measurements of the chemical energy of the solar ray." The papers were accompanied with photographic and experimental illustrations.

In discussing the second paper, Dr. Endemann remarked that Grotthuss had studied the action of the various rays upon starch iodides, and had found that the red and yellow rays bleached this substance, while the violet ray restored the color. The possibility of a greater energy of the violet ray at noon would correspond with the results obtained by Prof. Leeds.

The Vice-President resuming the chair.

Mr. Sherer read a paper entitled "A Method for the Determination of Dextro-glucose and Cane Sugar in Refined Sugars and Syrups,"* which was discussed by Dr. Behr.

Mr. Casamajor then read a paper "On the Influence of Variations of Temperature, and the Deviations of Polarised Light by Solutions of Inverted Sugar." After which the meeting adjourned.

S. A. GOLDSCHMIDT,
Recording Secretary.

IV.—RELATIONS BETWEEN THE TEMPERATURE AND VOLUME IN THE GENERATION OF OZONE, WITH DESCRIPTION OF A NEW FORM OF OZONATOR.

BY ALBERT R. LEEDS, PH. D.

THE methods usually employed to generate ozone by means of the slow oxidation of phosphorus, partly immersed in water, are quite unsatisfactory. Thus Miller (Elements of Chemistry, 2d. Ed., Part II., p. 23) directs that a stick of clean phosphorus, moistened with a few drops of water, should be placed in a bottle of atmospheric air. In an hour or two the production of ozone attains a maximum, when, if the phosphorus be not removed, the ozone disappears, owing to its combination with the phosphorus. Instead of a bottle, a large glass balloon is preferably employed, which Arendt (Lehrb. der Anorgan. Chem., p. 416) directs to be covered with a glass plate, and allowed to remain before using for twelve hours. Gorup-Besanez (Anorgan. Chem., p. 358) recommends, in addition to the foregoing, that the balloon should be maintained for several hours at a temperature of 16° to 20°. As means of studying, or even of exhibiting to a class, the properties of ozone, everyone who has used these and similar devices, will probably have found them disappointing. At times a

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* This paper has been withdrawn by the author, C. P. P.

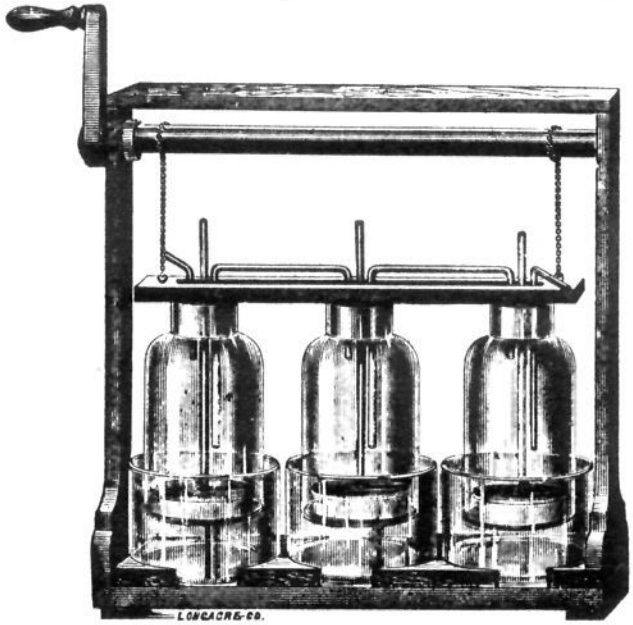
considerable evolution of ozone occurs; at others, little, or none. The causes of these variations will appear on examination of the experiments detailed later.

In a work published much earlier than the two last quoted, an apparatus is described and illustrated (Lecons de Chimie, A. Riche, Tome I., p. 106), which was a step in the right direction. The balloon was provided with an entrance and exit tube, the latter extending nearly to the bottom, so that a slow continuous current of air might be drawn through by means of an aspirator. The ozonized air was washed in the usual manner, and the liquids to be subjected to the action of ozone were placed in a second wash-bottle. This contrivance was adopted, a large bell-jar turned upside down and covered with a glass plate, being substituted for the wash-bottle, when it was desired to ozonize dyed goods, flowers and similar large objects. The apparatus was further improved by using a bell-jar in place of the balloon. The bell was set in a dish containing a number of sticks of phosphorus, the water with which they were partly covered acting as a seal. The disagreeable operation of occasionally cleansing the phosphorus, by scraping, was obviated by immersing them before using in a mixture of potassium bichromate solution and sulphuric acid.

