and that therefore the time required to produce 25 per cent. hydration in a 0.05 formular solution would be about 100 hours at 25° and 1030 at 0°, and even greater in more dilute solutions. From the same principle (expressed more generally by the equation log (k_{t_2}/k_{t_1}) = const. × $(t_2—t_1)$, it follows that the multiplication of the rate of this reaction for each 10° rise of temperature is about 2.57-fold, in conformity with the usual effect of temperature on reactions.

BOSTON, April, 1909.

[CONTRIBUTION FROM THE PHYSIKALISCH-CHEMISCHES INSTITUT, UNIVERSITY OF LEIPZIG.]

A QUANTITATIVE STUDY OF THE PHOTOCHEMICAL REACTION BETWEEN QUININE AND CHROMIC ACID.

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The original intention of this research was to follow the kinetics of a photochemical reaction in monochromatic light over a considerable period, and to construct equations showing the relation between speed of reaction and absorption of light throughout a long range of concentrations of the reacting substances. We chose the reaction between quinine and chromic acid, already studied by Goldberg,[1] whose results seemed to show that the velocity was dependent on the quantity of light absorbed by the chromic acid. Experiments with monochromatic light, however, soon convinced us that the *quinine* was the substance sensitive to light, and that the chromic acid acted only as an indifferent light filter, absorbing a part of the light and turning it into heat. This and other considerations led us to modify somewhat the plan of the research. The initial velocities of the reactions induced in various solutions by monochromatic light were measured, and the quantities of light absorbed by the quinine and by the chromic acid were calculated from measurements of extinction coefficients. The concentrations of the reacting substances, the intensity of the incident light, and the wave length of the same were varied, one at a time, in successive experiments. Finally the results were generalized and explained from the theoretical standpoint.

The apparatus in which the reaction mixtures were exposed to light is shown in Fig. 1. Three cylindrical glass tubes, *A*, *B*, and *C*, were set in a ring-shaped pan of sheet tin, *P*; their lower edges were made concentric by suitable pieces of brass soldered to the floor of the pan, their upper edges by bits of wood. The average distance between *A* and *B* was 0.71 cm., between *B* and *C* 1.56 cm. Two small glass tubes, not shown in the cut, were passed through holes in the pan, barely projecting into the spaces between *A* and *B*, and *B* and *C*, respectively; through

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[1] Dissertation, Leipzig, 1906.

these tubes a solution in either compartment could be drawn off at pleasure. The inner edge of the pan could be kept cool by a current of water flowing through *D*, a coil of small lead tubing. Next, the pan was filled with melted cement, which, on cooling, made the apparatus tight; special experiments showed that chromic acid mixed with sulphuric acid maintained its original titer for days when left in a bottle whose interior was coated with this cement. The method of supporting the vessel is clear from the diagram. The source of light was a uviol mercury vapor lamp *U* clamped in the axis of the apparatus.

Preliminary experiments indicated that the total reaction velocity was proportional to the concentration of the hydrogen ion. To make this velocity, under average conditions, large enough for convenient measurement, 2.7 mols. of sulphuric acid had to be present in each liter of reaction mixture. As will be proved later, the total velocity was the sum of the photochemical reaction proper and the spontaneous reaction of the same mixture in the dark. This "dark reaction," which at room temperature was often more than half the total reaction, ought to be greatly retarded by working at zero, while the photochemical reaction, having a very small temperature coefficient[1] could not be appreciably affected by so doing. Therefore the reaction mixture in the outer vessel was cooled by a glass tube wound in a double spiral, through which flowed brine at a temperature below zero from a large reservoir placed above the apparatus and filled with water, ice, and salt; the brine was forced back into the reservoir by a small mechanical pump driven by an elec-

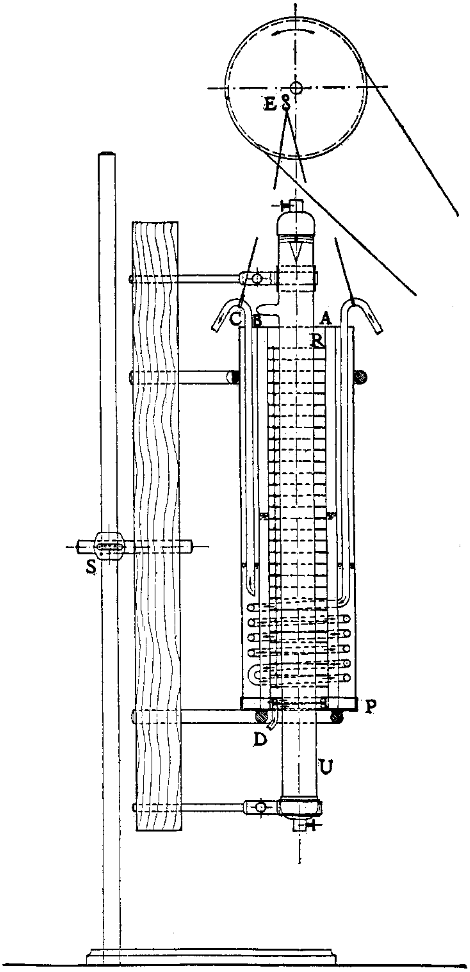

Fig. 1.

