

XXX.—ACTION OF LIGHT ON THE SOLUBLE IODIDES, WITH THE OUTLINES OF A NEW METHOD IN ACTINOMETRY.

BY A. R. LEEDS, PH. D.

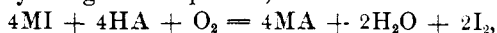
In the June number of the *Philosophical Magazine*, for 1879, I published an article with the above title, and gave an abstract of three preceding papers dealing with various parts of the same subject, viz.—“Upon the titration of hydrochloric acid for chlorine, and of sulphuric and nitric acids for hyponitric acid” (1st and 2nd papers, PROCEEDINGS AMERICAN CHEMICAL SOCIETY, 2, 1878, and JOURNAL AMERICAN CHEMICAL SOCIETY, I, 1879); also, “Upon the influence of light upon the decomposition of iodides” (JOURNAL AMERICAN CHEMICAL SOCIETY, I, 1879). In the first of these papers I gave an account of the anomalous reaction which first attracted my attention to the subject, and led me to undertake a series of laborious quantitative determinations extended over an interval of three months. This was, that on titrating very dilute solutions of the acids with potassium iodide (1 c.c. acid to 1000 c.c. water), no change occurred immediately, but at the end of two hours an amount of iodine had been set free, corresponding to 0.42 c.c. of a standard sodic hyposulphite solution, in the case of the hydrochloric acid; to 0.28 c.c. with the sulphuric acid, and to 0.24 c.c. with the nitric acid. After decolorisation with the hyposulphite, slow change again set in, and a series of titrations, beginning with October 27th, 1878, and extended to December 5th, 1878, eleven in all, was given, showing that a constant source of change was operating upon the mixtures of very dilute acids and iodide—the summations of the changes effected during the interval being for the hydrochloric acid 1.23 c.c., for the sulphuric acid 5.17 c.c., and for the nitric acid 2.41 c.c.

This source of constant change was thought to be the diffused light of the laboratory, and in the second paper the results of testing this hypothesis, under a great variety of conditions and with many precautions as to purity of acids, iodides, etc., were detailed at length. In the third paper, the various phenomena noted were brought into reconciliation by recognising that *oxygen was essential to the reaction*, no change whatsoever occurring either in the dark or in the strongest sun-light during several days exposure, in case the presence of oxygen were rigorously excluded. This observation likewise explained the real difficulty at the root of the acrimonious controversy between Schoenbein and Fischer, Houzeau and Sauvage,* as to whether or

* Journ. f. pr. Chem., 1845, 34, 492; Compt. Rend., 1868, 67, 663, 714, 1138.

no perfectly pure potassium iodide, in dilute solution, is decomposed by free sulphuric acid.* The answer to this question, as determined by the author from the experiments quoted, was that either in light or darkness free acid will decompose potassium iodide if oxygen is present, even when the dilution is carried to the one four-thousandth part; but in case oxygen is absent, solutions of potassium iodide, with excess of free acid, and both solutions of considerable strength, may be kept for days in the dark or in strong sun-light, without a liberation of iodine.

Furthermore, all the cases of soluble iodides experimented upon, and the acids, organic acids as well, were shown to undergo a change represented by the general equation,



where M indicates the monovalent basic, and A the monobasic acid radical.

In the earlier experiments (2d paper), before the indispensable co-operation of oxygen in the decomposition of the iodides, in presence of free acid, had been recognised, the law of change of the iodides in the dark appeared to be quite different from that operating when they were exposed to the light. In the former case, the amount of decomposition of the iodide was approximately proportional to the degree of concentration; in the latter, the reverse appeared to be true. This curious anomaly was done away with by the next step in the investigation: for in the preliminary trials, bottles of different forms and material had been used in holding the solutions; but it was evident that not only would the varieties in shape greatly alter the relative surfaces of exposure to the solar ray, but differences in tint of the glass (yellowish, white, pink, etc.) strongly affect the percentage of the transmitted actinic component of the beam. For these reasons, comparison tubes of uniform bore and dimensions (25 c.m. in length, 3 c.m. in diameter), such as the author has proposed in his color comparator,† all made of the same thin, perfectly colorless glass, were substituted. The anomalies now disappeared.

Before proceeding further, however, it was essential to determine to what extent the pure acids themselves underwent decomposition in the sunlight; and to this end, 50 c.c. of nitric acid, of sp. gr. 1.4, 50 c.c. of sulphuric acid, of sp. gr. 1.84, and 50 c.c. of hydrochloric

* See also Fischer, *Pogg. Ann.*, **66**, 168; *Journ. f. pr. Chem.*, **34**, 186; also Dulk, *Journ. f. pr. Chem.*, **34**, 344, Criticism on Schoenbein's paper, "Some notes upon potassium iodide."

† *Chem. News*, **37**, 229.

acid, of sp. gr. 1.202, were hermetically sealed in bottles, and exposed at a south window from December 10th, 1878, to January 21st, 1879.

“At the end of this period, 1 c.c. of each was taken, diluted with 1 liter water, potassium iodide and starch water added, and allowed to stand for 24 hours in darkness.” They gave, on titration:

1 c.c. HNO_3 = 14.80 c.c. $\text{Na}_2\text{S}_2\text{O}_3$.
 1 “ H_2SO_4 = None.
 1 “ HCl = “

This experiment was the first of a series, which are given at length in the articles referred to, by which it was shown that the decomposition of soluble iodides, in the presence of light and of free nitric acid, does not conform to the same general law which operates in the case of acids not of themselves decomposable by sun-light. The equations which explain the different deportment of nitric acid were given in full, and the necessity of rejecting its employment in making actinometric measurements was emphatically pointed out.

“This investigation suggested a convenient method for studying the variations in the actinic force of the solar ray, which was to determine the amount of iodine set free by its action, under identical conditions. In the following experiments, the first which were instituted in this direction, no attempt was made to determine absolute values. A series of comparison tubes, each containing 1 c.c. H_2SO_4 , 1 c.c. KI , and 5 c.c. starch water, with the amounts of water specified, were exposed at times and during intervals given, upon a comparator, the frame of which was kept normal to the solar ray.”

RELATIVE ACTION OF THE SUN'S RAYS (JAN. 22, 1879).

	20 c.c. H_2O	60 c.c. H_2O	100 c.c. H_2O
9.00- 9.30 A. M.	0.24 mgrm I	0.27 mgrm I	0.38 mgrm I
9.30-10.00	0.22	0.29	0.37
10.00-10.30	0.24	0.40	0.40
10.30-11.00	0.39	0.76	0.71
11.00-11.30	0.67	1.25	1.29
11.30-12.00	0.67	1.25	1.46
12.00-12.30 P. M.	0.55	1.25	1.54
12.30- 1.00	0.60	1.50	1.73
1.00- 1.30	0.50	1.13	1.31
1.30- 2.00	0.40 [clouded over]	0.75	0.92

CONTINUED, JANUARY 24TH.

