CCCLIX.—*The Photochemical Union of Hydrogen and Chlorine. Part I. The Effect of Light Intensity.*

By ARTHUR JOHN ALLMAND and EDWARD BEESLEY.

THE work described in Parts I and II of this series was carried out during the three sessions 1924—1927 inclusive, and a preliminary note has already been published (*Nature*, 1929, **123**, 164). The experiments recorded below arose out of the work of Baly and Barker (J., 1921, **119**, 653), according to whom the photochemical combination of hydrogen and chlorine proceeds at a rate proportional to a power of the intensity greater than unity. Only one case of a similar relation between velocity and intensity is recorded in the literature, *viz.*, the bleaching of aqueous solutions of certain fluorescing dyes in light (*e.g.*, Wood, *Phil. Mag.*, 1922, **43**, 757), and the conclusions of Baly and Barker were not in accord with the earlier work of Draper and of Bunsen and Roscoe. The results of (Mrs.) M. C. C. Chapman (J., 1924, **125**, 1521), which were in agreement with those of Draper over a range of intensity variation of 1 : 6, were published before our work was commenced. We nevertheless proceeded with our experiments, for reasons given below. During their course, papers were published by Marshall (*J. Physical Chem.*, 1925, **29**, 1453), working at low gas pressures, and using unfiltered light from a quartz–mercury lamp, and by Kornfeld and Müller (*Z. physikal. Chem.*, 1925, **117**, 242), using unfiltered light from metal-filament lamps. These investigators controlled their intensities by varying the distance of the light source and by the use of perforated metallic screens respectively. The extreme intensity ratios used were about 1 : 20 (M.) and 1 : 64 (K. and M.). In both cases, proportionality between intensity and velocity was found.

In spite of this further confirmation of the work of Draper, we present our results, as they constitute a more elaborate study of

the subject than has hitherto been made. Our scheme of work has included (i) experiments with monochromatic light; (ii) the quantitative measurement of the incident intensities; (iii) the use of more than one method of varying the intensity. Padoa and Vita (*Gazzetta*, 1926, **56**, 164) state that the velocity of the photo-reaction is greater in white light than in the equivalent dispersed spectral beam, a type of result in accordance with the statement of Baly and Barker (*loc. cit.*), and one which gives good reasons for experiments with monochromatic light.* Further, the relation between intensity and velocity has recently been found in some cases (Briers and Chapman, J., 1928, 1802; Allmand and Style, this vol., p. 606) to be a function of the intensity, which suggests that the intensities employed in work of this type should be measured. Finally, it seemed possible, if improbable, that the results of Baly and Barker, who varied their intensities by means of Nicol prisms, were due to their use of polarised light, and further experiments appeared desirable.

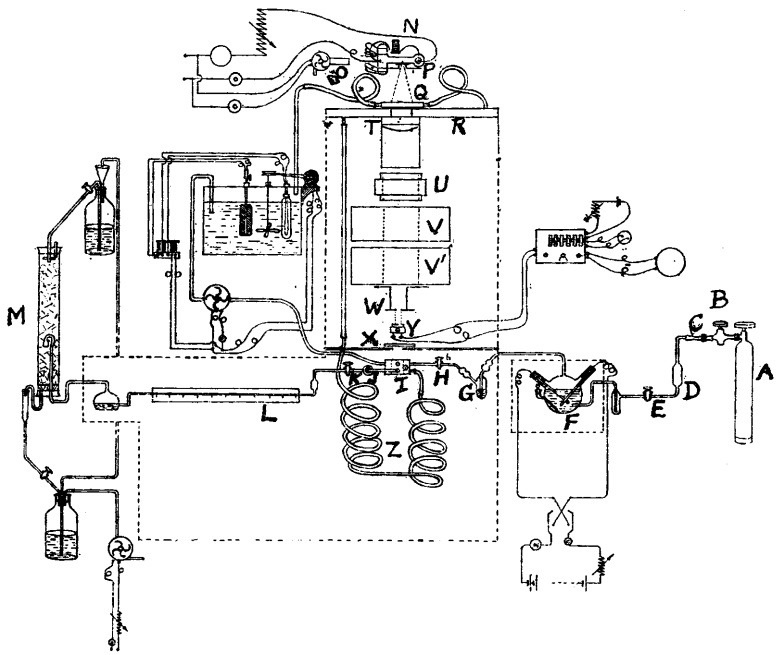
EXPERIMENTAL.

Reaction System.—The technique used was based on that of Bunsen and Roscoe, *i.e.*, we employed electrolytic gas, had a layer of water present in the photochemical cell, and followed the rate of reaction by observing the movement of a water meniscus in a horizontal capillary tube. Having gained much valuable information from extensive preliminary experiments with a glass cell (finally destroyed by explosion), we constructed the final apparatus, of which the lay-out is shown in Fig. 1. The chlorine cylinder A was connected with the rest of the apparatus by a silver-plated micrometer pressure-reducing valve B and a steel–glass joint C (*J. Amer. Chem. Soc.*, 1924, **46**, 287). Access of water vapour to B was prevented by the calcium chloride tube D. E, H, and K were mercury-sealed taps, lubricated with water. F was the electrolytic-gas generator, G a bubbler originally filled with boiled distilled water, and I the water-jacketed fused silica reaction vessel with optically flat and parallel ends, connected with the capillary tube L by way of K and a mercury-sealed quartz-to-soda-glass ground joint J. The liquid reservoir at the far end of L was connected with the tower M, down which percolated a slow stream of concentrated sodium carbonate solution for the absorption of chlorine. This solution was pumped up from time to time in the way indicated from the lower to the upper container.