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[1] Goldberg, Dissertation, p. 45.

tric motor. The spiral was made to act as a stirrer at the same time by hanging it to an eccentric E on a wheel high above the apparatus and rotated by the motor. To prevent the moisture which collected on the cold shafts of the spiral from flowing down and diluting the solution, a small cup of lead foil was cemented about each shaft; these cups never touched the reaction mixture.

The light filter solution in the inner vessel was cooled and stirred by a different device: A Liebig condenser with cold water jacket was suspended above the apparatus; a filter pump was connected through a capillary and a large bottle to the upper end of the condenser tube; from the lower end a finer tube ran down below the surface of the filter solution. When the pump was started, the liquid was drawn up into the condenser and cooled, but as soon as the liquid fell below the end of the tube, air rushed up through the condenser and restored normal pressure throughout the system; thereupon the liquid ran back into the light filter vessel before a partial vacuum could again be established through the capillary. This process repeated itself at regular intervals.

To insure nearly perpendicular incidence of light upon the reaction mixture, the more oblique rays were cut off by thirty horizontal rings of smoked mica, R. ., in the space between the lamp and the inner cylinder. Each ring was pierced with three holes through which ran fine copper wires; the rings were kept equidistant by small drops of solder on the wires. Since the width of the rings was equal to their distance from each other, no ray of light could fall upon the glass at an angle greater than 45° from the normal; on entering water this angle is reduced to 32°; hence the longest ray of light in a plane including the axis of the system would travel sec. 32° or 1.18 times the perpendicular distance between the tubes. Rays not lying in such planes must have slightly longer paths, necessitating a slight additional correction. The *average* path of a ray in the filter solution is therefore quite nearly 0.71 × 1.10 or 0.78 cm. which is d_1 the effective thickness of this solution. So also d_2 for the reaction mixture would be 1.56 × 1.10 or 1.72 cm., were it not for the transparent stirrer which diminishes its average value. Seven turns of tubing 0.6 cm. in external diameter are equivalent to a body of annular cross-section h centimeters in height and $\frac{\pi \times 0.3^2 \times 7}{h}$ cm. thick. Since h, the depth of solution during illumination, was 11 cm., the final value of d_2 is 1.72-0.18 or 1.54 cm.

The same uviol lamp was used throughout the work; all other light was excluded by working in a dark room and wrapping the vessel in cotton wool covered with black paper. The current was uniformly 2.00 ± 0.05 ampere to insure constant light emission; experiments 20, 21, 22 performed under conditions otherwise identical at the beginning, middle, and end of the research, respectively, gave results constant within the limit of error, which shows that constant light emission was indeed maintained. The spectrum of the lamp[1] gives six bands which must be considered; their centers of gravity are as follows: ultraviolet, λ = 313$\mu\mu$ and 362$\mu\mu$; violet, 406$\mu\mu$; blue, 433$\mu\mu$; green, 541$\mu\mu$; yellow, 571$\mu\mu$.

Light filters were prepared from uranine, quinine, and three stock solutions: (*a*) Fuchsine S, 0.57 gram per liter; (*b*) methylene blue, 0.40 gram per liter; (*c*) nitrosodimethylaniline, about one gram per liter. The fraction of each ray emerging from a layer of mixture 0.78 cm. thick was calculated from measurements with a König-Martens spectral photometer, the lower end of the lamp serving as a source of light. In working with the wave-length 362$\mu\mu$ equality in the halves of the optical field had to be determined photographically.[2] A Zeiss anastigmatic lens was adapted to the eyepiece of the instrument, and the rays, passing through an extensible brass tube, were to be focussed upon a strip of sensitive film. This strip was contained in a long, narrow, black paper envelope with open ends and a round aperture in the middle of the lower side, through which the rays could pass when the envelope was fastened in the proper position. The film was moved along by pulling an adhering strip of paper till a number written on the strip appeared outside the envelope, showing that the film was in position for the first exposure. This was made with a random but carefully recorded setting of the nicol; then the strip was moved to position two and another setting of the nicol made, and so on. When the film was developed, it was evident between what limits the proper settings must lie; then these regions were investigated with a fresh film, till pictures were obtained where the field was practically of uniform depth. This method is capable of considerable accuracy. Except in one case all solutions were twice investigated. The filter solutions were not perceptibly altered by light, for samples taken before and after exposure showed nearly the same absorptive power.

