XI.—INFLUENCE OF LIGHT UPON THE DECOMPOSITION OF IODIDES.

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Received March 31, 1879.

As long ago as 1845, a sharp controversy arose between Schönbein and Prof. Fischer, of Breslau, as to whether dilute solutions of potassium iodide would undergo decomposition in the presence of free acid. The latter had stated that all hydrous acids would turn paper, moistened with potassium iodide solution, brown. Schönbein, in reply (Jour. für prakt. Chem., 1845, xxxiv., p. 492), pointed out the numerous sources of error from impurities in the iodide, and asserted that had Fischer employed a pure salt, he would have obtained quite different results. Moreover, that atmospheric air, even when mingled with half its volume of carbonic acid, and enclosed in a flask, would not turn a piece of iodide-potassium-starch-paper exposed to its action, blue, however long the exposure might be continued.

It will appear probable, I think, after examination of the experiments detailed below, that Prof. Fischer's results were not due to the cause assigned them, and that both investigators might have legitimately arrived at discordant conclusions from sources of chemical perturbations at that time unsuspected.

A similar remark, perhaps, would apply to the dispute between M. Houzeau and M. L. Sauvage (Compt. Rend., 1868, LXVII., pp. 633, 714, 1138). The former stated that the decomposition noted by M. Sauvage, when he agitated dilute solution of potassium iodide with dilute sulphuric acid, was due to the ether employed to collect the iodine, this ether producing oxygenated water ; and that when chloroform was substituted, no evidences of decomposition could be detected.

Without further anticipating, however, it will be better first to relate the experiments themselves, beginning at the point arrived at in the conclusion of paper in the first number of the current volume, and afterwards deduce certain conclusions, having an important bearing on numerous operations performed in the laboratory.

I.—To determine whether a change of base influenced the rate of decomposition in the sunlight, when the same acid was employed ; or, with the same base, when different acids were used. Ten per cent. solutions of the iodides were employed :

Decompositions effected January 18th. 12—1 P. M.

100 cc	H_2O+5 cc	starch+1 cc	KI +1	cc H_2SO_4	$=2.25$	mgrm. I.
20 cc	“	“	1 cc NH_4I+1	cc H_2SO_4	$=1.35$	“
100 cc	“	“	“	“	$=2.20$	“
20 cc	“	“	1 cc KI +1	cc HNO_3	$=0.90$	“
100 cc	“	“	“	“	$=2.00$	“
20 cc	“	“	1 cc NH_4I+1	cc HNO_3	$=1.00$	“
100 cc	“	“	“	“	$=2.00$	“
20 cc	“	“	1 cc NH_4I+1	cc HCl	$=0.30$	“
100 cc	“	“	“	“	$=1.00$	“

The above experiments were performed with acids whose specific gravities were as follows: Sulphuric acid, 1.84; hydro-chloric acid, 1.202, and nitric acid, 1.4. In the subsequent experiments, the acids employed were some manufactured in the laboratory with especial care, and of such strength, that 1 cc of the sulphuric acid corresponded to 25 cc of a normal soda solution; 1 cc of the hydro-chloric to 10.7 cc, and 1 cc of the nitric acid to 12.6 cc of the normal soda solution.

(Strong sun-light) Feb. 4th. 1879. 1 P. M.—3:30 P. M.

100 cc	H_2O+5 cc	starch+1 cc	KI+1	cc H_2SO_4	$=16.0$	mgrm. I.
100 cc	“	“	“	1 cc HNO_3	$=17.5$	“
100 cc	“	“	“	1 cc HCl	$=16.0$	“
100 cc	“	“	1 cc NH_4I+1	cc H_2SO_4	$=14.5$	“
100 cc	“	“	“	1 cc HNO_3	$=16.5$	“
100 cc	“	“	“	1 cc HCl	$=13.5$	“
100 cc	“	“	1 cc CdI_2+1	cc H_2SO_4	$=11.0$	“
100 cc	“	“	“	1 cc HNO_3	$=14.5$	“
100 cc	“	“	“	1 cc HCl	$=11.0$	“

It will be noted that this series shows less of a definite character than the foregoing. The only constant feature being the greater amount of decomposition occurring in presence of the free nitric acid. One phenomenon made strikingly evident in this experiment was, that a great amount of decomposition took place after all the starch present had been precipitated, the supernatant liquid in every comparison-tube being dark yellow. It appeared, therefore, important to keep the starch in excess in each experiment. Repeated :—

Feb. 10th, 1879. Feeble sun-light for 2¼ hrs.

