CCCLX.—*The Photochemical Union of Hydrogen and Chlorine. Part II. The Effect of Wave-length. Measurements with Filtered Light.*

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THE work recorded in this paper is chiefly concerned with the relative quantum sensitivity of the reaction in moist gases as a function of wave-length. In view of current theories on the mechanism of the reaction, our measurements with the 546 $\mu\mu$ mercury line have an added interest. We have also incidentally made a determination of the relative effect of temperature on the quantum sensitivities at certain wave-lengths, and have done comparative experiments on the effect of simultaneous action of two different monochromatic rays.

A summary of our present scanty knowledge of these matters must first be given. It has long been known that the union of hydrogen and chlorine under ordinary experimental conditions takes place with increasing difficulty as the visible spectrum is passed through from the violet towards the red, and that it eventually stops, or apparently does so. Attempts have been made to determine the limiting wave-length at which, in practice, the reaction ceases, but these are rendered difficult by the rapid fall in extinction coefficient of chlorine with increasing wave-length. Coehn and Jung (*Z. physikal. Chem.*, 1924, **110**, 705) claimed to have found such a threshold frequency at 540 $\mu\mu$, and Taylor (*Phil. Mag.*, 1925, **49**, 1165) at 490 $\mu\mu$, but their respective conclusions were contested by Bowen (*ibid.*, **50**, 879), who pointed out that, owing to the low absorption in this region just referred to, their experimental results could be explained in quite a different way. According to Weigert and Nicolai (*Trans. Faraday Soc.*, 1926, **21**, 581), the threshold is about 590 $\mu\mu$, or just at the origin of the violet absorption band of chlorine. In a later paper (*ibid.*, 1927, **23**, 583), Taylor and Elliott interpret their experiments on the assumption that light down as far as 550 $\mu\mu$ is active, whilst Padoa and Butironi (*Rend. R. Accad. Lincei*, 1916, **25**, ii, 215) and Lind and Livingston (*J. Amer. Chem. Soc.*, 1930, **52**, 593) have published temperature-coefficient measurements in the 530—550 $\mu\mu$ region. The whole subject has acquired renewed interest as a result of the well-known views of Franck (*Trans. Faraday Soc.*, 1926, **21**, 536), according to which the absorption by a chlorine molecule of light of $\lambda < 4785$ Å. will necessarily cause immediate dissociation of the molecule to atoms, whatever the other experimental conditions, this effect extending down to 492—493 $\mu\mu$ if the gas pressure is sufficiently high. Beyond this limit, only molecules already containing an exceptional amount of internal energy will dissociate on absorption of a quantum. This conclusion definitely points to an atomic chain mechanism for the hydrogen–chlorine reaction, and some authors (*e.g.*, Cathala, *J. Chim. physique*, 1928, **25**, 182) assume as a consequence that the reaction must have a threshold at 492—493 $\mu\mu$, in agreement with the earlier paper of Taylor.

Although certain measurements of γ for the reaction have been reported from time to time, very little experimental work has been done on its dependence on wave-length. The results of Taylor and Elliott (*loc. cit.*) in complex visible light are explained by them on the two assumptions (i) that the rate of reaction between 350—550 $\mu\mu$ is proportional to the intensity (with which our own work is in agreement) and (ii) that the rate of reaction between the same limits is proportional to the absorbed energy, independently of the wave-length of the light, which means that γ must increase with frequency. Weigert and Nicolai (*loc. cit.*, p. 582) and Thon (*Fortschr. Chem.*, 1926, **18**, Heft 11) have come to the same conclusion. Finally, there is the work of Heymer (*Diss.*, Göttingen, 1927), who found values of $0{\cdot}75 \times 10^4$ for 436 $\mu\mu$, and for 254—260 $\mu\mu$, under otherwise identical conditions, $0{\cdot}2$—$0{\cdot}7 \times 10^4$, a result in disagreement with those just mentioned.

