THE PHOTOCHEMICAL OXIDATION OF HYDRIODIC ACID

BY

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I. The photochemical Oxidation of the hydriodic acid.

Introduction.

The earlier literature on this photolysis is found em-
bodied in EDER's Photochemistry[1]. Of more recent
works PLOTNIKOW's two papers[2] have more especially given
the impression of enlarging our knowledge of the said process
to a considerable degree. PLOTNIKOW's experiments were car-
ried out by exposure to an uviol-lamp of potassium iodide-
solutions, to which sulphuric acid and water containing
oxygen had been added. What was being measured was,
then, the decrease in the oxygen-concentration. No stirring
was employed. Neither induction-period nor after-action
was found. The velocity constant is proportional to the
light-intensity. The rates of the dark- and light processes are
added directly and occur after the same order of reaction,
so that the velocity of the total process may be expressed by:

$$\div \frac{d(O_2)}{dt} = [K_d 10^{\alpha T} + K_L 10^{\beta T}] (HCl)^{2/3} (KJ)^{2/3} (O_2).$$

K_d and K_L are the velocity constants for the dark- and
light-processes, $10^{\alpha T}$ and $10^{\beta T}$ the corresponding tempera-
ture-coefficients.

PLOTNIKOW furthermore found that the dark- and light-
process behaved quite differently in regard to catalysts, the
selfsame substance, ($CuSO_4$ f. inst.), being able to accelerate

[1] 3d Edition. P. 144 (1906).

[2] Zeitschr. f. physichal. Chemie. **58**, 214 (1907), **64**, 215 (1908).

the one and inhibit the other; that the process is especially
sensitive to blue light, less to violet and ultra-violet ($336\,\mu\mu$);
that an addition of iodine to the reaction-mixture does not
abate the velocity; and finally, that the reaction-mixture
itself, employed as a light-filter, does not reduce the velocity
of another portion of reaction-mixture which is placed
behind this light-filter. From this PLOTNIKOW concludes,
that a very slightly absorbing reaction-mixture is here
in question, which despite this has a considerable sen-
sitiveness. This interpretation, which is generally accepted,
is expressed by BODENSTEIN in his survey[1] on quantum-
sensitivities, where he computes the amount of molecules
oxidized in aqueous hydriodic acid for each absorbed
quantum to 10^6, the same order of magnitude, hence, as the
sensitiveness of the mixture of chlorine and hydrogen.

These statements of PLOTNIKOW's contain, however, such
extraordinary and improbable things, that it seems highly
necessary to submit his work to a critical examination.

In the first place, the found colour-sensitiveness seems to
be but little probable. In the course of time not a few cases
are known where the colour-sensitiveness occurs parallel
to (and is often proportional to) the absorption of the light-
sensitive substance, and several of the apparent exceptions
from this quantitative absorption-law can be explained
from the particular circumstance sprevailing in the indivi-
dual case[2]. But in this reaction-mixture no single substance
is found, the absorption of which is greater for blue than
for violet and nearest ultra-violet. Neither was the confidence
in PLOTNIKOW's results increased on a previous occasion[3]

[1] Zeitschr. f. physichal. Chemie **85**, 356 (1913).
[2] V. f. inst. Lasareff. Ann. d. Physik (4) **37**, (1912) and below S.
[3] Zeitschr. f. Elektroch. **19**, 394 (1913).

when I found that the light-filters employed by him were far from being monocromatic.

Then: If really, as generally assumed, hydriodic acid, or rather iodine-ion, is the actual sensitive substance, then the new formed iodine, or rather the tri-iodine-ion, the absorption of which for blue, violet and nearest ultra-violet is infinitely stronger than that of the iodine-ion, must absolutely reduce the light-intensity in the interior of the liquid to such a degree, that the process for this reason must come to a stand-still long before the oxygen is consumed. The circumstance, that an addition of iodine, hence a further strong augmentation of the absorption, does not influence the velocity, does not harmonise either with the assumption of the iodine-ion being the actual light-sensitive substance, but seems rather to point in the direction of the active co-operation of the iodine in the process.

But the most remarkable thing in PLOTNIKOW's works is the experiments with the reaction-mixture as a light-filter. Even if the lack of effect of the iodine in the reaction-mixture itself can be understood, it must — when formed in the light-filter — absolutely absorb blue, violet and ultra-violet, and as the velocity is proportional to the in-tensity, the process in the reaction-vessel behind must necessarily be gradually retarded, notwithstanding its nature and which substance is to be regarded as the actual sensitive substance.

Methods and Results.

These various mysterious or improbable statements made me decide to take up the investigation of this process. To start with, the colour-sensitiveness was examined. The mea-

surements were already carried out in 1913 by Mr. HEEGÅRD-POULSEN. The arrangement is more closely described else-where[1]. It consisted materially in a quartz-mercury-lamp, a couple of screening shades, to procure a fairly parallel light, a filter-couvette, furnished with quartz-walls, and a reaction-couvette cemented on to it, without front-wall and with back-wall of quartz. The rate of reaction was measured by means of the energy-measurer, the fluormeter (which I have previously described[2]), the amounts of light passing through the filter and the reaction-mixture being measured during the progress of the process. When the extinction of the tri-iodine-ion for the various wave-lengths are known, its concentration and therewith the decrease in the concentration of the oxygen can be calculated at different times. As the process during the given circumstances occured very rapidly, energy-measurements had to be taken at such short intervals, that the time only allowed 1 adjustment each time, and the measurements cannot, therefore, lay claim to any great accuracy. But the question being here only of quite a rough determination of the colour sensitiveness, the method might apply.

