CCXXI.—*The Action of Light on Mixtures of Ozone and Chlorine. Part I. Experimental. Results with Low Ozone Concentrations.*

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The sensitisation of the photo-decomposition of ozone for blue light by chlorine was discovered by Weigert (*Ann. Physik*, 1907, **24**, 243; *Z. Elektrochem.*, 1908, **14**, 591). He found the kinetics of the reaction to present one striking feature: the order in respect of ozone was zero until just before complete decomposition, whereat the rate of reaction rapidly rose. Weigert further showed that, under his conditions (quartz-mercury lamp light filtered through a glass plate; $[O_3]$ up to 4%; $[Cl_2] = 5$—70%), the rate was proportional to I_0, and the temperature coefficient was 1·17. The value of γ was estimated later by Bodenstein (*Z. Elektrochem.*, 1913, **19**, 840) from Weigert's results to be about 1·7. Further experimental work, more particularly on the energetics of the reaction, was carried out by Bonhoeffer (*Z. Physik*, 1923, **13**, 94). He employed Uviol-lamp light filtered through an ammoniacal copper sulphate solution (mean λ 416 $\mu\mu$), measured the incident energy by thermopile and galvanometer, and calculated the absorbed energy by the aid of absorption measurements on chlorine–air mixtures. Using 0·5—5% ozone and 40—75% chlorine, he confirmed Weigert's observation on the linear nature of the decomposition–time curve, and obtained for γ the value of $2 \pm 0{\cdot}2$.

Although no really satisfactory explanation of these results has been put forward, the facts as described have generally been accepted without question. We undertook a reinvestigation of the reaction, primarily to test the relation between γ and λ. The results obtained suggested experiments with higher ozone concentrations, and the whole forms a more complete study of the reaction than has yet appeared.

Apparatus and Method.

Principle of Method.—For following the reaction, we used essentially the same technique as did Bonhoeffer. Our apparatus consisted of two similar vessels filled with the same gaseous mixture, one kept dark and the other insolated, and each connected with one of the limbs of a sulphuric acid U-manometer. The movement of the latter measured the reaction velocity, and any disturbances due to thermal reaction, provided, of course, that they occurred to the same extent in the two vessels and were independent of the photoreaction, were automatically eliminated. By cleaning out the cells several times with the gaseous mixture before starting an experiment, the thermal reaction at our working temperature of 25° was usually reduced to a very small figure. Its order of magnitude could be estimated by completely decomposing the ozone in one vessel by light and then observing the movement of the manometer liquid with the whole apparatus darkened. On one occasion this rate of movement was 0·5 mm. (of concentrated sulphuric acid) in 15 hours, or less than 1% of the figure usually observed during insolation. That even such small effects essentially balanced out was shown by the fact, frequently noticed, that no change in manometer level occurred over-night when an insolation was interrupted after partial decomposition had taken place. This was usually not the case with concentrated ozone mixtures, but only work using relatively dilute ozone is described in the present paper.

Preparation of Ozone.—Oxygen was prepared by the electrolysis of 20% sodium hydroxide containing a little baryta, nickel gauze electrodes being used. The electrolysers, provided with central bell-jars containing the anodes, were used in series; a current of 4 amps. produced about 1·7 litres/hour of oxygen. This gas passed successively over palladised asbestos at 180°, through a sulphuric acid bubbler, a calcium chloride tube, a phosphoric oxide tube, and then into the ozoniser. Connexions throughout were glass-sealed, and all taps were lubricated with concentrated sulphuric acid.

The ozoniser was of the design and dimensions recommended by L. E. Smith (*J. Amer. Chem. Soc.*, 1925, **47**, 1844), three parallel generating tubes being contained in a single large Exide battery jar. Alternating current of 500 cycles was obtained from a small 500-volt alternator; this could be stepped up to 50,000 volts by a suitable transformer. Further regulation was effected by a lamp resistance in the field of the motor, and 16,000 volts were normally employed on the ozoniser. In most of the work, one generating tube only was used, giving 8% ozone by volume for indefinite periods.