	20 c.c. H_2O	40 c.c. H_2O	60 c.c. H_2O	80 c.c. H_2O	100 c.c. H_2O
2.30-3.00	0.125	0.24	0.33	0.38	0.40
3.00-3.30	0.110	0.18	0.24	0.27	0.28
3.30-4.00	0.070	0.10	0.12	0.13	0.12

It will be seen that the amounts of iodine liberated in the 40 c.c. solution and the 80 c.c. solution, are intermediate between those liberated in the solutions of 20 and 60, and 60 and 100, respectively. Moreover, the determination of the liberated iodine is so easily made, that we possess in this method a convenient form of actinometry, lending itself readily to various practical applications. The chlorine-hydrogen method of Draper, which received at the hands of Bunsen and Roscoe the various instrumental refinements essential to accurate quantitative results, requires a corresponding complexity of apparatus and nicety of manipulation, and is therefore carried into execution with difficulty by the working chemist. The method just described needs little or no apparatus beyond that essential to any well equipped laboratory.

The next question investigated (3d paper), was "*to determine whether a change of base influenced the rate of decomposition in the sun-light when the same acid was employed; or, with the same base, when different acids were used.*"

In solving this question, the intention was to employ chemically equivalent solutions of the acids, but, by an error in the calculation, the solutions actually employed in this and the subsequent parts of the work were of such strength, that 1 c.c. of the sulphuric acid corresponded to 0.43 c.c. of the hydrochloric, and to 0.504 c.c. of the nitric acid. The experiments were made and the wood-cuts executed before the error was discovered, which accounts for the publication of the results as given in the articles alluded to, and from which only I shall quote in the present communication. But, whilst I was unable at that time to undergo the expense of having new plates made, and published these somewhat imperfect results just as they stood, I repeated in March, 1879, the experiments with truly equivalent solutions, and shall in a subsequent paper make them known, with appropriate graphic representations.

In all the earlier trials starch-water was used in making up the solutions in the comparison tubes to the desired volume, since "*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.*" But a series of trials is given (3d paper) with the iodides of potassium, cadmium and lithium, and with the three mineral acids, which showed that in every instance the amount of decomposition was greater when the addition of starch was omitted. The dense precipitate of starch iodide suspended in the tubes, cut off to a large degree the action of the light upon the solutions. Moreover, the disturbing effect of such an opaque pre-

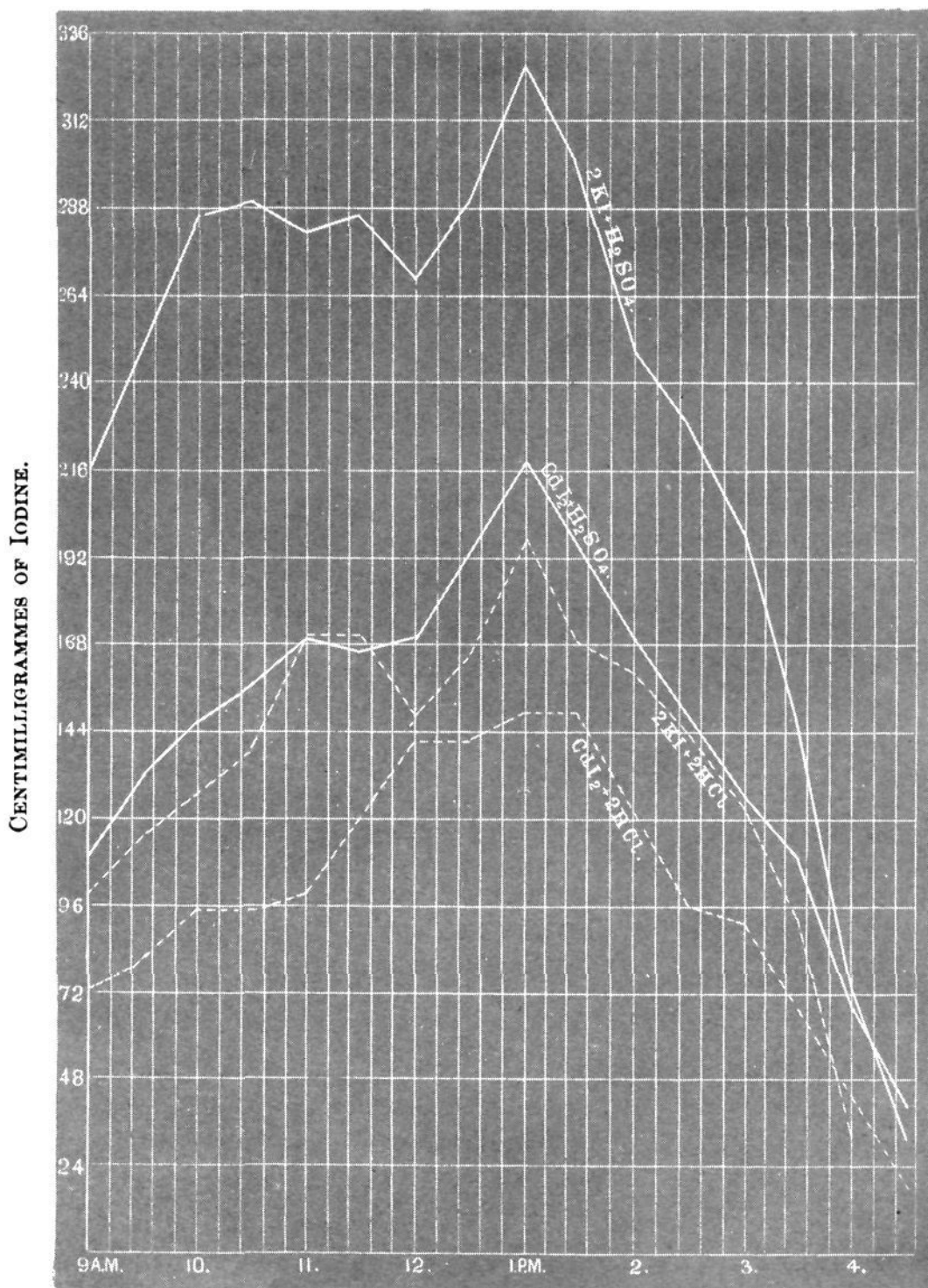
cipitate was so great, that the striking quantitative relationships exist-

ACTINOMETRIC DETERMINATIONS, February 27th, 1879.

REAGENTS.	9 A. M.—		10—		11—		12—		1 P. M.—		2—		3—		4—		MEANS
	9.30	10.30	10.30	11.30	11.30	12.30	12.30	1.30	1.30	2.30	2.30	3.30	3.30	4.30	4.30		
1 c.c. H ₂ SO ₄ + 1 c.c. KI	215	250	285	280	285	270	290	325	300	250	225	200	155	75	35	233	
1 c.c. HCl + "	100	125	140	170	170	155	165	200	170	160	145	125	90	35	23	131	
1 c.c. H ₂ SO ₄ + 1 c.c. CdI ₂	115	130	145	155	170	165	170	195	220	195	170	130	110	70	43	146	
1 c.c. HCl + "	75	85	100	100	120	140	140	150	150	120	95	90	65	35	20	99	
1 c.c. H ₂ SO ₄ + 1 c.c. LiI	120	130	135	145	150	160	170	155	145	150	140	125	105	65	43	131	
1 c.c. HCl + "	75	80	95	100	100	110	120	120	110	100	75	70	50	30	18	84	
1 c.c. H ₂ SO ₄ + 1 c.c. NH ₄ I	130	140	155	165	170	180	190	195	180	170	150	120	105	70	45	146	
1 c.c. HCl + "	85	95	100	100	115	115	120	115	115	110	85	90	60	30	18	92	

ing between the amounts of iodine liberated by the unequal chemism of different acid radicals for the same metallic base, were not made manifest, until by doing away with the starch, the reactions were rendered normal. The most important instance of this constant difference of chemism which as yet has been worked out, is that between $\frac{1}{2}$ H₂SO₄ and Cl in the presence of KI, CdI₂, NH₄I and LiI solutions exposed to sun-light.