100 cc	H_2O+5 cc	starch+1 cc	KI+1 cc	H_2SO_4	= 7.15	mgrm. I.
100 "	" 5 "	" 1 "	" 1 "	HNO_3	= 5.2	"
100 "	" 5 "	" 1 "	" 1 "	HCl	= 2.0	"
100 "	" 5 "	" 1 "	CdI_2+1 "	H_2SO_4	= 6.5	"
100 "	" 5 "	" 1 "	" 1 "	HNO_3	= 5.0	"
100 "	" 5 "	" 1 "	" 1 "	HCl	= 2.1	"
100 "	" 5 "	" 1 "	KI+1 "	HNO_3	= 6.4	"
100 "	" 5 "	" 1 "	" 1 "	HCl	= 2.2	"
100 "	" 5 "	" 1 "	CdI_2+1 "	HNO_3	= 5.3	"
100 "	" 5 "	" 1 "	" 1 "	HCl	= 2.9	"

In this series, though at the close of the experiment, the supernatant liquids were yellow, yet the amounts of liberated iodine were not so greatly in excess of the required amounts of starch, and more agreement will be found in the results. The experiments were therefore twice repeated, the times of exposure being made so short, that the liquids remained bright blue to the end. Any shade of greenish blue, arising from the admixture of the blue of the starch iodide with the yellow of free iodine, was avoided.

STARCH IN EXCESS.—Feb. 12th, 1879.

I, from 1—1:35 P.M. (sun-light).—II, 3:30—5 P.M. (cloudy).

								I.		II.	
100	cc H_2O	+5	cc starch	+1	cc KI	+1	cc H_2SO_4	—0.45	mgrm. I.	0.25	mgrm. I.
100	"	+5	"	+1	"	+1	HNO_3	—0.40	"	0.30	"
100	"	+5	"	+1	"	+1	HCl	—0.15	"	0.10	"
100	"	+5	"	+1	CdI_2	+1	H_2SO_4	—0.45	"	0.24	"
100	"	+5	"	+1	"	+1	HNO_3	—0.45	"	0.30	"
100	"	+5	"	+1	"	+1	HCl	—0.15	"	0.10	"
100	"	+5	"	+1	KI	+1	HNO_3	—0.55	"	0.30	"
100	"	+5	"	+1	"	+1	HCl	—0.15	"	0.10	"
100	"	+5	"	+1	CdI_2	+1	HNO_3	—0.50	"	0.30	"
100	"	+5	"	+1	"	+1	HCl	—0.15	"	0.10	"

This double series brought out strikingly the fact, which was confirmed in all subsequent trials *with sun-light*, that the amount of iodine liberated in presence of free sulphuric acid, bore a nearly constant ratio, when the same base was combined with iodine, to that occurring in case of hydrochloric acid. The deportment in presence of nitric acid was at variance with that anticipated, on account of a secondary action not investigated until later.

II.—As to the part played by the starch itself in these reactions, the supposition had been, that its affinity for the liberated iodine, though feeble, had nevertheless been one of the agencies at work in determining the fact of a decomposition.

To what extent its influence was exerted, was the object of the next experiment, in which to the contents of four comparison-tubes each containing 100 cc H_2O, 5 cc starch were added (column I), and to four other similarly prepared, no starch (column II.)

Feb. 13th, 1879. 1:15—2:15 P. M. (cloudy).

	I.	II.
1 cc KI + 1 cc H_2SO_4 =	Lost.	1.15 mgrm. I.
1 cc KI + 1 cc HCl =	0.45 mgrm. I.	0.90 "
1 cc CdI_2 + 1 cc H_2SO_4 =	0.55 "	1.15 "
1 cc CdI_2 + 1 cc HCl =	0.45 "	0.90 "

That omission of starch should have increased, and in fact have doubled the amount of iodine set free under these circumstances, was so opposite a result to what was anticipated, that the experiment was repeated in the expectation of finding the former figures incorrect; they were confirmed.

Repeated Feb. 15th, 1879 10:30 A.M.—12:45.

	I.	II.
1 cc KI + 1 cc H_2SO_4 =	3.70 mgrms. I.	7.5 mgrms. I.
1 cc CdI_2 " =	4.00 "	8.2 "
1 cc LiI " =	3.75 "	5.8 "

Further proof was obtained when each of the iodides was exposed with each of the acids, both being employed of same strengths and amounts as stated above, and the solutions made up to 100 cc.

