

over, at the maximum, yet since, by attaching the ozonator to the water-pump, it may be allowed to act during days and nights for several days without further attention, the yield of ozone may be indefinitely increased.

Since writing the above, attempts have been made to improve the ozonator in various details. It was thought that it might be simplified by substituting for the jars a rectangular trough of copper, lead, or wood painted inside with asphalt. The copper was rapidly attracted by the chromic acid (56 p. c. of copper in the form of turnings went into solution over night), and the asphalt likewise. In the case of lead, it was found that 16.543 grm. turnings increased in weight to 16.546 grms., on standing in the mixture 20 hrs., so that the superficial crust of insoluble salts formed would serve for protection. But its weight, if made thick enough to keep the shape, was objectionable. Moreover, it was important to make the trough of a material which could be heated directly by gas-jets, when it was desired to bring the apparatus to the temperature of maximum activity, or 24° c. This has been done by the addition of a suitable copper water-bath, in which the jars are placed, provided with proper arrangements for heating. Manifestly, the same bath will serve for cooling, when the summer temperature shall exceed 24°.

It gives me great pleasure to acknowledge the co-operation of my assistant, Dr. Edgar Everhart, in the performance of the foregoing experiments.

V.—UPON THE TITRATION OF HYDROCHLORIC ACID FOR CHLORINE,
AND OF SULPHURIC AND NITRIC ACIDS FOR HYPONITRIC ACID.
[2d PAPER.]

BY ALBERT R. LEEDS.

In a former paper I have given the results obtained on titrating eight specimens of so-called pure acids, the titrations beginning October 27th and continued, as notable amounts of starch iodide were formed, until December 5th. At this time solutions VI, VII and VIII were thrown away; the others were titrated giving the following amounts of standard sodium hyposulphite:

	I.	II.	III.	IV.	V.
Dec. 12th . . .	None	0.34 cc	1.04 cc	0.10 cc	0.10 cc
Jan. 3rd . . .	None	0.75	3.25	2.00	0.50
Totals	1.23 cc	4.91 cc	9.46 cc	5.70 cc	3.01 cc

It will be seen from column II, that the 5 cc of HCl in 1 liter water, had liberated nearly five times the amount of iodine as the 1 cc HCl under like circumstances (column I). The sulphuric acid (columns III and IV) had effected far more decomposition than the nitric (V), and this again much more than the hydrochloric acid of similar strength (I). The significance of these differences were not known when the five solutions were thrown away (Jan. 3rd), but the cause of the combined change was, having become known through the following experiment.

In place of solutions VI, VII and VIII, six two-liter bottles were taken, and 1000 cc water, 4 cc starch solution, and 1 cc KI solution of 10 per cent. added to each. Three of these, after addition of 1 cc H_2SO_4 , 1 cc HNO_3 and 1 cc HCl respectively (same acids as in columns VI, VII, VIII), were placed in diffused light; the other three, similarly treated, were set in the dark (Dec. 6th).

TITRATION OF ACIDS.

	H_2SO_4	Dark.			Light.		
		HNO_3	HCl	H_2SO_4	HNO_3	HCl	
Dec. 9th . . .	0.13 cc	0.30	0.13	0.96	0.79	0.49	
Jan. 3rd. . . .	None	None	None	4.70	3.00	3.20	
Jan. 4th. . . .							

Those in the dark having ceased to change, three similar new solutions were substituted :

Jan. 6th . . .	0.033	0.03	0.03			
Jan. 20th . . .	None	None	None	3.60	2.50	1.50

The three new solutions having ceased to change were thrown away; those in the light were exposed to *sun-light* for six hours.

Jan. 20th, (6 hrs.)	0.50	0.40	0.20			
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The last experiment was made in consequence of the results obtained in several preceding trials. Eight bottles, each containing 1 cc H_2SO_4 , 3 cc starch solution and 1 cc KI, were partly filled with various amounts of water, and four placed in light, four in darkness. After 24 hrs. they were titrated (column I). This experiment was repeated (column II); in this case, the same solutions being again titrated after the lapse of 5 days :

TITRATION OF 1 cc H_2SO_4 —(1.845 Sp. Gr.)