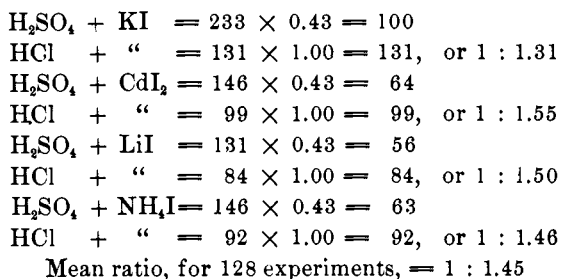
The progress which had been made in solving the question above italicised, will be gathered from an examination of § VII (3d paper), "*Upon the actinometric determination of sun-light,*" which begins by stating that "in order to compare the decomposition effected by the sun-light, after passing through various thicknesses of the earth's atmosphere, and 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 amounts of iodine are given in centigrammes. The solutions were all made up to 100 c.c.



February 27th, 1879. Hours of the day.

Unfortunately, as before stated, the solutions were not chemically equivalent, 1 c.c. of the H_2SO_4 corresponding to 0.43 c.c. HCl , and the potassium iodide solution being of 20 per cent., the other iodides of 10 per cent. But if we multiply the means of the numbers of centimilligrammes of iodine, in each case set free in the presence of

the sulphuric acid, by 0.43 (the number expressing the relative strength of the hydrochloric acid), and divide the products into the amounts of iodine liberated by the hydrochloric acid, we obtain the following ratios :



We have here a set of ratios obtained with 128 solutions exposed during the course of one day, under identical circumstances in each corresponding experiment, of time, of exposure, temperature, surface, intensity and quantity of light, size and nature of vessel, etc. The ratio 1/1.31, obtained with the potassium iodide solution, is retained, though it might without violence be thrown out, inasmuch as this solution contained 20 per cent. of the iodide, the other three but 10 per cent. of their respective iodides. We have reason, therefore, for bringing forward the hypothesis that the chemism of the Cl radical, as compared with that of the $\frac{1}{2}\text{SO}_4$ radical, and as made manifest by the amount of metathetical decomposition taking place in sun-light in mixtures of their hydrogen salts with the iodides of certain metallic radicals, may be expressed by a certain ratio. And without claiming any thing further than the suggestion of some quantitative relationship, not as yet fully apprehended, this ratio might be expressed as a law of specific actinic forces under the formula :

The chemism of the chlorine radical is to that of the $\frac{1}{2}\text{SO}_4$ radical (measured by the relative amounts of iodine liberated by each respectively, in solutions of the metallic iodides exposed to sun-light), as 1.45 : 1. This formula holds good, as was shown in the unpublished actinometric determinations made March 26th, 1879, for rigorously chemically equivalent solutions of the acids. But the ratio requires change when the actinic power emanates from a different source, the magnesium lamp for example. This will be forcibly shown further on. A similar law appears to be true of the amounts of iodine set free from iodides of different metals, when exposed to the action of sun-light in presence of the same acid—these amounts standing in definite ratios, one to another.

Before leaving this diagram, I wish to point out the remarkable depression in the $2KI + H_2SO_4$ curve, and the $CdI_2 + H_2SO_4$ curve, between the hours of 11 A. M. and 1 P. M. As soon as this tendency was noted, I naturally anticipated the passage of some visible mist or haze across the sun. Such, however, was not the case, the sky appearing just as brilliant and blue during this interval as before and after. I deemed it not improbable that this absorption of the actinic component of the solar ray, was due to the passage of some mass of aqueous vapor, or some other alteration in the physical or chemical constitution of an interjected atmospheric layer, which, though invisible to the sense of sight directly, had been written down in the sensitive chemical fluid by the blurred tracing of the actinic rays. This, indeed, was an animating thought—that we possess in the undulations of the solar beam, which are too rapid to affect vision, a delicate probe to reach down through various parts and thicknesses of the earth's atmosphere, and to tell what alterations of constituents may be taking place there. To test this idea, a set of experiments was undertaken upon the absorbing action of vapors, gases, etc., upon the chemical component of the solar, electric and magnesium light, under known conditions in the laboratory, prior to their extension to an actino-chemical analysis of the atmosphere. The circumstances narrated below will cause the publication of the results, though in a somewhat incomplete state, at once.

§ IX (3d paper) was devoted to the "*Influence of heat upon the decomposition of the iodides.*" Three series of trials were instituted in this direction. The first was made before the *hauptrolle* played by oxygen in these decompositions, was recognised. It consisted in noting the intervals through which the same amounts of potassium iodide, sulphuric acid, and starch-liquor, diluted with 20 c.c., 60 c.c., and 100 c.c., water, ran through a scale of colors (very faint rose, faint rose, rose, violet and blue), as the temperature rose from 30° to 95° . On continuing the heating, the colors disappeared in the inverse order, due to the gradual conversion of the indicator into dextrine, under the influence of the dilute acid.

The second series of trials was upon the "Effect of heat in closed flasks." Of course, the use of starch was abandoned in these and subsequent trials. The final result obtained, to quote from the original paper, was that—"In other words, when the potassium iodide was diluted 600 times, and heated nearly to the boiling point (93°), in a closed flask, for six 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."

The third series was upon the "Effect of heat in flasks entirely deprived of air." The previous displacement of the air held in solution in the liquids, was effected by a long-continued current of carbonic anhydride. When this was done, the solutions of potassium iodide, both with sulphuric and hydrochloric acid, were heated for two hours to a temperature five degrees above the boiling point of water, without any liberation of iodine whatsoever. Similar acidified solutions, heated to the same temperature, in contact with air, turned *yellow immediately*.

§ IV (3rd paper) was upon the "*Decompositions effected by the electric light.*" The experiments were performed by arranging the solutions in comparison tubes, so as to form the sides of a cylinder with the focus of the electric light at the geometric centre. "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 photometric measurements made by Prof. Morton and Mr. Beckmayer, between 7000 and 7500 candles." Reducing the observations in the same manner as was done above with the actinometric determination of sun-light, we have, the results being given in mgrms of iodine:

ACTINOMETRIC MEASUREMENT OF ELECTRIC LIGHT.