Feb. 19th, time 20 mins. (Without starch.)

1 cc H_2SO_4	+ 1 cc KI	= 2.85	mgrm. I;	CdI_2	= 3.85	mgrm. I;	LiI	= 2.35	mgrm. I.
" HNO_3	"	= 2.85	"	"	= 3.15	"	"	= 2.30	"
" HCl	"	= 2.00	"	"	= 2.45	"	"	= 1.35	"

The decomposition, as will be seen on comparing these results with the foregoing, was so much greater, that after the two following experiments, the use of starch was abandoned in most cases.

III.—Decomposition in Presence of Organic Acids.

To 1 cc of the potassium iodide solution, acetic, tartaric and oxalic acids were added, and the liquids made up to 100 cc. Three of the tubes contained starch—three without. At the end of 2 hours exposure to the sun-light, only the oxalic acid had effected decomposition ; after 8 hours all had changed ; they were left for 2 days, and titrated at the end of 48 hours.

Feb. 22d. ; 2 days. (Organic acids.)

	With starch.	Without.
Oxalic acid	= 6.15 mgrm. I.	8.25 mgrm. I.
Tartaric "	= 0.85 "	0.30 "
Acetic "	= 0.35 "	0.50 "

IV.—Decompositions Effected by the Electric Light.

A cylindrical stand was made, of such dimensions that the centre of the axis of the 100 cc column contained in each comparison-tube, should be at a distance of 6 in. from the focus of the electric light. The electric arc was taken between carbon points, and was produced by electricity generated with a dynamo-electric machine run by steam power, its illuminating capacity varying during the course of the experiment, according to the photometric measurements made by Prof. Morton and Mr. Beckmayer, between 7,000 and 7,500 candles. In the first experiment, the first nine solutions contained 5 cc starch-water, the last two none, and it will be noted that in the latter decompositions were twice as great.

ELECTRIC LIGHT.

	15 min. Mgrm. I.		20 min. Mgrm. I.		7½ min. Mgrm. I.
1 cc H_2SO_4 + 1 cc KI	= 1.65 ;	same	= 3.90 ;	same	= 3.00
1 HNO_3 + 1 "	= 1.80 ;	1 cc HCl	= 3.15 ;	——	
1 HCl + 1 "	= 1.05 ;	same	= 3.40 ;	same	= 2.00
1 H_2SO_4 + 1 CdI_2	= 1.80 ;	same	= 3.15 ;	same	= 2.25
1 HNO_3 + 1 "	= 1.40 ;	1 cc HCl	= 2.30 ;	——	
1 HCl + 1 "	= 1.25 ;	same	= 2.50 ;	same	= 1.35
1 H_2SO_4 + 1 LiI	= 0.90 ;	same	= 3.00 ;	same	= 2.10
1 HNO_3 + 1 "	= 0.95 ;	——		——	
1 HCl + 1 "	= 0.60 ;	same	= 1.70 ;	same	= 1.00
1 H_2SO_4 + 1 KI	= 2.35 ;				
1 " + 1 CdI_2	= 2.30 ;				
1 " + 1 NH_4I	= —— ;		= 2.50 ;		= 2.30
1 HCl + 1 "	= —— ;		= 1.50 ;		= 1.50
1 " + 1 "	= —— ;		= 1.85 ;		= ——

The potassium iodide solution in the first two trials was of ten per cent., in the third twice this amount. The other iodides were of a strength equivalent to the ten per cent. KI solution in each trial.

The highly actinic nature of the electric beam is made strikingly manifest by the large amounts of iodine set free. Moreover, its chemical energy is not the same in the three experiments, twice the amount of decomposition having been effected in the third, as in the second experiment, during the same interval of time. The reason of this variation is not quite clear, for while the light was remarkably uniform during the third experiment, there was no such corresponding difference in the apparent luminous effect.

V.—Comparison of Effects of Sun-light and Electric Light after passing through Absorbing Media.

One cc of a twenty per cent. solution of potassium iodide solution was used in these experiments, with the acids and water. The comparison-tubes were supported in the centers of tall, wide-mouth bottles, so as to be surrounded by an equal thickness (3 cm.) of the absorbing medium on every side. Their tops and those of the bottles were closed in with tin foil, so as entirely to prevent the access of light from that quarter. The blue medium was ammoniacal solution of copper ; the yellow, neutral potassium chromate ; the red, fuchsine. They were made of such strength that the outlines of an object could be seen through them with equal distinctness, though in each case feebly.