Preparation of Ozone–Chlorine Mixtures.—The ozone was collected by displacement of concentrated sulphuric acid from a 3-litre gas-holder. The latter (A) was made from a large flask by sealing off the neck, and simultaneously adding an entry tube (B) and a siphon-tube (C) which led to the bottom of the vessel. It was supported inside a deep sand-bed and blackened to exclude light. The incoming gas displaced the acid through C into the bottom of a large jar (D), communicating with the atmosphere by a tube packed with solid sodium hydroxide. The pressure furnished by the oxygen generator was ample to secure the movement of the sealing acid backwards and forwards between A and D. The chlorine came from a cylinder, passed through a silver-plated reducing valve and a metal–glass joint, streamed through a sulphuric acid bubbler, and thence was led to the gas-holder. A scale on D gave an indication of the volume of gas in A at any moment, and thus allowed of the preparation of chlorine–ozone mixtures of roughly the desired composition.

Analysis of Gaseous Mixture.—For this purpose, a bulb of volume 77 c.c., with a tap at each end lubricated with sulphuric acid, was used. This was attached to the apparatus at a side tap, and filled simultaneously with the reaction cells. Its contents were then swept out by an air-stream into neutral potassium iodide solution contained in two absorption flasks, and titrated with $0{\cdot}1N$-sodium thiosulphate after addition of dilute sulphuric acid. When commencing the work, we first determined the ozone content of the ozonised oxygen, and then made a second similar analysis after addition of chlorine. A combination of the two results gave the chlorine content of the final mixture to within about 1%. Later, we adopted the method, involving the use of potassium iodate, suggested by Bodenstein, Padelt, and Schumacher (*Z. physikal. Chem.*, 1929, *B*, **5**, 209) for the simultaneous determination of ozone and of chlorine. This procedure proved both more accurate and more convenient than the former one.

Reaction Cells.—For the main experiments, two pairs of cells with fused circular plane ends, made by Schott of Jena, were employed. The first pair was of "Suprax" glass, about 10 cm. in depth and 5 cm. in diameter. After considerable use, the end plates of the illuminated cell began to deteriorate, becoming visibly attacked and etched. On this account, we resorted to the second pair, made of "Geräte" glass, about 5 cm. both in depth and in diameter. These withstood the experimental conditions far better. Each cell had an inlet tube in its side, to which was sealed a special glass–soda glass graded joint. Extensions from these joints led to the manometer interposed between the cells. The reaction system thus constituted was isolated by taps from the rest of the apparatus, to which were connected the gas-holder, a supply of pure dry electrolytic oxygen for washing out the reaction system, the side tube for the attachment of the sampling bulb, and a tube leading through two potassium iodide wash-bottles to the water pump used for evacuation. All connecting tubes were blackened over, and the sides of the cells covered with tin foil to exclude stray light.

A single fused-quartz cell (depth 10 cm., diameter 5 cm.) with plane ends was employed in certain experiments, primarily with the 313 $\mu\mu$ mercury line. It was used in conjunction with a "dark" cell of Suprax glass, and was joined up by a quartz–soda glass graded joint just as before. As will be seen, it gave rise to specific irregular effects.

Thermostat.—The reaction was carried out in an electrically heated thermostat, fitted with a 10-cm. crystal quartz window, and regulated in the usual fashion to within 0·005°. The majority of the work was done at 25°, 20° and 30° being used for temperature-coefficient measurements. The cells were supported in a copper frame which hung from an optical bench erected above the thermostat. The taps were above the water level, as were also the side connexions leading to the manometer outside the thermostat. The volumes of dead space between cell taps and manometer liquid were the same in the two cases; the volume outside the thermostat was only 1·5% of the total, and errors due to inequality of temperature were negligible. However, all connecting tubes outside the thermostat, save the capillary leads to the manometer, were lagged with cotton wool, and the thermostat itself was enclosed in a wooden cover.

Manometer, and Calculation of Reaction Rate.—The manometer with its connecting leads was of 1·15-mm. internal-diameter tubing. A tap at the base of the U permitted of the admission or withdrawal of the indicating strong sulphuric acid. The illuminated meniscus levels were measured by a cathetometer and extemporised reading microscope, mounted on a concrete pillar and placed in focus 4½″ from the manometer. The meniscus image was of high magnification, and measurements could be rapidly made. The reproducibility and accuracy of the readings (0·03 mm.) were satisfactory. Where height differences exceeding 16 mm. were involved, the cathetometer was used in conjunction with a scale behind the meniscus.

The volume of the cells and connecting tubes (V) was measured before the apparatus was sealed together. From a knowledge of Δp, the pressure increase, the degree to which the reaction had proceeded was calculated by the relation $\Delta p \, . \, V = \Delta n \, . \, RT$, from which figure, by introduction of the equation $2O_3 \longrightarrow 3O_2$ and the relation $N = 6{\cdot}07 \times 10^{23}$, the number of ozone molecules decomposed was obtained. A correction was applied for the slight volume change due to the movement of the manometer liquid.