The results showed that the transformed amount of substance per absorbed energy-unit was largest in violet ($405\,\mu\mu$) and somewhat smaller in blue ($436\,\mu\mu$) and ultra-violet (336 and $313\,\mu\mu$).

The question was now allowed to rest until the spring of 1918. The preliminary experiments were executed by Mr. V. A. LARSEN, the final measurements by me.

The necessary extinction-measurements were partly, for the lines 436 and $405\,\mu\mu$, carried out by means of König-

Martens spectrophotometer, and partly, for the lines 366 and 313 $\mu\mu$, with the fluormeter. The absorption of the iodine being very powerful and therefore only measurable with highly dilute solutions, the re-calculation factor becomes very great and the accuracy of the final figures consequently slight. The found extinction coefficients have the following values:

Table 1.

Konc. af KJ	Konc. af J_2	436	405	366	313 $\mu\mu$
0,2—n	$5,75 \cdot 10^{-5}$	600	2100	6900	4150 -
1,0—n	„	900	2800	8050	4300 -
0,2—n	$11,50 \cdot 10^{-5}$	1000	2600	8600	3900 -
1,0—n	„	900	2500	9350	— -
		900	2500	8200	4100 $\mu\mu$

In the insolation experiments I reasoned as follows: If PLOTNIKOW's discovery, that the velocity is proportional to the oxygen-concentration, be correct, we must, by keeping the latter constant, be able to obtain constant velocity and thereby be able to investigate in the easiest and most accurate way the significance of the absorption of the tri-iodine-ion.

The applied arrangement was as schematisised in fig. 1.

L is the quartz-mercury-

Fig. 1.

lamp, the electrode potential and current-strength of which was controlled all the time during the experiments and, where necessary, kept constant by variation of the inserted
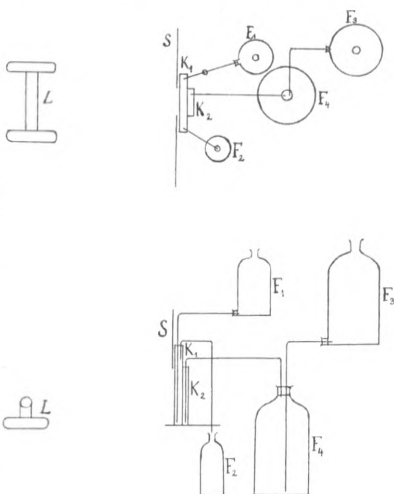
resistance. S is a shade of card-board in which is an aperture of the same size as the reaction-couvette K_2. This as well as the large filter-couvette K_1 is made of glass having plan-parallel side-walls. Only in the experiments with the wave-length 313 µµ a couvette furnished with quartz-walls was used. The filter-liquid runs slowly from the flask F_1 down into the filter-couvette, and from there through a siphon over into the flask F_2. By this slow circulation of the filter-liquid we gain the advantage that the temperature in the reaction-couvette keeps very nearly constant. When the hydrochloric acid is furthermore heated so much as to just adopt the temperature of the room by the subsequent solution of potassium iodine, this temperature keeps sufficiently constant ($\pm 1°$) during the experiment. It must here be remembered, that the temperature-coefficient of the photolysis is so small (1,4, according to Plotnikow), that this variation is without any significance at all, and that the dark-process by ordinary temperature is so exceedingly slow, that its high temperature-coefficient plays no rôle whatever. The oxygen-concentration was kept constant by having a current of air bubbling through the reaction-mixture. The air was pressed out of the flask F_4 by means of water which ran down from the flask F_3. It was thus always saturated with water-vapour and was therefore unable to bring about any evaporation of the reaction-liquid, even if the current of air was very strong. As filters were employed those previously [1] described by me.

The final experiments took place, then, in the following manner. The lamp having reached constant tension and the filter-liquid having been put into slow circulation, the hydrochloric acid was heated (2—7° according to the

[1] Zeitschr. f. Electrochemie **19,** 390 (1913).

concentration of the potassium iodide). In the darkened room, where all the measurements were carried out, the weighed amount of potassium iodide was then dissolved in hydrochloric acid by shaking, the temperature of the mixture measured and the couvette filled and put in its place. While this was going on the aperture in the shade S was covered with a shade of card-board. When now the air had been made to bubble through the reaction-mixture with the desired velocity, the aperture in the shade was uncovered and the time together with the voltage and current-strength of the lamp were noted. After the lapse of a suitable time a certain amount (as a rule 2 cm³) of the reaction-mixture was taken out with a pipette, starch solution added and it was titrated with $^1/_{400}$-n thiosulphate of sodium. Immediately thereupon the voltage and the current-strength of the lamp were again read and, if necessary, regulated. After the majority of the liquid had been consumed in this manner, the couvette K_2 was removed, the fluormeter put up close behind the couvette K_1 and the incident energy measured, generally at various potentials of the normal lamp.

