CCLXVII.—*The Photochemical Reaction between Oxygen and Hydrogen Chloride.*

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Isolated observations on the oxidation of hydrogen chloride by oxygen in light have been made in the past, but very little systematic work has been done. McLeod (J., 1886, **49**, 608), Backelandt (*Bull. Acad. belg.*, 1886, **11**, 194), Richardson (*Brit. Assoc. Reports*, 1889, 59), and others all report that if a sufficiently concentrated solution of hydrochloric acid be exposed to oxygen or air in sunlight, a certain amount of chlorine is produced. In a first paper (*Ann. Chim.*, 1890, **19**, 515) M. Berthelot asserts that perfectly pure solutions will not behave in this way, a trace of dissolved manganous or ferric chloride being necessary; and in a second paper (*Ann. Chim. Phys.*, 1904, **3**, 295) he states that contact with gold or platinum has the same effect. The most conclusive experiments are those of Backelandt and of Richardson.

Experiments on the corresponding gaseous system were carried out by Backelandt (*loc. cit.*), Richardson (J., 1887, **51**, 801; *Brit. Assoc. Reports*, 1888, 89), and Thiele (*Ber.*, 1907, **40**, 4914; *Z. angew. Chem.*, 1909, **22**, 2472), the first two authors working with glass vessels in sunlight, and the last using quartz vessels and a quartz–mercury lamp. All found the oxidation to take place under suitable conditions. There were, however, differences in detail. Richardson could obtain practically complete oxidation of the hydrogen chloride if the gases were moist, with definite indications that the reaction was photosensitised by the chlorine produced, but found the rate to diminish with partly dried, and to fall to zero with phosphoric oxide-dried, gases. On the other hand, Backelandt reported the formation of chlorine in a " perfectly dry " gaseous mixture. Thiele, employing light of shorter wave-length and sulphuric acid-dried gases, also found the reaction to take place.

Thermodynamic Considerations.—The reaction $2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2$ tends to take place spontaneously in dilute aqueous solution and can be effected in practice by the action of light (some chloric acid is produced in addition to the oxygen). The question arises as to whether the reverse reaction taking place in a concentrated hydrochloric acid solution is also spontaneous, or whether it is not rather accompanied by an increase in free energy derived from the light, *i.e.*, is endoenergetic. The point can be answered in the following way. We know that the equilibrium in the Deacon reaction moves in favour of the chlorine–water vapour side of the equation with fall in temperature. Extrapolating the data given by Nernst (*Z. Elektrochem.*, 1909, **15**, 689) for the constant $K_p = p^2_{Cl_2} \cdot p^2_{H_2O}/p^4_{HCl} \cdot p_{O_2}$, down to 25°, we find $\log K_p = 13{\cdot}9$ (pressures in atmospheres). Combining this figure with data for the partial pressures of hydrogen chloride and water vapour over various aqueous solutions of hydrochloric acid, we can calculate whether the free energy decrease associated with the reaction

$$4HCl(p_1) + O_2\ (1\ \text{atm.}) \longrightarrow 2Cl_2\ (1\ \text{atm.}) + 2H_2O(p_2)$$

is positive or negative.

TABLE I.

Normality of solution.	p_1, mm.	p_2, mm.	Log $p^2_{H_2O}/p^4_{HCl}$ (pressures in atmospheres).	Log $K_p - \Sigma\nu \log p$.
10·5	37·5	6·28	1·05	+12·85
8·0	3·01	10·5	5·83	+ 8·07
6·5	0·57	13·4	8·99	+ 4·91
3·33	0·0133	19·64	15·85	− 1·95

We have used for the purpose the data of Dobson and Masson (J., 1924, **125**, 668), with the results shown in Table I. Thermodynamically, then, there is no reason why irradiation of the three more concentrated acid solutions in presence of oxygen at 1 atm. pressure should not result in the formation of chlorine at very considerable pressures. A 3·33*N*-solution is, however, not capable of forming chlorine even at 1 atm.; the maximum developable pressure is clearly governed by the relation

$$2 \log p_{Cl_2} = -1{\cdot}95, \text{ or } p_{Cl_2} = 0{\cdot}106 \text{ atm.}$$

No quantitative data have hitherto been published on this reaction. The object of the present experiments was to fill this gap, particularly as regards the reaction in the liquid phase, working under well-defined conditions, investigating the energetics, and attempting to discover why the reaction apparently proceeds to a far less degree than is predicted on thermodynamical grounds.

EXPERIMENTAL.

Apparatus and Methods.—The majority of our experiments were carried out with a cell similar in construction to those described in J., 1925, **127**, 829. The glass block was 5 cm. deep, the volume of the cell cavity being about 220 c.c. The quartz faces were cemented on by a very thin layer of pitch. A tap (A), sealed into a hole which was drilled through the base of the glass block, allowed samples of the photolyte to be drawn off for analysis. A vertical tube (B), sealed into a similar hole, which entered the cell cavity vertically and tangentially to the horizontal diameter of the latter, served to pass oxygen or air into the cell. A third hole, 1 cm. in diameter, was drilled vertically through the middle of the top of the glass block into the cavity. It was closed by a ground joint (C). Through the latter was introduced a rotating glass stirrer which passed through a seal (G) of the usual type, fitting on to the outside of C, and filled with a hydrochloric acid solution of the concentration under experiment. The seal was sufficiently deep, and the wing attached to the stirrer rod sufficiently long, to allow of the stirrer being raised right out of the liquid, which filled the lower part of the cell, into the top part of the cell (filled with gas) during insolation. Connected with B was a reservoir of oxygen (D) of about the same capacity as the cell, sealed with a solution of hydrochloric acid, the height of which could be adjusted by a levelling bulb (E) in the usual manner. A side tube (F) allowed of oxygen being passed directly into D when E was lowered.