Optical Train.—A quartz-mercury lamp was used, which burnt very constantly (Tirrill voltage regulator) at 4 amps. and 55 volts. Close up against the arc was placed a diaphragm with a 9-mm. circular aperture, the whole being outside the wooden cover surrounding the thermostat. The beam entered this cover through a suitable aperture (shutter), passed the light filter, and fell on a quartz lens (10 cm. focal length) placed immediately outside the window of the thermostat. The resultant convergent ray passed through the window, through the reaction vessel, and finally was brought to a focus on a surface thermopile contained in a water-tight case provided with a quartz window.

Filters.—The following were employed (transmissions in percentages) :

313 μμ. (i) Potassium chromate (0·2034 g./l.), 0·5 cm.; (ii) *p*-nitrosodimethylaniline (0·014 g./l.), 0·5 cm., contained between quartz plates. Two solutions of potassium chromate were used, the second from specially purified material. The figures below show the great importance of this purification.

λ, in μμ	303	313	365	405	436	546
Transmissions (*a*) ...	3	21	0	0·2	5·3	78·8
(*b*) ...	—	48·4	0	0·2	2	—

365 μμ. Corning Filter G. 586 A ; 3·6 mm.

λ, in μμ	313	365	405
Transmission	1	71·6	20

365 μμ. Corning Filter G. 586 AW ; 7·7 mm.

Passed 11·4% of 365 μμ ; no detectable trace of other lines.

420 μμ (*circa*). Corning Filter G. 552 PY; 4·2 mm.

λ, in μμ	365	405	436	546
Transmission	4	60	71·4	2

420 μμ (*circa*). Corning Filter G. 40 D; 8·24 mm.

λ, in μμ	405	436
Transmission	28·9	45·4

436 μμ. (i) Quinine sulphate in 2*N*-sulphuric acid (20 g./l.), 0·5 cm.; (ii) Victoria-blue (0·425 g./l.), 0·5 cm., made up between glass plates. These are preferable to quartz, as most of the short wave-length light, which assists photo-oxidation of the quinine sulphate by dissolved oxygen, is thereby cut out. Much use of Victoria-blue filters in this laboratory has shown them very liable to changes in extinction. Three different preparations gave the following results :

λ, in μμ	405	436	492
Transmissions (*a*)	4·3	30·7	—
(*b*)	0	47·5	5
(*c*)	1	49·4	—

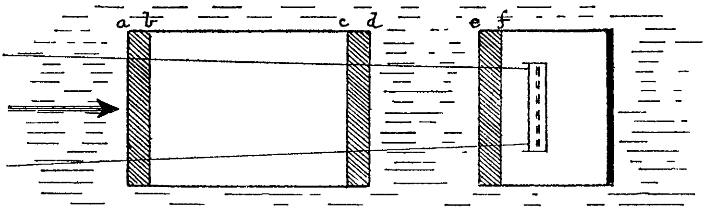
Thermopile and Energy Measurements.—The majority of the measurements were done with a 2-cm. Moll surface thermopile, of which the outer cone had been removed and the inner stepped down and blackened (Allmand and Beesley, J., 1930, 2701). As already stated, it was enclosed in a brass case provided with a quartz window, and could thus be immersed in the thermostat. Any zero correction was thereby eliminated, the *E.M.F.* in absence of incident light being definitely zero. The thermopile case was attached to a long rod, pivoting on a support mounted on the optical bench, the beam roughly focused on the thermopile surface by the aid of a small mirror, and the final adjustment made by means of a screw on the pivoted arm. When the thermopile was once thus set for maximum deflexion, the same readings were always reproduced if it were removed and replaced. The instrument was calibrated against a Hefner candle and also against some standard metal-filament lamps from the U.S.A. Bureau of Standards. Its sensitivity was $40{\cdot}3 \times 10^{-6}$ volt per H.K. at 1 metre. When in use, the *E.M.F.* was measured by a micro-potentiometer reading to 1×10^{-7} volt.