The provisional experiments now showed, in accordance with those of Mr. HEEGÅRD POULSEN, that a very good parallelism was really present between the absorbed amounts of energy of various wave-lengths and the corresponding amounts of substance transformed. But the provisional experiments having later turned out to have been made on false assumptions, I only shall mention them very briefly in order to obtain an opportunity of showing where the error came in. The velocity-curve in most of these experiments was as in fig. 2.

The velocity increased rapidly in the beginning, slower

later on, and ended by becoming fairly constant. In some of the experiments sufficient temperature constancy had not been provided for, the hydrochloric acid — having room-temperature — being much cooled by solving
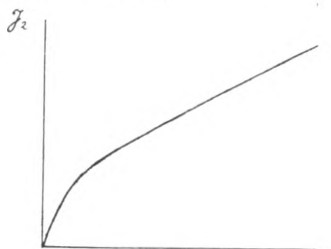

Fig. 2.

the potassium-iodide, and the temperature of the mixture therefore increased, first rapidly, later more slowly towards room-temperature. This source of error having been corrected, the velocity curve was directly from the beginning fairly rectilinear, as was to be expected. An addition of iodine did not alter the velocity, as was also found by PLOTNIKOW.

This fact, in connection with the parallelism between the absorption of the tri-iodine-ion and the colour sensitiveness of the reaction-mixture which had been shown both by HEEGÅRD-PAULSEN and especially by V. A. LARSEN's experiments, made it probable to a high degree, that the tri-iodine-ion must be the actual light-sensitive substance, and that the course of the reaction-velocity might be computable when the amount of energy was known which in each single moment is absorbed by the tri-iodine-ion. If now we imagine a transverse section of there action-mixture at various times after the begin-

Fig. 3.

ning of the exposure, it will be like fig. 3, where the inserted curves indicate the light-intensity in various depths of the liquid at the times t_1, t_2, etc. The simultaneously absorbed amounts of energy increase steadily, until at the

moment t_4, the absorption is complete, hence equal to 1. In this first phase of the exposure the reaction velocity, presupposed to be proportional to the absorbed amount of light, must constantly increase until the absorption becomes complete. From this moment the velocity must become constant.

When the exposure is continued the absorbed amount of light remains the same, but the exposed layer of the liquid is all the time decreasing in thickness. The process takes place in this exposed layer, and thereafter the reaction products are to be mixed with all the dark liquid-volume in the back part of the couvette. If the process is to advance with its full velocity, if, hence, the absorbed light is to be utilised as well as possible, this mixing-process — which may be accelerated by stirring — must take place so quickly, that even the velocity of the light-reaction in comparison herewith is negligible. Augmented stirring must, consequently, augment the rate until a certain limit.

The correctness of the theory can accordingly by tested in three ways. Partly by examining the occurrence of the reaction velocity in the beginning of the exposure, partly by examining the influence of the stirring, and finally by examining the relation between the maximum, constant, velocity and the simultaneously absorbed amount of energy of various wave-lengths.

The Initial Velocity.

The object being to get as many measurements as possible before the absorption becomes complete, these experiments were carried through for blue light of the wave-length 436 µµ, where the extinction-coefficient is comparatively slight (900), and with a couvette with only 5 mm

thickness of layer. The employed solution consisted of 3,32 gms. ($^1/_{50}$ mol) potassium-iodide which was dissolved in 20 cm^3. 1-n hydrochloric acid.

In the following tables:

t means the time, expressed in minutes.

x the liberated amount of iodine, in equivalents per liter.

Δx the increase in the amount of iodine.

$1-10^{-\frac{\alpha}{2}x}$ the relative absorption.

$\Delta x : \left(1-10^{-\frac{\alpha}{2}x}\right)$ the transformed amount of substance per unit of absorption. Δx corresponds to the period which comes after each single determination of absorption.

Table 2.

Experiment 1.

Distance 30 cm. 340 Watt. $T = 26°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1-10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1-10^{-\frac{\alpha}{2}x}\right)$
2	0	—	—	—
4	0	—	—	—
6	0	—	—	—
9	0,28	—	0,30	—
12	0,35	0,07	0,36	0,23
15	0,53	0,18	0,49	0,50
18	0,71	0,18	0,59	0,37
21	0,95	0,24	0,70	0,41
				0,38

$$\frac{\Delta x \cdot 10^3}{1-10^{-\frac{\alpha}{2}x}} : \Delta t = 0,13$$

Experiment 2.