Example of Calculation.—Required the fraction of the violet ray which will pass through 0.78 cm. of filter F described below. When *d*, the thickness of the layer in the photometer vessel was 1 cm., uniformity in the optical field was attained at 29°55′ and 42°12′. If L° is the incident light and L the emerging light we have for this solution, according to the law of Beer and Lambert, $L = L_0\ 10^{-Ed}$, where ε = log tan 42°12′— log tan 29°55′ = 0.2054. If $d = 0.78$, $L = L_0\ 10^{-0.2054 \times 0.78}$; now $10^{-0.1602} = 1/10 \times 10^{0.8398} = 0.69$. Hence, 69% of the ray of wave length 406$\mu\mu$—abbreviated 0.69[406]—will pass through the filter.

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[1] Ladenburg, *Physik. Z.*, **5**, 525 (1904).

[2] Compare Glatzel, *Ibid.*, **2**, 173 (1901).

Typical Light Filters.—A contained uranine, quinine, and fuchsine S in quantity sufficient to absorb everything but the yellow ray, $\lambda = 571\mu\mu$.

B contained 20 cc. of (*a*), 40 cc. of (*b*), 8.4 grams quinine and 300 cc. of water; it let through 0.02[406[and 0.62[433].

F_4 contained 40 cc. of (*a*), 18 cc. of (*b*), 0.3 gram quinine and 300 cc. of water; it let through 0.69[406] and 0.55[433], which latter was disregarded after the blue ray was proved inactive.

G_1 contained 67 cc. of (*a*), 20 cc. of (*b*), 20 cc. of (*c*), and 380 cc. of water; it let through 0.25[362] and a trace of [571].

F_4 and G_1 are types of two series of filters in which the concentrations of the components were varied to transmit different fractions of [362] and [406] respectively without any other active rays. All filters contained either quinine[1] or fuchsine S[2] which, together with common glass,[3] absorb [313] very strongly.

Analytical Precautions.—The change in concentration of the chromic acid was followed by iodimetry. The reaction mixture had to be diluted sixfold that the acid might not interfere with the blue color of the starch and that compounds of iodine and quinine might not be precipitated; but then the dissolved oxygen introduced a serious error. To avoid this the water and the one per cent. potassium iodide solution were evacuated in large bottles sealed with cement, and pure carbon dioxide bubbled through for a long time; then the pressure of this gas was raised above atmospheric, to discourage leakage of air from outside. The bottle of thiosulphate solution and its attached burette were similarly treated with pure hydrogen. The titration flasks were filled with carbon dioxide before use, and a slow stream of the gas was passed in during titration. The reaction mixture still contained air, but this error was small in proportion to those eliminated, and constant as well, as is proved by four analyses of a given solution, (1) and (3) without precaution, (2) and (4) with exclusion of air. (1) 19.20, (2) 18.53, (3) 19.09, (4) 18.53.

The dark reaction was investigated in flasks wrapped with black cloth, and kept in cracked ice and water. Titrations were made at suitable intervals, and the initial velocity of the reaction in each solution at zero calculated in cubic centimeters of $0.0085N$ thiosulphate solution per 25 cc. of mixture per hour. All reaction velocities given in this paper are thus expressed; concentration of quinine C_1 is always expressed in grams per liter; and concentration of chromic acid C_2 in gram equivalents per liter $\left(\frac{CrO_3}{3} = 33.4 \text{ grams}\right)$.

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[1] Kayser, *Handbuch der Spectroscopie*, III, 493.

[2] Krüss, *Z. physik. Chem.*, 51, 283 (1905).

[3] Kayser, *Handbuch der Spectroscopie*, III, 378–9.

TABLE I.

	C_1.	C_2.	Time.	ΔC_2.	Speed.
(1)	0.5	0.006	24.0	0.62	0.027
(2)	4.5	0.006	22.5	0.51	0.23
(3)	1.5	0.006	27.0	2.35	0.087
(4)	1.25	0.002	32.0	0.79	0.025
(5)	1.5	0.012	6.0	0.98	0.16

The velocity is proportional to the concentration both of the quinine and of the chromic acid; the preliminary experiments indicated that it is also proportional to the concentration of the hydrogen ion.

The temperature coefficient of the dark reaction was determined, using a solution in which $C_1 = 1.5$ and $C_2 = 0.006$. One portion was kept at 0° in ice, another in a stream of tap water constant at 8.5°, a third in a room whose average temperature during the experiment was 22°.

