

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.

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

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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.

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

The solutions were of such strength, that 1 c.c. of each of the acids employed was chemically equivalent to 12.6 c.c. of a normal caustic soda solution; the iodides were each exactly equivalent to the 20 per cent. solution of the potassium iodide; 1 c.c. of the iodide and 1 c.c. of the acid were used in each trial, the volume of the test being made up to 100 c.c. by the addition of distilled water. The tests were contained in comparison tubes made of thin, perfectly colorless glass, of uniform bore and dimensions, which were supported on frames in such a manner that each tube should be normal to the incident ray, and in the case of the magnesium and electric lamps, 6 in. from the focus of the light.

The first set of trials was made to determine whether the addition of starch as an indicator facilitated the decomposition under the influence of light, as had been originally supposed, or whether, as later on, there had been reason to think, it retarded the reaction. In this, as in succeeding experiments, the amounts of iodine liberated are given in milligrammes.

## EFFECT OF STARCH UPON THE RATE OF CHANGE.

March 18th, 1879. (Brilliant Sun.)

Reagents	1.30—2.30 P.M.	2.30—3.30	3.30—4.30
	5 c.c. starch-water	30 c.c. starch-water	No starch
H <sub>2</sub> SO <sub>4</sub> + KI	0.48	0.51	1.65
HCl + “	1.18	1.46	3.50
HNO <sub>3</sub> + “	3.10	2.57	3.50
H <sub>2</sub> SO <sub>4</sub> + CdI <sub>2</sub>	0.49	0.82	1.65
HCl + “	1.90	1.11	3.55
HNO <sub>3</sub> + “	2.80	2.83	3.40
H <sub>2</sub> SO <sub>4</sub> + LiI	0.34	0.40	0.30
HCl + “	0.59	0.72	1.75
HNO <sub>3</sub> + “	2.70	3.86	2.75
H <sub>2</sub> SO <sub>4</sub> + KI	0.48	....	....

MARCH 19TH, 12 M.-1 P.M. (Feeble Sun-light.)

H <sub>2</sub> SO <sub>4</sub> + KI	0.26	....	1.8
HCl + “	0.40	....	2.4
H <sub>2</sub> SO <sub>4</sub> + CdI <sub>2</sub>	0.22	....	1.6
HCl + “	0.40	....	2.2
H <sub>2</sub> SO <sub>4</sub> + LiI	0.20	....	1.2

The experiments of March 18th, performed as they were with a sun approaching the horizon, having been less decisive than could have been desired, they were repeated upon the following day, but with the disadvantage of feeble sun-light, with the result of showing that six times more iodine was set free in the absence than in the presence of starch. The suspended precipitate of starch iodide cut off the light except upon the superficies of the solution. Henceforth the employment of starch was abandoned.

The next set of trials was instituted in order to observe the influence upon the rate of change, of larger access of oxygen than that derivable from the air already dissolved, or in contact with the solution at its upper surface. To this end tests were prepared in duplicate, and through one pair of these duplicate solutions, the comparison tubes being connected together in the manner of wash-bottles, a slow current of oxygen was passed.

INFLUENCE OF INCREASED SUPPLY OF OXYGEN,  
March 19th, 1879. 11 A.M.-12 M. (Feeble sun-light.)

	With Oxygen.	Without.
H <sub>2</sub> SO <sub>4</sub> + KI	7.15	2.9
HCl + "	10.60	4.3

Also with Nitric Acid. 1-2 P.M. (Snowing at time.)

	With Oxygen.	Without.
H <sub>2</sub> SO <sub>4</sub> + KI	5.25	1.5
HNO <sub>3</sub> + "	6.75	2.5

Since 100 c.c. of water, when saturated with air under the ordinary circumstances of temperature and pressure, would hold in solution only about 1 mgrm of oxygen, the maximum amount of iodine which could be liberated during one of these tests, in case no fresh absorption of oxygen took place from the upper surface, would be 16 mgrms. The influence of these conditions upon the accuracy of the estimations made with the iodo-acid actinometers, is being submitted to further investigation.

In order to study the influence of mineral acids, trials were made as above, the solutions being of such strength that 1 c.c. of each was chemically equivalent to the same amount of the mineral acid.

EFFECT OF ORGANIC ACIDS, MARCH 20TH, 10.10 A.M.-1.10 P.M.  
(Good sun-light.)

Oxalic acid	+ potassium	iodide	= 6.50	mgrms I.		
"	"	+ cadmium	"	= 6.00	"	"
"	"	+ lithium	"	= 5.75	"	"
Tartaric acid	+ potassium	"	= 0.10	"	"	"
"	"	+ cadmium	"	= 0.00	"	"
"	"	+ lithium	"	= 0.00	"	"

No change with acetic acid during this three hour interval.