With regard to the temperature coefficient of the reaction, Padoa and Butironi (*loc. cit.*) give the following data:

Light.	White.	Green.	Blue.	Violet.	Ultra-violet.
Wave-length, $\mu\mu$	—	550—530	490—470	460—440	400—350
Temp. coeff.	1·29	1·50	1·31	1·21	1·17

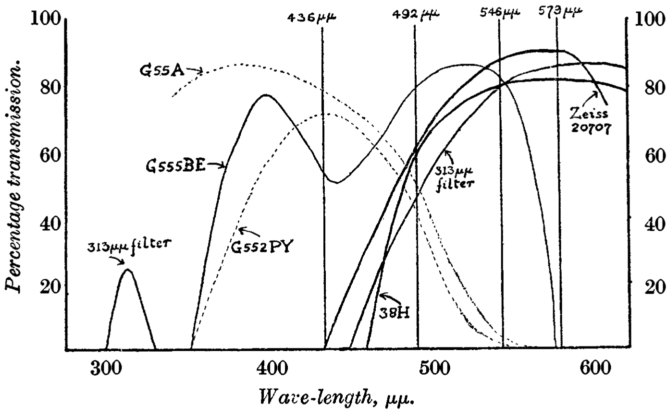
These figures, which show a marked dependence on λ, refer to the effect of temperature on the velocities observed at constant incident intensity, and it has been suggested by Wulf (*Proc. Amer. Acad. Sci.*, 1930, **16**, 27), amongst others, that they may to a great extent simply be due to increased absorption at the higher temperatures, and that the temperature coefficient referred to the same number of absorbed quanta may be smaller and less dependent on λ. Lower figures have, in fact, been found by Porter, Bardwell, and Lind (*J. Amer. Chem. Soc.*, 1926, **48**, 2603) and by Lind and Livingston (*loc. cit.*), the latter authors, when using white and green light, obtaining some evidence of the effect of wave-length claimed by Padoa and Butironi.

Finally, in the matter of the effect of complex as compared with monochromatic light, there are the experiments of Padoa and Vita (*Gazzetta*, 1926, **56**, 164), who found the rate of reaction to be considerably greater in white light than in the equivalent dispersed spectrum. The quoted ratio between the velocities is 1·56 : 1·0. This curious result would accord with a dependence of velocity on a power of the intensity greater than one. But their results for white light, like those of most other workers, point to proportionality between intensity and velocity.

Experimental.

The apparatus and method of work employed have been described in Part I. Any essential further details will be mentioned in their place.

Fig. 1.



In addition to the filters already described, two others were brought into use, compounded as follows.

(1) 546 μμ. Made up of four components :

(*a*) Corning glass filter—38 H. Noviol—3·5 mm. thick
(*b*) Corning glass filter—G. 555 B E—4·3 mm. thick
(*c*) Zeiss yellow filter—Batch 20707—3 mm. thick
(*d*) (i) 5 mm. 0·00376% *p*-nitrosodimethylaniline } in
(ii) 5 mm. 0·0486% potassium chromate } glass

[Note. (*d*) is identical with the filter for 313 μμ + 303 μμ described in Part I, except that glass plates are substituted for quartz.]

The transmissions of the different components * are shown in Fig. 1. The compound filter passes 49% of incident 546 μμ light, and no detectable trace of other mercury lines. In order, however, to make quite certain that the effect observed when using this

* The data plotted for the 313 μμ + 303 μμ filter are those obtained using a *quartz* cell. The transmission in the ultra-violet region will be considerably less in the present case.

filter was actually due to the 546 $\mu\mu$ line, and not to traces of the 313 $\mu\mu$ and the weak 492 $\mu\mu$ line, an experiment was done in which were superadded two additional Corning glass filters, of which the transmission curves are shown by dotted lines. The reaction was completely stopped.