* Their results differ from those of Baly and Barker when using white light of varying intensity.

Electrolytic-gas Generator.—This is shown in detail in Fig. 2. It was three-quarters filled with pure concentrated aqueous hydrochloric acid, and was operated with a maximum current of 0·75 amp. The electrodes were of Le Carbone graphite, the maximum *C. D.* being 0·023—0·024 amp./cm.^{2}. The pitch seals proved satisfactory, provided that the pitch had been extracted several times with boiling distilled water. Towards the end of the work, it was found that a more sensitive gas mixture could be obtained if the current used were very slowly alternated—once every 5 seconds. This is

FIG. 1.

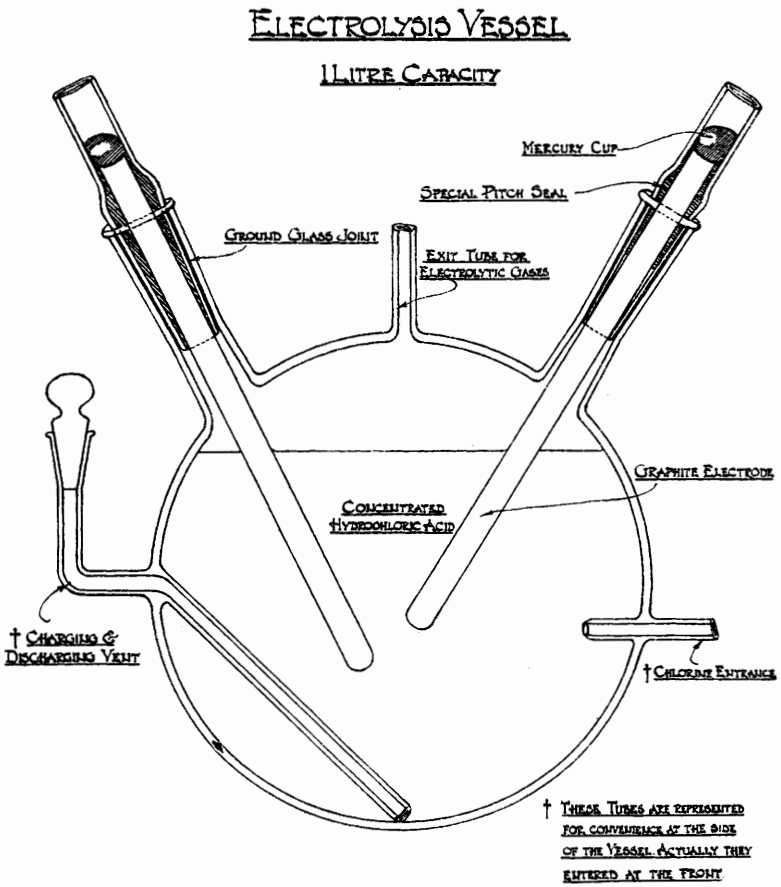


probably due to the oxygen formed during the anodic pulse being adsorbed by the electrode and reduced to water during the succeeding cathodic pulse.

Reaction Vessel.—This is shown in detail with dimensions in Fig. 3. It will be seen that the electrolytic gas entered through the aqueous layer which covered the bottom of the cell, a mercury-sealed quartz-to-soda-glass ground joint (not shown in Fig. 1) being interposed between the cell and tap H (Fig. 1). The cell itself was contained in a copper water-jacket, provided with suitable apertures for the two plane ends and for the gas entrance and exit tubes. The quartz–metal joints were sealed satisfactorily by means of pitch.

Capillary Indicating Tube.—The apparatus set up was provided with two such tubes, either of which could be connected with the reaction cell by means of a three-way tap. They were respectively of internal diameter 0·85 and 2·14 mm. In practice, the former (not shown in Fig. 1) was found to give untrustworthy readings