TABLE II.

	t.	Time.	ΔC_2.	Speed.	$K = \frac{\log S_2 - \log S_1}{t_2 - t_1}$
(1)	0.0°	21.7	1.74	0.080	0.024
(2)	8.5°	5.3	0.67	0.126	0.025
(3)	22.0°	4.5	1.16	0.26	

Using this constant and the data in the previous table, the dark reaction velocity in any solution could be interpolated for temperatures above zero, and extrapolated for several degrees below. While each reaction mixture was being exposed to light the temperature was frequently recorded, and the corresponding velocities calculated; then the total progress of the dark reaction for the interval in question was found by graphical integration. Lastly, the change in concentration due to the photochemical reaction alone was provisionally determined by subtraction.

Before starting an experiment the apparatus was cleaned and emptied and rotated through 90° about the swivel *S* (Fig. 1). The current was turned on and the lamp lighted by re-establishing the vertical position. If the lamp continued to burn, the light filter solution was introduced into its compartment. Then the quinine, dissolved in a little sulphuric acid, was combined with the sulphuric and chromic acids, and the containing bottle well shaken. The reaction vessel, a small flask, and a pipette were rinsed with the mixture; then all portions were returned to the bottle, and the whole, after more shaking, poured into the vessel. The cooling and stirring devices were set in operation, and after waiting five or ten minutes to avoid the influence of possible initial disturbances, the portion of liquid which had been in contact with rubber in the outlet tube was discarded. Then about 90 cc. were drawn off into a flask wrapped in black cloth, noting the time, and quickly warmed to 17°; two portions were successively pipetted off and analyzed, the results being corrected for the dark reaction during the interval between drawing off and diluting for titration. After several hours new analyses of the illuminated mixture were made with the same precautions. In cases where the dark reaction at 17° would have been too rapid to allow of certain correction the flask was both times kept at 0° and the corresponding corrections applied; this variation in the process could not influence the result for change in concentration by more than two-tenths of a per cent.

Quantitative determinations of the action of the various wave lengths were made in a solution where $C_1 = 1.5$, $C_2 = 0.006$, and 2.7 gram molecules of sulphuric acid were present in each liter. The second column of the table describes the light incident upon the reaction mixture, the third and fourth the speed of the dark and light reactions, respectively, and the last column the speed for the whole ray calculated by simple proportion:

TABLE III.

	Filter.	Incident light.	Dark.	Light.	Time.	Speed.	Speed (λ).
(1).................	A.	0.5±[571]	0.455	0.025	5.0	0.005	....
(2).................	B.	0.62[433]	0.355	0.04	3.1	0.013	....
(3).................	B.	0.62[433]	0.27	0.04	3.6	0.011	0.01
(4).................	B.	0.62[433]	0.36	0.015	4.2	0.004	....
(5).................	F_1..	0.34[406]	0.36	0.18	3.1	0.06	0.18
(6).................	F_2..	0.24[406]	0.66	0.30	6.9	0.043	0.18
(7).................	F_3..	0.71[406]	0.55	1.08	7.1	0.15	0.21
(8).................	F_4..	0.69[406]	0.64	1.16	7.7	0.15	0.22
							0.20
(9).................	G_1	0.25[362]	0.54	0.80	6.3	0.13	0.51
(10).................	G_2	0.16[362]	0.54	0.46	5.9	0.08	0.47
							0.49

Since the yellow ray is very slightly absorbed by the reaction mixture it cannot cause appreciable chemical change; hence experiment (1) indicates that the dark correction is adequate, and the consistency of the following results points to the same conclusion. The blue ray is virtually inactive; in the table, correction is made for 0.02[406] which filter B transmits. The violet and the ultraviolet rays are active, and the constancy of the results in the last column show that the photochemical action is proportional to the incident light in each case.

The effect of concentration changes in the reaction mixture was studied in violet and ultraviolet light, respectively, using filters of types F and G.

The probable error of (12) is considerable, owing to the magnitude of the dark reaction and the difficulty in finding the incident light with great percentage accuracy. But it is clear that the speed of reaction in either violet or ultraviolet light is diminished by increasing the concentration of the chromic acid. In ultraviolet light the velocity appears independent of the concentration of the quinine, but in violet light these two quantities are roughly proportional to each other.

TABLE IV.

	Incident light.	C.	C_2.	Dark.	Light.	Time.	Speed.	Speed (λ).
(11)......	0.166[362]	1.25	0.002	0.16	0.45	5.2	0.085	0.52
(9–10)......	... [362]	1.5	0.006	....	....	...	...	0.49
(12)......	0.11 [362]	1.5	0.012	0.81	0.23	5.0	0.046	0.42
(13)......	0.25 [362]	0.5	0.006	0.19	0.80	6.4	0.125	0.50
(9–10)......	... [362]	1.5	0.006	....	....	...	...	0.49
(14)......	0.16 [362]	4.5	0.006	0.99	0.345	4.37	0.079	0.49
(15)......	0.54 [406]	1.25	0.002	0.15	0.64	4.9	0.13	0.24
(5–8)......	... [406]	1.5	0.006	....	....	...	...	0.20
(16)......	0.37 [406]	1.5	0.012	1.53	0.53	8.1	0.067	0.18
(17)......	0.38 [406]	1.5	0.012	1.03	0.45	6.0	0.075	0.20
(18)......	0.45 [406]	0.5	0.006	0.16	0.23	5.9	0.04	0.09
(5–8)......	... [406]	1.5	0.006	....	....	...	...	0.20
(19)......	0.29 [406]	4.5	0.006	0.96	0.64	3.9	0.162	0.56

The joint action of two rays was followed using light filter M, identical with solution (*a*), which transmitted 0.22[362] and 0.30[406].