	15 min	20 min	7½ min	MEANS.	RATIOS.
1 c.c. H ₂ SO ₄ + 1 c.c. KI	1.65	3.90	3.00	2.85 × 0.43 = 1.22	
1 c.c. HCl + "	1.05	3.40	2.00	2.15 × 1.00 = 2.15	1 : 1.76
1 c.c. H ₂ SO ₄ + 1 c.c. CdI ₂	1.80	3.15	2.25	2.40 × 0.43 = 1.03	
1 c.c. HCl + "	1.25	2.50	1.35	2.02 × 1.00 = 2.02	1 : 1.96

The same remarks are true of the chemical decompositions of the iodides effected by the electric-, as when the decomposition resulted from the sun-light. But the amount of iodine liberated in each trial was relatively several lines greater, and the coefficient of chemical energy of the chlorine radical, 1.86 instead of 1.46. This exaltation of the relative chemical energy of the chlorine under the influence of the electric light, will be still more strikingly exhibited when the results obtained with rigorously equivalent solutions are published.

§ V (3d paper) was devoted to the "*Comparison of effects of sun-light and electric light, after passing through absorbing media.*"

The experiments were performed as usual, except that the comparison tubes were surrounded by a layer, 3 c.m. in thickness, of the absorbing medium: ammoniacal solution of copper for the blue, neutral potassium chromate for the yellow, and fuchsine for the red. 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. Reducing the observations as before, we have :

EFFECT OF ABSORBING MEDIA.

		Sun-light (1 hour).	Ratios.	Electric Light (1 hr.)	Ratios.
Blue	1 c.c. H_2SO_4	$2.38 \times 0.43 = 1.02$	1 : 2.2	$6.00 \times 0.4325 = 2.595$	1 : 1.7
	1 c.c. HCl	$2.22 \times 1.00 = 2.22$		$4.50 \times 1.00 = 4.50$	
Yellow	1 c.c. H_2SO_4	$0.67 \times 0.43 = 0.2881$	1 : 1.4	$0.50 \times 0.43 = 0.215$	1 : 2.0
	1 c.c. HCl	$0.45 \times 1.00 = 0.45$		$0.45 \times 1.00 = 0.45$	
Red	1 c.c. H_2SO_4	$1.53 \times 0.43 = 0.6579$	1 : 1.3	$4.95 \times 0.43 = 2.1285$	1 : 1.5
	1 c.c. HCl	$0.83 \times 1.00 = 0.83$		$3.00 \times 1.00 = 3.00$	

The fact most striking in this tabular view is, that while the greater strength of the actinic component of the electric beam is very manifest, the *yellow* absorbing medium absorbed 85 per cent. of the actinic energy which was transmitted through the blue solution, and 83 per cent. of that which passed through the red. Of the actinic energy of the sun-light, 32 per cent. of that which passed through the blue was absorbed by the yellow, and 50 per cent. of that going through the red. But the actinic energy of that part of the *sun's* actinism which passed through the fuchsine, was but one-third of that of the *electric light*. I have said actinic energy, rather than actinic rays, because the absorption spectra for the invisible part of the spectra of the sun and electric light, possessed by these substances, has, so far as I know, not been mapped. To quote from the original: "Better to understand what occurs in this instance, a study of the absorption spectra (chemical) of the media, and of the various iodides in the several portions of the sun and electric light, has been entered upon" (February, 1879).

§ VI (3d paper) was upon the "*Decomposition effected by the magnesium light.*" Reducing the observations (one set obtained by an hour's exposure) to the same standard as before, we have :

				Ratios.
1 c.c. H ₂ SO ₄ + 1 c.c. KI	=	0.050 mgrm I	× 0.43 = 0.0215	
“ HCl + “	=	0.075 “	× 1.00 = 0.0750	1 : 3.5
“ H ₂ SO ₄ + 1 c.c. CdI ₂	=	0.035 “	× 0.43 = 0.0150	
“ HCl + “	=	0.050 “	× 1.00 = 0.0500	1 : 3.3
“ H ₂ SO ₄ + 1 c.c. LiI	=	0.040 “	× 0.43 = 0.0170	
“ HCl + “	=	0.050 “	× 1.00 = 0.0500	1 : 3.0
“ H ₂ SO ₄ + 1 c.c. NH ₄ I	=	0.060 “	× 0.43 = 0.0260	
“ HCl + “	=	0.070 “	× 1.00 = 0.0700	1 : 3.0

The results were very surprising for their smallness, because the experiments were arranged in the same way as with the electric light, the focus of the lamp being at the geometric centre of a cylinder, formed by the comparison tubes, the cylinder being of 6 in. radius. For, while to the eye, the white light of the burning magnesium was painful, the chemical decomposition effected by it was but the $\frac{1}{17}$ th part of that effected by the electric light during the same interval, and but $\frac{1}{3}$ d part of that effected by the sun. The coefficient of comparative chemical energy exhibited by the chlorine atom under these circumstances, is 3.2 as against 1.86 in case of the electric light, and 1.45 in that of the sun.

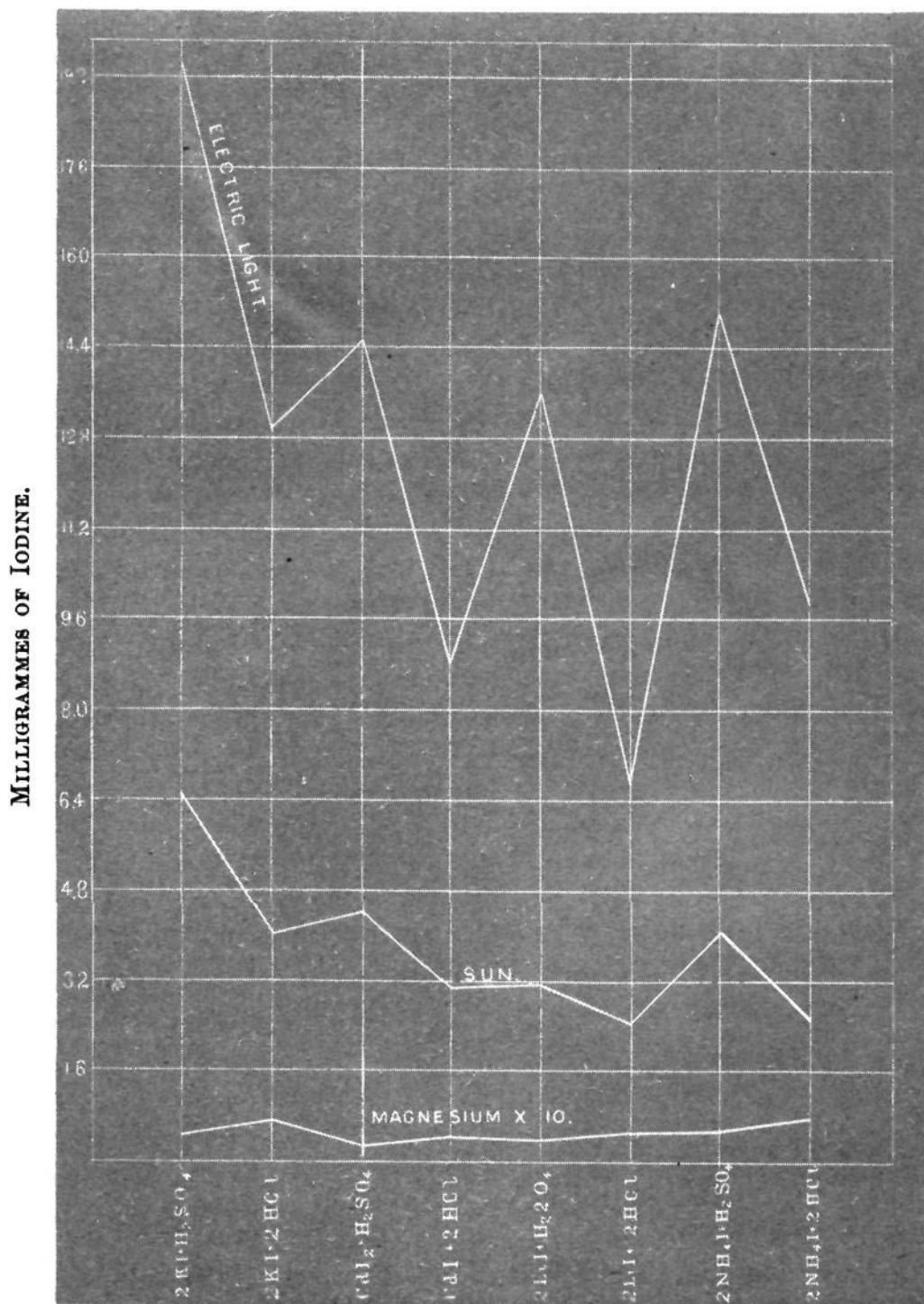
§ VIII (3d paper) was devoted to the “*Comparison of actinic intensities for equal times.*” Reducing these observations as before, the amounts of liberated iodine being given in mgrms, we have :