The actual measurements during an experiment were (i) reading with cell full of air or oxygen $= A$, (ii) reading with cell full of gaseous mixture $= B$; A was redetermined at the end of the experiment, and furnished a check on the constancy of the light source. The optical conditions of the experiment are shown diagrammatically in Fig. 1. There are six reflexion surfaces involved between the first face of the cell and the thermopile, and the contributions of two of these (c and f) to the absorbed light have been taken into account. If a, b, c, etc., represent the fractional transmissions of these same surfaces for the light beam, and x the fractional transmission of the layer of gas, we can calculate (neglecting absorption by glass and quartz plates) the total absorbed light to be

$$\frac{A-B}{cdef}\left\{1+\frac{B}{A}[(1-c)+(1-f)c^2d^2e^2]\right\}$$

The values of c, d, e, f were determined by the usual formula, using the appropriate refractive indices, and the correction was applied where necessary. This, of course, was primarily the case where the values of $x(B/A)$ were high (blue light and low chlorine concentration), when each of the two correction terms might amount to as much as 3—3·5%. With 365 μμ and 313 μμ, and with high chlorine pressures, the simpler formula

Fig. 1.



$$\text{Absorbed light} = (A-B)/cdef$$

could be used.

Course of an Experiment.

The lamp was allowed to burn for an hour, and then, with the light filters in position and the reaction system filled with air or oxygen, the thermopile *E.M.F.* was measured (reading A). The cell was darkened, evacuated by the water-pump, and filled with the reaction mixture. This operation was repeated a number of times, and a sample of gas taken for analysis. A sufficient time having elapsed for the setting up of thermal equilibrium, the manometer taps were closed, the gaseous mixture illuminated, and manometer readings immediately commenced. At the same time, the thermopile reading was again taken (B), this being repeated from time to time during the course of the experiment. Any change would denote an alteration either in light intensity or in chlorine concentration.

The pressure readings were made at intervals of a minute or longer, depending on the rate of reaction, and were plotted on a pressure–time graph. At the end of the experiment, whether carried through or not to the stage of complete decomposition, the light was cut off and the pressure readings were followed for some time longer until constant. The apparatus was then several times alternately evacuated by the water-pump and refilled with dry oxygen, and a final thermopile reading (A') taken.

The pressure changes observed during the course of a run were complex, and depended on the experimental conditions. They will first be described qualitatively for the case of a dilute ozone mixture (up to about 7% ozone) in glass vessels.

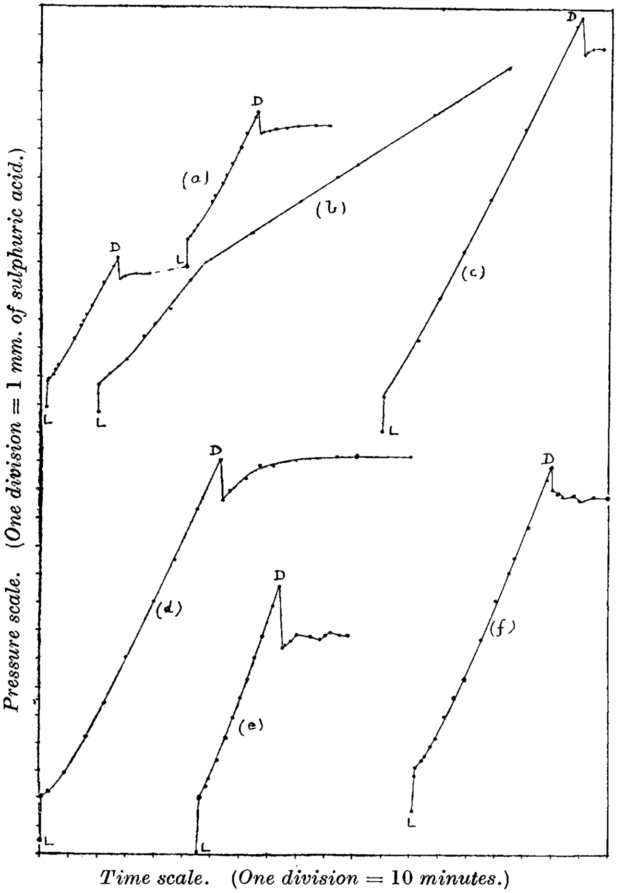
When the gas was first insolated, the pressure rapidly rose by an amount of the order of 1 mm. (of sulphuric acid). This rapid *initial rise* (Fig. 2) was normally immediately succeeded by a considerably lower rate of increase of pressure, which rose somewhat and soon became constant. The result is a curve showing a slight *induction period* (Fig. 2). The constant rate of pressure increase (*constant slope*, see Fig. 2) remained substantially the same until shortly before the stage of complete decomposition, whereupon the curve began to turn up rapidly (*final rise*, see Fig. 3). The cessation of reaction was sometimes very abrupt, the curve suddenly becoming horizontal, frequently after exhibiting a small depression; sometimes the flattening of the curve set in just before decomposition was complete and on other occasions the curve was irregular in this region. When the light was subsequently cut off, the pressure sharply dropped (*final fall*, Fig. 3) by an amount which was perhaps half of the initial rise, and remained constant.