To determine more precisely the rate of change effected by the organic, as compared with the mineral acids, it will be necessary to make simultaneous estimations, but even with oxalic acid, the most active of them all, it is evident that the amount of decomposition was relatively small.

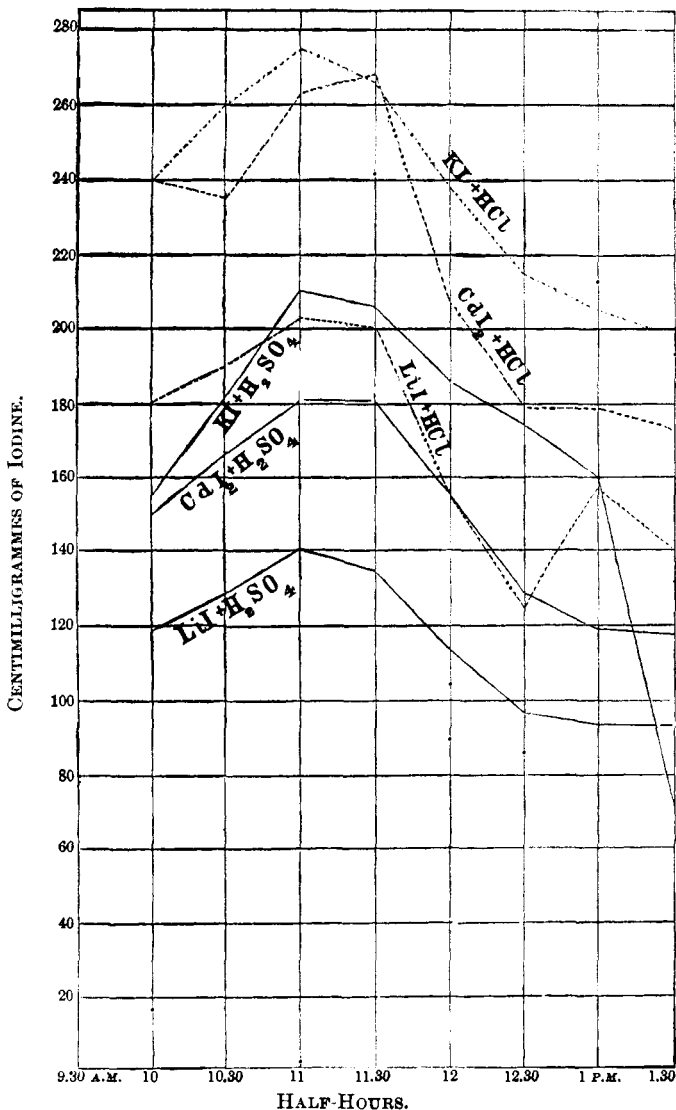
An actinometric measurement of the solar ray was made with the equivalent solutions of various iodides and acids, the principal object being to note the effect upon the rate of decomposition of different acids in the presence of the same base, and of different basic radicals of the iodides in the presence of the same acid. The sun-light, which was good during the early part of the day, declined towards noon, and shortly after the sky became overcast.

ACTINOMETRIC MEASUREMENT OF THE SOLAR RAY, MARCH 26TH, 1879.

	9.30- 10 A.M.	10- 10.30	10.30- 11	11- 11.30	11.30- 12 M.	12 M.- 12.30	12.30- 1 P.M.	1- 1.30	MEANS	RATIOS.
H <sub>2</sub> SO <sub>4</sub> + KI	155	181	21	206	187	17	16	75	168	H <sub>2</sub> SO <sub>4</sub> : HCl 1 : 148
HCl + "	24	26	275	266	239	215	205	20	250	
H <sub>2</sub> SO <sub>4</sub> + CdI <sub>2</sub>	15	162	181	181	156	129	119	118	149	H <sub>2</sub> SO <sub>4</sub> : HCl 1 : 146
HCl + "	24	235	263	268	209	179	179	175	218	
H <sub>2</sub> SO <sub>4</sub> + LiI	118	128	141	135	113	96	93	93	115	H <sub>2</sub> SO <sub>4</sub> : HCl 1 : 147
HCl + "	183	19	203	20	156	125	158	14	169	

These results are represented graphically on the diagram on the following page.