			Sun-light.	Electric Light.
			Mch. 3d, 12 M.—3 P.M.	20 min.
Blue	1 cc	H_2SO_4	= 7.15 mgrm. I.	= 2.00 mgrm. I.
	1	HCl	= 6.65 "	= 1.50 "
Yellow	1	H_2SO_4	= 2.00 "	= 0.165 "
	1	HCl	= 1.35 "	= 0.15 "
Red	1	H_2SO_4	= 4.60 "	= 1.65 "
	1	HCl	= 2.50 "	= 1.00 "

Computed for equal intervals, they would be :

			Sun-light (1 hour).	Electric Light (1 hour).
Blue	1 cc	H_2SO_4	= 2.38 mgrm. I.	= 6.00 mgrm. I.
	1	HCl	= 2.22 "	= 4.50 "
Yellow	1	H_2SO_4	= 0.67 "	= 0.50 "
	1	HCl	= 0.45 "	= 0.45 "
Red	1	H_2SO_4	= 1.53 "	= 4.95 "
	1	HCl	= 0.83 "	= 3.00 "

Now, while in the preceding experiments, the action in the electric light had been approximately three times the maximum of that in the sun-light, this ratio, when absorbing media were used, was approached only in case of the blue and red solutions. In other words, the yellow medium absorbed a much larger relative proportion of the actinic rays of the electric, than of the sun-light. Better to understand what occurs in this instance, a study of the absorption-spectra (chemical) of the media, and of the decomposition of the various iodides in the several portions of the spectra of the sun and electric light, has been entered upon.

VI.—Decomposition effected by the Magnesium Light.

The light was furnished by a single-ribbon magnesium lamp, run by clock-work. The reason for repeating the experiment *three* times was that the ratio of decomposition in presence of free hydro-chloric acid was greater instead of less (as when sun and electric light were employed), than in the presence of free sulphuric acid, the acids being of strength before given. This difference is probably connected with the fact, long since recognized in photography, that the maximum of sensitiveness for certain sensitive salts is located in different parts of the spectrum. The potassium iodide was of 20 p. c., the other iodides were equivalent to a 10 p. c. KI solution.

MAGNESIUM LIGHT.