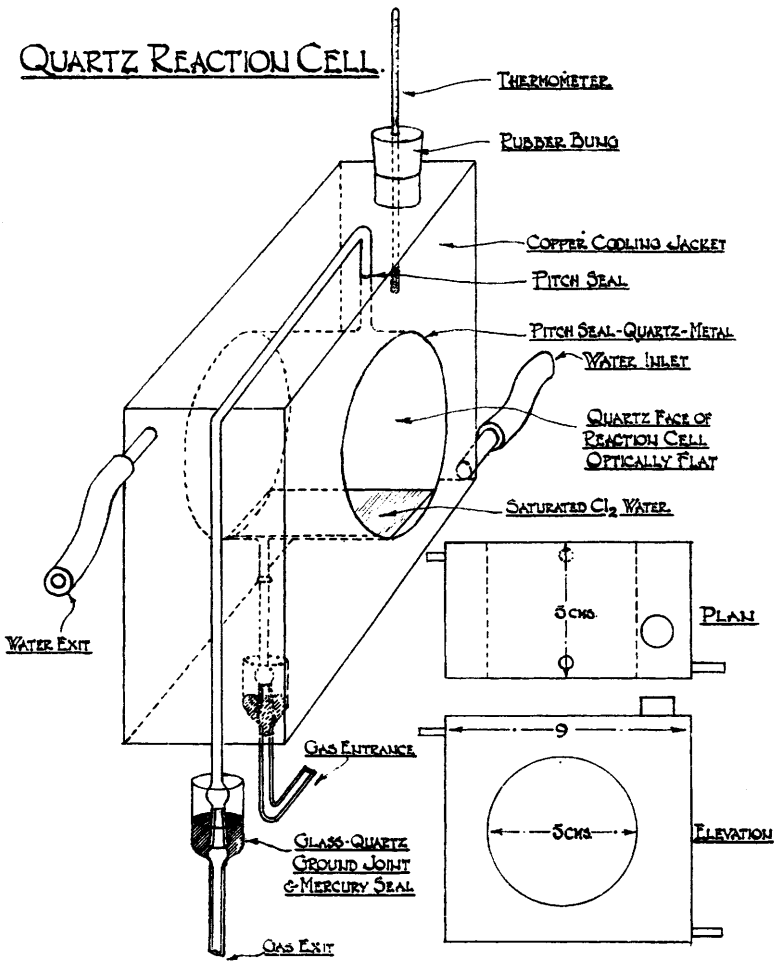
FIG. 2.



(although the preliminary experiments had not indicated this as likely) and only the latter was employed. Its horizontal length was 65 cm., of which the central 45 cm. were used for the readings, the standard procedure being to measure the time required for a movement of 10 cm. The calibration showed a maximum volume error, on lengths of 8·5 cm., not exceeding 3%. The liquid level in the reservoir supplying the indicating water thread was so arranged as

to be about 5 cm. below the capillary tube. This had the effects of minimising irregular movements of the meniscus due to capillary action and of preventing the inclusion of bubbles of gas in the capillary column. The scale was graduated in mm.

FIG. 3.



Optical Train.—The quartz–mercury lamp employed (N, Fig. 1) was of the atmospheric pressure type, and was cooled by the electric blower O. It was fed by a 110-volt D.C. generator, the voltage of which was kept to within $\pm$ 0·5 volt by means of a Tirrill regulator, and burned at a very constant load of 3·5 amps. at 78·5 volts. Immediately in front of the lamp was placed a thick copper screen P,

pierced by a 3 mm.-diameter hole opposite the centre of the arc. The light from what was practically a point source fell on to the water-cooled shutter Q and, when this was raised, passed through the aperture in the water-cooled screen R on to the quartz lens T (focal length for 579 μμ, 11·5 cm.; for 260 μμ, 10·6 cm.), which converted the divergent ray into a parallel beam of 8 cm. diameter. This successively passed the 5 cm. plane-parallel quartz water cell U, the filters, and the device for varying the light intensity, supported on stands V V′, finally falling on an adjustable iris diaphragm W, the aperture diameter of which could be varied between the limits of 40 and 1·5 mm. When measuring the incident intensity quantitatively, a Moll surface thermopile Y was placed on the far side of the diaphragm. When a reaction was being carried out, the beam leaving W passed through an aperture (provided with a shutter) in the partition X, and thus into the reaction cell. T, U, V V′, W and Y were mounted on an optical bench.

Precautions against External Light.—The gas generator was enclosed in two concentric light-tight boxes, and the electrolytic-gas delivery tube was coated successively with insulation tape and with black velvet. The reaction system and the optical train from T onwards were enclosed in a large "dark box," of three-ply wood, dead-blackened inside, provided with removable panels and shown by dotted lines in Fig. 1. Its front R facing the lamp was hollow, made of copper, and water-cooled. It was divided into two parts by the partition X, as ready access to the filters, etc., was necessary during the course of the experiments. The capillary tube L was observed through a red glass screen, illumination being provided from outside. All glass taps could be operated from without by means of "Meccano" chains and bevelled gears.

Maintenance of Constant Temperature.—Water was pumped from an external thermostat as shown (Fig. 1) through (*a*) the jacket of the reaction cell, (*b*) about 30 feet of coiled lead tubing Z inside the dark box, (*c*) the dark box front R, (*d*) the shutter Q, then returning to the thermostat. This was done for 4 hours before the start of any experiment; the stream was shut off during the actual readings. From H onwards, all glass connexions were made of thick-walled tubing in order to minimise the effects of any rapid local temperature variations. The temperature of the reaction cell was taken as that of the thermometer in its water jacket (Fig. 3).

Light Filters.—The filters used were as shown below. The front, separating and back-end plates of the composite filter cells were of optically flat quartz in all cases. The transmissions were measured by a quartz spectrograph, linear thermopile and Paschen galvanometer.