DECOMPOSITION DURING EQUAL TIMES (1 hour).

REAGENTS.	ELECTRIC LIGHT.		SUN.		MAGNESIUM.		RATIOS.
	Obs'rd	Reduced	Obs'rd	Reduced	Obs'rd	Reduced	
H ₂ SO ₄ + KI	19.5	12.38	6.5	2.3	0.050	0.022	560 : 100 : 1
HCl + “	13.0	13.00	4.0	4.0	0.075	0.075	173 : 53 : 1
H ₂ SO ₄ + CdI ₂	14.6	6.28	4.4	1.9	0.035	0.015	420 : 126 : 1
HCl + “	8.8	8.80	3.0	3.0	0.050	0.050	176 : 60 : 1
H ₂ SO ₄ + LiI	13.7	5.99	3.1	1.3	0.040	0.017	350 : 83 : 1
HCl + “	6.5	6.50	2.4	2.4	0.050	0.050	130 : 48 : 1
H ₂ SO ₄ + NH ₄ I	15.0	6.45	3.9	1.7	0.060	0.026	248 : 65 : 1
HCl + “	9.8	9.80	2.3	2.3	0.070	0.070	140 : 33 : 1
Means of H ₂ SO ₄							395 : 94 : 1
“ HCl							155 : 50 : 1
Means of all							275 : 72 : 1

These phenomena are graphically represented in the following diagram, the observed results being taken for abscissas and ordi-

nates, and the magnesium ordinates multiplied by 10 to bring its curve up into the field of view.



REAGENTS.

SUMMARY.

I.—The part played by oxygen is the essential fact in the decomposition of soluble iodides in acidified solutions; no decomposition taking place either in darkness or in the strongest sun-light, in case

oxygen is absent. The principal exception to this rule is when nitric acid is employed.

II.—In case oxygen is present, the reaction takes place according to the equation, $4MI + 4HA + O_2 = 4MA + 2H_2O + 2I_2$, where **M** stands for any monovalent basic radical, and **A** a monobasic acid radical. This is true of the solutions both in darkness and in light.

III.—In case sufficient oxygen is present to permit of a normal reaction, the amount of iodine liberated in the darkness is strictly proportional to the degree of concentration, up to the limit to which the above equation is true. In the light, the same law holds good; the surface of exposure, the quantity and intensity of the light remaining the same, the degree of concentration the variable.

IV.—In case sufficient oxygen is present, and the degree of concentration is fixed, the amount of iodine liberated increases in the same ratio as the time of exposure to the light. There is likewise much reason for supposing that it stands in a similar numerical relation to the number and intensity of the chemical rays falling upon the solution.

V.—With a constant actinic energy, and with equivalent solutions of acids, the amounts of iodine liberated differ by constant quantities, which appear to be coefficients of comparative chemical energy of the acid radicals under these conditions. A similar law appears to apply to the various basic radicals of the iodides in the presence of the same acid.

VI.—In the absence of oxygen no decomposition takes place either in light or darkness, nor in dilute nor quite strong solutions, when the solutions are *heated* for hours to a temperature 5° above the boiling point of water. In the presence of oxygen, instantaneous and abundant decomposition sets in at this temperature, and correspondingly at lower temperatures.

Applications of the iodo-acid method. 1st. To determine the amount of chemical work done by the sun's rays while passing through various layers of the earth's atmosphere, either during each hour in the same day at any given place, or at different places for each day and season of the year. Curves representing such actinometric measurements at Hoboken, for January 22nd and 24th, 1869, and February 27th, 1879, are given.

2d. To determine the absorptive coefficients for the chemical rays of the sun (or other powerfully actinic light) of various gases, vapors, etc., under known conditions in the laboratory, and then apply the knowledge thus obtained to an actino-chemical analysis of the atmosphere.

3d. To map the actinic spectra of the sun, electric, magnesium, and other powerfully actinic illuminants, and the absorption bands for the invisible rays, when the light from these sources passes through solids, mineral and organic compounds, in dissolved or liquid form, and vaporous or gaseous bodies.

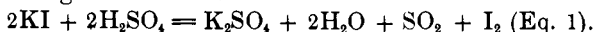
4th. To determine the comparative coefficients of combining and decomposing power of elements in compounds subject to metathesis, by actinic forces, and to find these actino-equivalents for invisible rays of various refrangibility.

Besides the extended account published in the June number of the *Philosophical Magazine*, for 1879, I sent about the same time to different gentlemen in Europe, and among them, directed to his address in Manchester, to Dr. R. Angus Smith, reprints of the three original articles. Nothing then could exceed the surprise I felt when I saw an article published in the *Chemical News* for May 7th, 1880, being "A paper read before the Royal Society, April 29th, 1880," under this gentleman's name, in which beneath the title "Measurement of the actinism of the sun's rays and of daylight," he gives a meagre account of the process, which in every point runs parallel with and coincident with my own, except in several vital omissions. This, I think, will appear on consideration of the following resumé of Dr. Smith's work. He states—"The fundamental fact is, that when iodide of potassium in solution is treated with nitric acid, so small in quantity as to cause no change of color in dull diffused light, a change takes place when the same mixture is brought into clear light; iodine is set free and the solution becomes yellow. The amount of iodine freed can be titrated with great exactness, by the use of hyposulphite, as is well known. In these two facts lies the whole process; the first is the new part, the second makes the first quantitative, and it is, of course, part of the novelty."