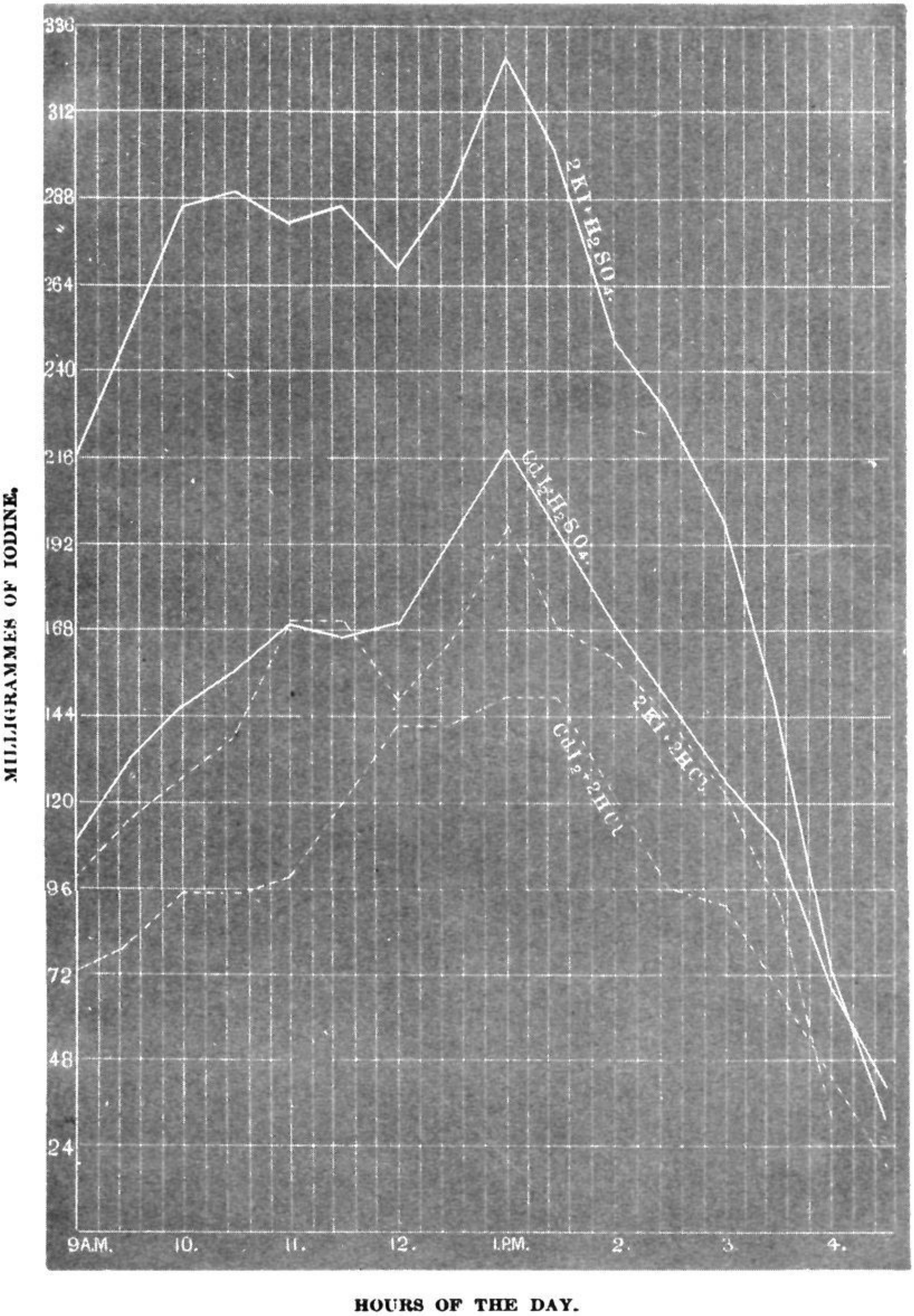
	I.	II. (1 hour). Mgrm. l.	III. (½ hour.) Mgrm. l.
1 cc H_2SO_4 + 1 cc KI	= lost ;	same = 0.050 ;	same = 0.015.
" HCl "	= 0.225 ;	" = 0.075 ;	" = 0.050.
" H_2SO_4 + 1 cc CdI_2	= 0.080 ;	" = 0.035 ;	" = 0.010.
" HCl "	= 0.150 ;	" = 0.050 ;	" = 0.050.
" H_2SO_4 + 1 cc LiI	= 0.075 ;	" = 0.040 ;	" = indet.
" HCl "	= 0.165 ;	" = 0.050 ;	" = 0.060.
" H_2SO_4 + 1 cc NH_4I	= 0.115 ;	" = 0.060 ;	
" HCl "	= 0.200 ;	" = 0.070 ;	

ACTINOMETRIC DETERMINATIONS, FEB'RY 27th, 1879.

	A. M. 9–9:30	9:30–10	10–10:30	10:30–11	11–11:30	M. 11:30–12	12–12:30	P. M. 12:30–1	1–1:30	1:30–2	2–2:30	2:30–3	3–3:30	3:30–4	4–4:30	4:30–5
1 cc H_2SO_4 + 1 cc KI	2.15	2.50	2.85	2.90	2.80	2.85	2.70	2.90	3.25	3.00	2.50	2.25	2.00	1.55	0.75	0.35
1 " HCl "	1.00	1.15	1.25	1.40	1.70	1.70	1.55	1.65	2.00	1.70	1.60	1.45	1.25	0.90	0.35	0.23
1 cc H_2SO_4 + 1 cc CdI_2	1.15	1.30	1.45	1.55	1.70	1.65	1.70	1.95	2.20	1.95	1.70	1.50	1.30	1.10	0.70	0.43
1 " HCl "	0.75	0.85	1.00	1.00	1.05	1.20	1.40	1.40	1.50	1.50	1.20	0.95	0.90	0.65	0.35	0.20
1 cc H_2SO_4 + 1 cc LiI	1.20	1.30	1.35	1.45	1.60	1.50	1.60	1.70	1.55	1.45	1.50	1.40	1.25	1.05	0.65	0.43
1 " HCl "	0.75	0.80	0.95	1.00	1.00	1.00	1.10	1.20	1.20	1.10	1.00	0.75	0.70	0.50	0.30	0.18
1 cc H_2SO_4 + 1 cc NH_4I	1.30	1.40	1.55	1.65	1.80	1.70	1.80	1.90	1.95	1.80	1.70	1.50	1.20	1.05	0.70	0.45
1 " HCl "	0.85	0.95	1.00	1.05	1.15	1.15	1.15	1.20	1.15	1.15	1.10	0.85	0.90	0.60	0.30	0.18

VII. — Actinometric Determination of Sunlight.

In order to compare the decomposition effected by the sunlight, after passing through various thicknesses of the earth's atmosphere, and to compare the relative amounts of iodine set free under these circumstances, when different salts were employed, the determinations summarized in the accompanying table were made. The day was unusually brilliant and unclouded, from beginning to close. The potassium iodide was 20 p. c.; the other iodides were equivalent to one-half this quantity; the acids were of same strength as before given. An inspection of the accompanying diagram, in which the potassium and cadmium curves are given, will exhibit these results more clearly.