Distance 30 cm. 350 Watt. $T = 26°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1-10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1-10^{-\frac{\alpha}{2}x}\right)$
4	0	—	—	—
8	0	—	—	—
12	0	—	—	—
16	0,19	—	0,21	—
20	0,38	0,19	0,38	0,90

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1-10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1-10^{-\frac{\alpha}{2}x}\right)$
24	0,60	0,22	0,53	0,58
28	0,95	0,35	0,70	0,66
32	1,25	0,30	0,79	0,43
				0,64

$$\frac{\Delta x \cdot 10^3}{1-10^{-\frac{\alpha}{2}x}} : \Delta t = 0,16$$

Experiment 3.
Distance 30 cm. 390 Watt. $T = 25°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1-10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1-10^{-\frac{\alpha}{2}x}\right)$
10	0,65	—	0,56	—
14	0,90	0,25	0,68	0,45
18	1,28	0,38	0,80	0,56
22	1,70	0,42	0,89	0,52
26	1,95	0,25	0,92	0,28
30	2,21	0,26	0,94	0,28
34	2,85	0,64	0,98	0,68
38	3,23	0,38	0,99	0,39
42	3,63	0,40	0,99	0,40
				0,45

$$\frac{\Delta x \cdot 10^3}{1-10^{-\frac{\alpha}{2}x}} : \Delta t = 0,11$$

Experiment 4.
Distance 30 cm. 360 Watt. $T = 26°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1-10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1-10^{-\frac{\alpha}{2}x}\right)$
22	0	—	—	—
30	0,29	—	0,30	—
34	0,65	0,36	0,56	1,2
38	0,81	0,16	0,64	0,29
42	0,98	0,17	0,71	0,27
46	1,39	0,41	0,83	0,58
50	1,65	0,26	0,88	0,31
54	2,00	0,35	0,92	0,40
58	2,38	0,38	0,95	0,41
				0,49

$$\frac{\Delta x \cdot 10^3}{1-10^{-\frac{\alpha}{2}x}} : \Delta t = 0,12$$

Experiment 5.

Distance 60 cm. 310 Watt. $T = 26°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1 - 10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1 - 10^{-\frac{\alpha}{2}x}\right)$
0	0,11	—	0,13	—
10	0,39	0,28	0,39	(2,20)
20	0,66	0,27	0,56	0,69
30	1,04	0,38	0,73	0,68
40	1,46	0,42	0,84	0,58
50	1,75	0,29	0,89	0,35
60	2,23	0,48	0,94	0,54
70	2,70	0,47	0,97	0,50
80	2,98	0,28	0,98	0,29
				0,52

$$\frac{\Delta x \cdot 10^3}{1 - 10^{-\frac{\alpha}{2}x}} : \Delta t = 0,052$$

The four first experiments, where the lamp was placed in 30 centimeters' distance from the reaction-couvette, give the following amounts of substance transformed per unit of absorption and time:

Table 3.

Experiment	$\dfrac{\Delta x \cdot 10^3}{1 - 10^{-\frac{\alpha}{2}x}} : \Delta t$
1	0,13
2	0,16
3	0,11
4	0,12
	0,13

Hence the velocity formula becomes:

$$\frac{\Delta x \cdot 10^3}{1 - 10^{-\frac{\alpha}{2}x}} = 0,13 \, \Delta t.$$

By means of this formula the drawn curve in fig. 4 is calculated, and the observed points are entered here upon, each row of points being displaced in horizontal direction,

until the mean deviations from the curve are as small as possible. The zero-point being uncertain (it depends upon the degree of purity of the sample of potassium iodide) this way of proceeding is fully justifiable.

The figure and the tables show the following facts. For the experiments 1 and 2 a very pure sample of potassium iodide was employed, which even in acid liquid and with admittance of air, kept constant for a long time without giving colouring with starch. Even by exposure a measur-
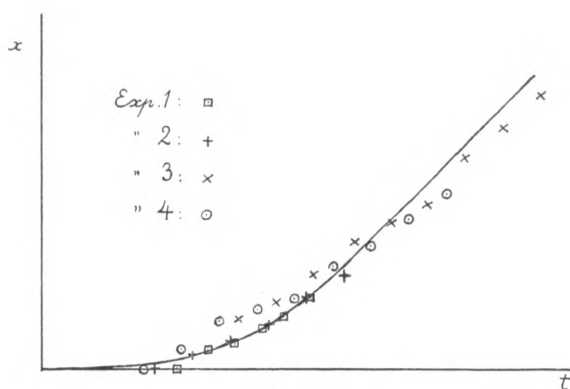

Fig. 4.

able iodine-separation does not occur until after 9—16 minutes respectively, but it then continues with increasing velocity, exactly as demanded by the theory. In these cases the process consequently shows both zero-period and induction-period, — contrary to PLOTNIKOW's assertion. All the induction-periods, the cause of which we have hitherto been able to trace, originate, however, in the fact that some inhibiting impurity has had to be removed before the process can be properly set going. This is, f. inst. the case with the mixture of chlorine and hydrogen, where the impurity is not indeed known with certainty,

but is supposed to be ammonia or an ammonia-derivative[1], with photochlorination of benzene and similar substances, where the impurity is oxygen[2], and with Eder's liquid, where it is likewise oxygen which is removed in the course of the induction-period[3].