If insolation were interrupted whilst appreciable amounts of ozone were still present, the pressure rapidly fell (*final fall*, Fig. 2) by an amount equal to the initial rise, and then increased again by a variable but usually considerably lesser amount, and slowly (*after-effect*, Fig. 2). The curve was frequently irregular at this stage. Re-insolation reproduced the same phenomena, the constant slope having the same value as previously.

When glass cells were used, the above phenomena were in general very reproducible (for instance, the values of the constant slopes under identical conditions varied by 4—5% only), with the exception that an unusually marked induction period was sometimes observed during the first experiment after the cells had been cut down, cleaned with chromic acid and distilled water, and re-erected.

The initial rise, for a given cell, was proportional to the rate of energy absorption and, for example, was about 1 mm. (of acid) per 100 microvolts absorbed in the case of the 10-cm. Suprax glass cell. The importance of the induction period varied from one experiment to another. It was particularly marked with mixtures low in chlorine and with 365 μμ light, a ray sufficiently absorbed even under these conditions to give an appreciable rate of reaction. Two related phenomena were noticed during such experiments, which will be referred to later. The transmission of the gaseous mixture at 365 μμ, measured by the thermopile, was found to increase during the first ten minutes or so of insolation, subsequently remaining constant. Simultaneously, marked formation of a mist, which gradually disappeared, was noticed to occur in the insolated gases.

Fig. 2.



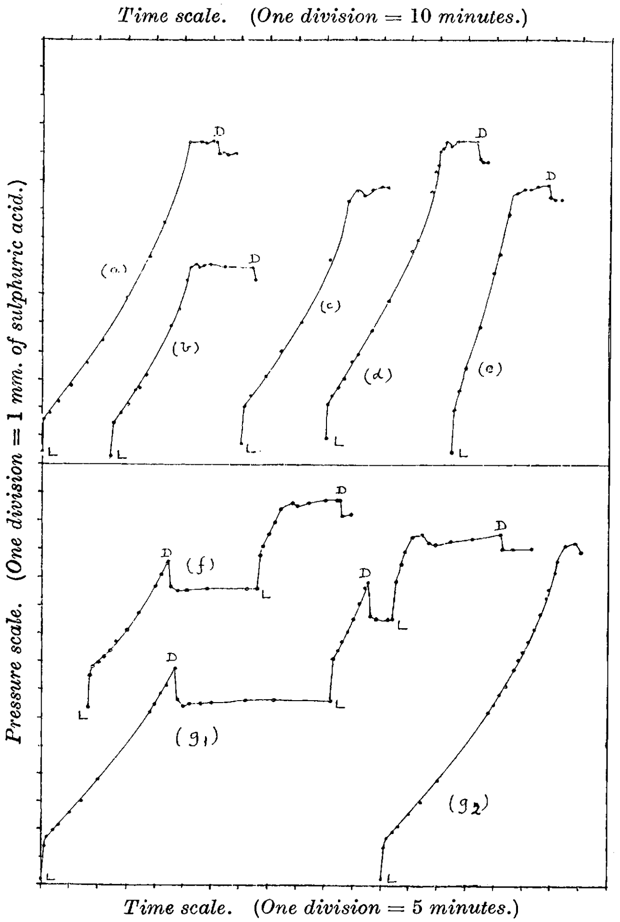
Time scale. (*One division* = 10 *minutes.*)

(*a*) *Expt.* 195—365 μμ; (*b*) *expt.* 21—365 μμ, *then* 420 μμ; (*c*) *expt.* 62—365 μμ; (*d*) *expt.* 30—365 μμ; (*e*) *expt.* 54—420 μμ; (*f*) *expt.* 133—365 μμ.

L = *light started.* D = *light cut off.*

The pressure changes attending the decomposition of the last traces of ozone were studied in detail in a few cases. If the light were cut off in the middle of the final rise, the normal final fall resulted, followed by no further change in the dark. On re-insolation, the original curve was continued. On one occasion, two such interruptions were made during the final rise; the three sets of light readings, allowance being made for the initial rise and final fall pressure changes and for the slight after-effect, could be plotted as a continuous curve (Fig. 3, g_1, g_2), indicating that the final rise is a photochemical effect.