We most cheerfully admit the novelty exhibited by Dr. Smith in selecting of all others, nitric as the acid forming part of the fundamental fact of the process as he states it. For it is true, that in the 128 determinations of the iodine liberated from four iodides in the presence of sulphuric and hydrochloric acids, and titrated by the use of standard (1 c.c. = 5 mgrms I) sodic hyposulphite and $\frac{1}{16}$ standard, these 128 determinations being all made in one day, February 27, 1879, I did not use nitric acid. And the reason for its omissions are stated in many places (2d and 3d papers). For while the reaction in dilute solution (Eq. 2, § X, 3d paper) for sulphuric acid is $4KI + 2H_2SO_4 + O_2 = 2K_2SO_4 + 2H_2O + 2I_2$, and for hydrochloric acid

(Eq. 6), $4\text{KI} + 4\text{HCl} + \text{O}_2 = 4\text{KCl} + 2\text{H}_2\text{O} + 2\text{I}_2$, that for nitric acid is not only the normal one of $4\text{KI} + 4\text{HNO}_3 + \text{O}_2 = 4\text{KNO}_3 + 2\text{H}_2\text{O} + 2\text{I}_2$ (Eq. 3), but the secondary ones of $2\text{HNO}_3 = \text{N}_2\text{O}_4 + \text{H}_2\text{O} + \text{O} = 2\text{HNO}_3$ (in sun-light) $= \text{N}_2\text{O}_3 + \text{H}_2\text{O} + \text{O}_2$ (Eq. 4),* and $2\text{KI} + 2\text{HNO}_3 + \text{N}_2\text{O}_3 = 2\text{KNO}_3 + \text{H}_2\text{O}_2 + \text{N}_2\text{O}_2 + \text{I}_2$ (Eq. 5). It had been abundantly demonstrated by many experiments (what was well known before) that nitric acid of itself, no iodides being present, spontaneously breaks up into one or more lower oxides of nitrogen and free oxygen, in the sun-light, and generates in the body of the solution itself an abnormal supply of that oxygen, which is the fundamental factor in these cases of actino-chemical change. Later on, Dr. Smith suspects that the nitric acid itself, in dilute solution, was subject to decomposition, and substitutes for his new and fundamental fact, the use of sulphuric acid. This I shall venture to assure Dr. Smith certainly is not new, inasmuch as he will find it stated at great length, *Philosophical Magazine*, for 1879, 396. Neither, however, is it fundamental, for an equivalent amount of hydrochloric acid possesses a greater coefficient of iodine-liberating power when placed in an actinic field.

Dr. Smith furthermore states: "3. It is known that strong acid liberates iodine; weak acid does so after a long time, but the process is hastened by light." This generalized statement cannot fail to lead to confusion and error, if left unqualified by a precise idea of the conditions under which it is false, and those under which it is true: for when oxygen is excluded,† "decomposition of an acid solution of potassium iodide occurs only after the concentration has attained to some point between one-third and one-tenth the weight of the water employed." The acidifying body, referred to in the experiments quoted, is sulphuric acid, and a more precise limit of concentration is not given, because of the undue multiplication of trials thereby entailed. But decomposition ensues, in this instance, from the production of an entirely different set of conditions on the attainment of the limit, and the sulphuric acid splits up, thereby furnishing the essential oxygen by an endo-chemical change. Instead of $4\text{KI} + 2\text{H}_2\text{SO}_4 + \text{O}_2 = 2\text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{I}_2$ (Eq. 2, § X, 3d paper), the equation given for this case is



* Gay-Lussac states that the decomposition is into nitrous acid. He adds that nitric acid, whose density is as low as 1.3235, is not decomposed by light, except in the presence of a certain quantity of concentrated sulphuric acid, when even the most dilute acid undergoes change.—Ann. Chim. Phys., 1816, 397.

† Upon the detection and estimation of nitrous acid in potable waters, acids, &c., with potassium iodide, by the Author: Chem. News, Aug. 8th, 1879, 61.

With regard to the statement, that weak acid liberates iodine after a long time, but the process is hastened by light, it appears to the author that herein is contained the fundamental proposition of Dr. Smith's labors, and that, as such, it demanded elaborate experimental verification. For although, in a qualified sense, the proposition is true, yet the working out of the exact conditions under which it holds good, constituted the preliminary and most laborious portion of the work performed by the author, in the three papers previously referred to, and in others following them. Moreover, if these facts and conditions be so well known, and generally accepted, that a method of actinometry might be founded upon them without further independent proof, yet the evidence of their being commonly ignored is to be seen in the very frequent publication of erroneous observations and conclusions, concerning processes in which soluble iodides are concerned. Let me instance again the bitter controversy between Schoenbein and Fischer, Houzeau and Sauvage, as to the fact of a dilute potassium iodide solution being decomposed in the presence of very dilute sulphuric acid. More striking still, the universal employment of an acidified solution of potassium iodide for titrating a current of air or oxygen, carrying with it ozone, or ozone and peroxide of hydrogen. It is but a few weeks ago since, in certain experiments instituted to discover whether or no ozone is given off by the slow oxidation of phosphorus in moist air, the most abundant reaction for ozone was obtained when the current of ozonised air was heated to 200°, before its passage into an acidified solution of potassium iodide; but at a temperature of 200°, 97 per cent. of the ozone present in ozonised air or oxygen is *destroyed at once*, and the residue very speedily.*

* Peroxide of hydrogen and ozone, Chem. News.

NOTE.—It is earnestly to be hoped, in the controversy alluded to in this reference, that the indisposition, either to become acquainted with, or to recognise the labors of preceding investigators, will not be continued. I would respectfully ask the gentlemen concerned to refer as far back as 1840, to the article by Schoenbein, entitled, "Researches on the nature of the odor given off by certain chemical reactions" (Compt. Rend., 10, 706; Ann. Elec., 6, 108); also to this article upon the "Production of ozone by chemical means" (1844) (Arch. de l'Elec., 4, 333, 454). Let me ask them to read, likewise, the critique, by Fischer (Berl. Jahresb. f. wissensch. Kritik, 1844), upon Schoenbein's pamphlet, "Ueber die Erzeugung des Ozons auf chemischen Wege," followed, as it was, by a second attack from the savan of Breslau (Schles. Gesell. Uebersicht, 98, 107; Pogg. Ann., 66, 163; Journ. pr. Chem., 35, 851), in which he advanced the hypothesis, that the ozone discovered by Schoenbein was probably a peroxide of hydrogen. We have seen how, 35 years