But in the case here investigated the induction-period, on the contrary, arises from the fact, that the actual light sensitive substance, the tri-iodine-ion must first be procured before the process can proceed by means of the energy absorbed by this light sensitive substance. The first small amount of tri-iodine-ion cannot, accordingly, be procured by the light itself, as the effect of the light only begins when absorbing tri-iodine-ion is present. It must be secured by means of the slow oxidation, which also takes place in the dark, and we thereby reach the peculiar conclusion, that the condition of processes of this kind being light sensitive is their possession of a measurable darkness-velocity. Thereby they form a separate group, as will be more closely developed in another section (v. p. 24).

If now the employed sample of potassium-iodide contains a little iodate or another oxidating impurity which immediately by solving in hydrochloric acid liberates a little iodine, the zero-period will be quite omitted, and the induction-period be materially shortened, the light immediately finding tri-iodine-ion to work with. This was the case in the experiments 3 and 4, where the employed potassium iodide immediately after the solution in hydrochloride acid gave colouring with starch.

[1] Burgess and Chapman, Journ. Chem. Soc. **89**, 1402 (1906).

[2] Luther and Goldberg, Zeitschr. für phys. Chemi **56**, 43 (1906).

[3] Winther, Zeitschr. f. wiss. Photogr. **8**, 197 (1910).

The Effect of Stirring.

Already the form of the velocity curve in the provisional experiments showed that the slow bubbling-through of air which was employed, produced a too feeble stirring to make the mixing-process occur very rapidly in comparison with the light-process. This is corroborated by the three following experiments which were made under the same circumstances as the experiments 1—4, with the difference, only, that the air-current in the last named experiments was far stronger than in the experiments 6—8.

Table 4.

$\lambda = 436 \ \mu\mu$. Thickness of layer $^1/_2$ cm. Distance 30 cm.

Experiment 6.
360 Watt. $T = 26°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1-10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1-10^{-\frac{\alpha}{2}x}\right)$
6	0	—	—	—
12	0	—	—	—
18	0	—	—	—
24	0	—	—	—
30	0,28	—	0,30	—
40	0,78	0,50	0,63	1,67
50	1,34	0,56	0,82	0,89
60	1,93	0,59	0,91	0,72
70	2,56	0,63	0,96	0,69

Experiment 7.
340 Watt. $T = 26°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1-10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1-10^{-\frac{\alpha}{2}x}\right)$
16	0	—	—	—
24	0	—	—	—
30	0,25	—	0,27	—
36	0,55	0,30	0,50	1,11
42	0,90	0,35	0,68	0,70
48	1,20	0,30	0,78	0,44
54	1,50	0,30	0,85	0,38
60	1,73	0,23	0,89	0,27
66	2,15	0,42	0,94	0,47

Experiment 8.

340 Watt. $T = 26°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$1-10^{-\frac{\alpha}{2}x}$	$\Delta x \cdot 10^3 : \left(1-10^{-\frac{\alpha}{2}x}\right)$
18	0,96	—	0,70	—
22	1,29	0,33	0,81	0,47
26	1,65	0,36	0,88	0,44
30	1,88	0,23	0,91	0,26
34	2,06	0,18	0,93	0,20
38	2,26	0,20	0,95	0,22
42	2,50	0,24	0,96	0,25

The tables show, that the quotient $\Delta x : \left(1-10^{-\frac{\alpha}{2}x}\right)$
i. e. the transformed amount of substance per absorbed unit
of energy, decreases greatly when the absorption increases,
and that it is almost everywhere smaller than it ought to
be according to the experiments 1—4. In experiment 6 it
ought to be $10 \cdot 0,12 = 1,20$, in experiment 7, 0,72 and
in experiment 8, 0,48. The slow stirring has accordingly
prevented the absorbed light from being utilised to its
full degree.

The same result is attained by a couple of experiments,
in which the stirring-velocity was altered during the ex-
periment. The further details having no interest in this
place I shall only give the transformed amounts of sub-
stances. The wave-length was in both experiments 366 $\mu\mu$.

Table 5.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	t	$x \cdot 10^3$	$\Delta x \cdot 10^3$
	strong stirring			strong stirring	
6	0,50	—	6	0,58	—
12	1,13	0,63	12	1,12	0,54
18	1,63	0,50		feeble stirring	
24	2,03	0,40	18	1,30	0,18
	feeble stirring			strong stirring	
30	2,35	0,32	24	1,75	0,45
	strong stirring		30	2,10	0,35
36	2,88	0,53			
	feeble stirring				
42	3,19	0,31			

A comparison between the provisional and the final experiments finally showed, that the constant velocities which were attained in the former, are everywhere much smaller than in the same circumstances in the latter, where the stirring was stronger.

The Colour Sensitiveness.

For the wave-lengths 405, 366 and 313 $\mu\mu$, the extinction is so strong that the absorption even with very small amounts of iodine is practically complete. With regard to these wave-lengths there could therefore be no question of examining the induction-period as in the case of 436 $\mu\mu$, but we had to keep to the constant velocity which occurs in complete absorption. In order to obtain constant velocity also with the blue line (436 $\mu\mu$) without exposing too long, so much iodine-solution was in this case previously added as to make the absorption very nearly complete at the beginning of the exposure. In the experiments 9—13, 0,5 cm thickness of layer was employed and a lamp-distance of 30 cm. The solution was, as before, normal, both with regard to hydrochloric acid and potassium iodide.