TABLE V.

	C_1.	C_2.	Dark.	Light.	Time.	Speed.
(20)......	1.5	0.006	0.51	0.99	4.9	0.20
(21)......	1.5	0.006	0.46	0.82	5.25	0.16
(22)......	1.5	0.006	0.52	0.96	5.3	0.18
						0.18
(23)......	4.5	0.006	0.47	0.47	1.95	0.24

The reaction velocity induced in experiments (20–22) by 0.22[362] should be 0.49 × 0.22 = 0.11; and that induced by 0.30[406] should be 0.20 × 0.30 or 0.06. The total velocity, calculated by addition, 0.17 agrees well with the observed value, 0.18. This shows that the action of two rays is strictly additive; this is the first quantitative treatment of the joint action of two rays to be published.

The total velocity calculated for experiment (23) is (0.49 × 0.22) + (0.56 × 0.30) = 0.28, while the observed value was 0.24. The value 0.56, taken from (19), will be proved excessively large in Table IV, but we can find by subtraction a good value for the velocity induced by 0.30[406] by subtracting (0.49 × 0.22) from 0.24. This result, 0.13 for 0.30[406] or 0.43 for [406], will be used in Table IV.

The explanation and mathematical treatment of these results required a knowledge of the extinction coefficients of quinine and of chromic acid in 5.4 equivalent normal sulphuric acid. The method is described in the section on light filters; $L = L_0^{-Acd}$ where $A = \frac{e}{cd}$, the extinction coefficient of the substance in unit concentration and unit thickness.

TABLE VI.

Quinine.					Chromic acid.				
λ.	c_1.	d_1.	e_1.	A_1.	λ.	c_2.	d_2.	e_2.	A_2.
433	1.5	2.0	0.006	0.004	433	0.006	1.0	0.335	56.0
406	1.5	2.0	0.342	0.11+	433	0.006	1.0	0.335	56.0
406	1.5	2.0	0.370	0.12+	406	0.006	1.0	0.242	40.3
406	10.0	1.0	1.18	0.12	433	0.006	1.0	0.249	41.5
362	1.5	0.1	1.43	9.5	362	0.006	0.1	0.15	250.0
362	1.5	0.1	1.40	9.3[1]					

The value of A_2 for [362] is doubtless too high, because of the presence of 1.9 cm. of glass in the absorption vessel. In $5.4N$ H_2SO_4, chromic acid absorbs [433] more strongly than [406], while in neutral solution the reverse is the case. Hantzsch and Clark[2] measured the absorption of [485] by chromic acid in neutral solution and in sulphuric acid of various concentrations, and finding it nearly constant postulated the same conclusion for all lines in the spectrum. It is intended to investigate this matter further in the near future.

TABLE VII.

$\lambda = 362\mu\mu$, $A_1 = 9.5$, $A_2 = 250$.

	C_1.	C_2.	L_a.	L_1.	L_2.	Speed.	$K_{362} = \frac{\text{Speed}}{L_1}$.
(11).....	1.25	0.002	1.00	0.96	0.04	0.52	0.54
(9–10).....	1.5	0.006	1.00	0.91	0.09	0.49	0.54
(12).....	1.5	0.012	1.00	0.83	0.17	0.42	0.51
(13).....	0.5	0.006	1.00	0.76	0.24	0.50	0.66
(14).....	4.5	0.006	1.00	0.97	0.03	0.49	0.51
							0.55

$\lambda = 406\mu\mu$, $A_1 = 0.12$, $A_2 = 41$.

	C_1.	C_2.	L_a.	L_1.	L_2.	Speed.	$K_{406} = \frac{\text{Speed}}{L_1}$.
(15).....	1.25	0.002	0.56	0.36	0.20	0.24	0.66
(5–8).....	1.5	0.006	0.77	0.33	0.44	0.20	0.61
(16–17).....	1.5	0.012	0.91	0.25	0.66	0.19	0.76
(18).....	0.5	0.006	0.66	0.13	0.53	0.09	0.68
(19).....	4.5	0.006	0.95	0.66	0.29	0.56	[0.85]
(23).....	4.5	0.006	0.95	0.66	0.29	0.43	0.66
							0.67

$\lambda = 433\mu$, $A_1 = 0.004$, $A_2 = 56$.