Sun-light.

	I.	II.	III.
With 100 cc H_2O	0.18 cc	0.23 cc	1.20 cc
“ 50 cc “	0.15	0.17	0.98
“ 25 cc “	0.23	0.23	1.06
“ 20 cc “	0.20	0.20	1.00

Darkness.

	I.	II.	III.
With 100 cc H_2O	Trace.	0.03 cc	0.10 cc
“ 50 cc “	0.06 cc	0.06	0.20
“ 25 cc “	0.15	0.10	0.30
“ 20 cc “	0.23	0.18	0.30

An inspection of these figures developed the curious fact, that in the dark, the amount of decomposition of the potassium iodide, was approximately proportional to the degree of concentration. In the light, similar solutions appeared to obey no similar law, or indeed any law of a definite character. To determine to what degree of dilution the above law held true, a number of bottles, each containing 2 cc KI solution, and 5 cc starch, but with various amounts of water, were placed, some in sun-light, others in darkness, allowed to stand over night, and titrated at the end of 24 hours.

TITRATION OF 1 cc H_2SO_4 —(1.845 Sp. Gr.)

	Sun-light.	Darkness.
With 500 cc H_2O .		Indeterminable.
“ 400 “ “	0.70 cc	“
“ 300 “ “		“
“ 250 “ “		“
“ 200 “ “	0.56	0.01 cc
“ 150 “ “		0.006
“ 100 “ “	0.44	0.06
“ 75 “ “		0.15
“ 50 “ “	0.30	0.06
“ 25 “ “		0.80
“ 20 “ “	0.30	

This experiment brought out the fact that in sun-light, the action was the reverse of that in darkness, although the law governing the rate of change did not directly appear. In the dark, it appeared that at ordinary temperatures, no appreciable amount of change had taken

place at the end of 24 hours, when the dilution exceeded 200 times the volume of the acid or potassium iodide solution. But in both series of trials, the figures conforming to no exact rule, they were repeated with the following more satisfactory results :

TITRATION OF 1 cc H_2SO_4 —(1.845 Sp. Gr.)

	Sun-light.	Darkness.
With 200 cc H_2O .	0.67 cc	
“ 150 “ “	0.47	0.018 cc
“ 100 “ “	0.60	0.03
“ 75 “ “	0.37	0.06
“ 50 “ “		0.13
“ 25 “ “	0.33	0.26

The potassium iodide used in these and the following experiments was some especially prepared, and free from all impurities, except a trace of iodic acid. The amount was so small that none of the tests for iodic acid, except that with sulphurous acid, revealed its presence, and then only a scarcely recognizable indication. The same remark is true of the cadmium iodide; which was next tried, in order to learn whether the above laws were general in their application.

TITRATION OF 1 cc H_2SO_4 —(With CdI_2).

	Sun-light.	Darkness.
With 200 cc H_2O .	1.15 cc	0.023 cc
“ 150 “ “	1.07	0.048
“ 100 “ “	1.09	0.03
“ 50 “ “	1.07	0.25
“ 25 “ “	0.95	0.13

On reviewing the methods pursued up to this point, three sources of serious error became apparent. 1st. The bottles, while placed in the sun-light during the day, were not titrated until the following morning, and during the intervening period, the law regulating the decomposition in darkness had the opportunity of operating, and that, too, in a contrary direction. 2d. The bottles were of various tints, some of yellowish or even pinkish tinge, which would affect the actinism of the solar ray very differently from quite colorless glass. 3rd. The bottles were of different shapes and dimensions, the latter circumstance causing the surface of exposure to increase in a very different ratio from that of the increase in bulk of the contained liquid only. For these reasons, comparison-tubes were substituted. In these, the increase in the surface of exposure of liquid would be directly proportional to the increase in its volume.

JAN. 18TH. SUNNED IN COMPARISON-TUBES (1 cc H_2SO_4).