(2) *Short ultra-violet* (average wave-length about 260 $\mu\mu$). A 5-cm. plane-parallel quartz cell containing chlorine at one atmosphere pressure, with transmission

248 $\mu\mu$	254 $\mu\mu$	265 $\mu\mu$	405 $\mu\mu$	436 $\mu\mu$	546 $\mu\mu$	579 $\mu\mu$
60%	63%	42%	14·5%	40%	84%	87·5%

The general scheme of work adopted for comparing the effects of different wave-lengths was similar to that used when comparing different intensities (Part I). A succession of some 10—20 velocity readings was taken with filter A and filter B alternately placed in the parallel light beam, between water cell and iris diaphragm (Part I, Fig. 1). When two successive readings with filter A showed no appreciable difference from one another, indicating that the sensitivity had remained constant over the time required for the sequence A–B–A, the average value for the A readings was compared with the reading for B. The mean of a number of such ratios, which agreed well amongst themselves, was taken as the final figure derived from the series of readings. When the sensitivity proved constant over the whole series, an alternative and simpler procedure was to compare the arithmetic mean of an equal number of A and of B readings. Several such series were done; the results were concordant. Having thus obtained an A/B ratio, similar measurements were carried out with filters B and C, B and D, etc., and thus a set of relative velocities was obtained covering all the filters used, comparable with one another on the assumption that the relative values of γ for different wave-lengths are independent of small changes in the sensitivity of the gas. The relative numbers of quanta absorbed by the gas when the different filters were in use were calculated from (i) the spectral energy distribution in the radiation of the quartz–mercury lamp (*J. Physical Chem.*, 1925, **29**, 713; 1928, **32**, 861); (ii) the spectral transmission of the filters concerned; (iii) the absorption coefficient data for chlorine (von Halban and Siedentopf, *Z. physikal. Chem.*, 1922, **103**, 71). Corrections were applied for the change with wave-length of the reflexion losses at the front face of the cell and at the water filter. Comparison between the relative velocities and relative numbers of absorbed quanta furnished values of relative quantum efficiencies.

Simultaneous Effect of Two Monochromatic Rays.—These measurements are taken first as, besides their intrinsic interest, they have a bearing on experiments carried out with the chlorine gas filter and the filter for 313 $\mu\mu$ light, both of which reduce mercury arc radiation to light which is still far from monochromatic. In this work, the reaction cell I (Part I, Fig. 1) was insolated through opposite ends by two filtered monochromatic rays, the one (A) passing as shown in the figure, and the other (B) coming from a second quartz–mercury lamp placed outside the dark box, and entering the latter through a special aperture cut in the wall. The lens for rendering the light parallel and the filter were, as before, inside the dark box, and matters were so arranged that the two horizontal beams entered the cell at the same height. A set of readings was taken with A, B, and A + B acting in succession. The observed velocities in cm./sec. are shown in Table I. The variations between the figures quoted for any one ray are partly due to fluctuations in gas sensitivity, and partly to changes in incident intensity.

TABLE I.

	(a)							
A	0·0795	0·077	0·074	0·074	0·169	0·179	0·328	0·285
B	0·060	0·080	0·097	0·093	0·240	0·254	0·235	0·205
Sum of A and B	0·1395	0·157	0·171	0·167	0·409	0·433	0·563	0·490
(A+B) together	0·137	0·152	0·169	0·162	0·408	0·430	0·565	0·505

