that found for the total chlorine, showing that it is present as hypochlorous acid.

Analysis of the residual solution in the retort, after aspiration for 2 hours in the cold, gave for the total residue: active chlorine, absent; total chlorine = 29.3 c.c. $N/10$ $AgNO_3$.

This value, which is seen to be largely in excess of the total chlorine found in the distillate, shows that under the conditions of the experiment the reacting chloride is not equally divided between the two acids. It seemed probable, however, that this result might be due to the gradual decomposition of part of the hypochlorous acid, under the prolonged action of heat, which was inevitable during distillation for 6 hours at temperatures below the boiling point; the process was therefore modified to overcome this difficulty.

Chlorine water was now distilled at the boiling point in a stream of

chlorine gas, the solution being heated in a distilling flask, through which a stream of chlorine was passed by means of an inlet tube ground into the neck of the flask, and sealed to the water bulb connected with the washing apparatus of the chlorine generators. The side tube was sealed to the inner tube of a Liebig's condenser, the distillate being collected in the small open distilling flask from which excess of free chlorine was removed by means of a side tube attached to an aspirator. After 400 c.c. of chlorine water had been rapidly distilled in a current of the gas until 195 c.c. of distillate had passed over, the free chlorine was removed from the distillate and residue by aspiration for 4 hours, and the two solutions were analysed:

Total distillate (195 c.c.).	Total residue (205 c.c.)
Active chlorine = 48.7 c.c. $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$	Active chlorine absent.
Total ,, = 25.9 ,, AgNO_3	Total chlorine = 25.6 c.c. $N/10$ AgNO_3

This experiment indicates that at the boiling point, as at lower temperatures, hypochlorous acid passes over when chlorine water is distilled, and that the values obtained for the total chlorine in the distillate and residue are now in close agreement, showing that the reacting chlorine is equally divided between the two acids. Under these conditions, therefore, the change is represented by the equation:

Even under these more favourable conditions, the proportion of hydrochloric acid tends to increase with slow distillation and prolonged digestion. Thus, in one case, in which 50 c.c. only were allowed to distil over in 8 hours, the total chlorine in the residue reached a value double that found in the distillate.

This led me to test the stability of chlorine water at the boiling point when distillation and the consequent separation of the two acids were altogether prevented, the object being to determine whether hydrochloric acid was a decomposition product of the action of heat on chlorine water, or whether it was strictly a dissociation product depending for its separation on the isolation of hypochlorous acid in the distillate. To decide this, a fresh quantity of chlorine water was heated in the same apparatus as before, but in this case the flask was fitted with an upright condenser so that the distillate returned to the distilling flask. A continuous stream of chlorine was passed through 400 c.c. of the solution, which was kept at the boiling point for 5 hours, the free chlorine being then removed in the cold. Analysis gave for the total volume: active chlorine absent; total chlorine = 4 c.c. $N/10$ AgNO_3 .

In a second experiment, when the solution was boiled for 3 hours, it contained, after aspiration, no active chlorine, and total chlorine = 1.7 c.c. $N/10$ $AgNO_3$.

The small amount of chloride found under these conditions shows that, when the separation of the two acids is prevented, chlorine water undergoes very little decomposition at the boiling point. These results also indicate that the formation of the two acids during distillation is due to the removal of one of the acids from the sphere of action, and not to the action of the chlorine water on the alkali contained in the glass. We are therefore led to the conclusion that hypochlorous and hydrochloric acids are separated during distillation as the products of the partial change of chlorine water.

This conclusion is further justified by the fact that, on mixing the residue and distillate obtained by distilling chlorine water, a solution having all the properties of the original chlorine water is reproduced. Thus, in one experiment, 160 c.c. of distillate were collected from 400 c.c. of chlorine water distilled in a current of chlorine gas; the free chlorine was then removed from the residue and distillate by aspiration until the air-current, when passed through a solution of potassium iodide, failed to liberate a trace of iodine. The two solutions were then analysed:

Total distillate.	Total residue.
Active chlorine = 52 c.c. $N/10$ $Na_2S_2O_3$.	Active chlorine absent.
Total chlorine = 26.5 c.c. $N/10$ $AgNO_3$.	Total chlorine = 28 c.c. $N/10$ $AgNO_3$.

Half of the residue and a similar proportion of the distillate were then mixed, with the result that the product now smelt of free chlorine, and on renewed aspiration, the escaping air freely liberated iodine from potassium iodide.

Analysis of the aspirated solution now gave: active chlorine absent, total chlorine = 3 c.c. $N/10$ $AgNO_3$, thus showing that mutual decomposition of the two acids with evolution of free chlorine had taken place.

The conditions which influence the change were now further studied. In the first place, an experiment was made to determine whether the two acids are actually formed by the action of chlorine on water at the boiling point, or whether they have their origin in the cold solution, distillation in such a case serving only to separate the acids first formed. To decide this, 400 c.c. of pure water were first heated to the boiling point and then saturated with chlorine gas, the distillation being carried out as before; 100 c.c. of distillate contained, after aspiration: active chlorine = 40 c.c. $N/10$ $Na_2S_2O_3$; total chlorine = 21 c.c. $N/10$ $AgNO_3$.

The residue contained no active chlorine, and total chlorine = 36.5 c.c. $N/10$ AgNO_3 .