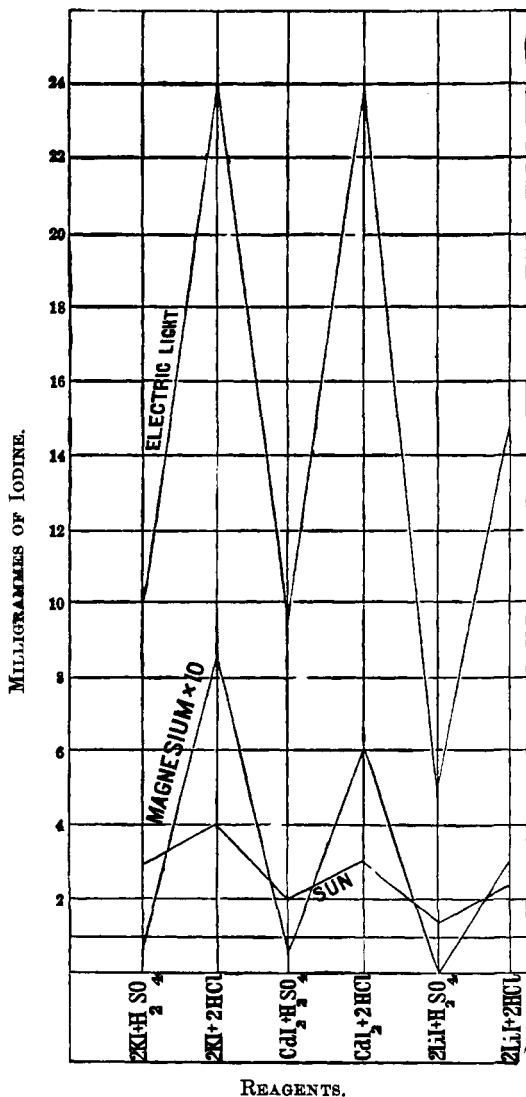
On comparison of the arithmetical means of the results obtained in 54 trials made during the course of the same day, the striking fact is brought out, that the amounts of iodine liberated by the two acids in the presence of the same base, stand in a constant ratio to one another. The law of actinic force herein indicated may provisionally be expressed by the formula—the chemism of the chlorine radical is to that of the  $\frac{1}{2}$ SO<sub>4</sub> radical (measured by the relative amounts of iodine liberated by each respectively, in solutions of the metallic iodides exposed to sun-light) as 1.47 : 1. There is reason for inferring from the experiments, that a similar definite ratio exists between the amounts of iodine liberated from different soluble iodides in the presence of the same acid.



COMPARISON OF THE ACTINIC INTENSITIES OF THE SOLAR, ELECTRIC AND MAGNESIUM LIGHT.

In making this comparison, the amounts of iodine liberated at the hour of maximum actinic intensity (1-1.30 P.M.) were taken in the case of the sun. The electric light was that emanating from a lamp of 7000 candle power, falling upon the solutions at a distance of six

inches; the magnesium light, that derived from the burning of a single ribbon in the ordinary lamp, placed at the same distance. The time of exposure to the electric light was 10 minutes; to the magnesium light, 25 minutes; to the sun, one-half hour; in the table, all are calculated to one hour.



	Solar.	Electric.	Magnesium.
H <sub>2</sub> SO <sub>4</sub> + KI	2.70	10.0	0.084
HCl + "	4.00	24.0	0.870
H <sub>2</sub> SO <sub>4</sub> + CdI <sub>2</sub>	2.04	9.5	0.072
HCl + "	3.00	24.0	0.600
H <sub>2</sub> SO <sub>4</sub> + LiI	1.44	5.0	none
HCl + "	2.40	15.0	0.300

On examining this table, and still more readily the graphic illustration preceding it, two phenomena become forcibly manifest:— 1st. The very much greater actinic intensity of the electric, as compared with the solar ray, when compared in the manner indicated, and the very much less intensity of the magnesium. In order to bring the magnesium curve into the same diagram as the others, the numbers in the magnesium column in the table were all multiplied by ten. 2d. Instead of the relative chemism of the chlorine atom, as estimated by its iodine-liberating power under these conditions, being 1.5 in all three cases, it is 6 with the electric, and 10 with the magnesium light. The examination of these differences, as related to the actinic forces of different sources of light, and to different acid and basic radicals, is being investigated further.

Finally, the influence of absorbing media upon the invisible rays of the sun and electric light were determined, the comparison tubes being surrounded with a thickness of 3 c.m. of ammonio-sulphate of copper, neutral potassium chromate and fuchsine, each solution being brought to the same apparent degree of translucency, for the blue, yellow, and red respectively. The exposure to the sun was from 9.30 A.M. to 5.30 P.M.; to the electric light, 20 minutes; but both are reduced to the interval of 1 hour.

	Sun.	Electric Light.
Blue H <sub>2</sub> SO <sub>4</sub> + KI	0.74	1.800
HCl + "	1.12	6.750
Yellow H <sub>2</sub> SO <sub>4</sub> + KI	0.11	0.000
HCl + "	0.25	0.125
Red H <sub>2</sub> SO <sub>4</sub> + KI	0.28	0.600
HCl + "	0.56	2.250

These figures show that the selective action of absorbing media upon the invisible rays of different illuminants, varies greatly; and suggests the employment of this method for the mapping out of absorption spectra for the actinic portion.