436 μμ. (*a*) 5 mm. 0·085% Victoria blue;
(*b*) 5 mm. 4% acid quinine sulphate.
Passed 48·5% of 436 μμ; no trace of other lines.

405 μμ. (*a*) 5 mm. 0·02% Diamant fuchsin;
(*b*) 5 mm. 0·2% quinine sulphate.
Passed 31·7% of 405 μμ; <1% of 436 μμ.

365 μμ. Corning Glass Filter G. 586 A W, 7·7 mm. thick.
Passed 11·45% of 365 μμ; no trace of other lines.

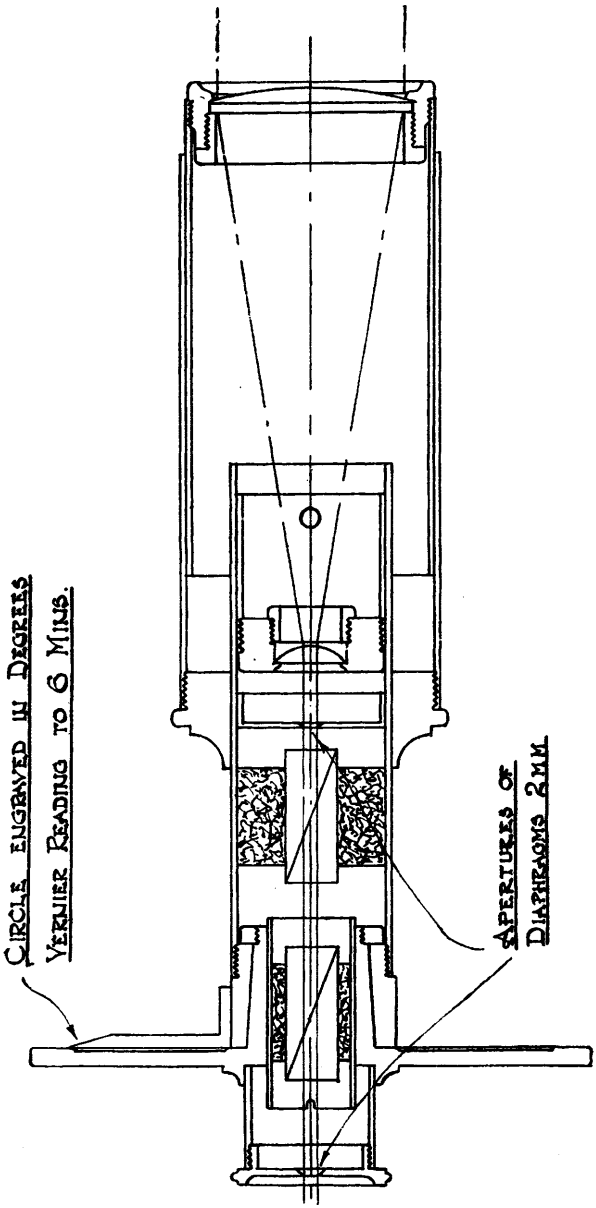
313 + 303 μμ. (*a*) 5 mm. 0·00376% *p*-nitrosodimethylaniline;
(*b*) 5 mm. 0·0486% potassium chromate.
Passed 22·5% of 313 μμ, 4·4% of 303 μμ, 80·5% of 546 μμ, and 86% of 579 μμ.

The figures quoted were measured in each case immediately after the comparative measurements of γ for their lines recorded in Part II. The solutions used in the liquid filters were changed from time to time, and the filter transmissions re-determined. The differences found were usually very small, except in the case of the 436 μμ filter (see Part II—experiments with 546 μμ filter and chlorine filter). Past experience in this laboratory has shown this filter to give very variable transmission values.

Variation of Light Intensity.—For the most important series of experiments, four wedges of neutral tint and of continuously varying density, made by Ilford, Limited, were employed. These consisted of a suspension of colloidal silver particles in gelatin, enclosed between optically flat glass plates about 6 inches in length, and made possible a measured intensity reduction to about 0·001 of the unweakened intensity. For this purpose, they were mounted on adjustable slides, and provided with scales so that the light beam could at will be passed through the wedge at a point of known density. Density–length data for white light were furnished by the makers. We recalibrated the wedges for monochromatic 436 μμ and 405 μμ radiation, using the spectrograph–thermopile–galvanometer combination. The curves obtained for the two wave-lengths differed slightly from one another and deviated very appreciably from the white light figures.

In the second method, the intensity variation was effected by crossed Nicol prisms. The instrument employed, designed and made by Adam Hilger, Limited, is shown in Fig. 4. The lenses were of quartz, and the resulting parallel beam of plane-polarised light was 3 cm. in diameter. Owing to the relatively low intensities furnished, the complete radiation of the quartz–mercury lamp was worked with. When in use, the instrument was placed outside the

FIG. 4.


CIRCLE ENGRAVED IN DEGREES
VERNIER READING TO 6 MINS.
APERTURES OF
DIAPHRAGMS 2 MM.

dark box, up against Q (Fig. 1), and the lamp with its shield P was placed as closely as possible; the lens T was removed, and the emergent beam, after passing the water cell U and the diaphragm W, fell directly on thermopile or reaction cell.