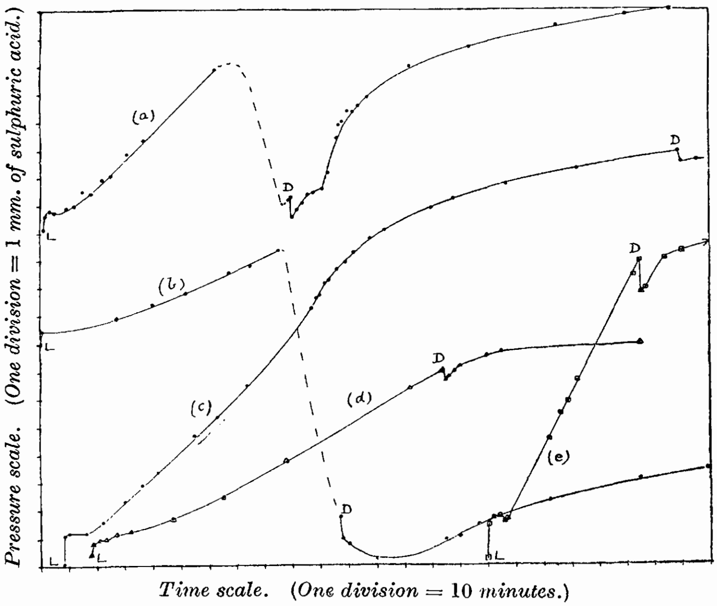
FIG. 3.



(*a*) *Expt.* 47—365 $\mu\mu$; (*b*) *expt.* 40—365 $\mu\mu$; (*c*) *expt.* 53—365 $\mu\mu$; (*d*) expt. 182—365 $\mu\mu$; (*e*) *expt.* 134—365 $\mu\mu$; (*f*) *expt.* 200—365 $\mu\mu$; (*g*) expt. 203—365 $\mu\mu$.

With the quartz cell, exceptional and unexpected phenomena were noticed. The dark reaction was sometimes considerable. Mist formation was unusually pronounced. The induction effects were very marked. Sometimes no perceptible pressure increase took place for some time after the initial rise (Fig. 4, *c*), or the pressure actually fell off (Fig. 4, *a*, *e*). The *p–t* curve was frequently irregular (Fig. 4, *a*), and sometimes, after normal behaviour at the start, the pressure would suddenly decrease (Fig. 4, *a*), even to figures below its initial value (Fig. 4, *b*). The end of the reaction was not abruptly apparent, as when working in glass. Instead, the slope of the *p–t* curve gradually became *less* as complete decomposition was approached, and sometimes this happened at an earlier stage (Fig. 4, *c*). Very large after-effects were noticed (Fig. 4, *d*, *e*), perhaps even continuing until all the ozone had been decomposed. In addition, the values of γ, calculated, as was usual, from the constant slope of the main *p–t* curve, were much lower than when working in glass; and the rate was not proportional to the intensity under conditions when this would have been the case in glass.

FIG. 4.



(*a*) *Expt.* 237—365 $\mu\mu$; (*b*) *expt.* 232—313 $\mu\mu$; (*c*) *expt.* 240—365 $\mu\mu$; (*d*) *expt.* 231—313 $\mu\mu$; (*e*) *expt.* 230—365 $\mu\mu$.

After the cell had been cut down, cleaned, re-erected, and used many times with chlorine–ozone mixtures, the results became more regular and reproducible. But the after-effects still remained large, and γ (calculated as above) low.

Results with Mixtures containing less than 7% of Ozone.

Effect of Intensity.—Using 365 $\mu\mu$ light, a number of experiments were carried out in the glass cells, the intensity being varied in a ratio of 2/1—3/1 by means of perforated zinc gauze screens, of which the transmissions were determined in each case by thermopile readings made on the cell filled with air. For mixtures containing $<7\%$ of ozone and at least 2—3% of chlorine, the constant slopes were proportional to the intensities. The results are in Table I, where the fraction of light absorbed is given by the thermopile readings $(A—B)/A$. With mixtures containing $<2—3\%$ of chlorine, this relation no longer holds, the velocity increasing less rapidly than the intensity (Table II).

TABLE I.