If more evidence were needed to show that the spontaneous decomposition of a soluble iodide in presence of dilute acid and oxygen, is a fact generally ignored, it is to be found in the tests recommended in Fresenius' Qual. Analysis for the detection of free chlorine in hydrochloric acid, and of hyponitric in sulphuric acid—the latter “when diluted with twenty parts of water, must not impart a blue tint to a solution of iodide of potassium mixed with starch paste.*” But if the trial be made in an atmosphere of carbonic acid, care being used to expel previously all traces of air in reagents and in the

later, this hypothesis was again brought forward by Mr. Kingzett, without reference to the battle of these illustrious teachers of a past generation, and without comment upon Schoenbein's reply to Fischer's attack (Journ. f. pr. Chem., 34, 492; Pogg. Ann., 65, 190), Mr. Kingzett asserting that “*there is no known process of slow oxidation, which has been established to produce ozone,*” and that the substance formed in the aerial oxidation of phosphorus is peroxide of hydrogen. Whilst the controversy was raging in Germany between Schoenbein and Fischer, it was opened in England by Prof. Williamson's “Researches on ozone” (Chem. Soc. Mem., 2, 395; Liebig Ann., 54, 127; Phil. Mag., 27, 372; Compt. Rend., Mar., 1845)—in which Dr. Williamson states, as the result of elaborate experiments, performed with exceeding care, that there were reasons for believing in the existence of two kinds of ozone: one the ozone given off in electrolysis, and which he regarded as a higher oxide of hydrogen, differing from the previously well known peroxide; and the other formed by the action of phosphorus on moist air. I cannot regard the rejoinder of Schoenbein (Pogg. Ann., 66, 292; Phil. Mag., 27, 450)—in which he showed 1st, that the chemical and physical properties of ozone are not the properties of peroxide of hydrogen, and 2d, that whatever might be the true nature of ozone, the gaseous matter obtained in the electrolysis of water, was in all respects identical with that formed by the action upon air of moist phosphorus—otherwise than as a masterpiece of cogent reasoning, and as an argument *for the identity of ozone from whatever source produced*, even at the present day unsurpassed. His eminent English antagonist never replied, and the doctrines of Schoenbein on this point passed into the text books, and remained there without a dissenting voice until, unsupported by any show of evidence that he had performed more precise experiments on his own part, or that he had in any particular demonstrated errors in the work of those whom he so assertively attacked, Mr. Kingzett pronounced them *faise*.

Perhaps even more surprising, as certainly more novel, are the polemical methods adopted by Prof. McLeod. For, stepping down unasked of the two principals in the fight, into this particular arena of controversy, and without even the fine courtesy, traditional to a free lance, of previous salutation by name or token of reference, Prof. McLeod proceeds forthwith to demolish his two antagonists, and makes them both to be in error. This too, without invoking, by *as much as a single foot note*, the shades of the mighty contestants, who took part in the much greater battle fought on these points more than a quarter of a century before, to be spectators of the fray!

* Fresenius' Qualitative Analysis, 6th Ed., 32, 35.

dilute acid solution, the test and estimation of percentage may be satisfactorily performed.* A like proof may be found in the customary mode of applying Trommsdorf's method for the detection and estimation of nitrous acid in potable waters.† When the zinc-iodide-starch reagent and water, under examination, are left without previous expulsion of dissolved oxygen, the amount of iodine set free by spontaneous decomposition, even in the diffused light of a laboratory, may much exceed the total quantity of nitrous acid present. In truth, an amount admitting of quantitative determination may apparently be found, when, as examined by the Griess test (metadiamidobenzole), not a trace of nitrous acid is actually present.

Finally, examine in this connection the admirable memoir of Schoene, "upon the quantitative estimation of hydrogen peroxide.‡" For in one series of trials, this investigator employs concentrated solutions of potassium iodide and hydrochloric acid to determine minute amounts of hydrogen peroxide dissolved in different quantities of water. In another series, the solutions were boiled in contact with the air, and the amounts of hydrogen peroxide found, which in most trials exceed the quantities taken, corrected by a figure obtained by boiling similar solutions, *but containing no hydrogen peroxide*, during an equal interval. True values, it appears to me, might have been found in both series of trials, had the experiments been performed with the exclusion of every trace of oxygen from the solutions. It is the more surprising, inasmuch as in the same article, this most careful experimenter calls attention to the method of Gernez † for freeing solutions of oxygen by a current of an indifferent gas, and the experiments of Baumert, § Payen || and Lehmann, ¶ upon the decomposition of hydriodic acid by oxygen.

* Chem. News, 63; *ibid.*, 62.

† *Zeitschr. f. anal. Chem.*, 18 (1879), 144.

‡ *Compt. Rend.*, 63, 883; *Zeitschr. f. Chem.* [2], 2, 717.

§ *Pogg. Ann.*, 99, 92.

|| *Compt. Rend.*, 62, 254.

¶ *Arch. Pharm.* [3], 2, 25; *Chem. Centr.*, 1873, 152.

NOTE.—The historical aspect of this important question is of great interest. In 1853, Baumert thought he had succeeded in proving the existence of two kinds of ozone; the one prepared by the electric discharge, which he regarded as allotropic oxygen; the other, afforded by the electrolysis of acidulated water, to which he assigned the formula H_2O_3 , teroxide of hydrogen (Breslau, *Schles. Gesell. Verhandl. Uebersicht*, 24; *Ann. de Chim. et Phys.*, 39, 477; *Journ. f. pr. Chem.*, 59, 350; *Journ. de Pharm.*, 24, 381; *Phil. Mag.*, 6, 51; *Ann. der Chem. u. Pharm.*, 88, 221; *Pogg. Ann.*, 89, 38). He passed the electrolytic oxygen, evolved in such a manner as to exclude the presence of hydrogen, through a

Dr. Smith goes on to state: "4. Heat, even to the boiling point, does not act so well as light (experiments being made in sealed tubes to prevent loss of iodine)." With regard to this point, it is a mild criticism to make, that Dr. Smith could not have arranged the conditions of his experiment in a manner better calculated to lead him to conclusions utterly false: for, in sealing up the tubes, Dr. Smith prevented the access of oxygen, the very element whose presence is essential to the occurrence of the reaction with dilute solutions, whether the experiment be performed in light or darkness, in the heat or cold. And the sum total of the iodine which Dr. Smith could have liberated, under the conditions given, even had the tubes been kept at the boiling heat, or several degrees above (see results obtained at 105°, *supra*), for hours, would have been the small amount equivalent to the oxygen sealed up at the same time with the solutions in the tubes.

very long sulphuric acid tube, and thence into an absorption apparatus containing *potassium iodide*, and provided with a proper sulphuric acid guard. In case the matter of ozone and oxygen were identical, the weight of oxygen equivalent to the weight of iodine set free by the ozone, should have been equivalent to the total gain in weight by the absorption apparatus. But, according to the experiments, this weight was less, and the numbers apparently assigned to electrolytic ozone the formula H_2O_3 .

Three years later, the conclusions of Baumert were overthrown by Andrews, in his classic research upon the "Constitution and properties of ozone" (Phil. Trans., 1856, 1; Roy. Soc. Proc., 7, 475; Ann. de Chim., 67, 181; Journ. de Pharm., 30, 3; Ann. der Chem. u. Pharm., 97, 371; Pogg. Ann., 98, 435). He demonstrated the fatal error in Baumert's experiments, in that the electrolytic ozone had contained a minute but determinable quantity of carbonic acid, which, unless exceeding precautions be taken, is always present in the evolved gas. Finding that the results obtained with a *neutral solution of potassium iodide*, varied irrationally and uncontrollably, Andrews in despair abandoned the use of the *neutral* and substituted a slightly *acidified* solution of potassium iodide. The free hydrochloric acid prevented the fixation of any traces of carbonic anhydride by the liberated base of the iodide, the anomalies disappeared, and by very numerous experiments, he succeeded in establishing that the weight of the substance which produced the decomposition (the active oxygen or ozone), was exactly equal to the weight of the iodine set free, and therefore no hydrogen, as well, could have been present.