Finally, a number of experiments with intermittent monochromatic light were done, using a rotating disc with two adjustable open sectors in opposite quadrants. By this means, of course, a variation of the total energy incident over a finite time is effected, and not a true intensity variation. In actual use, the total rate of energy flux was varied over a range of 100 : 1. Measurements were also done on the effect of rate of rotation at constant sector aperture, using suitable gearing and a resistance-controlled motor.

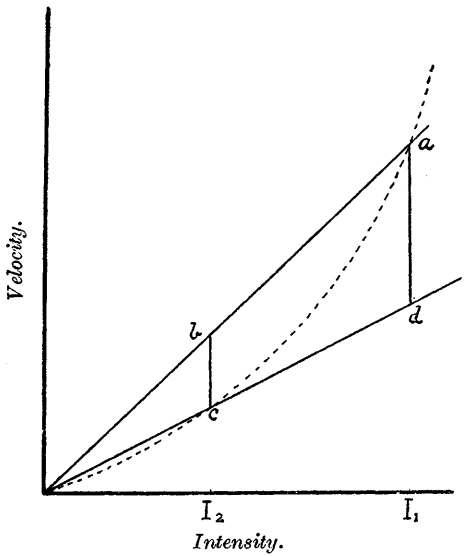
Measurement of Light Intensity.—As already indicated, this was done by a Moll surface thermopile. The diameter of the circular receiving surface was 2 cm. The outer cone of the instrument was removed, and the small inner cone was stepped down and dead-blackened, thus eliminating any uncertain factor bound up with reflexions from the latter. The *E.M.F.* furnished by this thermopile when irradiated by a Hefner candle at 1 m. under the usual standard conditions was 38×10^{-6} volt, measured by a Kelvin–Varley potentiometer and galvanometer. A comprehensive series of measurements showed incident intensity and *E.M.F.* to be closely proportional to one another up to a flux of at least 1·5 H.K. In carrying out an intensity measurement, the thermopile was placed in the path of the parallel light ray in front of the reaction cell (Fig. 1), and the aperture W adjusted until the circular beam just covered the thermopile junctions. The *E.M.F.* could be determined with an accuracy approaching 1×10^{-7} volt $\simeq 6 \times 10^{-8}$ g.-cal./cm.^{2}/sec.

Experimental Procedure.—The electrolyser was charged with concentrated A.R. hydrochloric acid, and thoroughly boiled distilled water at 70° was put into G, I, and L (Fig. 1). A slow stream of chlorine was then passed through the reaction system from A, and the whole of the apparatus intensely illuminated for 3 days. The chlorine stream was then shut off, the reaction system shielded from light, and electrolysis commenced. After 24 hours passage of gas, the sensitivity of the mixture was tested. In all the definitive experiments, it was found to be high at this stage, and the gas suitable for experiment. Taking the work as a whole, the sensitivity of the gas used varied considerably, corresponding to a variation in γ_{436} between, perhaps, 1000—250,000 molecules of chlorine per absorbed quantum. In all the experiments of which we quote the numerical data, γ was relatively high; there was no trace of induction period, and the Draper effect was marked.

When beams of large cross section and high intensity were used,

with a consequent rapid rate of reaction, the cooling effect of the water-jacket on the cell was unable to cope with the heat produced by the reaction and that thermally absorbed (an obvious Budde effect could be observed when the cell containing chlorine or an insensitive mixture was strongly illuminated), and the tendency of the actinometer gases to expand thermally partly counteracted the contraction due to reaction. This was, of course, particularly pronounced with sensitive gas mixtures, and put an upper limit to the rate of reaction which could be measured. In addition, however, and apart from this effect, it was found that sufficiently reproducible results could only be obtained with successive readings involving an intensity change (i) if the ratio between the velocities of the water index in such readings did not exceed about 4 : 1, and (ii) if the absolute values of movement of the index were kept within certain limits. In practice these conditions were satisfied by working as far as possible within the velocity limits of 1 cm./3 secs. and 1 cm./12 secs. In order to cover a large range of specific intensity variation, it was necessary from time to time to alter the aperture of W (Fig. 1) in a sense opposite to that of the changes in intensity, and thus to keep the total light flux falling on the cell, and consequently the total rate of reaction, within the same approximate limits.

FIG. 5.