Depth of cell (cm.)...	10	10	10	10	5	5	5	5
Chlorine, %	45	12	4	—	29·6	29·6	3	3
Fraction of light absorbed	0·91	0·88	0·66	0·60	0·85	0·85	0·30	0·26
Ratio of intensities	2·32	2·21	2·32	2·32	2·69	2·69	2·29	2·40
Ratio of velocities	2·36	2·21	2·32	2·34	2·58	2·57	2·28	2·47

TABLE II.

Depth of cell (cm.)	10	10	10	5	5
Fraction of light absorbed	0·48	0·24	0·06	0·16	0·16
Ratio of intensities	2·40	2·24	2·20	2·33	2·33
Ratio of velocities	2·17	1·99	1·77	2·07	2·00
Depth of cell (cm.)	5	5	5	5	5
Fraction of light absorbed	0·10	0·10	0·08	0·06	0·06
Ratio of intensities	2·28	2·23	2·32	2·33	2·29
Ratio of velocities	1·88	1·77	1·92	1·77	2·14

Our intention had been to do similar experiments with blue light, using the 10-cm. Suprax cell; but by this time the latter had deteriorated too far, and measurements with the shorter " Geräteglas " cell were not undertaken, in consequence of the low velocities to be anticipated.

Measurements with the 420 $\mu\mu$ group of lines, as well as with 365 $\mu\mu$, were, however, carried out with the quartz cell. As already stated, the latter was usually associated with abnormal results. For example, in this matter of intensity, a mixture containing 4% of chlorine, and therefore absorbing about 0·7 of the incident 365 $\mu\mu$ light, did not obey the I_0 law. This was also the case in the other experiments. Table III contains the results.

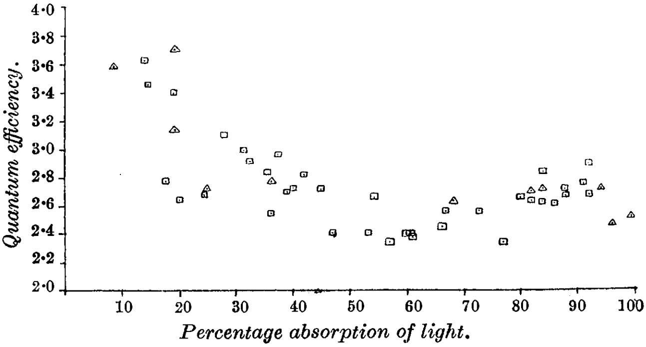
Effect of Chlorine Concentration.—Seven experiments were carried out in glass cells with 436 $\mu\mu$ light. The percentages of chlorine varied between 40 and 65, and the fractions of absorbed light between

TABLE III.

Wave-length, $\mu\mu$	365	365	365	420	420	420
Chlorine, %	—	4	1·2	39	29	25
Ratio of intensities	2·32	2·36	2·5	6·9	2·38	2·25
Ratio of velocities	1·97	1·85	1·83	4·89	2·08	1·74
Square root of velocity ratio	1·52	1·54	1·58	2·63	1·54	1·50

0·35 and 0·45 in the 10-cm., and between 0·20 and 0·31 in the 5-cm. cell; γ fluctuated between 1·92 and 2·39, the mean being 2·09. No dependence on $[Cl_2]$ was observable. Thirteen similar experiments, all in 10-cm. cells, were carried out with one or another of the 420 $\mu\mu$ filters. The chlorine percentages varied between 4 and 57, and those of absorbed light between 11·6 and 61·6; γ fell between the limits of 2·02 and 2·73, the mean being 2·40. Here again $[Cl_2]$ seemed to be without effect.

FIG. 5.



This was, however, not the case with 365 $\mu\mu$ light, with which the majority of the experiments were carried out (11 with 5-cm. cells, chlorine percentage 0·5—42, fraction of absorbed light 0·043—0·88; 37 with 10-cm. cells, chlorine percentage 0·7—45, fraction of absorbed light 0·14—0·91). The γ values obtained in these measurements are plotted in Fig. 5 against the percentage of incident light absorbed. In order to make the results with the 5-cm. (triangles) and 10-cm. (squares) cells more comparable with one another, the experimental figures for absorption in the 5-cm. cell have been recalculated on a 10-cm. basis. Down to about 55% absorption of light (roughly 2·5—3% of chlorine), γ is seen to vary between extreme limits of 2·32—2·90, the mean value of the figures obtained with the 10-cm. cell being 2·58, and with the 5-cm. cell 2·62. It is difficult to say whether the tendency to a minimum figure at about 50% absorption represents a real effect. We are inclined to think that it does not. No γ values below 2·47 were obtained with the 5-cm. cell, and in this case the lowest values were found at the highest and not at intermediate $[Cl_2]$ figures. Further, all the low figures given by the 10-cm. cell were observed at about the same time, relatively early in the work.