	C_1.	C_2.	L_a.	L_1.	L_2.	Speed.	$K_{433} = \frac{\text{Speed}}{L_1}$.
(2–4).....	1.5	0.006	0.69	0.01	0.68	0.01	1 ±

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[1] Some chromic acid was present also, hence this determination has only approximate accuracy.

[2] *Z. physik. Chem.*, **63**, 373 (1908).

The portion of the incident light absorbed by either quinine or chromic acid in any reaction mixture can now be calculated. The law of Beer and Lambert is assumed, and the formulas developed by Luther and Weigert[1] are applied:

Let L_0 be that quantity of light of wave length λ which the uviol lamp, with a transparent light filter, delivers to each 25 cc. of reaction mixture.

Let L_a be the light absorbed by the reaction mixture.

Let A_1A_2 be the respective extinction coefficients for λ.

Let C_1C_2 be the respective concentrations.

Let L_1L_2 be the respective quantities of light absorbed by quinine and by chromic acid, respectively.

Then $$\frac{L_a}{L_0} = 1 - 10^{-(A_1C_1 + A_2C_2)d}, \quad L_1 = L_a \frac{A_1C_1}{A_1C_1 + A_2C_2}, \quad L_2 = L_a \frac{A_2C_2}{A_1C_1 + A_2C_2};$$

d is here 1.54, the effective thickness of the reaction mixture. L_0 is taken as unity for each wave length.

It will be noted that $K\lambda$ is numerically equal to the velocity which would result if *all* the ray of wave length λ that could pass between the mica rings were absorbed completely by the quinine in the reaction mixture. These constants can also be used to calculate the velocity of the light reaction for any mixture in the annular vessel if only $F_{1,2}$, the fractions of the given rays passing through the filter, and C_1 and C_2 are known. The sulphuric acid is $5.4N$.

$$\text{Speed}_{362} = F_1 \times \frac{9.5\ C_1}{9.5\ C_1 + 250\ C_2} \times (1 - 10^{-(9.5\ C_1 + 250\ C_2)d}) \times 0.55.$$

$$\text{Speed}_{406} = F_2 \times \frac{0.12\ C_1}{0.12\ C_1 + 41\ C_2} \times (1 - 10^{-(0.12\ C_1 + 41\ C_2)d}) \times 0.67.$$

The sum of these, plus the dark reaction, gives the total reaction velocity.

The figures thus far exhibited prove (1) that the amount of chemical change in each unit of time is proportional to the fraction of a given ray absorbed by *quinine* in the same period. (2) The amount of light absorbed by the chromic acid has no effect on the result. From (1) and (2) the apparent inertness of the blue ray is no longer surprising. (3) No sensible error is involved in finding the light reaction by difference.

Conclusion (2) was now tested over a greater range of concentration. A solution in which $C_1 = 4.5$ and $C_2 = 0.003$ at the start was exposed with a filter of pure water, which intercepted little of the active rays. Analyses were made at suitable intervals, using a 37.50 cc. pipette. The dark reaction was calculated and subtracted in the usual manner; results are based on a volume of 25 cc.

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[1] *Z. physik. Chem.*, **53**, 408 (1905).

TABLE VIII.

	Interval.	Average C_2.	Dark.	Light.	Speed.
(24)	1.47	0.0026	0.25	1.62	1.11
(25)	1.57	0.0019	0.18	2.07	1.31
(26)	0.82	0.0013	0.06	1.09	1.33
(27)	1.1	0.0010	0.06	1.11	1.01
(28)	1.73	0.0005	0.05	1.52	0.87
(29)	0.50	0.00015	0.01	0.25	0.50
(30)	0.50	0.00007	0.00	0.13	0.26

From these figures it is inferred that the photochemical reaction takes place in two stages: first, the formation of sensitized quinine with a velocity proportional only to light absorption; then a reaction in the ordinary sense between this product and chromic acid, with a velocity proportional to the concentration of chromic acid and of sulphuric acid, as in the dark reaction. At very small concentrations the second stage is so slow that it determines the speed of the reaction as a whole; but when $C_2 > 0.0013$ the speed of the second stage is very great, and the speed with which sensitized quinine is produced regulates the progress of the reaction; this sensitizing is probably a reversible reaction, otherwise the product would accumulate rapidly when C_2 became small and prevent any approach to a reaction of the first order. Finally, the smaller the value of C_2, the more in proportion should the hydrogen ion accelerate the photochemical reaction as a whole.