Table 6.

	Experiment 9.				Experiment 10.		
$\lambda =$ 436 $\mu\mu$. 365 Watt. $T = 26°$.				$\lambda =$ 405 $\mu\mu$. 360 Watt. $T = 26°$.			
t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$\Delta x \cdot 10^3 : \Delta t$	t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$\Delta x \cdot 10^3 : \Delta t$
0	2,75	—	—	8	0,75	—	—
4	3,10	0.35	0,09	14	1,23	0,48	0,08
8	3,50	0,40	0,10	20	1,59	0,36	0,06
12	3,78	0,28	0,07	26	2,00	0,41	0,07
16	4,19	0,41	0,10	32	2,44	0,44	0.07
24	4,93	0,74	0,09	38	2,85	0,41	0,07
32	5,55	0,62	0,08	44	3,34	0,49	0,08
40	6,38	0,83	0,10	50	3,75	0,41	0,07
			0,090				0,071

Experiment 11.

λ = 405 μμ. 345 Watt. $T = 24°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$\Delta x \cdot 10^3 : \Delta t$
6	0,56	—	—
12	0,94	0,38	0,06
18	1,38	0,44	0,07
24	1,69	0,31	0,05
30	2,00	0,31	0,05
36	2,41	0,41	0,07
42	2,78	0,37	0,06
			0,060

Experiment 12.

λ = 366 μμ. 405 Watt. $T = 25°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$\Delta x \cdot 10^3 : \Delta t$
6	0,50	—	—
12	1,13	0,63	0,11
18	1,63	0,50	0,08
24	2,03	0,40	0,07
30	2,56	0,53	0,09
36	2,90	0,34	0,06
			0,082

Experiment 13.

λ = 366 μμ. 335 Watt. $T = 26°$.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$\Delta x \cdot 10^3 : t$
6	0,58	—	—
12	1,13	0,55	0,09
18	1,46	0,33	0,06
24	1,81	0,35	0,06
30	2,08	0,27	0,05
36	2,42	0,34	0,06
42	2,83	0,41	0,07
48	3,11	0,28	0,05
			0,063

Experiment 14.

λ = 313 μμ. 360 Watt. $T = 25°$, thickness of layer 1 cm.

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$\Delta x \cdot 10^3 : \Delta t$
10	0,81	—	—
20	1,56	0,75	0,08
30	2,38	0,82	0,08
			0,080

Experiment 15.

λ = 313 μμ. 360 Watt. $T = 27°$, thickness of layer 1 cm.

t	$x \cdot 10^3$	$x \cdot 10^3$	$x \cdot 10^3 : t$
10	0,75	—	—
20	1,63	0,88	0,09
30	2,50	0,87	0,09
			0,090

These experiments show that the velocity — by complete absorption and constant oxygen-concentration — actually is as nearly constant as can be expected with the relatively big experimental errors which are inevitable in photochemical measurements of this kind, where it is important to work in as thin layers as possible, and where the amounts of substances which are to be measured must consequently be very small.

Table 7 contains the found velocities together with the simultaneously measured absorbed amounts of energy (in erg per mm² and second) and the quotients of these figures.

Table 7.

λ	$\Delta x \cdot 10^3 : \Delta t$	$E_{abs.}$	$\dfrac{\Delta x \cdot 10^5}{\Delta t} : E_{abs.}$
436	0,090	5,9	1,5
405	0,071	2,9	2,5
—	0,060	2,3	2,6
366	0,082	5,5	1,5
—	0,063	3,5	1,8
313	0,080	3,1	2,6
—	0,090	3,5	2,6
			2,2

When considering the inaccuracy which an energy-measurement with the fluormeter is always beset with, the proportionality between the absorbed amounts of energy and the transformed amounts of substance can hardly be expected to be shown in a better manner.

According to PLOTNIKOW's experiments, which were, however, carried out under quite different circumstances — no stirring, decreasing oxygen-concentration — the velocity should be proportional to the oxygen-concentration, for which reason a single series of experiments was executed with the passage of pure oxygen. It hereby appeared that the darkness-velocity increased more than the oxygen-concentration. While the darkness-velocity in the former experiments on an average is $0,11 \cdot 10^{-3}$ equivalents per liter in the course of 15 minutes, by saturating with oxygen it was found to be $0,66 \cdot 10^{-3}$. The light-velocity, on the contrary, increased in far slighter degree. In order to be able to eliminate the great darkness-velocity the experiment was carried through with alternating exposing and darkening.

Table 8.

$\lambda = 366.$ 350 Watt. $T = 25°.$

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$\Delta x \cdot 10^3 : \Delta t$
0	0	—	—
darkness			
6	0,25	0,25	—

t	$x \cdot 10^3$	$\Delta x \cdot 10^3$	$\Delta x \cdot 10^3 : \Delta t$
light			
12	1,91	1,66	0,23
darkness			
18	2,13	0,22	—
light			
24	3,46	1,33	0,17
darkness			
30	3,79	0,33	—
light			
36	4,90	1,11	0,15
			0,18

The mean of the darkness-velocities is $0,27 \cdot 10^{-3}$ per 6 minutes. If this velocity is subtracted from the velocity of the total amounts transformed, we obtain the light-velocities per minute, given in the last column. By comparison with the experiments 12 and 13 it is seen, that the velocity has only increased abt. $2^1/_2$ times, simultaneously with the oxygen-concentration having been augmented 5 times. The absorbed energy here being 3,7 erg, we have:

$$\frac{\Delta x \cdot 10^5}{\Delta t} : E_{abs} = 4,9$$

2,2 times as great, then, as the average for the experiments with air-passage.