Like other workers (*e.g.*, Porter, Bardwell, and Lind, *J. Amer. Chem. Soc.*, 1926, **48**, 2603), we found it difficult to avoid sudden changes in the sensitivity of the gas used. In experiments with constant intensity, these changes were relatively small, became less important the greater the sensitivity of the gaseous mixture, and could usually be traced to the entry of fresh gas from the electrolyser into the reaction cell during the course of an experiment.* During

* It is recognised that the introduction of fresh gas through the aqueous layer in the bottom of the cell represents a fault in design; this has been corrected in more recent experiments.

the preliminary work, however, when relatively insensitive gas mixtures were used, and considerable changes made in intensity between successive readings, another effect was encountered, which is best explained diagrammatically (Fig. 5). If the gas be insolated by an intensity I_1, and a velocity measurement taken a little later, a value corresponding to point a is obtained. If the intensity be now reduced to I_2, and a reading immediately taken, it will correspond to b, lying on a straight line drawn from a to the origin. This velocity, however, steadily falls off, and, after a certain time, attains a constant value corresponding to c. If now the intensity be altered again to I_1, and the velocity at once measured, it will correspond to d, but will immediately commence to rise, finally becoming constant at a value corresponding to a. Similar behaviour is observed if the lower intensity be used first—the apparently definitive points on the curve are a and c. As the figure indicates, this drift in the readings will become less obvious the smaller the ratio of the two intensities, and it was also found to decrease with increased sensitivity of the gas mixture. Thus, with a gas of $\gamma_{436} = 2500$ (molecules of chlorine) and an intensity ratio of 10 : 1, there was a noticeable fall in velocity at the lower intensity after 30 secs. With a gas of $\gamma = 5000$, no such result could be detected after one minute, but appeared at once when the intensity ratio was changed to 100 : 1.

This phenomenon is, we think, capable of a simple explanation. Insensitive gases, such as gave the effect, will contain traces of some inhibitor, which are gradually destroyed under the action of light. The volume of gas actually under insolation in the reaction vessel was surrounded by a volume (usually larger) of unilluminated gas. During insolation, therefore, there must have been a difference in inhibitor concentration between the gas in the light path and the gas outside the beam, a constant influx of inhibitor into the illuminated volume by diffusion and convection, and the gradual setting up of a stationary concentration of inhibitor inside the beam, which would be lower the higher the light intensity. The result would be a drift in velocity as found experimentally, and a dependence of the sensitivity of the gas *actually under irradiation* on the light intensity. We further think that the same phenomenon may account for the experimental results of Baly and Barker. Like us, they also used a beam which only filled a fraction of the cross-section of their cell, and the type of intensity–velocity curve they obtained (broken line in Fig. 5) would qualitatively be the logical outcome of our observations. Their description of the gradual drift in velocity on illumination, and the effect of the length of time elapsing between successive insolations is consistent with the view put forward here. Their light beam entered vertically through the

upper surface of their cell, and they mention that their experiments were affected by the liberation of oxygen from the chlorine water layer on the bottom of the vessel.

Results and Discussion.

In order to obtain the true relation between velocity and intensity under our conditions of work, it was necessary, then, (i) to take into account small arbitrary sensitivity changes arising from the introduction of fresh gas into the cell, (ii) to keep the velocity of the water index in the capillary tube within certain limits, (iii) to avoid large changes in intensity between successive readings [even when simultaneously altering the cross-section of the beam in accordance with (ii)], and (iv) to use a sensitive gas mixture. These conditions were fulfilled in the following manner.

(i). When comparing the effects of two intensities A and B, some 8—12 sets of readings A–B–A′ were taken, the readings of any set being made in rapid succession, and fresh gas being introduced into the cell when required between successive sets of readings and not between the separate readings of any one set. If the difference between A and A′ in any given set were negligible, it was assumed that the gas sensitivity had remained unchanged and the mean value of the velocity ratios A/B found in the different sets of readings was taken as characteristic of the intensity ratio. Examples are contained in Table I, which gives, first, an average specimen of data, followed by readings given by a mixture of particularly constant sensitivity and by a mixture in which a quite exceptional change in sensitivity took place half-way through the series of observations. These data were obtained with monochromatic 436 $\mu\mu$ light, the intensity being varied by neutral wedges.

TABLE I.

Relative intensities and their ratios.	Times (secs.) required for the meniscus to traverse 1 cm. of capillary, and their ratios.										Average times, and their ratios.
0·593	4·23	4·20	4·24	4·23	4·10	4·00	4·21	4·50	4·48	4·32	4·25
0·366	6·45	6·39	6·45	6·42	6·20	6·10	6·38	6·83	6·79	6·53	6·46
1·62	1·52	1·52	1·52	1·52	1·51	1·52	1·52	1·52	1·52	1·51	1·52
0·366	6·53	6·53	6·45	6·30	6·42	6·31	6·36	6·38			6·41
0·244	9·90	9·96	9·89	9·58	9·81	9·63	9·75	9·78			9·79
1·50	1·52	1·53	1·53	1·52	1·53	1·53	1·53	1·53			1·53
0·0425	13·40	13·35	12·58	12·32	8·98	9·62	10·40	10·22	10·43	10·63	11·19
0·0199	25·80	26·00	24·60	22·82	17·62	19·02	20·50	20·50	21·02	21·16	21·90
2·14	1·93	1·95	1·96	1·85	1·96	1·98	1·97	2·01	2·02	1·99	1·96

(ii). In the great majority of the measurements, the velocity of the water meniscus was kept between the limits already mentioned, *viz.*, 0·33—0·083 cm./sec. When working with very low intensities, as in the third example in the above table, this was not always

practicable, and it will be seen that, in the case referred to, the velocity ratios found for the two intensities were by no means as constant as in the first two examples.