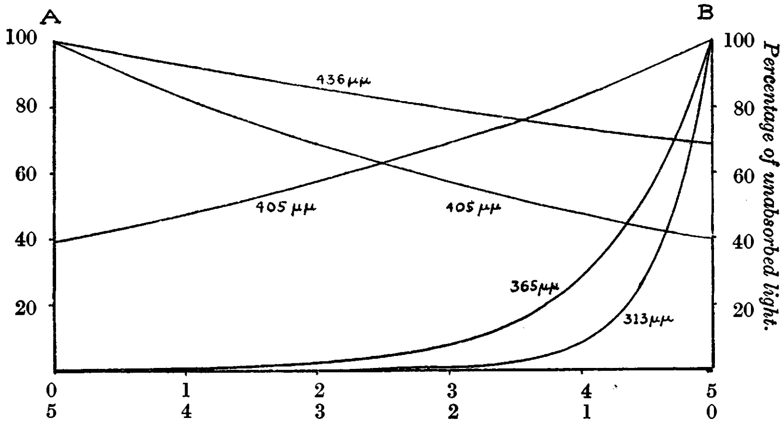
	(b)				(c)			(d)	
A	0·033	0·040	0·370	0·368	0·119	0·167	0·167	0·0406	0·0470
B	0·0405	0·049	0·249	0·244	0·094	0·070	0·074	0·0445	0·0519
Sum of A and B	0·0735	0·089	0·619	0·612	0·213	0·237	0·241	0·0851	0·0989
(A+B) together	0·0735	0·088	0·600	0·611	0·213	0·233	0·244	0·0844	0·0980

A and B were 436 $\mu\mu$ and 365 $\mu\mu$, 405 $\mu\mu$ and 365 $\mu\mu$, 436 $\mu\mu$ and 405 $\mu\mu$, and 405 $\mu\mu$ and 313 $\mu\mu$ respectively in sections (*a*), (*b*), (*c*), and (*d*) of Table I. It will be seen that, within experimental error, the simultaneous effect of the two rays is, in every case, equal to the sum of their separate effects. The action of light of a given wave-length is then neither enhanced nor reduced by the simultaneous presence of light of another wave-length.

It may be objected that, as insolation took place from opposite sides of the cell, the effect of the two rays, when acting simultaneously, was bound more or less to be equal to the sum of their individual effects, on account of the extinction of the chlorine, which will have tended to confine the absorption of each ray to the vicinity of the face at which it entered. To what extent this is true is shown in Fig. 2, where the intensity of unabsorbed light is plotted against the thickness of the cell. Even in the last, most unfavourable, case, although the action of the 405 $\mu\mu$ line could in no circumstances have been much influenced by the 313 $\mu\mu$ ray, the latter was absorbed in an environment where the intensity of the 405 $\mu\mu$ line was practically 40% of its incident intensity inside the other face.

Relative Quantum Efficiencies of the Lines 436 $\mu\mu$, 405 $\mu\mu$, 365 $\mu\mu$, *and* 313 + 303 $\mu\mu$.—The method of comparison used has been described. Table II contains the relevant data. The measurements were carried out at 19·7°. The absolute value of γ_{436} was about 10^5 (molecules of chlorine).

FIG. 2.



Thickness, cm.

The significance of the headings to the different columns is as follows :

A, relative intensities of lines in radiation of lamp (ergs).

B, percentage transmission of filters.

C, relative intensities incident on water cell (ergs), *i.e.*, A $\times$ B $\times$ 10^{-1}.

D, relative fractional reflexion losses in water cell and reaction cell (0·00 for 579 $\mu\mu$).

E, relative intensities incident inside reaction cell (ergs), *i.e.*, C $\times$ (1 − D).

F, fractions of incident light absorbed.

G, relative amounts of light absorbed (ergs), *i.e.*, E $\times$ F.

H, relative numbers of quanta absorbed, *i.e.*, G $\times$ λ (in μ).

I, relative velocities.

J, relative values of effective photochemical equivalent (ϕ), *i.e.*, I/G (ϕ_{313} = 1).

K, relative values of quantum efficiency (γ), *i.e.*, I/H (γ_{313} = 1).

Relative Quantum Efficiencies of the Lines 546 $\mu\mu$ *and* 436 $\mu\mu$.—In this experiment, owing to the small effect, if any, to be anticipated with the green line on account of its low absorption, beams of very

TABLE II.