The usual experimental procedure was to fill the greater part of the cell through C with the acid, already pre-saturated with oxygen, and then, with G open, to lower E, and to pass oxygen *via* F successively through D, B, the acid in the cell, and out through C. When the gas space in the cell had been swept out and the acid well saturated with oxygen, G was closed, the oxygen stream stopped, and F just sealed by raising E. The residual gas space in the cell was shielded from the light source by an aluminium screen (this was invariably done when the liquid phase was insolated), and insolation commenced. After a given time, the stirrer was lowered, the acid stirred, and one-third drawn off through A for analysis, the oxygen pressure in the cell being kept constant by raising E. After readjustment of the aluminium screen and raising the stirrer, a further insolation was made, and another one-third of the cell's contents withdrawn. A similar procedure was adopted for the insolation of the final third part of the solution.

In the first experiments, a water-cooled tungsten arc lamp was used, but it proved erratic in behaviour owing to deposition of tungstic oxide on the electrodes. Quartz mercury lamps were subsequently employed, placed a few inches in front of the cell without any lens system. The filters used for monochromatic light will be described later. A 1-cm. quartz cell, through which distilled water flowed, was normally placed between the lamp and the reaction cell in order to keep down the temperature of the latter.

The course of the reaction was followed iodometrically. The potassium iodide used was iodate-free, and a solution was freshly prepared for each experiment, as also was the " soluble starch " indicator. A progressive liberation of traces of iodine was found to occur when aqueous potassium iodide was added to pure concentrated (10—12N) hydrochloric acid solutions, but on diluting the latter five-fold with water, no detectable amount appeared until after 20 minutes. The procedure finally adopted was to dilute the chlorine solutions until the acid concentration was 2—2·5N, add the potassium iodide and starch solutions, and titrate with 0·01N-sodium thiosulphate. Tested on solutions of known chlorine content, the titration figures were found to be raised very slightly by the presence of the acid, but to be consistent. In titrating 50 c.c. of the photolyte, the end-point could be determined to a single drop of thiosulphate, corresponding to an error in the chlorine concentration of $0{\cdot}006 \times 10^{-3}N$. Blank tests for the presence of traces of chlorine or other oxidising agents in the concentrated acid solutions used were invariably made before these were insolated.

Preliminary Experiments.—After first observing that solutions of concentrated hydrochloric acid saturated with oxygen and exposed to the full radiation of the tungsten or mercury arcs for an hour or so did, in fact, develop chlorine, it was shown that no such reaction took place either in the dark or in the diffused light of the laboratory. A glass plate, 0·6 cm. thick, placed before the cell prevented any perceptible reaction during the course of 3½ hours, the conclusion being that the essentially active rays, under our experimental conditions, lay in the short or medium ultra-violet.

Experiments were then done in which concentrated solutions of acid saturated with oxygen were exposed in the apparatus described above (i) successively for 1, 2, and 3 hours, (ii) for 3 hours, (iii) for 4, 5, and 6 hours. The concentrations of chlorine produced, $[Cl_2]$, are shown below as normalities, the same convention being adopted throughout this paper.

	i.			ii.	iii.		
Time, hours	1	2	3	3	4	5	6
$[Cl_2] \times 10^3$	0·15	0·23	0·28	0·28	0·34	0·37	0·41

If these data are plotted, the curve is seen gradually to flatten out, indicating an asymptotic approach to a limiting chlorine concentration. It appeared possible that this result might be due to loss of chlorine from the liquid to the gas phase, but one or two experiments, confirmed later, showed this diffusion loss to be negligibly small. In the present instance, a $0{\cdot}14 \times 10^{-3}N$-solution had become $0{\cdot}11 \times 10^{-3}N$ after 46 hours in the dark; another solution, originally $0{\cdot}19 \times 10^{-3}N$, was still $0{\cdot}15 \times 10^{-3}N$ after 67·5 hours in the dark. The average fall in concentration was thus only of the order of $0{\cdot}0006 \times 10^{-3}N$ per hour, and therefore quite insufficient to explain the course of the observed curve.

In view of the emphasis laid by Berthelot (*loc. cit.*) on the accelerating effect of manganese chloride on the reaction, a few experiments were done with air-saturated acid solutions containing small quantities of this salt. Parallel experiments in absence of manganese chloride were carried out. In every case under our conditions, the addition of the salt resulted in a definite retardation of the reaction, of the order of 20%. Incidentally, it was shown that chlorine is slowly formed when concentrated acid solutions are insolated in thin glass test-tubes, although at a rate quite negligible compared with that of its production in quartz vessels. This point is of interest, as it shows that light of wave-length greater than 300 μμ is active; such radiation is present in quantity in sunlight, which most of the previous workers had used.

Experiments were next done on the effect of the oxygen concentration. On insolation of 11*N*-acid in quartz test-tubes by the total light of the mercury arc, the chlorine concentration was $0{\cdot}44 \times 10^{-3}N$ after one hour, a photolyte saturated with oxygen being used, whilst the figure for air-saturated acid was $0{\cdot}30 \times 10^{-3}N$ (in both cases the mean of several experiments). In order definitely to show that, in absence of oxygen, the reaction ceased, a quartz test-tube was provided with a ground tubulus, which permitted of oxygen-free atmospheric nitrogen being passed through the solution before insolation. In two such experiments, no formation of chlorine could be detected after 2—3 hours, whereas acid containing dissolved air gave figures of the order of $0{\cdot}1 \times 10^{-3}N$ (lower than before owing to the " ageing " of the lamp).

Experiments were also done to test the effect of the acid concentration. In one hour's insolation, the following comparable chlorine concentrations were produced :

Acid concentration	11*N*	5·5*N*	2·5*N*
$[Cl_2] \times 10^3$	0·16	0·05	0·02

It is of interest to compare the results obtained in this respect by previous observers (*locc. cit.*), working with sunlight in glass vessels.