(iii). Except very occasionally, the ratios of the actual intensities used in successive readings did not exceed the value 2 : 1. A ratio of 3 : 1 was never exceeded.

(iv). γ_{436} for the gas used was never allowed to fall below the order of 10^5 (molecules of chlorine).

The results of such pairs of measurements showed a departure from proportionality between velocity and intensity never exceeding 10%, *whatever the values of the intensities used* (see successive values of ratios in the last lines of Tables II and III).

It will be clear that the actual velocities observed in any one complete series of measurements are not directly comparable with one another for two reasons, *viz.*, alterations in the sensitivity of the gaseous mixture, and alterations in the cross-section of the light-beam. Our results indicate that the relation between velocity and intensity is independent of the sensitivity of the gas when, as in our case, relatively sensitive mixtures are used. Further, a detailed inspection of the experimental data showed that any changes in sensitivity during the course of such a complete series of measurements were relatively small: the increases and decreases observed largely counterbalanced one another. In the matter of the beam area, it was usually necessary to increase this three or four times during measurements covering a large range of decreasing intensities, and we have every reason for thinking that the total light flux into the cell was proportional to the cross-section of the beam. Intensity and beam area were never altered simultaneously, so that there was always a connecting link between successive sets of measurements carried out with different beam areas. In these circumstances, it is possible to transform the observed relative velocities into what they would have been if beam area and gas sensitivity had remained constant throughout the whole series of measurements, and thus render them comparable with one another. Thus, let a, b, c, d, e, f be a series of decreasing intensities; α, β, γ a series of increasing beam areas; $V_{a\alpha}$, $V_{b\alpha}$, $V_{c\alpha}$ mean velocities observed with the beam area α, $V_{c\beta}$, $V_{d\beta}$, $V_{e\beta}$ with beam area β, and $V_{e\gamma}$, $V_{f\gamma}$ with beam area γ. Then comparable velocities for this set of intensities will be as follows:

Intensity	a	b	c	d	e	f
Velocity	$V_{a\alpha}$	$V_{b\alpha}$	$V_{c\alpha}$	$V_{d\beta}\times\frac{V_{c\alpha}}{V_{c\beta}}$	$V_{e\beta}\times\frac{V_{c\alpha}}{V_{c\beta}}$	$V_{f\gamma}\times\frac{V_{e\beta}}{V_{e\gamma}}\times\frac{V_{c\alpha}}{V_{c\beta}}$

Our experimental data have all been recalculated in this manner. Unit intensity in each series is arbitrarily defined as the intensity of

the unweakened light, *i.e.*, working with zero contact density in the neutral wedge experiments, with zero angle between the two prisms in the measurements with the crossed Nicols, and with maximum aperture in the measurements with intermittent light (in this case unit intensity representing the maximum possible average intensity). Further, in each series, the velocity for the maximum intensity *actually used* has been arbitrarily given the same figure as this intensity, *i.e.*, V_{aa} has been put equal to a. For this intensity then, the ratio velocity/intensity is unity. The following tables contain the results.

TABLE II.

Neutral wedge. 405 μμ. Maximum incident intensity $2{\cdot}42 \times 10^{-6}$ g.-cal./cm.^{2}/sec. γ about 200,000 (molecules of chlorine).

Contact density	0·099*	0·275	0·452	0·629	0·805	0·979*	0·984*
Relative intensity ...	0·796	0·531	0·353	0·235	0·157	0·105	0·104
Relative velocity ...	0·796	0·499	0·337	0·217	0·143	0·105	0·104
Velocity/intensity ...	1·00	0·94	0·95	0·92	0·91	1·00	1·00
Contact density	1·152	1·328	1·503	1·679	1·855*	2·110	2·372
Relative intensity ...	0·0705	0·0470	0·0314	0·0209	0·0140	0·0078	0·0043
Relative velocity ...	0·0659	0·0441	0·0280	0·0203	0·0135	0·0074	0·0040
Velocity/intensity ...	0·93	0·94	0·89	0·97	0·96	0·95	0·93

TABLE III.

Neutral wedge. 436 μμ. Maximum incident intensity $5{\cdot}85 \times 10^{-6}$ g.-cal./cm.^{2}/sec. γ about 120,000 (molecules of chlorine).

Contact density	0·052*	0·088*	0·227*	0·436	0·612	0·789	1·113
Relative intensity ...	0·887	0·817	0·593	0·366	0·244	0·163	0·0771
Relative velocity ...	0·887	0·827	0·592	0·389	0·255	0·177	0·0827
Velocity/intensity ...	1·00	1·01	1·00	1·06	1·05	1·09	1·07
Contact density	1·302	1·635	1·781*	1·991	2·182	2·372	2·702
Relative intensity ...	0·0499	0·0232	0·0166	0·0102	0·0066	0·0043	0·0020
Relative velocity ...	0·0577	0·0258	0·0191	0·0115	0·0072	0·0046	0·0023
Velocity/intensity ...	1·16	1·11	1·15	1·13	1·09	1·07	1·15

TABLE IV.