	A.	B.	C.	D.
436 $\mu\mu$	237·0	48·5	1149·0	0·009
405 $\mu\mu$	110·8	31·7	351·2	0·012
365 $\mu\mu$	351·1	11·45	402·0	0·018
313 $\mu\mu$ + 303 $\mu\mu$ ...	158·7+44·5	22·5, 4·4	357·2+19·5	0·029, 0·032
	E.	F.	G.	H.
436 $\mu\mu$	1139·0	0·318	362·1	157·9
405 $\mu\mu$	346·9	0·608	210·9	85·4
365 $\mu\mu$	394·8	0·998	394·1	143·8
313 $\mu\mu$ + 303 $\mu\mu$ ...	346·8+18·9	1·00, 1·00	346·8+18·9	108·6+5·7
	I.	J.	K.	
436 $\mu\mu$	194·5	1·96	1·41	
405 $\mu\mu$	153·9	2·67	2·06	
365 $\mu\mu$	136·2	1·26	1·08	
313 $\mu\mu$ + 303 $\mu\mu$ ...	100	1·00	1·00	

different areas were employed in the two cases. That used with 436 $\mu\mu$ was 0·28 cm.^{2} in area and gave an average velocity of 0·33 cm./sec.; that with the 546 $\mu\mu$ light was 10 cm.^{2} in area, and gave an average velocity, which, although small, was unmistakable, of 1 cm. in 144 secs. The results are contained in Table III, where the lettering has the same meaning as in Table II. The relative velocities given under I are corrected for the different beam areas used, on the assumption of direct proportionality.

TABLE III.

	A.	B.	C.	D.	E.	F.
546 $\mu\mu$	287·5	49	1409	0·001	1408	0·00041
436 $\mu\mu$	237·0	53·3	1263	0·009	1251	0·318
	G.	H.	I.	J.	K.	
546 $\mu\mu$	0·577	3·15	0·000695	0·79	0·45	
436 $\mu\mu$	398	1736	1·19	1·96	1·41	

Experiments with the Chlorine Filter.—In order to gain an idea of the relative quantum effect of the group of lines passed by this filter in the neighbourhood of 260 $\mu\mu$, it was necessary to allow for the action of other lines transmitted. In this connexion, the 405 $\mu\mu$ and 436 $\mu\mu$ lines are of far greater importance than the 546 $\mu\mu$ line, and experiments were accordingly done in the normal way in which the effect of the chlorine-filtered light was compared with the effects of the rays passed by the 405 $\mu\mu$ and 436 $\mu\mu$ filters. The transmissions of the latter were remeasured immediately after the experiment, and were found to be 31·5% and 53·5% for their respective lines. The results were as follows :

	Average time required for 10-cm. movement of water meniscus.	Velocity, cm./sec.
436 $\mu\mu$	45·5 secs.	0·22
405 $\mu\mu$	68·0	0·147
Chlorine filter..............	42·5	0·236

It has been shown (Part I) that the rate of reaction is proportional to the light intensity, and further, that the simultaneous actions of two rays are independent of one another. (A special experiment, done in the manner described earlier in this paper, showed that the presence of 579 $\mu\mu$ light has no influence on the rate of reaction brought about by monochromatic rays.) As the unfiltered intensity of the mercury lamp was maintained quite constant during the experiment, we feel justified, therefore, in assuming that the component contributed to the total velocity observed with the chlorine filter by the 405 $\mu\mu$ light present in the beam would bear the same relation to the total velocity obtained with the 405 $\mu\mu$ filter as the fraction of this ray transmitted by the chlorine filter does to the fraction transmitted by the 405 $\mu\mu$ filter. A similar relation would hold for 436 $\mu\mu$ light. We therefore have:

$$v_{405} = \begin{array}{l}\text{velocity component}\\ \text{due to 405 } \mu\mu \text{ passed}\\ \text{by chlorine filter}\end{array} = 0{\cdot}147 \times \frac{14{\cdot}5}{31{\cdot}5} = 0{\cdot}0682 \text{ cm./sec.}$$

$$v_{436} = \begin{array}{l}\text{velocity component}\\ \text{due to 436 } \mu\mu \text{ passed}\\ \text{by chlorine filter}\end{array} = 0{\cdot}22 \times \frac{40{\cdot}0}{53{\cdot}5} = 0{\cdot}1645 \text{ cm./sec.}$$