These results show that at the boiling point chlorine reacts with water, forming the oxy- and hydr-acids. The composition of the distillate before and after removal of the free chlorine by aspiration was now determined, in order to gain some idea as to the proportion of hypochlorous acid to free chlorine passing over in solution in the distillate. To do this, the last experiment was repeated, 160 c.c. of distillate being collected from the distillation of 400 c.c. of solution. Analysis gave for the total distillate :

Before aspiration, active chlorine = 162.0 c.c. $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$.					
After	„	„	„	= 42.4	„ „ „
„	„	total	„	= 20.9	„ „ AgNO_3 .

Here it is seen that about one-quarter of the active chlorine in the original distillate is present as hypochlorous acid.

In very dilute solutions, the whole of the free chlorine taken appears to enter into reaction with the water. Thus, in a series of experiments in which solutions of chlorine water of different degrees of dilution were distilled from a retort, the values for the active and total chlorine found in the distillates without previous aspiration approached more nearly to the ratio 2 : 1 as dilution increased ; finally, chlorine water containing active chlorine (= 20 c.c. of $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$) in 2000 c.c. of water were distilled ; 90 c.c. of distillate gave, without previous aspiration, active chlorine = 3.6 c.c. $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$, total chlorine = 1.8 c.c. $N/10$ AgNO_3 , showing that, in this case, all the free chlorine taken had reacted with the water, hypochlorous acid alone passing over into the distillate.

The next experiment was made to determine the amount of hypochlorous acid formed at the different stages of the distillation. Three fractions (each of 80 c.c.) were collected from 400 c.c., of pure water distilled in a stream of chlorine gas, the rate of the gas current and of the distillation being kept as nearly uniform as possible. Analysis after removal of free chlorine gave the values tabulated on p. 389.

These numbers show that the yield of hypochlorous acid steadily diminishes as distillation proceeds ; though in each fraction the close agreement between the values found for the active and total chlorine with those required by theory for hypochlorous acid is well maintained. This decrease in yield is such as might be expected, since the removal of the oxy-acid in the distillate is attended by the separation of fresh hydrochloric acid in the residual solution, reaching in this case a value = 54.2 c.c. $N/10$ AgNO_3 when the last fraction had passed over ; the concentration of the acid already formed also tends to increase as the water distils off in the process.

Fraction.	Active chlorine.	Total chlorine.
Distillate (1). 80 c.c.	40.2 c.c. $N/10$ $Na_2S_2O_3$	20.6 c.c. $N/10$ $AgNO_3$
„ (2). 80 „	23.4 „ „	11.6 „ „
„ (3). 80 „	16.1 „ „	8.7 „ „
Total distillate = 240 c.c.	79.7 „ „	40.9 „ „
Residue = 160 c.c.	Absent	54.2 „ „

The influence of hydrochloric acid on the dissociation was further studied in the following experiment, in which the solutions described below were distilled in a stream of chlorine; 60 c.c. of distillate in each case were collected, the active chlorine, as hypochlorous acid, being estimated after the removal of free chlorine by aspiration.

(1) 150 c.c. of pure water gave active chlorine in the distillate = 28.8 c.c. $N/10$ $Na_2S_2O_3$.

(2) 150 c.c. of water containing $HCl = 25.9$ c.c. $N/10$ $AgNO_3$ gave a distillate containing active chlorine = 12 c.c. $N/10$ $Na_2S_2O_3$.

(3) 150 c.c. of the residual solution from a previous experiment, in which $HCl = 25.9$ c.c. $N/10$ $AgNO_3$ had already been formed during distillation, was again distilled; the distillate contained active chlorine = 13 c.c. $N/10$ $Na_2S_2O_3$. Thus the presence of hydrochloric acid, whether added to or formed in the solution, causes a marked decrease in the yield of hypochlorous acid passing over during distillation.

The results of a large number of experiments made to determine the strength of hydrochloric acid required to arrest entirely the formation of the oxy-acid during distillation—that is, to ensure complete stability of the chlorine water—showed that it was not until a strength equal to 1 part of concentrated HCl to 8 parts of chlorine water had been reached that the oxy-acid ceased to distil over.

In conclusion, an experiment was made to investigate the dissociation of chlorine water at the ordinary temperature; this was done by distilling the solution under diminished pressure in the apparatus indicated (p. 390). This consisted of a bolt-head flask, *A*, the neck of which was enlarged at *B* and contained a tube *C* of 15 c.c. capacity, previously filled with dry chlorine and sealed, the end of *B* being also drawn out and sealed. Water (500 c.c.) was boiled in *A* until all the air had been expelled by the side tube, *D*, which was then sealed up at its drawn-out extremity. When the water in *A* was cold, the bulb *C* was broken inside *B* and the flask shaken until the chlorine was absorbed. By means of the india-rubber tube

and mercury cup *G*, the end of *E* was tightly fixed in the neck of the flask *F*, which was provided with a side tube, *H*, and contained 50 c.c. of water and a globule of mercury. The water in *F* was now boiled to expel all the air, and *H* was sealed off. The two flasks were then connected by breaking the capillary *E* inside the neck of *F*, and, on placing *F* in a freezing mixture, the liquid in *A* distilled into *F*. The distillate, when finally shaken with the mercury, gave rise to the brownish-yellow precipitate characteristic of

hypochlorous acid, showing that the oxy-acid passes over from chlorine water under diminished pressure at the ordinary temperature.

From these experiments it is shown:—

- (1) That when chlorine water is distilled, it undergoes partial change with formation of hypochlorous and hydrochloric acids,
- (2) That when the separation of the two acids is prevented, chlorine water is practically stable at the boiling point,
- (3) That the amount of change decreases as distillation proceeds, owing to the formation of hydrochloric acid in the original solution, and that in the presence of a large excess of the acid only free chlorine passes over in the distillate.

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