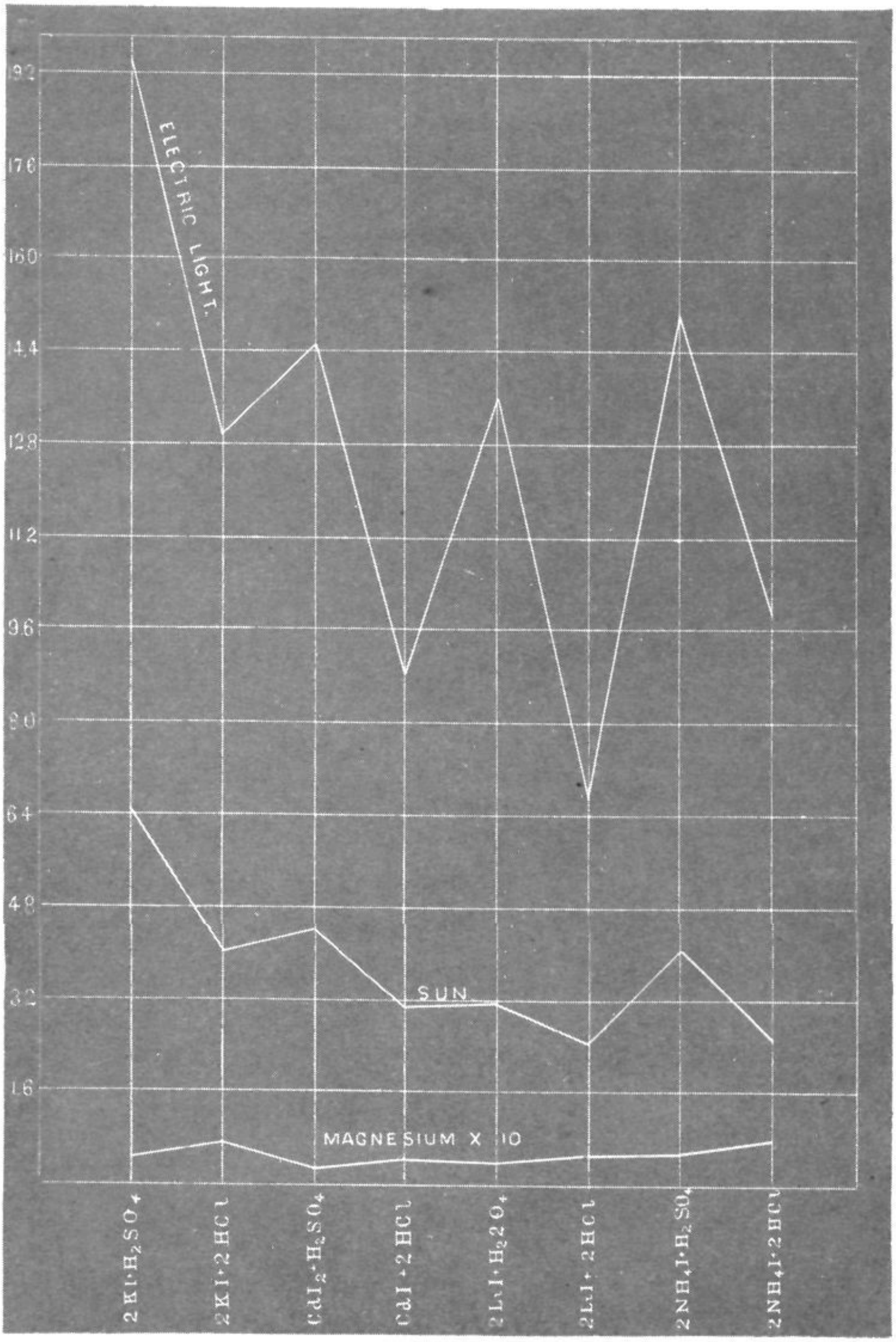

MILLIGRAMMES OF IODINE.
336
312
288
264
240
216
192
168
144
120
96
72
48
24
9A.M.
10.
11.
12.
1.P.M.
2.
3.
4.
HOURS OF THE DAY.
2KI+H2SO4.
CdI2+H2SO4.
2KI+2HCl.
CdI2+2HCl.