The sum of these velocities is 0·233 cm./sec., which falls short of the total velocity obtained with the chlorine filter by 0·003 cm./sec., which is within the experimental error. It is clear that the effect produced by the short wave-length and green light absorbed is very small. Knowing the spectral energy distribution in the radiation from the lamp,* the spectral transmission of the chlorine filter, and the extinction coefficient of chlorine for the mercury lines concerned, the relative numbers of quanta of different wavelengths absorbed by the reacting gas can be calculated. This has been done, incorporating the usual correction for reflexion. The results, omitting the intermediate steps, are shown in Table IV. No account has been taken of the 579 $\mu\mu$ line.

TABLE IV.

λ, $\mu\mu$.	Relative intensity in radiation of lamp.	Percentage transmission of filter.	Relative intensity incident inside reaction vessel (ergs.).	Relative fraction of incident light absorbed.	Relative number of quanta absorbed.	
546	287·5	84	241·3	0·00049	6·5	
436	237·0	40	93·9	0·322	1319	
405	110·8	14·5	15·9	0·611	393	
265	42·4	42	17	0·252	113	171
254	48·8	63	29·2	0·0552	40·9	
248	24·2	60	13·7	0·0500	17·1	

* Determined after the lamp had been burning for 80 hours. The work with the chlorine filter was done about 20 lamp-hours later. Any change in energy distribution will have been small.

The number of absorbed ultra-violet quanta is seen to be just 10% of the number of absorbed quanta of blue and violet light. Consequently their insignificant effect can only be due to a relatively low quantum efficiency in the ultra-violet. If the small residual velocity of 0·003 cm./sec. calculated above be assumed to be real, and not due to experimental error, a rough estimate can be made of this quantum efficiency. It is first necessary to realise the part which may be played by the absorbed 546 μμ quanta. The ratio of $\gamma_{436} : \gamma_{546}$ has already been shown to be 3·1 : 1. The relative numbers of absorbed quanta are known (Table IV) and we have calculated that, in the chlorine-filter experiment, the velocity component due to the 436 μμ line is 0·164 cm./sec. This gives us

$$v_{546} = 0{\cdot}164 \times \frac{6{\cdot}5}{1319} \times \frac{1}{3{\cdot}1} = 0{\cdot}00026 \text{ cm./sec.}$$

This value, less than 10% of the residual velocity, is quite negligible, and certainly undetectable under our experimental conditions. It follows that the residual velocity, in so far as it is real, must be ascribed to the ultra-violet light. Calculating on this basis, we have

$$\frac{\gamma_{u.v.}}{\gamma_{436}} = \frac{0{\cdot}003/171}{0{\cdot}164/1319} = 0{\cdot}14.$$

It has been made clear that this is a figure of little more than qualitative value. From a consideration of the experimental data and possible errors involved, we conclude, however, that the *maximum* value for this ratio cannot exceed 0·5. On the other hand, if the residual velocity is largely or entirely due to experimental error, as it may be, then the ratio may have any value less than 0·14 down to zero.

The following is a summary of the relative values of ϕ and of γ found, putting the figures for 313 (303) μμ as unity.

TABLE V.

Wave-length, μμ	546	436	405	365	313 (303)	248—265
ϕ	0·79	1·96	2·67	1·26	1·00	—
γ	0·45	1·41	2·06	1·08	1·00	0·20 (possible correction + 250% to − 100%)

Both ϕ and γ are seen to increase with decreasing λ as far as 405 μμ, and then to fall off unmistakably, though irregularly, in the ultra-violet.