Before leaving this section we have only to note, that PLOTNIKOW's assertion, that the reaction-mixture employed as a light-filter, does not decrease the velocity, must either be due to a misunderstanding, an incorrect statement in the said paper, or to quite incredible experimental errors.

For the investigation of this point a couvette of 1 cm thickness was divided into two partitions by means of a thin glass-wall, each partition of abt. 0,45 cm thickness, and both filled with the usual reaction-mixture and stirred by an aircurrent, the stirring — which was insufficient for a complete utilising of the light — being as nearly uniform

in both halves as possible. The light had consequently to pass the one partition with the reaction-mixture before it reached into the other partition. At the same time the velocity of the dark-process was determined.

Table 9.

$\lambda = 405\ \mu\mu.\ 350\ \text{Watt}.\ T = 26°.$

$x \cdot 10^3$

t	1st partition	2nd partition	darkness	2nd part.÷darkness
15	—	0,73	0,12	0,61
17	1,04	—	—	—
31	—	1,00	0,24	0,76
33	1,75	—	—	—
45	—	1,13	0,33	0,80
47	2,44	—	—	—
60	—	1,25	0,45	0,80
62	3,23	—	—	—
75	—	1,46	0,57	0,89
77	3,88	—	—	—
90	—	1,58	0,69	0,89
92	4,55	—	—	—
105	—	1,75	0,78	0,97
107	5,19	—	—	—

While the process in the first partition takes its even course, it soon stops in the second partition, of course on account of the absorption of the iodine in the reaction-mixture standing before it. To make certain that this stop in the 2nd partition was not due to peculiarities in the walls of this partition or in the medium wall, it was filled, in a fresh experiment, with the same reaction-mixture, but in such a way that the 1st partition was filled with 1 normal hydrochloric-acid.

Table 10.

$\lambda = 405\ \mu\mu.\ 420\ \text{Watt}.\ T = 26°.$

t	$x \cdot 10^3$
15	1,10
30	2,36
47	3,75
60	4,69

By comparison with the last experiment it is seen that the 2nd partition acts quite normally, if only the active light is not kept away.

II. The Optical Auto-Sensitisation.

The previous investigations show that, by the photo-chemical oxidation of the iodine-hydrogen, it is the tri-iodine-ions, themselves formed by the process, which determine the course of the process, the amount of energy, absorbed by these tri-iodin-ions, being decisive for the reaction-velocity. The absorption of the iodine-ion lies further out in ultra-violet. The figures 5 and 6 show the course of the absorption by the formation of the tri-iodine-ion. They are the result of spectrographical investigation partly of solutions of a certain amount of iodine in varying concentrations of potassium-iodide (fig. 5), partly of varying amounts of iodine in 1-normal potassium-iodide-solution (fig. 6). In fig. 5 are furthermore inserted the absorption-limits for varying con-centrations of potassium-iodide. It is seen from this that the absorption of the potassium-iodide only becomes strong at abt. $280\,\mu\mu$, while the absorption of the tri-iodine-ion reaches into the visible spectrum, forming two bands having maxima at abt. 350 and abt. 290, the latter being, however, deformed on account of the absorption of the potassium-iodide in this region. Fig. 5 shows how the absorption of the solution decreases greatly with falling potassium-iodide-concentration, hence, with decreasing tri-iodide-concen-tration, the tri-iodide, thus, being undoubtedly the bearer of the strong absorption.

The energy absorbed by the tri-iodine-ion must in one way or other be transmittable to the iodine-ion, and thereby

give rise to the oxidation of the latter. As will be shown in another paper, the question here, probably, is of a transformation of the absorbed radiation to a radiation of such wave-length as can be absorbed by the iodine-ion.

In this place we have only to point out what is essential in the process, namely 1) that the optical sensitiser is first formed in the process itself, which consequently 2) must possess a measurable darkness-

Fig. 5.

velocity, in order that this sensitiser can be formed and act at all, and 3) that the optical sensitiser is formed by simple oxidation of the substance which is to be oxidated by the process, hence by the process itself which it is to accelerate.
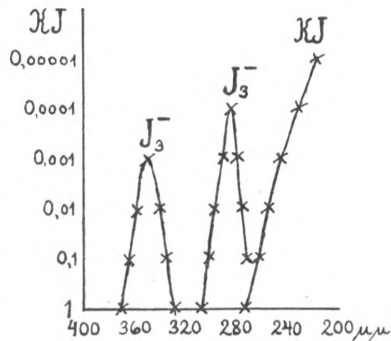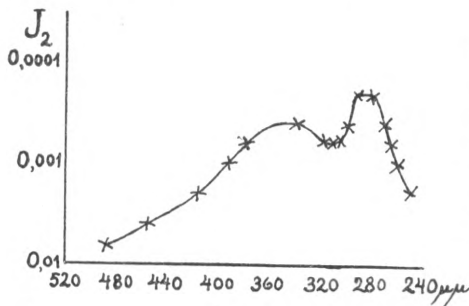

Fig. 6.