VIII.—Comparison of Actinic Intensities for Equal Times.

The foregoing results are brought together in the following table, and likewise illustrated in the diagram. The numbers found for the magnesium light have been multiplied by ten, in order that the corresponding curve may be brought into the same illustration with the others.

DECOMPOSITION DURING EQUAL TIMES (1 hour).

	Electric Light.	Sun.	Magnesium.
H_2SO_4 + KI =	19.5 mgrm. I.	6.5 mgrm. I.	0.05 mgrm. I.
HCl + " =	13.0 "	4.0 "	0.075 "
H_2SO_4 + CdI_2 =	14.6 "	4.4 "	0.035 "
HCl + " =	8.8 "	3.0 "	0.050 "
H_2SO_4 + LiI =	13.7 "	3.1 "	0.04 "
HCl + " =	6.5 "	2.4 "	0.05 "
H_2SO_4 + NH_4I =	15.0 "	3.9 "	0.06 "
HCl + " =	9.8 "	2.3 "	0.07 "



192
176
160
14.4
128
11.2
9.6
8.0
6.4
4.8
3.2
1.6
ELECTRIC LIGHT.
SUN
MAGNESIUM X 10
$2KI\cdot H_2SO_4$
$2KI\cdot 2HCl$
$CdI_2\cdot H_2SO_4$
$CdI + 2HCl$
$2LiI\cdot H_2 2O_4$
$2LiI + 2HCl$
$2NH_4I\cdot H_2SO_4$
$2NH_4I\cdot 2HCl$

IX.—Influence of Heat upon the Decomposition of the Iodides.

These experiments were made at that period in the investigation, when the effect of light had been recognized, but the concurrent action of oxygen was unknown. The first experiment was made in comparison-tubes, each containing 1 cc KI (of 10 p. c.), 5 cc starch water, and 1 cc H_2SO_4. But I was made up to 20 cc with water, II to 60 cc and III to 100 cc. The times given in the upper line are those at which the change of color first occurred ; those in the second line, when the same tint appeared on further heating. The change is quite gradual, running through the scale of colors indicated.

I. (20 cc).

Very Faint Rose.	Faint Rose.	Rose.	Violet.	Blue.
(30°C.) 5 mins.	(33°) 10 mins.	(36°) 16 mins.	(38°) 20 mins.	(45°) ½ hr.
(95°) 95 mins.	(86°) 1½ hr.	(65°) 50 mins.	(56°) 40 mins.	

At boiling point, slowly became colorless.

II. (60 cc).

(32°) 7 mins.	(34°) 12 mins.	(39°) 24 mins.
(61°) 44 mins.	(50°) 39 mins.	

Became colorless at 85°, at the expiration of 1 hr. 25 mins.

III. (100 cc).

(34°) 11 mins.	(41°) 27 mins.
(50°) 35 mins.	

Became colorless at 59°.

In other experiments different figures were obtained, and since the starch is converted into dextrin on heating with dilute acid, its use as an indicator under these circumstances was abandoned.

Effect of Heat in Closed Flasks.—To three flasks, each containing 60 cc H_2O and 1 cc H_2SO_4 were added ½ cc, 1 cc and 2 cc of a 10 p. c. KI solution respectively. They were closed with valve-stoppers, so as to exclude the air, and heated to 93° C. for 6 hours. After cooling, starch was added and they were titrated. The first contained no free iodine, the second gave a very faint rose color to the starch, but too little to titrate, the third contained 0.1 mgrm. I. In other words, when the potassium iodide was diluted 600 times, and heated nearly to the boiling point in a closed flask for 6 hours, the amount of iodide set free was so small that it could not be estimated, and when diluted 1200 times, no change whatever took place.

Effect of Heat in Flasks Entirely Deprived of Air.—Three comparison-tubes were connected in the manner of wash-bottles. Each contained 100 cc water and 1 cc KI solution of 20 p. c., but the first had 1 cc H_2SO_4, the third 1 cc HCl as well. After passing a stream of carbonic anhydride, previously washed with KI solution, through them for ½ hour, they were immersed in a salt bath and the temperature raised to 105° C. After two hours exposure, a current of carbonic anhydride constantly flowing, no iodine had been liberated in either of the three vessels. Similar acidified solutions, heated to the same temperature, in contact with air, turned yellow immediately.