	1st Series (A).	2d Series (B).
With 100 cc H_2O .	1.366 cc	1.366 cc
“ 80 “ “	1.83	1.40
“ 60 “ “	1.20	1.20
“ 40 “ “	1.00	1.00
“ 20 “ “	0.60	0.60

They were exposed from 12:20 P. M. to 2:45 P. M.

The changes of color were as follows, counting from beginning of experiment :

	TO VERY FAINT ROSE.	FAINT ROSE.	ROSE.	VIOLET.	BLUE.
100 cc A..	In 16 min.	In 19 min.	In 22 min.	In 30 min.	In 35 min.
100 “ B..	8 “	14 “	17 “	25 “	31 “
80 “ A..	10 “	16 “	21 “	28 “	33 “
80 “ B..	13 “	17 “	23 “	28 “	33 “
60 “ A..	15 “	20 “	26 “	28 “	34 “
60 “ B..	19 “	19 “	25 “	28 “	34 “
40 “ A..	21 “	25 “	27 “	30 “	35 “
40 “ B..	20 “	25 “	27 “	29 “	35 “
20 “ A..	24 “	27 “	32 “	35 “	40 “
20 “ B..	22 “	25 “	30 “	32 “	38 “

From this and similar experiments, it would appear that the amount and rate of decomposition is proportional to the increase in the dilution, when this increases in the same ratio as that of the exposure to the sun's rays.

The next problem was, to determine the amount of decomposition in the presence of the same acid, when the iodine was united to different bases. Also, in the presence of different acids, when the iodine was united with the same base. The following solutions were therefore exposed from 10:45 A. M. to 4 P. M., to the sun's rays (Jan. 20th):

WITH DIFFERENT BASES.

20 cc H_2O + 1 cc KI + 5 cc starch	+ 1 cc H_2SO_4 = 6.5 mgrm. I.	CdI ₂ = 6.5
40 “ “ + 1 “ “ + 5 “ “ + 1 “ “	= 8.0	“ = 7.5
60 “ “ + 1 “ “ + 5 “ “ + 1 “ “	= 9.3	“ = 9.5
80 “ “ + 1 “ “ + 5 “ “ + 1 “ “	= 10.5	“ = 10.3
100 “ “ + 1 “ “ + 5 “ “ + 1 “ “	= 9.5	“ = 12.0

WITH DIFFERENT ACIDS.

20 cc H ₂ O	+ 1 cc H ₂ SO ₄	+ 5 cc starch	+ 1 cc KI	= 6.5 mgrm. I.	HCl = 6.8
40 "	" + 1 "	" + 5 "	" + 1 "	" = 7.8 "	" = 7.5
60 "	" + 1 "	" + 5 "	" + 1 "	" = 9.6 "	" = 8.3
80 "	" + 1 "	" + 5 "	" + 1 "	" = 11.0 "	" = 9.0
100 "	" + 1 "	" + 5 "	" + 1 "	" = 12.0 "	" = 9.8

REPEATED, FROM 12 M. to 1 P. M.

100 cc H ₂ O	+ 1 cc KI	+ 5 cc starch	+ 1 cc H ₂ SO ₄	= 2.25 mgrm. I.
100 "	" + 1 " NH ₄ I	+ 5 "	" + 1 "	" = 2.20 "
20 "	" + 1 " KI	+ 5 "	" + 1 " HNO ₃	= 0.90 "
100 "	" + 1 " "	+ 5 "	" + 1 " "	" = 2.00 "
20 "	" + 1 " NH ₄ I	+ 5 "	" + 1 " "	" = 1.00 "
100 "	" + 1 " "	+ 5 "	" + 1 " "	" = 2.00 "
20 "	" + 1 " "	+ 5 "	" + 1 " HCl	= 0.30 "
100 "	" + 1 " "	+ 5 "	" + 1 " "	" = 1.00 "

In these trials, equal volumes of acid of usual strength were employed, not equivalent amounts of real acid, and the exact ratio of decomposition has yet to be determined.