It is next desirable to compare $\frac{K_{406}}{K_{362}}$ with the ratio of the corresponding absolute light energies. Ladenburg[1] has investigated the distribution of energy in the spectrum of a quartz mercury lamp and found the relative energy of two rays independent of the electrical energy consumed by the lamp. Hence the relative absolute energies E_{406} and E_{362} as determined by graphical integration of their curve can be assumed for our lamp without serious error:

$$E_{406} : E_{362} = 1 : 3.2,$$

but

$$K_{406} : K_{362} = 1 : 0.82.$$

Hence the *photochemical efficiency* of [406] is seen to be nearly four times as great as that of [362]. Since further $A_{406} : A_{362} = 0.12 : 9.5$, it appears that the photochemical efficiency of the light decreases as the wave length of maximum absorption in the ultraviolet, $330\mu\mu$,[2] is approached.

The theory of forced vibrations which are damped leads to similar conclusions. The energy of a vibrating body (electron) is given by the expression

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[1] *Physik. Z.*, 5, 525 (1904).

[2] See Schmidt, *Physik. Z.*, 1, 466 (1900).

$$\varepsilon_1 = \frac{A^2\theta^2}{4m\pi^2} \frac{\left(\frac{T^2}{\theta^2} + 1\right)}{\left(\frac{T^2}{\theta^2} - 1\right)^2 \frac{\theta^2}{T^2} + 4\gamma^2}.$$

where m is the mass, θ the free period, γ the logarithmic decrement of the damping, T the period of the exciting vibration, and A its amplitude. This stationary "resonance energy" or "photokinetic potential" (Wildermann) is evidently closely related to the tendency of the absorbing molecule toward chemical change. This tendency, and therefore the speed of reaction, clearly increases with this resonance energy heaped up in the molecule.[1] The energy transformed into heat in unit time by the damping is given by the expression:

$$\varepsilon_2 = \frac{A^2\gamma\theta}{m\pi} \frac{1}{\left[\left(\frac{T^2}{\theta^2} - 1\right)^2 \frac{\theta^2}{T^2} + 4\gamma^2\right]}.$$

The photochemical efficiency of the absorbed energy, ε_2 is

$$\frac{\varepsilon_1}{\varepsilon_2} = \frac{\theta}{4\pi\gamma}\left(\frac{T^2}{\theta^2} + 1\right).$$

Other things equal, the efficiency will be the greater, the smaller the damping is, *i. e.*, the steeper the absorption band is. For a given substance the efficiency increases with T, the period, or in other words with the wave length of the light; our results are in harmony with this conclusion.

Influence of the Thickness of the Layer.—Since A_{362} for quinine is 9.5, the first millimeter of a solution where C_1 = 1.5 must absorb practically all the ultraviolet ray; thus a thin layer having no chance to mix with unilluminated solution behind should show a very great reaction velocity. This conclusion was tested in a second type of vessel (Fig. 2) made of three thin glass plates 40 cm. x 8 cm. carefully cemented together. The light filter vessel in front is 0.7 cm. thick, the reaction vessel 0.13 cm. thick; the method of filling or emptying is clear from the cut. Light filter M, in thickness 0.7 cm., transmits 0.26[362] and 0.33[406] C_1 = 1.5, C_2 = 0.006; the source of light was a uviol lamp, the duplicate of the first, but without mica rings. The speed was found in essentially the usual way, and the dark reaction subtracted,

(31) distance = 10 cm., speed = 1.17;

(32) distance = 13 cm., speed = 0.93.

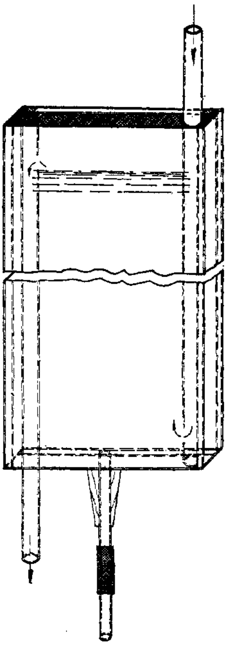

Fig. 2.

It can be shown that if the thin layer had been 3.6 cm. from the axis of the lamp as is the first millimeter of solution in the annular vessel and if the mica rings had been in place, the velocity would have been about 1.6. If now the quinine in the

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[1] Luther, *Z. Elektrochem.*, 1908, 471.

annular vessel had absorbed the same amount of light as the quinine in the thin layer under the above conditions, namely $0.26 \times 0.97[362]$ and $0.33 \times 0.05[406]$, the speed would have been $(0.24 \times K_{362} + 0.02 \times K_{406})$ or 0.14, that is, one-eleventh as great. But the annular vessel is about eleven times as thick as the thin layer. Hence for given light absorption the velocity induced is inversely proportional to the thickness of the layer.