[HCl].	Result of insolation.	Observer.
Fuming acid (13*N*)	Chlorine formed	Berthelot
12·6*N*	Marked action	Backelandt
9·5*N*	Definite action	Richardson
6·8*N*	Less pronounced action	Backelandt
4·3*N*	Trace of chlorine	Richardson
1·0*N*	No action	Backelandt

Having settled these preliminary points, attention was next directed to the factors responsible for the fall off in rate of reaction with time of insolation noted above.

The Stationary State with 11N-*Acid Solutions.*—A series of experiments was carried out in which 11*N*-acid, saturated with oxygen, was insolated under identical conditions for increasing periods of time, varying between 2 and 160·5 hours, by the full light of the mercury lamp. The gradual development of a marked yellow colour in the photolyte during insolation was first noticed in these experiments. In order to obtain the eleven readings taken, four successive cell fillings were required. The results, shown below, indicate once more a slow approach to a limiting chlorine concentration.

Time of insolation, hours ...	2	4	6	8·5	10	12
$[Cl_2] \times 10^3$	0·13	0·18	0·22	0·26	0·29	0·31
Time of insolation, hours ...	21·5	48	71·5	96	160·5	
$[Cl_2] \times 10^3$	0·44	0·72	0·79	0·85	0·96	

Further experiments showed that loss of chlorine from the photolyte by diffusion was negligible. The alterations in concentration during a period of 18 hours' standing in the dark in the reaction cell are as follows :

$[Cl_2] \times 10^3$, initially	0·76	1·49	1·51	1·50	1·62
,, ,, finally	0·75	1·46	1·51	1·48	1·60
Loss by diffusion	0·01	0·03	nil	0·02	0·02

The change in acid concentration during the insolation is imperceptible, and in view of the small quantity of oxygen consumed and the slow rate of reaction, any retardation due to delayed solution of this gas would be negligible. We are led, then, to the conclusion that the chlorine formed in the reaction is responsible for the retardation of the latter. This view was confirmed by insolating in the same apparatus solutions of 11*N*-acid, saturated with oxygen and containing various small but definite concentrations of added chlorine. After each insolation and titration, the residual solution was allowed to stand in the cell in the dark, and the rate of loss of chlorine by diffusion determined, this figure being subsequently corrected for the difference between the conditions during the insolation and during the dark observations on the assumption that the rate of change of concentration by diffusion would be proportional to the ratio surface/volume of the liquid. The results, contained in Table II, are somewhat irregular, but plainly show that there is a tendency towards a stationary chlorine concentration of about $1{\cdot}6 \times 10^{-3}N$, this figure being very slowly approached during insolation from the sides both of lower and of higher concentration.

TABLE II.

Time of insolation, hours.	$[Cl_2] \times 10^3$ initially.	$[Cl_2] \times 10^3$ finally.	Diff. $\times 10^3$.	Fall in $[Cl_2] \times 10^3$ by diffusion.
23·5	0·95	0·99	+0·04	Not determined
42	1·06	1·09	+0·03	
66	1·06	1·11	+0·05	
24	1·56	1·56	nil	
48	1·56	1·56	nil	
20	1·95	1·90	−0·05	0·02
22·25	2·30	1·95	−0·35	0·07
21·5	2·28	2·19	−0·09	—
24·5	2·48	2·44	−0·04	0·03
22	5·12	4·40	−0·72	0·39
22	5·58	4·47	−1·11	0·32

The yellow colour of the solution was very marked at $1{\cdot}56 \times 10^{-3}N$ (chlorine water of this concentration is colourless, even in presence of enough dilute hydrochloric acid to repress the hydrolysis), and it was further noticed that at higher chlorine concentrations, the colour became less pronounced, and at 5—6 × $10^{-3}N$ had practically disappeared.

Further, it was remarked when making up the solutions that, up to about 2·5 × $10^{-3}N$, there was very little loss of chlorine during saturation with oxygen, but that this loss became relatively far greater when working with more concentrated chlorine solutions. This fact is reflected in the diffusion losses in the last column of the table.

In view of the calculation at the beginning of this paper, the decomposition by light of solutions of chlorine of concentrations of 2—5·5 × $10^{-3}N$ was unexpected, as were, on general grounds, the maximum in visible colour and the sudden rise in chlorine volatility.

Separate test-tube experiments, done with $11N$-acid solutions saturated with air, and using a far higher light intensity, gave a final chlorine concentration of 1·48 × $10^{-3}N$ after 20·75 hours, and suggest that the stationary concentration may be independent both of the light intensity and of moderate changes in oxygen concentration.

Stationary State with 5·5N-*Acid Solutions.*—Similar experiments were done with $5{\cdot}5N$-solutions. Commencing with the photolyte saturated with oxygen, but free from chlorine, a limiting chlorine concentration of 0·08 × $10^{-3}N$ was reached after 25 hours (unchanged at 45·5 hours) when the complete light of the lamp was used—this is a far lower figure than was given with the $11N$-acid. Results with the same solution pre-charged with various chlorine concentrations are shown in Table III. Parallel dark experiments were carried out to determine the diffusion loss correction.

TABLE III.

Time of insolation, hours.	$[Cl_2] \times 10^3$ initially.	Loss in chlorine normality × 10^3 due to light.	due to diffusion.
24	0·096	(0·01 gain)	nil
21·5	0·21	0·01	0·01
20·25	0·39	0·01	0·025
18	0·75	0·01	0·07
20·75	1·60	0·07	0·08
18	3·06	0·26	0·47
18	3·58	0·23	0·80

It will be noticed that any photodecomposition between 0·096 and 0·75 × $10^{-3}N$ is very small and comparable with the experimental error. At 1·6 × $10^{-3}N$ and at higher concentrations, on the other hand, it is quite definite. The chlorine diffusion losses are far greater than with the $11N$-acid solutions (Table II). The depth of colour in solutions of equal chlorine content is considerably less in $5{\cdot}5N$- than in $11N$-acid, and the colour maximum, which is less marked, occurs at about $0{\cdot}8 \times 10^{-3}N$. It would seem as if, in this case, the stationary state concentration lies below that of the colour maximum and that, between these concentrations, a slow decomposition of chlorine occurs on exposure to light. Above the colour maximum, both chlorine volatility and photosensitivity markedly increase. That fraction of the chlorine present as the non-volatile form of strong visible colour would seem to be insensitive to light.