Decomposition of Pure Acids in Sun-Light.—To determine whether the acids underwent decomposition in sun-light, nitric acid, of sp. gr. 1.4; hydrochloric acid, sp. gr. 1.202; sulphuric acid, sp. gr. 1.845, were taken; 50 cc of each were placed in 100 cc glass-stoppered bottles, the stoppers luted in with paraffine, and the three bottles exposed at a south window, from Dec. 10th to Jan. 21st. At the end of this period, 1 cc 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 cc HNO ₃	= 14.80 cc Na ₂ S ₂ O ₃
1 " H ₂ SO ₄	= none.
1 " HCl	= "

To determine whether the *diluted acids*, with and without organic matter, changed by exposure to sunlight, 1 cc of each of the pure acids of densities given above, was diluted with 500 cc water. To three, starch-water was added. The six were sunned during six weeks, when potassium iodide and fresh starch-water added to each, and they were then titrated, after standing in darkness 24 hours. They gave:

THE THREE WITH STARCH.

THE THREE WITHOUT.

500 cc dilute HNO_3	= 0.50 cc $\text{Na}_2\text{S}_2\text{O}_3$	= 0.30 cc $\text{Na}_2\text{S}_2\text{O}_3$.
500 " " H_2SO_4	= none	= none.
500 " " HCl	= "	= "

The presence of the organic matter appears, in this experiment, to have facilitated the decomposition of the nitrate in sunlight.

Chemical Energy of the Solar Ray.—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 cc H_2SO_4 , 1 cc KI and 5 cc starch, 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.

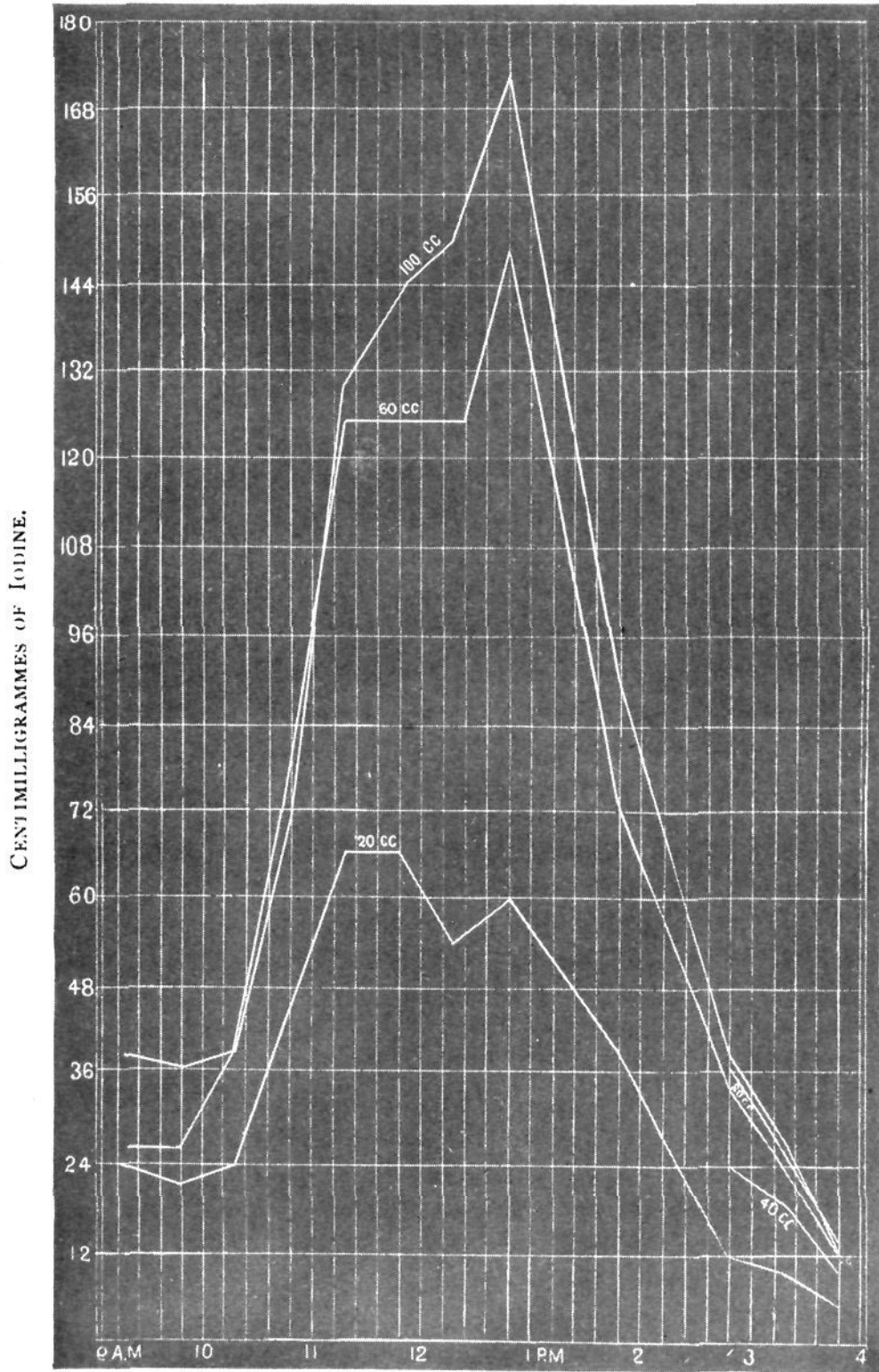
RELATIVE ACTION OF THE SUN'S RAYS (JAN. 22d, 1879).