The fact that the foregoing, which is the main truth, was thus triumphantly established by Andrews, has probably been the reason why the method he followed, of titrating ozone in an acidified solution of iodide, has been generally adopted and practised, even up to the present day, with, as we have previously seen, the commission of very serious error. For while Baumert failed in his reply (Pogg. Ann., 99, 88) to invalidate the principal conclusion of Andrews, he nevertheless did succeed in experimentally proving that all of them were vitiated

It is possible that in the experiment performed by Dr. Smith, a small amount of the dilute nitric acid may have undergone resolution, by heating, into hyponitric acid and oxygen. But this is extremely improbable, and there is reason for believing that the total amount of iodine set free in the experiment cited, was the exact chemical equivalent of the oxygen of the air, which was sealed up at the same time with the acidified solution in the tube. And, as a corollary to this proposition, that, had Dr. Smith taken the precaution to exclude every trace of free oxygen from the tube, even with the dilute nitric acid, no change of the potassium iodide solution would have occurred on heating to the boiling point, and on continuing the heating for hours.

The 7th point is:—"The solution of iodide of potassium as hitherto obtained, is subject to change. An old solution, that is, one nearly a month old, was found more sensitive than a new one in all

by a constant error. Baumert showed that when a stream of electrolytic ozone was passed through three absorption apparatuses, the first and second containing a neutral, the third an acidified solution of potassium iodide, all the ozone underwent decomposition in the first, no iodine whatsoever was liberated in the second, but in the third, *the acidified solution*, an amount of iodine was set free equivalent to many times (from 4 to 10) that corresponding to the ozone reaction in the neutral solution. This last, Baumert correctly ascribed to the decomposing action of oxygen upon an *acidified* solution of potassium iodide, and the curious fact remains that both the total increments in weight due to the fixation of absorbed ozone (and oxygen), and the amounts of oxygen as determined by titration equivalent to the iodine liberated, were both false in Andrews' experiments, and in excess of the absolute quantities of ozone operated upon. Yet, inasmuch as these two weights in the absence of an extraneous third body, like carbonic acid, which could be fixed by the titrating fluid, were necessarily equal, the constant error in Andrews' results did not excite general attention. Fortunately, as above remarked, the conclusions arrived at by Andrews were true, and the accompanying fallacy, concealed beneath the halo surrounding a great name, was perpetuated in the works of later experimenters, and has led many astray.

Ten years later than the memoir referred to, the facts made known by Baumert, concerning the decomposition of an acidified iodide solution in the presence of oxygen, were rediscovered by Payen (*loc. cit.*), who extended his trials to the action of acetic, nitric, oxalic, and other acids, in dilute condition, upon solutions of potassium iodide, in and out of contact with air, but without accompanying them with the beautifully quantitative methods of Baumert. While both experimenters noted the essential participation of oxygen in the change, they appeared to have overlooked the role of actinism.*

* Since writing the above, I have found (*Chem. News*, 86, 100, from *Gazz. Chim. Italiana*, 7, Fas. 6) a note entitled, "Action of light and carbonic acid upon aqueous solutions of iodide of potassium, and on ozonoscopic paper, by G. Pellagri." I am unable to judge, from this short note, to what extent the above results have been anticipated by the Italian experimenter, and have no means of present access to the original paper.

cases tried." I find it difficult to understand the precise meaning of the epithet "sensitive," as applied in this connection, unless the sensitiveness be due to a decomposition of the nitric acid employed, and a corresponding liberation of iodine. In this case, however, instead of being styled sensitive, the solution might, with more propriety perhaps, be termed spoiled, and as such unfit for employment in actinometry.

Dr. Smith states in the ninth place:—"The amount of allowance to be made for temperature is not made out. It is not certain that any is required in the cases when weak acid is used. The weather has not allowed any combined action of great light and heat, but with heat and light in the rays from an electric light with a parabolic reflector, the action was very rapid."

I fail to find in the experiments detailed by Dr. Smith upon the effects of temperature (see above), a basis for the above generalization. Neither do I perceive the reason for this dependence upon the weather, when it might be deemed the essential prerequisite of accurate experiment, that the changes due to the two separate causes should be carefully discriminated, and the effects properly assignable to each, determined by previous trials under conditions admitting of exactitude and control. Nor do I recognize a test of the latter character, in the experiment performed in the concentrated beam from an electric light.

Finally, the manner in which the iodo-acid method is applied to solar actinometry, appears to me irrational. For Dr. Smith proposes to expose this actinometer during successive hours of "sunshine and cloud alternately"; during times when the weather is "changeable"; during intervals of "sun and showers"; during weather which is "foggy, with a gleam of sunshine." I am quite unable to understand in what way the value of a meteorological observation is enhanced, by knowing that, during periods in which the sun may or may not have been shining, a few milligrammes, more or less, of iodine were set free, in an acidified solution.

When, however, we call to mind the frequent experience in photography, that there are states of the atmosphere when, with a clear sky, the quality of the light does not appear to be favorable to the making of a successful picture; or the fact previously noted, that no visible change being manifest in a brilliant blue sky, the curve of chemical intensity underwent a great depression; or note the immense amount of chemical work done as the horizontal ray passes through the myriad organisms and pestilential germs, miasms,

vapors, and countless emanations from the earth's surface, that admit of oxidation under solar influence, then, I think, we become impressed with the large practical value of an easy and rapid method of actinometry. The actinic component of the solar ray has its units of work, as well as the thermal, and the day has come when, in the utilization of available energy, if it will not repay us to "extract sun-beams from cucumbers," it is because we can more profitably store up the wasted forces in the sun-beams ready made.

XXXI.—LAWS GOVERNING THE DECOMPOSITION OF EQUIVALENT SOLUTIONS OF IODIDES UNDER THE INFLUENCE OF ACTINISM.

BY ALBERT R. LEEDS, PH.D.

In a paper published in the *Philosophical Magazine* for June, 1879, I have given a brief review of the controversy as to whether potassium iodide, in very dilute solution, is decomposable by sulphuric acid. I likewise pointed out that the explanation of the opposite views entertained by experimenters upon this question, was due to their having overlooked the essential part played by air or oxygen in this reaction.

In former papers,* a summary of which is given in the *Philosophical Magazine* (loc. cit.), I have shown that the presence of oxygen not merely facilitates, but is absolutely essential to the occurrence of the reactions in all cases, and whether the reaction occurs in open or closed vessels, in the heat or cold, in darkness or in light. The only exception to this law is in the case of an acid like nitric acid, which under the influence of light (the action of heat alone in the absence of light and oxygen is being investigated) spontaneously breaks up, and supplies by internal change the essential oxygen. The experiments made to determine the rates of decomposition when various iodides in the presence of different acids, were submitted to the influence of the magnesium, electric and solar rays, were made with solutions of known, though not of chemically equivalent, strength. To supply this defect, a new series of experiments was performed immediately after the publication of those cited above, and it is to make known certain remarkable laws of actino-chemical change deduced from these later experiments, that the present article is written.

* Compt. Rend., 62, 254; PROCEEDINGS AMERICAN CHEMICAL SOCIETY, 1878, 2, 4; JOURNAL AMERICAN CHEMICAL SOCIETY, 1879, 1, 18; *ibid*, 65.