Relative Temperature Coefficients for the Lines 436 μμ, 405 μμ, 365 μμ, *and* 313 + 303 μμ.—Comparative velocity measurements were made with these lines at 19·7° and 25·0°. The relative velocities are shown in lines (i) and (ii) of the following table :

	436 $\mu\mu$.	405 $\mu\mu$.	365 $\mu\mu$.	313 $\mu\mu$ + 303 $\mu\mu$.
(i)	194·5	153·9	136·2	100·0
(ii)	203·7	156·1	138·1	100·0
(iii)..................	208·3	158·7	138·1	100·0
(iv)..................	1·047	1·014	1·014	1·0
(v)	1·071	1·031	1·014	1·0

Under our conditions, however, the work being always at atmospheric pressure, the rise in temperature has the effect of slightly diminishing the quantities of light absorbed in cases where such absorption is incomplete. On the assumption that the extinction coefficients for 405 $\mu\mu$ and 436 $\mu\mu$ are unaffected by this small rise in temperature, we have corrected the figures in line (ii) with the results given in line (iii) of the table [the correction is negligible both for 365 $\mu\mu$ and 313 (303) $\mu\mu$]. Line (iv) contains the relative temperature coefficients—for a temperature rise of 5·3°—for the observed velocities, calculated from (i) and (ii), the value for 313 $\mu\mu$ being put as unity. Line (v) contains, calculated from (i) and (iii), the corresponding temperature coefficients of the quantum efficiencies. Although the differences are small, their regular trend inclines us to think that they represent a real effect, *i.e.*, that the temperature coefficient of γ, as determined experimentally, increases with increasing wave-length.

The actual velocities measured at 25° were considerably greater than those at 19·7°. Thus, in the experiment just discussed, the velocities obtained with 365 $\mu\mu$ were respectively 0·498 and 0·388 cm./sec., which correspond to a temperature coefficient, for 10°, of 1·61. This high figure was doubtless chiefly due to the gas becoming more sensitive at the higher temperature owing to destruction of inhibitors, a view which was confirmed in another experiment by finding that the original low-temperature sensitivity of the mixture had considerably increased when, after a measurement at 25°, it was again examined at room temperature.

Discussion.

The above experiments were carried out a few years back. Since then, some of the work has been repeated in this laboratory, using a rather different technique. The main results have been confirmed, and the new measurements will shortly be published, but there are differences in detail, and on that account, a full discussion will be reserved. What follows refers only to such points as either have not been reinvestigated (temperature coefficient and effect of polychromatic light), or have been confirmed by the later work.

Activity of the Mercury-green Line.—This seems proved. The observed velocities were definite, and it is exceedingly improbable that, with the precautions taken, the filter combination transmitted any other light which could have caused the reaction. Assuming, as we do, the validity of Franck's conception of the result of quantum absorption by chlorine molecules on either side of the continuum limit (4785 Å.), it seems plausible to conclude that, depending on the wave-length of the active light, the mechanism of hydrogen chloride formation may involve either chlorine atoms or activated chlorine molecules. It is, however, possible that a closer examination of the nature of chlorine absorption in the green may lead to modification of this view.

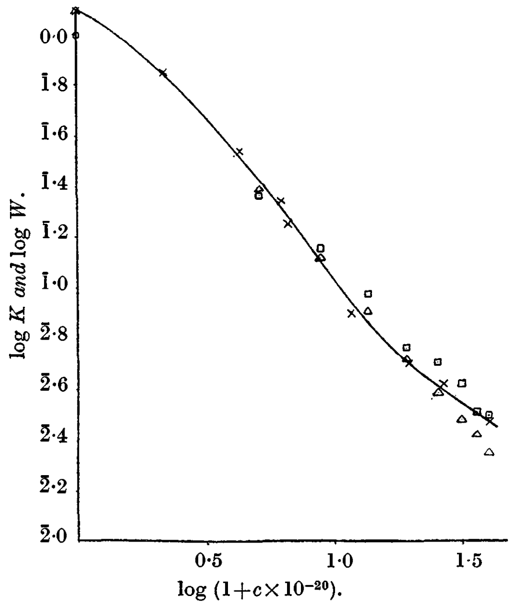
The Dependence of Quantum Efficiency on Wave-length.—A surprising feature of our results is the fact that although, as frequently happens in photochemical work, we find γ first to increase with decreasing wave-length, yet it later passes through a maximum and then falls off rapidly in the ultra-violet. To explain this result, if it is assumed not to be due to some cause unconnected with the main reaction, will require special assumptions. Experimentally, it receives some support from the work of Heymer (*loc. cit.*). His results have already been quoted. We find that γ_{260} cannot be greater than half of γ_{436}, and indeed may be very much smaller. Heymer concludes that they are probably identical, and attributes his lowest value for γ_{260} to the presence of inhibitor.