It is now beyond all doubt that these peculiarities are re-found in a series of other processes and are so characteristic that we are fully justified in comprising these processes in a group which may suitably be called the optical auto-sensitisation[1].

[1] I. PLOTNIKOW in his photochemical system (Zeitschr. f. physikal. Chemie 77, 472) has a group which is called »photochemische Autokatalyse« which should approximately approach the one given here, but wanting in several of the essential features of the latter, and without statement of any example.

In the literature we find the following cases:

The oxidation of the leuco-compounds to colour-substances. This process possesses a measurable dark-ness-velocity. It is, as shown by GROS[1], light-sensitive and is — as shown by the same author — accelerated by the colour substances themselves which are formed by the oxidation, the rays which are absorbed by these colour-substances being thus those which accelerate the oxidation also of the, to begin with, (apparently) colourless leuco-compounds. Starting from the indicated theory of the trans-formation of the absorbed radiation, it is of interest to note, that the leuco-compounds and the corresponding colour-sub-stances according to P. KRÜSS[2] possess a common absorption-domain in ultra-violet, quite like iodine-ion and tri-iodine-ion.

The oxidation of the pyrogallic acid in alcaline liquid. This process, according to TRAUTZ and THOMAS[3], is sensitive to red light, which is quite mysterious as long as the pyrogallic acid itself is considered as the actual sensitive substance. The oxidation product is brown. Its extinction-curve Mr. ORLA SAEBYE has determined with KÖNIG-MARTENS spectrophotometer. The solution contained 2 cm^3 5 per cent pyrogallic acid, 2 cm^3 10 per cent sodium hydroxide, 300 cm^3 water, and was oxidated by shaking with air. The concentration of the pyrogallic acid was 0,00262-molar. The molar decadic extinction-coefficients are given in table 11 and fig. 7.

Table 11.
Solution:

	I			II	
wave-length	fresh	1 day old	wave-length	fresh	1 day old
694 μμ	—	65	692 μμ	90,5	47,5
656 ·	—	8,7	667 ·	103	0

[1] Zeitschr. f. physikal. Chemie 37, 157 (1901).

[2] Jahrbuch d. Photographie 1906, 83.

[3] THOMAS, Inaug, Dissert. Freiburg i. Br. 1908, 39.

Solution:

wave-length	I fresh	1 day old	wave-length	II fresh	1 day old
579 μμ	220	23,1	646 μμ	144	3,2
546 -	257	105	626 -	192	22
436 -	404	591	607 -	242	77
			579 -	340	117
			546 -	445	232
			436 -	1185	—

It is seen from this, that by simple oxidation of pyro-gallic acid at any rate there may be formed a product which has selective absorption in red. Whether it is just that substance which is formed by the insolation of pyrogallic acid must be determined by direct experiments, but the sensitive-ness has, however, been found to be so small that even a slight amount of this substance is suffi-cient to explain it.

Also this process has a mea-surable darkness-velocity.

The oxidation of sodium sulphide in aqueous solu-

Fig. 7.

tion. The process possesses a measurable darkness-velocity. According to Trautz[1] it is not light-sensitive, as long as the solution is pure, but becomes so when by oxidation free sulphur (or polysulphides) are formed. The sensitive-ness lying also here in red, it must be specially investi-gated whether the light-product also here has a selective ab-sorption in this spectral-section.

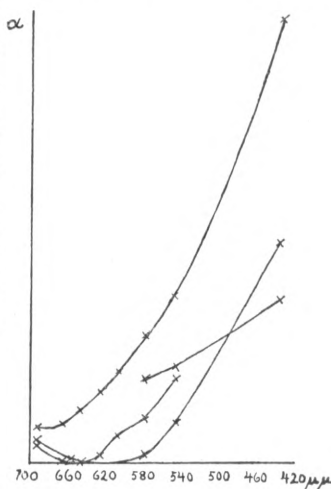Provisionally we thus know four photolyses which

[1] Jahrb. d. Photographie 1909, 39.

undoubtedly fall within this group, and several other light-
processes will no doubt on closer examination be referable
to it.

Results of this work.

When solutions of hydriodic acid are insolated in thin
layer, strongly stirred and kept at a constant concentration
of oxygen, the rate of oxidation is at first zero, then in-
creases during an induction period and finally becomes
constant.

The sensitiveness of the oxidation of hydriodic acid is
— both for the same wavelength and different concen-
trations and for different wavelengths — proportional to
the absorption of the triiodine-ion.

It is possible to form a certain group of optical sen-
sitisations — the optical autosensitisation — the characteri-
stics of which are, that the optical sensiser is formed by the
very process which it is to accelerate, and that this process
therefore must possess a measurable velocity in darkness.

Royal Technical College of Copenhagen,
May 1919.