Effect of Wave-length.—The filter vessels used were of the same general construction as the insolation cells and water filter. The solutions employed and the transmission of the completed filters for the mercury arc lines as measured by a combination of monochromator, thermopile, and galvanometer (filter 1 was measured photographically) were as follows :

Solutions.	Fractional transmissions.
1. 5 Mm. 0·0087% *p*-nitrophenol + 5 mm. 0·002% *p*-nitrosodimethylaniline.	365 $\mu\mu$, 0·04; 265 $\mu\mu$, 0·08; 254 $\mu\mu$, 0·15; much of 546 and 579 $\mu\mu$; smaller amounts of other visible lines; traces of other ultra-violet lines.
2. 5 Mm. 0·0125% auramine O + 5 mm. 0·0125% acid fuchsine.	313 $\mu\mu$, 0·19; 303 $\mu\mu$, 0·09.
3. 5 Mm. 0·075% acid fuchsine.	436 $\mu\mu$, 0·08; 405 $\mu\mu$, 0·27; 365 $\mu\mu$, 0·18.
4. 5 Mm. 4% quinine sulphate + 5 mm. 0·085% Victoria blue.	436 $\mu\mu$, 0·59.

In addition, a 1-cm. cell filled with chlorine gas at 1 atm. was used. Its transmission was about 50% between 250 and 290 $\mu\mu$, in addition to which it passed appreciable amounts of 365 $\mu\mu$ and proportions of the visible lines, increasing with increase in wave-length.

Formation of chlorine. In confirmation of the preliminary experiments, which indicated that the effect of ultra-violet rays transmitted by glass is relatively very slight, we found that no appreciable reaction took place when $11N$-acid saturated with oxygen was insolated for 8 hours with light passed by filters 2 and 3, whilst the reaction was definite when filter 1 was used.

Concentrations above the stationary state. Solutions of chlorine of about $4 \times 10^{-3}N$ concentration in $11N$-acid were prepared, saturated with oxygen, and insolated by filtered light for about 18 hours with filters 2—4 and the chlorine gas filter and for 43 hours in the case of filter 1. In *every* case there was marked loss of chlorine after correction for the diffusion * loss. In the particular case of

* This was considerable with these relatively concentrated chlorine solutions and, as the insolation cell was always found to rise 3—4° in temperature during insolation, experiments were done to see if this temperature rise was of any significance. It was found not to be the case. Working under our conditions, the rate of loss of chlorine from the photolyte was practically the same in a thermostat at 25° as at a room temperature of 16°.

filter 1, this loss was 3—4 times as great as could be accounted for by the small amount of 365 μμ light present. In view of the particular interest of this point, the experiments were repeated several times, always with the same result. Further, it was shown, by combining a quinine filter with filter 1, that the visible mercury lines passed are inactive. It seems, therefore, that light in the wave-length region 250—270 μμ causes the formation of chlorine at concentrations below the stationary state, and brings about the disappearance of chlorine at concentrations above this value.

The stationary state concentration. A $1{\cdot}64 \times 10^{-3}N$-chlorine solution in oxygen-saturated $11N$-acid was insolated by light passed by filter 3 for 18 hours. There was no perceptible decomposition or formation of chlorine, although, at rather higher concentration, the decomposition was marked (see above). Since, when the complete light of the lamp is used, the concentration at this point does not change on insolation, it is reasonable to assume that all wave-lengths are, at the most, only slightly active at the stationary state.

Concentrations below the stationary state. A number of experiments were done, using filters 3 and 4, on oxygen-saturated $11N$-acid solutions with chlorine concentrations below $1{\cdot}6 \times 10^{-3}N$. In no case was there any change in chlorine concentration exceeding the experimental error as the result of 18 hours' insolation. Hence those wave-lengths which bring about reaction of chlorine at higher concentrations have no such action below the stationary state.

Summarising, it appears (i) that ultra-violet light can cause formation of chlorine from oxygen and concentrated hydrochloric acid solutions up to a certain limiting concentration, the shorter wave-lengths being far more effective in this respect than the longer; (ii) that these solutions of chlorine, of strong visible colour and low chlorine pressure, are insensitive to light; (iii) that, at the stationary state, both formation and decomposition of chlorine are very slight; (iv) that light of all wave-lengths between 254 and 436 μμ can decompose solutions in concentrated acid of chlorine of concentrations exceeding that of the stationary state, these solutions being of relatively less extinction in the visible and having relatively high chlorine pressures.

Some Properties of Dilute Solutions of Chlorine in 11N-*Hydrochloric Acid.*—The striking dependence on the chlorine concentration of the colour of these solutions and of their chlorine vapour pressures was investigated more closely.

Colour of the solutions. Ten different solutions of chlorine in $11N$-acid, covering a concentration range of $0{\cdot}13N$ to $0{\cdot}00015N$, were filled into Nessler tubes, and their colours compared qualitatively. Table IV shows that, as the chlorine concentration *fell* from 0·00533 to 0·00258N, the colour (i) became far more marked and (ii) changed in quality. Its maximum intensity was reached at 0·0013N, after which it fell off on further dilution. Comparison between two solutions of different colour quality must, of course, be made with caution, but it may be recorded that, visually, the solutions of concentration $130 \times 10^{-3}N$ and $0{\cdot}3 \times 10^{-3}N$ appeared to have equal depth of colour, as did $5{\cdot}33 \times 10^{-3}N$- and $0{\cdot}15 \times 10^{-3}N$-solutions. A second set of tests gave a similar result; the solution of minimum greenish colour lay at $8 \times 10^{-3}N$, the change in quality was commencing at $3{\cdot}36 \times 10^{-3}N$, and the solution of maximum brown colour was one of $1{\cdot}76 \times 10^{-3}N$. In a third set of observations, a $1{\cdot}54 \times 10^{-3}N$-solution was found to have a distinctly darker tint than either a $0{\cdot}82 \times 10^{-3}$ or a $2{\cdot}42 \times 10^{-3}N$-solution; all were of a deep brownish-yellow.