X.—Reactions Involved in the Decomposition of Iodides.

The fact of the decomposition of the dilute iodides in presence of free acid having been established, it was essential to explain the accompanying reactions. The following might be legitimately conceived of :

[1.] $2\ KI + 2\ H_2SO_4 = K_2SO_4 + 2\ H_2O + SO_2 + I_2.$

[2.] $4\ KI + 2\ H_2SO_4 + O_2 = 2\ K_2SO_4 + 2\ H_2O + 2\ I_2.$

[3.] $4\ KI + 4\ HNO_3 + O_2 = 4\ KNO_3 + 2\ H_2O + 2\ I_2.$

[4.] $2\ HNO_3$ (in sun-light) $= N_2O_3 + H_2O + O_2.$

[5.] $2\ KI + 2\ HNO_3 + N_2O_3 = 2\ KNO_3 + H_2O + N_2O_2 + I_2.$

[6.] $4\ KI + 4\ HCl + O_2 = 4\ KCl + 2\ H_2O + 2\ I_2.$

It was evident the equation [1], which is true of concentrated solutions, could not apply to these very dilute ones, for two reasons : 1st. Because, as a fact, no sulphurous acid was given off. 2d. Because free sulphurous acid and free iodine could not co-exist in the same solution. It was, therefore, necessary to adopt the supposition contained in the second equation, the required oxygen being supplied by the air. No such alternative was possible in the case of hydrochloric acid. And with nitric acid, since it had been found (see preceding paper) that nitric acid contained in hermetically sealed flasks and exposed to sunlight, contained much nitrous acid, besides a primary decomposition, similar to the foregoing, a secondary reaction was not only possible, but probable. To this secondary reaction, the amount of which could be readily foretold, the high results obtained with nitric acid were attributed.

Effect of Oxygen in Sun-light.—To test the above hypothesis, two opposed methods were desirable—a negative, when the iodides in the entire absence of oxygen, should undergo no change, and a positive, when the iodides in presence of excess of oxygen, should change at a correspondingly accelerated rate. No method of carrying into execution the first method was found very feasible, except that of replacing the air held in solution and the atmosphere itself, by another gas. In this case, carbonic acid, which was employed for the purpose, appeared especially suitable, since it was in the presence of free acid, that the experiments were to be performed. Three comparison-tubes were filled up in the manner of wash-bottles, the joints being perfectly air-tight. 100 cc water and 100 cc potassium was put in each. The first contained as well, 1 cc sulphuric acid, the third, 1 cc hydrochloric acid, the middle tube no acid. After displacing air in solution by a current of washed carbonic acid continued for three hours, the tubes were exposed at a sun-window, and kept there during 48 hours, the sun shining upon them during the whole of two days. At the end of this time, a slow current of the gas having been kept flowing through the solutions, they were found to have experienced no change. Without changing the contents of the tubes, or any of the arrangements further than replacing the stream of carbonic acid by a current of oxygen, the exposure was continued, when a change quickly began, and at the expiration of 2¼ hours, during much of which time the sun was overclouded, the two solutions containing free acid had become deep yellow, the one without was entirely colorless. On titration, the first was found to contain 12.1 mgrms. of free iodine, the third 9.5 mgrms., the middle tube none.

These experiments put in a striking light the *role* which oxygen plays in the decomposition of iodides in presence of certain free acids. But two other points which they likewise render conspicuous should not be overlooked—that solution of pure potassium iodide, even when exposed to sun-light, is permanent not only in presence of excess of oxygen, but likewise in presence of excess of carbonic acid. These two points are important in their bearing upon ozonometry.

Effect of Air or Oxygen in the Dark.—When air had been completely replaced by carbonic acid, no decomposition occurred. Otherwise, not only did the rate of decomposition increase with the concentration (as shown in a preceding paper), but did not fall off to zero, even when the acid had been diluted four thousand, and the iodide forty thousand times. At the expiration of five days, with solutions one-half so dilute as those above (1 cc acid and 1 cc KI solution, in two liters), the iodine set free amounted to 0.25 mgrm.

CONCLUSION.—It is evident that the above results necessitate the use of corresponding precautions and modifications, in cases where potassium iodide is employed in titration, more especially in the determination of nitrates in potable waters, acid solutions, etc.; but the work instituted in this direction has not as yet been completed.