Crossed Nicol combination. Total light of lamp. Maximum incident intensity $0{\cdot}46 \times 10^{-6}$ g.-cal./cm.^{2}/sec. Average γ for absorbed light approximately as in Table III.

Angle of crossed Nicols	0°	20°	30°	40°	50°	60°
Relative intensity.....	1·000	0·883	0·750	0·587	0·413	0·250
Relative velocity	1·000	0·876	0·745	0·583	0·404	0·248
Velocity/intensity.....	1·00	0·99	0·99	0·99	0·98	0·99

TABLE V.

Rotating sector. 313 μμ + 303 μμ. Maximum true intensity $3{\cdot}7 \times 10^{-7}$ g.-cal./cm.^{2}/sec.

Relative average intensity	1·000	0·794	0·501	0·316	0·100
Relative velocity	1·000	0·793	0·508	0·307	0·100
Velocity/average intensity	1·00	1·00	1·01	0·98	1·00

TABLE VI.

Rotating sector. 365 μμ. Maximum true intensity $1{\cdot}1 \times 10^{-6}$ g.-cal./cm.^{2}/sec.

Relative average intensity	1·000	0·794	0·631	0·501	0·316	0·199	0·100	0·010
Relative velocity ...	1·000	0·790	0·645	0·503	0·318	0·196	0·101	0·010
Velocity/average intensity	1·00	0·99	1·02	1·00	1·01	0·98	1·01	1·00

TABLE VII.

Rotating sector. 405 μμ. Maximum true intensity $6{\cdot}2 \times 10^{-7}$ g.-cal./cm.^{2}/sec.

Relative average intensity ...	1·000	0·794	0·631	0·316	0·199	0·100
Relative velocity	1·000	0·789	0·626	0·311	0·199	0·098
Velocity/average intensity ...	1·00	0·99	0·99	0·98	1·00	0·98

TABLE VIII.

Rotating sector. 436 μμ. Maximum true intensity $2{\cdot}7 \times 10^{-6}$ g.-cal./cm.^{2}/sec.

Relative average intensity	1·000	0·794	0·631	0·501	0·316	0·199	0·100	0·010
Relative velocity	1·000	0·791	0·628	0·507	0·317	0·196	0·0991	0·0098
Velocity/average intensity	1·00	1·00	1·00	1·01	1·00	0·98	0·99	0·98

The maximum average intensities, in the intermittent light experiments, when the opposed sectors were fully open, were half of the values quoted in Tables V—VIII. No estimates for quantum efficiency can be given for these experiments, as the cross-sections of the light beams used were not measured.

As mentioned earlier, experiments with intermittent light were also done in which the sector opening was maintained constant whilst the rate of rotation was altered. No variation in velocity could be detected as the number of interruptions per minute was progressively lowered from 2600 to 75. At this stage the Draper effect became appreciable at each separate exposure. The meniscus began to move jerkily, and observations at still lower rates of rotation proved impracticable.

We think that the results show conclusively that the velocity of the reaction under the experimental conditions is directly proportional to the intensity of the incident light. It is true that the ratios in the last line of Table III exhibit a slight tendency to drift towards lower values as the intensity is raised. Some of Mrs. Chapman's figures (*loc. cit.*) show a similar trend. This is the opposite effect to that observed by Baly and Barker, and it has been suggested by Chapman (*Trans. Faraday Soc.*, 1926, **21**, 551) that such behaviour might perhaps be shown by gases completely free from oxygen, in

which there would be a greater tendency for the " catalyst " molecule (chlorine atoms in the Nernst chain) to disappear from the system by intercombination. After due consideration, we suggest that the drift referred to is due rather to experimental error arising from the use of the neutral wedges. Apart from any error in calibration, their setting was liable to be least accurate when the light beam was passing through them near their ends, *i.e.*, at points of highest and lowest optical density. We have denoted by an asterisk in Tables II and III the density readings which for this reason are possibly open to suspicion. If they are not taken into account, it will be seen that the concordance in both tables is far better, and that the " drift " shown in Table III largely disappears. A further argument in favour of some such explanation is the fact that nothing of the sort was found with 405 μμ light.

We have already stated our views as to the probable cause of the experimental results of Baly and Barker, and it is further clear that the I_0 rule holds for linearly polarised complex light in the same way as for unpolarised monochromatic light.

The results with intermittent light were as anticipated, and in concordance with those found for continuous insolation.

Summary.

1. The effect of the light intensity on the rate of photochemical combination of hydrogen and chlorine has been investigated, quantitatively measured intensities being used.

2. With monochromatic light of wave-lengths 405 μμ and 436 μμ, the rate was found proportional to the intensity over measured intensity ratios of about 180 : 1 and 440 : 1 respectively.

3. With plane-polarised complex light, the same relation held over a measured intensity ratio of 4 : 1.

4. An explanation is offered of the divergent results obtained earlier by Baly and Barker.

5. Using intermittent monochromatic light of wave-lengths 313 + 303 μμ, 365 μμ, 405 μμ and 436 μμ, and of quantitatively measured intensity, the rate of reaction was found proportional to the average light intensity, and independent, within the limits employed, of the rate of intermission.

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