TABLE IV.

$[Cl_2] \times 10^3$	130	65	32	16	5·33	2·58	1·3	0·6	0·3	0·15
Nature of colour	←Greenish-yellow→					←Brownish-yellow→				
Depth of colour	Very definite	Decreasing →			Barely perceptible	Pronounced	Deepest tint	Decreasing →		

In the second and third series, after the above observations had been made, the solutions were diluted with an equal volume of distilled water, thus halving both acid and chlorine concentrations, and their colours again examined. Apart from the diminished depth of colour observed in every case, it was found that the diluted solutions which had the deepest tint were derived from those with the maximum colour before dilution, *i.e.*, in 5·5N-acid, the chlorine solutions of strongest yellow colour were $0{\cdot}88 \times 10^{-3}N$ and $0{\cdot}77 \times 10^{-3}N$ in the second and third series respectively. The position of the colour maximum would appear to depend on the ratio $[Cl_2]/[HCl]$, and the depth of colour at the maximum on $[HCl]$. Dilution of the acid was, as before, accompanied by a marked increase in chlorine vapour pressure for solutions of the same chlorine concentration.

Absorption spectra. A number of photographic measurements were made on solutions of 11N-hydrochloric acid and on such solutions containing various amounts of dissolved chlorine. A Judd Lewis sector photometer and a Hilger quartz spectrograph were employed, together with a series of special absorption cells, consisting of 4-cm. quartz plates cemented over 3-cm. cavities drilled through plane-parallel glass blocks or plates of various thicknesses down to 1 mm. The results are not given in detail; they covered the spectral region 250—380 μμ only, and have since been repeated with greater accuracy and extended by Dr. D. W. G. Style, who will publish his data later. Our figures for hydrochloric acid solutions were in moderate agreement with those of Brannigan and Macbeth (J., 1916, **109**, 1277) obtained for $12M$-acid, the two sets of extinction coefficients practically coinciding at 283 μμ, but our values being definitely the greater both at higher and at lower frequencies. In the case of the solutions of chlorine in $11N$-acid, the Beer–Lambert law appeared to hold (within our not inconsiderable experimental error) up to $0{\cdot}0015N$-, and possibly up to $0{\cdot}0017N$-, solutions, a tendency for extinction coefficients to fall with increase in $[Cl_2]$ being most marked for the longer wave-lengths. Above the concentrations named, the extinction coefficients fell off rapidly; thus, for $0{\cdot}004N$-solutions, they were of the order of one-third of the values at lower concentrations. This decrease was again most marked for the longer wave-lengths. The band found at 330 μμ in chlorine gas could not be detected; the extinction coefficients appeared to increase throughout with frequency over the range investigated (Dr. Style has since shown this statement to require modification) and, for dilute chlorine solutions, were of the order of 10,000 at 260 μμ (cm.; common logarithms), compared with about 0·024 for hydrochloric acid in $11N$-solutions and 0·24 for chlorine gas (von Halban and Siedentopf, *Z. physikal. Chem.*, 1922, **103**, 71).

Our measurements therefore sufficed to show (i) that the great increase * in the extinction coefficients of chlorine caused by the addition of concentrated hydrochloric acid, apparent to the eye in the visible region, persists in the ultra-violet, and is very pronounced in the region of these rays which bring about the oxidation of the hydrogen chloride; and (ii) that, when the stationary state concentration of chlorine is exceeded, these extinction coefficients fall off, thereby more nearly approaching, though still far exceeding, those for ordinary chlorine.

Partial pressure of chlorine. A few preliminary experiments were done to confirm the obvious conclusion drawn from the sudden rise in diffusion and manipulation losses on passing the stationary chlorine concentration. Three 100-c.c. wash-bottles were connected in series in a thermostat at 25°, filled (the first two partly, the third nearly completely) with the solution under experiment, and allowed to stand for a few hours. A sample was withdrawn from the third bottle and analysed for chlorine, and a slow stream of air (200—300 c.c./hour) passed through for 2—5 hours, the

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* The extinction coefficients of chlorine in water, when allowance is made for partial hydrolysis, are similar to those of chlorine gas. See the preliminary results in J., 1927, 657.

chlorine carried forward being trapped in potassium iodide solution and titrated. After the run, the chlorine content of the last bottle was again determined. The total volume of air passed was measured by a calibrated aspirator. The results are contained in Table V.

TABLE V.

$[Cl_2] \times 10^3$, initially.			$\frac{[Cl_2] \text{ in gas}}{[Cl_2] \text{ in soltn. (average)}}$.	Partial pressure of chlorine at 25°, mm.
initially.	finally.	in gaseous phase.		
0·52	0·48	0·0046	0·0092	0·042
1·65	1·61	0·0113	0·0069	0·10
2·61	2·61	0·0212	0·0081	0·19
3·35	3·31	0·0522	0·0157	0·48
3·72	3·52	0·0835	0·0231	0·76
4·26	3·78	0·198	0·0493	1·8

Though no particular accuracy can be claimed for them (the concentrations in the last saturator changed during most of the runs), they suffice to show that the fugacity coefficient of the chlorine remains practically constant up to about $2{\cdot}5 \times 10^{-3}N$ (if indeed it does not pass through a flat minimum at or very near the stationary concentration), and then proceeds to rise rapidly. This confirms in every way our previous observations.