For $[Cl_2]$ values $<2\cdot5$—3% ($<50\%$ absorption in a 10-cm. cell), the curve definitely changes in direction, γ increasing as the absorption decreases, the maximum value actually observed being 3·71. It is significant that the $[Cl_2]$ figure below which this effect sets in is the same as that at which the I_0 law commences to break down.

The results given by the quartz cell are too irregular to be analysed in the above way. The actual figures obtained for γ, assuming that these can be calculated from the constant slopes, are given in the following table, in which, for each wave-length, the experiments are arranged in the order in which they were carried out. As already stated, experiments in the quartz cell became steadily more reproducible as time went on. In spite of this, they remained abnormal compared with those obtained in glass. Thus, the values for γ_{365} found at the end of the work, though considerably higher than those first measured, were still about 10—15% less than those shown in Fig. 5.

TABLE IV.

	313 $\mu\mu$.						
Absorption			Total in every case				
Quantum efficiency	2·36	2·32	2·0	2·67	2·66	2·62	
	365 $\mu\mu$.						
Percentage absorption	74	82·5	71	31	31	23	87
Quantum efficiency	1·63	1·55	1·68	2·10	1·92	1·77	2·3
Percentage absorption	62	56	73	85			
Quantum efficiency	2·2	2·33	2·3	2·23			
		420 $\mu\mu$.				436 $\mu\mu$.	
Percentage absorption	42	42	51	37·5		34	
Quantum efficiency	1·31	1·30	1·35	1·5		1·69	

Effect of Wave-length.—The average values of the figures recorded above, as found in glass vessels for conditions under which the I_0 relation holds, are 2·1 for 436 $\mu\mu$, 2·4 for 420 $\mu\mu$, and 2·6 for 365 $\mu\mu$. The figures suggest a dependence on frequency of the usual type, *i.e.*, an increase of γ with decreasing λ. This conclusion was confirmed by experiments with 365 $\mu\mu$ and 420 $\mu\mu$ light, in which the two different filters were used successively with the same gas mixture, and the constant slopes compared (Fig. 2). The values found for the ratio $\gamma_{365}/\gamma_{420}$ were, in eight such experiments, 1·12, 1·19, 1·19, 1·07, 1·04, 1·13, 1·07, and 1·06, giving a mean value of 1·11, compared with 1·08 from the preceding section. Two similar experiments with 313 $\mu\mu$ and 365 $\mu\mu$, carried out towards the end of the work with the quartz cell, when the latter was giving reproducible results, yielded 1·16 and 1·19 for $\gamma_{313}/\gamma_{365}$. We therefore feel justified in concluding that γ decreases with increasing λ, and in approximately the following fashion

$$\gamma_{313} : \gamma_{365} : \gamma_{420} : \gamma_{436} = 1 : 0{\cdot}84 : 0{\cdot}77 : 0{\cdot}67 \ (?).$$

The relative magnitudes of the respective quanta concerned are as 1 : 0·86 : 0·75 : 0·72.

Effect of Temperature.—These experiments were carried out in the 5-cm. glass cell on mixtures with 16·3% and upwards of chlorine. The value of the constant slope was first determined in the neighbourhood of 20°. The temperature of the thermostat was then raised to 30°, a similar measurement made, the bath cooled once more to 20°, and the first measurement repeated. The mean of the almost identical first and second readings at 20° was compared with the value for 30°. The incident intensity was maintained constant throughout. In one case (436 $\mu\mu$), it altered by about 10% when passing from 20° to 30°; for this reason, the 20° measurement was not repeated, but the intensity change was allowed for on the assumption of the I_0 relation. The results are in Table V.

TABLE V.

Wave-length.	Working temperatures.	Ratio of quantum efficiencies.	Temp. coeff. for 10°.
365 $\mu\mu$	20 —29·7°	0·986	0·985
	21 —30·1	0·970	0·967
420 $\mu\mu$	19·9—29·4	0·998	0·998
436 $\mu\mu$	20·3—29·5	1·021	1·023

We conclude that γ is independent of temperature within our experimental error over the wave-length range covered.

Part II of this work will contain the results of work with more concentrated ozone mixtures, and a discussion of the whole.

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