The influence of the thickness of the layer upon the results is a general question of great practical importance. For the sake of simplicity, let us assume that only the sensitive substance absorbs, a condition nearly fulfilled in the present research when $\frac{C_1}{C_2}$ is especially large. Let the mixture be exposed successively to those quantities of $[\lambda_1]$ and $[\lambda_2]$ for which K_1 and K_2 have been determined; m_1 and m_2 are the extinction coefficients of the sensitive substance for the two rays, and L_1 and L_2 the fractions of the incident light absorbed for given values of c and d.

$$\text{Speed}_1 = K_1L_1 = K_1(1-e^{-m_1cd}).$$
$$\text{Speed}_2 = K_2L_2 = K_2(1-e^{-m_2cd}).$$

If now d is very great, the parenthesis approaches unity and

$$\frac{\text{Speed}_1}{\text{Speed}_2} = \frac{K_1}{K_2}; \text{ in our case } \frac{\text{Speed}_{362}}{\text{Speed}_{406}} = \frac{55}{67} = 0.82.$$

But if d approaches zero, it is shown by the use of logarithms that

$$\frac{\text{Speed}_1}{\text{Speed}_2} = \frac{K_1m_1}{K_2m_2}; \text{ in our case } \frac{\text{Speed}_{362}}{\text{Speed}_{406}} = \frac{0.55 \times 9.5}{0.67 \times 0.12} = 73.$$

The relative chemical effect of two given lines of the spectrum is thus reversed by exchanging very thin for very thick layers. These considerations perhaps explain observations showing that the maximum of "chemical absorption" lies nearer the red than the maximum of optical absorption. The layers used in these cases were not infinitely thin.

Summary.

The reaction between quinine and chromic acid in monochromatic light is investigated; an apparatus of novel construction is used and all variables are measured with special precautions.

The photochemical reaction is exactly the difference between the total reaction and the dark reaction.

The joint effect of two rays is found additive, a fact not hitherto treated quantitatively.

The percentages of each ray passing through the light filters, and the percentages absorbed by quinine and by chromic acid, respectively, in each experiment, are calculated.

The speed of the light reaction is proportional to the quantity of light of given wave length absorbed by the quinine alone unless the concentration of chromic acid is very small; this is consistent with the hypothesis that the light reaction runs in two stages.

Formulas are worked out from which the velocity produced by the incidence of known amounts of light of various wave lengths upon any mixture of quinine and chromic acid under the conditions prevailing throughout the research can be calculated.

The photochemical efficiency of a given amount of absolute light energy is found to decrease as the wave length of maximum absorption is approached. This result is predicted by theoretical considerations.

The effect of changing the thickness of the layer is tested experimentally. It is shown that the relative effect of two rays of different wave length must depend entirely on the thickness of the layer.

The experimental work described in this paper was carried out in the Physikalisch-Chemisches Institut of the University of Leipzig during the winter semester 1906-7.

ON THE OXIDATION OF HYDRAZINE. IV.

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Historical.

E. Fischer[1] has shown that by the oxidation of a cold aqueous emulsion of phenylhydrazine with an excess of Fehling's solution, benzene and aniline are formed. Baeyer[2] has made use of the action of copper sulphate upon the hydrazines in the preparation of hydrocarbons. Gallinek and V. v. Richter[3] have called attention to the possible use of copper sulphate in the gasometric determination of the nitrogen in certain hydrazine derivatives. Strache[4] has suggested the use of hot Fehling's solution in the determination of phenylhydrazine. By measuring the excess of unused phenylhydrazine he has also effected the determination of carbonyl oxygen in aldehydes and in ketones. In a subsequent communication[5] he calls attention to two possible sources of error in his method, and finally states[6] that no aniline is formed when boiling hot Fehling's solution is employed,

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[1] *Ann.*, **190**, 67–183 (1878).

[2] See Haller, *Ber.*, **18**, 89–94 (1885). See also Kijner, *J. Russ. Phys. Chem. Soc.*, **31**, 1033–62 (1899); *J. Chem. Soc.*, **78**, I, 333 (1900).

[3] *Ber.*, **18**, 3172–78 (1885).

[4] *Monatsh. Chem.*, **12**, 524–32 (1891). See also de Vries and Hollemann, *Rec. trav. chim.*, **10**, 228–30 (1891); Strache and Iritzer, *Monatsh. Chem.*, **14**, 33–38 (1893); Benedikt and Strache, *Ibid.*, 14, 270–77 (1893); de Vries, *Ber.*, **27**, 1521–2 (1894); *Ibid.*, **28**, 2611–2 (1895); Kitt, *Chem.-Ztg.*, **22**, 358 (1898); *Chem. Centr.*, **1898**, I, 1310.

[5] *Monatsh. Chem.*, **13**, 299–315 (1892).

[6] Strache and Kitt, *Ibid.*, **13**, 316–19 (1892).