Solutions of Chlorine in Concentrated Aqueous Lithium Chloride.—In view of the above results, some observations were made on the colour of dilute solutions of chlorine in concentrated aqueous solutions of the alkali-metal chlorides. 0·03—0·04*N*-Chlorine solutions in pure saturated aqueous potassium or sodium chloride were of a pale yellow colour, which decreased normally on dilution with the saturated salt solution. With concentrated lithium chloride (330 g./litre) remarkable results were obtained. The colour of a 0·034*N*-chlorine solution was a pale yellow, as with solutions in potassium and sodium chlorides. On the addition of fresh concentrated lithium chloride, a deep brown-yellow appeared, far more intense than any observed with hydrochloric acid solutions, only to disappear on further dilution. If chlorine gas were passed into the solution when the colour was at its greatest intensity, the latter disappeared in a few moments. A further experiment gave the same type of result, the colour maximum lying near $[Cl_2] = 0{\cdot}0175N$.

All chlorine solutions of concentration below the colour maximum had so low a chlorine partial pressure as to be practically undetectable by smell. Dilution with an equal volume of water simply lessened the intensity of the colour, as with hydrochloric acid solutions but less markedly. Solutions of chlorine in saturated calcium chloride and in concentrated (225 g./litre) lithium sulphate solutions behaved normally.

The analogy between the results shown by chlorine dissolved in concentrated aqueous hydrochloric acid and lithium chloride solutions led us to test the behaviour of the latter when exposed to air in quartz vessels and insolated by the full radiation of a mercury lamp. Small amounts of chlorine, readily detectable by the yellow colour, were produced; thus, in two experiments, the concentration after one hour was $0{\cdot}1 \times 10^{-3}N$, about one-third of what would have been formed in $11N$-aqueous hydrochloric acid under the same conditions. Dr. Style has suggested to us that this production of chlorine may be the result of slight hydrolysis of the salt, combined with very low solubility of lithium carbonate in concentrated lithium chloride solutions. Similar experiments with concentrated calcium and potassium chloride solutions gave negative results.

Nature of the Stationary State.—As pointed out, the cessation of the oxidation of the acid solutions when the stationary state concentration is reached is clearly due to the chlorine formed. Our extinction coefficient measurements, although only approximate, enable us to decide whether this limit to the concentration is merely an apparent one, *i.e.*, whether the internal light filter action of the non-photosensitive chlorine is simply so great at this point as to make undetectable the further formation of chlorine which nevertheless takes place, or whether it is a true one, characterised by equality between rates of oxidation of hydrochloric acid by oxygen and of water by chlorine, *i.e.*, to the setting up of the dynamic equilibrium, $4HCl + O_2 \rightleftarrows 2H_2O + Cl_2$.

Measurements of the energy distribution in the radiation of the mercury lamps used and of the extinction coefficients of the acid solutions, together with our experiments with monochromatic light, made it clear that the only rays actively concerned in the formation of chlorine in our experiments were those centred on 254 μμ and 265 μμ. For these lines our measurements give the following approximate molecular extinction coefficients :

	HCl (in $11N$-solution).	Cl_2 (below stationary state).
254 μμ	0·026	15,000
265 μμ	0·022	6,500

With their aid, one can calculate, for a 2-cm. cell, (i) that about 70% of the incident active light is absorbed by an $11N$-acid solution free from chlorine, and (ii) that practically all the incident radiation of the 254 μμ and 265 μμ lines is absorbed when $[Cl_2]$ has become $0{\cdot}25 \times 10^{-3}N$ and $0{\cdot}5 \times 10^{-3}N$, respectively. The distribution of the absorbed energy between the two absorbing constituents for different chlorine concentrations is indicated in the following table, which contains the fractions of each wave-length absorbed by the acid. In the calculation of the figures at $[Cl_2] = 4 \times 10^{-3}N$, the provisional values assumed for α_{Cl_2} were 5000 and 2200 at 254 μμ and 265 μμ respectively.

$[Cl_2] \times 10^3$		0·2	0·6	1·0	1·4	1·6	1·8	4
Fraction absorbed by acid	254 μμ	0·160	0·060	0·037	0·027	0·023	0·021	0·028
	265 μμ	0·271	0·110	0·069	0·051	0·044	0·040	0·052

These figures make it clear that we are dealing with a true, not an apparent, stationary state, and that the internal light filter effect is simply to delay the establishment of this state. Formation of chlorine was found experimentally to occur in solutions in which its concentration had already reached $1{\cdot}0 \times 10^{-3}N$. At the stationary state ($1{\cdot}6$—$1{\cdot}8 \times 10^{-3}N$), the amount of active light absorbed by the acid is still 60% of that absorbed at $1 \times 10^{-3}N$. The fact that no further perceptible production of chlorine takes place can only then be caused by the slow rate of formation being balanced by a slow rate of decomposition, due to a sufficient fraction of the chlorine being present in the photosensitive form of high fugacity and low extinction. At concentrations above the stationary state, such as $4 \times 10^{-3}N$, the two opposed reactions must still both take place simultaneously on insolation with light of wave-length absorbed by the acid, as the figures at the end of the table indicate. The net result, as has been shown, is a disappearance of chlorine, due, of course, to the greater proportion of this substance being present in the photosensitive form.

Quantum-efficiency Measurements.—A number of determinations were carried out on $11N$-acid solutions saturated with oxygen (in one case with air) using both the whole light and filtered light from a quartz–mercury lamp. The latter was of the vacuum type, U-shaped, of 3000 c.p., and taking about 2 amps. at 150 volts. The first experiments gave irreproducible results, the chlorine yield falling off in successive runs. This was traced to a diminution in the ultra-violet radiation of the lamp as its life lengthened. The experiments recorded below were all carried out when the lamp was well " aged," radiation of $\lambda < 254$ μμ being practically absent, and were concordant with one another. As soon as they had been completed, measurements both of the total energy in the beam employed for the insolation and of its spectral distribution were made by standard methods * and used in the subsequent calculations.