It was stated earlier that Taylor and Elliott (*loc. cit.*) interpreted the results of their own experiments by assuming that the rate of reaction per absorbed g.-cal. (proportional to ϕ, the effective photochemical equivalent) was independent of the wave-length between 350 $\mu\mu$ and 550 $\mu\mu$. On this assumption, their calculated and experimental curves coincide with a fair degree of accuracy. If, however, their calculations are modified in accordance with the relative ϕ values contained in Table V, then the degree of concordance between calculation and experiment is decidedly improved. Fig. 3 contains the logarithms of the K function (data from their Table I) and the W function (uncorrected and corrected) of Taylor and Elliott, plotted against the logarithm of ($c \times 10^{-20} + 1$), where c represents, in molecules/cm.^{2}, the optical density of the chlorine gas used in their filter.

The Relative Temperature Coefficients.—When temperature coefficients, as here, increase with increase in wave-length, it is frequently found that γ is also a function of wave-length, increasing with increasing frequency. Our experiments, however, show γ to fall off in the ultra-violet, and the well-known interpretation usually given to the simultaneous changes of γ and of $d\gamma/dT$ cannot be applied here. We have stated that (in agreement with the results of Porter, Bardwell, and Lind, and of Lind and Livingston, *locc. cit.*) we imagine the true temperature coefficients of this reaction, uninfluenced by inhibitors, to be low. It is natural to attempt to explain the variation in temperature coefficient with wave-length on similar lines. There are, however, certain difficulties involved in this conception and more work is required before discussion of the subject can be fruitful.

The Additive Nature of the Effects of Monochromatic Rays.—Given the found proportionality between intensity and velocity, the results obtained are as anticipated. They are in conflict with

FIG. 3.



× *K* function—observed velocities.
□ *W* function—calculated velocities (T. and E.).
△ *W* function—corrected calculated velocities (A. and B.).

those of Padoa and Vita (*loc. cit.*), who, however, used dispersed white light, and not, as we did, two superposed monochromatic rays. Allmand and Webb (J., 1929, 1527), in the case of the decomposition of aqueous potassium ferrioxalate, found that the result of two or three monochromatic beams, acting together, was greater than that of their sum, acting singly,* but observed no corresponding difference exceeding the experimental error when the effect of white light was compared with the effect calculated for its spectral components with monochromatic light. A similar effect

* Unpublished work by Mr. K. W. Young has confirmed this result.

in the opposite sense may perhaps account for the difference between the results of Padoa and Vita and our own.

Summary.

1. The quantum efficiency in the photochemical reaction between hydrogen and chlorine has been studied as a function of wave-length between the limits of 260 $\mu\mu$—546 $\mu\mu$. It was found to pass through a maximum in the violet, falling off towards the green and the ultra-violet.

2. The threshold of the reaction lies to the long wave-length side of 546 $\mu\mu$.

3. The temperature coefficient of the quantum sensitivity as experimentally found increases with increasing wave-length between the limits of 313 $\mu\mu$—436 $\mu\mu$.

4. The sum of the effects of two monochromatic rays acting successively is equal to their total effect when acting simultaneously.

5. The results are briefly discussed.

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