	20 cc H_2O .	60 cc H_2O .	100 cc H_2O .
9 — 9:30 A.M.	0.24 mgrm. I.	0.27 mgrm.	0.38 mgrm.
9:30—10	0.22	0.29	0.37
10 — 10:30	0.24	0.40	0.40
10:30—11	0.39	0.76	0.71
11 — 11:30	0.67	1.25	1.29
11:30—12	0.67	1.25	1.46
12 — 12:30 P.M.	0.55	1.25	1.54
12:30— 1	0.60	1.50	1.73
1 — 1:30	0.50	1.13	1.31
1:30— 2	0.40 [clouded over]	0.75	0.92

CONTINUED, JAN. 24th.

	20 cc H_2O .	40 cc H_2O .	60 cc H_2O .	80 cc H_2O .	100 cc H_2O .
2:30—3	0.125	0.24	0.33	0.38	0.40
3 — 3:30	0.11	0.18	0.24	0.27	0.28
3:30—4	0.07	0.10	0.12	0.13	0.12

It will be seen by the inspection of the accompanying diagram, that the curve representing the amount of iodine set free in the 40 cc



HOURS IN THE DAY.

solution and the 80 cc solution, was intermediate between the curves 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.

VI.—ON THE INFLUENCE OF VARIATIONS OF TEMPERATURE ON THE DEVIATION OF POLARIZED LIGHT BY SOLUTIONS OF INVERTED SUGAR.

By P. CASAMAJOR.

Received February 18, 1879.

The researches, of which I propose to give an account in this paper, were suggested by an interesting communication of Dr. Ricketts to this Society, which was presented at our last meeting.

Dr. Ricketts found that the temperature at which the deviation of a solution of inverted sugar becomes 0 is not 90° C., as given by some authors, but 92° , or rather 91.7° C. From this Dr. Ricketts concluded, that if a solution of commercial sugar is inverted in the ordinary way, if, originally, the two constituents of the sugar were cane sugar and inverted sugar, after inversion there must only remain inverted sugar, and, if we bring this solution in the saccharometer tube to have the temperature of 92° C., the indication of the saccharometer scale must be 0.

As the inversion of sugar solutions in testing sugars is now almost entirely neglected, it struck me that the introduction of this subject before this Society was of great importance, as it is likely to excite inquiry in this direction, and must lead to interesting discussions which will throw much light on a ground which has not recently been explored. I hope the following remarks may be considered as a contribution to this important subject.

To enable me to present in a clear light, the results I have reached, it becomes necessary to bring before you some theoretical points relating to the inversion of sugar solutions.