In the actual experiments, the light from the lamp, made approximately parallel by means of a quartz lens, was passed

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* See Franklin, Maddison, and Reeve (*J. Physical Chem.*, 1925, **29**, 713), the calculations being modified in accordance with the later work of Ridyard and Style (*ibid.*, 1928, **32**, 861).

through a quartz–water cell, and then either directly or through a filter into the reaction cell, which was 2 cm. deep, of the same type as previously used, and contained 55 c.c. of acid. The filter used consisted of 5 mm. of 0·0087% *p*-nitrophenol and 5 mm. of 0·002% *p*-nitrosodimethylaniline, between quartz plates. Its transmission over the mercury spectrum was determined photographically, three plates showing excellent agreement. The only figures relevant here are 15% for 254 μμ and 8% for 266 μμ, either the filter transmission or the unfiltered intensities of the other ultra-violet lines being so low as to make it possible to neglect them. The total intensity of the beam falling on the front of the reaction cell after passing through the water-filter varied considerably from point to point, owing to the shape of the lamp. The average of 16 readings taken in different parts of the beam in the plane occupied previously by the front face of the reaction vessel was 50·6 H.K. Of this amount, 2·05% and 1·81% represented 254 μμ and 265 μμ respectively.

Using the filter, about 24 hours' exposure was given, and about 6 hours with the complete light of the lamp. During this period, it was necessary to keep the lamp current constant by hand regulation. The concentrations of chlorine, estimated as previously, were always so low as to render diffusion and back reaction losses both quite negligible. The calculation of the total number of quanta absorbed by the acid during the experiment, as distinct from the number absorbed by the chlorine, was carried out by a graphical integration method, the extinction coefficients for 11*N*-hydrochloric acid and for the thermally-absorbing variety of chlorine already given being used. The final results are contained in Table VI. It is considered that the errors in the last column are of the order of 15%. In the experiments with whole light, the calculations are made on the assumption that only the rays at 254 μμ and 265 μμ are active. The agreement between the values obtained under these conditions and those given by the filtered light is evidence that this assumption is very near the truth.

TABLE VI.

Conditions.	Time of insolation, hours.	$[Cl_2] \times 10^3$.	Quanta absorbed per molecule of HCl oxidised.
254—265 μμ filter. Acid saturated with oxygen.	23·5	0·148	4·6
	23·5	0·148	4·6
	26·0	0·168	4·2
Whole light. Acid saturated with oxygen.	5	0·237	4·2
	7·5	0·316	3·9
Whole light. Acid saturated with air.	5·5	0·187	6·7

The Reaction in the Gaseous Phase.—A few experiments on this problem are briefly described. An equimolecular mixture of chlorine and water vapour, contained in sealed glass tubes and subjected to the complete radiation of a quartz–mercury lamp at a distance of 4·5 cm. gave no detectable trace of hydrochloric acid in 19 hours at a temperature of 155°. The chlorine content of the tubes after insolation showed that any formation of acid subsequently taken up by the alkali in the glass was negligible.

Moist hydrogen chloride–oxygen mixtures, insolated in a similar way for 17—19 hours, gave 0·46% and 0·60% conversion of the acid into chlorine in two experiments. Blank experiments showed no dark reaction at 155° in the same period. Roughly drying the gases by sulphuric acid reduced these figures to 0·08% in one case, and to a mere trace in another experiment (compare Richardson, *loc. cit.*). The prior addition of chlorine exerted no retarding effect—indeed, if anything, it seemed to sensitise the reaction (compare *idem, ibid.*). Thus, with 3% and 5·3% of the total chlorine present initially as chlorine gas, the conversion figures rose to 0·77% and 1·06% respectively. It is thus clear that light of wave-length $>$ 300 $\mu\mu$ can slowly bring about the oxidation of gaseous hydrogen chloride just as it does the oxidation of the aqueous acid. The retarding effect of the removal of water vapour is of interest.

Further experiments were done in sunlight at ordinary temperatures, working with

(*a*) gaseous hydrogen chloride and oxygen dried by sulphuric acid;

(*b*) moist gaseous hydrogen chloride and oxygen;

(*c*) moist gaseous hydrogen chloride and oxygen standing over 11*N*-hydrochloric acid;

(*d*) as (*c*), but with some manganese chloride dissolved in the aqueous acid.

The period of insolation (June 6th to July 7th, 1924) included many bright sunny days. In cases (*a*) and (*b*), the oxidation of the hydrochloric acid was complete. In (*c*), the chlorine concentration in the liquid phase (pale yellow in colour) was $2{\cdot}5 \times 10^{-3}N$, whilst the total chlorine in the gas phase was 0·75 of that in the liquid phase. More chlorine was produced in (*d*), in qualitative agreement with Berthelot (*loc. cit.*); the concentration in the gas phase remained as in (*c*), but that in the deep brown liquid phase had risen to $6{\cdot}9 \times 10^{-3}N$.

The significance of these results, which agree closely with the work of Richardson, seems clear. In absence of any liquid phase, prolonged insolation of a gaseous mixture of hydrogen chloride and oxygen with intense light of wave-length$>$300 $\mu\mu$ will lead, even when the gases are partially dried, to a state not far removed from thermodynamic equilibrium. In the presence of aqueous hydrochloric acid, however, a complex stationary state is set up, corresponding to equality in the velocities of the opposed photochemical reactions

$$4HCl + O_2 \xrightleftharpoons[\text{liquid phase}]{\text{gas and liquid phases}} 2Cl_2 + 2H_2O.$$

The addition of manganese chloride, owing presumably to the formation of some manganese tetrachloride, leads to a higher potential chlorine concentration in the liquid phase at this stationary state. The contribution of the gaseous reaction to the total velocity read from left to right is probably far more important than that of the liquid reaction.

Discussion.

We have seen that, using light of average wave-length 260 $\mu\mu$, γ is about 0·23 and 0·15 for 11*N*-hydrochloric acid saturated with oxygen and with air respectively. This fall with decreasing oxygen concentration at once suggests as the primary mechanism the formation of an activated acid molecule, this reacting with an oxygen molecule only when the necessary collision occurs during the life-time of the activated state. Such a mechanism is rendered the more probable by the fact that radiation by $\lambda > 300$ $\mu\mu$ can bring about the formation of chlorine (a rough estimate of the value of γ_{365} gives about 2% of the figure obtained with 260 $\mu\mu$). Whilst the dissociation of hydrochloric acid into hydrogen and chlorine atoms (q = 101 Cals. = 281 $\mu\mu$) would be possible with 260 $\mu\mu$ light, it would be practically excluded when light of $\lambda > 300$ $\mu\mu$ is used. In addition, some kind of a chain reaction might be anticipated in the case of primary optical dissociation of the acid molecule, but of this there is no sign.

We suggest therefore a mechanism of the following type :

(i) $HCl + h\nu \longrightarrow HCl^*$,

followed by

(ii*a*) $HCl^* + O_2 + HCl \longrightarrow Cl_2 + H_2O_2 - 29{\cdot}3$ Cals.,
(iii*a*) $H_2O_2 + 2HCl \longrightarrow Cl_2 + 2H_2O$,

or

(ii*b*) $HCl^* + O_2 + HCl \longrightarrow Cl_2 + H_2O + O - 74{\cdot}3$ Cals.,
(iii*b*) $2HCl + O \longrightarrow H_2O + Cl_2$,

or

(ii*c*) $HCl^* + O_2 + HCl \longrightarrow 2HClO - 18{\cdot}8$ Cals.,
(iii*c*) $2HClO + 2HCl \longrightarrow 2Cl_2 + 2H_2O$.

The ternary collision involved in stage (ii) does not seem improbable when the high concentration of the solution is considered, quite apart from the possibility that partial association of the acid molecules may take place. And the fact that γ_{260} is of the order of 0·2 instead of 4 signifies, of course, that all but 5% of the absorbing hydrochloric acid molecules lose their energy of activation before undergoing such a ternary collision. It is also clear that all three alternatives under (ii) are thermochemically possible, even with 365 μμ light ($\approx$ 78 Cals.). But the fact that γ is undoubtedly far less for 365 μμ than for 260 μμ suggests that (ii*b*) and (iii*b*) represent the most likely of the three alternatives.

In the case of the gaseous reaction, the mechanism is more difficult to appreciate. Dry hydrogen chloride only commences to absorb at 215 μμ, and it is generally agreed that absorption in this region results in optical dissociation into hydrogen atoms and metastable chlorine atoms. It would seem, then, highly improbable that any reaction should take place in sunlight in completely dried gases, a conclusion which agrees with the results of Richardson. On the other hand, in agreement with earlier workers, we found the reaction to go to completion in daylight in glass vessels, using moist or incompletely dried gases, and we also noticed that water vapour had an accelerating effect. In default of any data on the absorption of moist as compared with that of dry gaseous hydrogen chloride, it seems possible that the " gaseous " oxidation actually takes place in a surface film of concentrated aqueous acid formed on the walls of the containing vessel, and therefore essentially proceeds in accordance with the main reaction investigated in this paper.

With regard to the very curious properties of dilute solutions of chlorine in concentrated aqueous hydrochloric acid, we can say little further at this stage. We have written throughout of two different states of chlorine, the one highly absorbing, insensitive to light and of low fugacity, the other of relatively weak absorption, photosensitive, and of high fugacity. The effect of changing concentration on the proportions of these two assumed forms seems to forbid any application of the ordinary laws of chemical equilibrium to the conditions of their co-existence.* We imagine rather that the phenomena observed are due to the attraction and distortion exerted on a proportion of the molecules of chlorine by the molecular and ionic fields of the dissolved acid. It may, in fact, be the case that the suggested two definite states of chlorine do not exist, and that the effects of variation of chlorine concentration are

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* It should be mentioned that those workers who have concluded that such complexes as HCl_3 are present in solutions of chlorine in hydrochloric acid (*e.g.*, Mellor, J., 1901, **79**, 232) were dealing with solutions of the gas of far higher concentrations.

explicable in terms of a continuously varying function of the electrical environment of the hydrogen chloride molecules. It is interesting to note that very recently Vaillant (*Compt. rend.*, 1930, **190**, 170) has been led to correlate the extinction coefficient of the cobaltous ion with its activity, a rise in the former being accompanied by a fall in the latter. In our case we find that a rise in the extinction coefficient of chlorine in concentrated hydrochloric acid solutions is accompanied by a fall in its fugacity coefficient.

Summary.

1. The photochemical oxidation of concentrated aqueous hydrochloric acid solutions by dissolved oxygen has been studied.
2. The reaction is found to take place in ultra-violet light of wave-length 254—365 $\mu\mu$.
3. At 260 $\mu\mu$, the quantum efficiency is of the order of 0·2, and falls off rapidly at longer wave-lengths.
4. The chlorine concentration produced is limited by the setting up of a stationary state, determined by the equality of two opposing photochemical reactions. Ultra-violet light can both form and destroy chlorine under these conditions, whilst visible light can only effect the latter reaction. The chlorine concentration at the stationary state is lower the lower the concentration of the acid.
5. The oxidation of gaseous hydrogen chloride by oxygen takes place slowly in ultra-violet light under laboratory conditions, goes to practical completion in sunlight, and is sensitised by chlorine and retarded by the removal of water vapour. It is suggested that in reality the oxidation takes place in a liquid film on the surface of the vessel. If concentrated aqueous acid also be present, a complex stationary state, involving both liquid and "gaseous" reactions, is set up in sunlight.
6. Dilute solutions of chlorine in concentrated aqueous hydrochloric acid or lithium chloride behave anomalously on change of concentration, in respect both of their extinction coefficients and of their chlorine partial pressures. Further work on this subject is in progress.

The experimental work described above was carried out between December 1922 and July 1924. We are indebted to Messrs. Brunner Mond and Company, Limited, for a grant which enabled us to purchase the quartz lenses and cells employed. The junior author (R. G. F.) also wishes to acknowledge the grant received by him from the Department of Scientific and Industrial Research whilst a student-in-training.

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[*Received, June 7th,* 1930.]