These improvements, however, were of small importance compared with that effected by substituting the bichromate mixture for the water in the generator itself. The scanty, fitful evolution of ozone was replaced by a copious and constant supply. The dish was now replaced by a jar capable of holding a considerable amount of the bichromate solution, and by permitting a considerable change of level in the liquid, the air could either be drawn through by aspiration or forced through by pressure. Instead of placing the phosphorus on the bottom, the sticks were supported on a glass disc, which dropped into a cell connected with a paraffined iron rod sliding up and down, through the cork at top. In another generator, the cell was replaced by a brass stirrup, electroplated with gold; but this had to be abandoned, the solution speedily eating away the metal.

A difficulty now arose from the danger of inflammation, resulting from the great energy of oxidation. This danger seemed largely due to irregular melting down of the phosphorus, ridges being formed which protruded too far above the liquid. This unequal action also greatly diminished the amount of surface which could be safely exposed. To obviate these difficulties, watch-glasses were placed in a shallow tin dish filled with water, sufficient fragments of phosphorus placed in dish, and the temperature raised until, by melting of the phosphorus, a number of rounded cakes of uniform size had been made. Six of these could be placed upon the stage at one time, and the stage adjusted so that each cake exposed about 9 c.m.^{2} of surface area. As the convexity of the exposed portions was small, the liquid, by surface action, was constantly drawn over it in thin streams, and not only kept the phosphorus wet, but always clean and in condition of maximum chemical activity.

It was found, as will be seen by results stated below, that the air ozonized in one bell, could have its ozone percentage notably increased by passing through a second bell similar to the first, through a third, and so on. But as the manipulation of three, or even two bells, connected with glass tubes, was troublesome, it became necessary to arrange suitable machinery. The bells were, therefore, cemented into heavy brass caps. Through these caps and the paraffined cork beneath, connecting tubes of heavy glass were passed, and a sliding glass rod, which terminated below in a horizontal circle. The latter carried a disc of sheet lead, with a slot permitting its removal. The caps were then screwed fast to a board having a suitable opening down its middle to permit of passage of tubes, etc., and this again fastened to chains by which it might be readily raised or lowered. The frame is made of such height that the jars may be easily slipped from under the bells when desirable.* Thermometers are fastened into the side of each bell, their bulbs dipping just below the surface of the liquid.



It was evidently essential to convenient working of this apparatus to have a flexible connection between exit tube and wash bottle. But herein arose a very serious difficulty, India-rubber tubing being destroyed. Through suggestion of Prof. Silliman, and by kindness of Mr. A. G. Day, the patentee, I became provided with a great variety

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* These ozonators are manufactured by S. Hawkridge, successor to Wales & Co., Stevens' Institute of Technology, at the price of thirty dollars.

of kerite tubing. Weighed samples of each kind were subjected to equal amounts of ozone for equal intervals, their changes and the products of decomposition noted. Without detailing these experiments, suffice it to say that the specimens which gained most in weight underwent greatest decomposition, some indeed crumbling to pieces, while others which gained none, also did not change in appearance or physical characters. Of these, the most satisfactory was selected, and from it as a guide Mr. Day manufactured the ozone-resisting kerite, which is now used in connection with the ozonator, and generally during the progress of this investigation.

The improvements effected in the ozone-generating apparatus, were due, as has been said above, to a series of quantitative trials, the results of each set of experiments suggesting modifications in the next series. In the first place, phosphorus was used with water alone, one bell only being employed. The ozonized air was washed, and afterwards drawn through two Peligot tubes, containing a ten per cent. solution of potassium iodide. The second tube was added as a guard, but in practice is unnecessary, complete absorption occurring in the first. The liberated iodine, after acidifying with sulphuric (free from nitrous) acid, was titrated with sodium hyposulphite. In each experiment, 9 liters of air were drawn over. It soon became evident that widely differing results were obtained at different temperatures, the percentage of ozone falling off with decrease of temperature, to nought. Starting from this point, it appeared to increase, according to some unknown law, to a maximum, and then decreased again with further increase of temperature, until the point of inflammation of the phosphorus was attained. The volume ratio is given in terms of 0.005 Vpc. taken as a convenient unit :—

I.—OZONE FROM PHOSPHORUS IN WATER.

T	Mgrm. per Liter air.	Wpc.	cc per Liter.	Volume Ratio.	Wpc. of O.	Vpc. of O.
2°	none		none			
19°.5	0.615	0.0478	0.290	5.8	0.2065	0.139
25°	0.882	0.0682	0.413	8.3	0.2946	0.198
25°	1.050	0.0812	0.494	9.9	0.3508	0.237
30°.5	0.326	0.0252	0.153	3.1	0.1088	0.073

For convenience of comparison between these experiments and others, in which oxygen, not air, has been ozonized, columns VI and

VII have been added, the former giving the percentage by weight of ozone in the oxygen passed over, disregarding the nitrogen, the latter the percentage by volume. It will be seen that the maximum was obtained at about 25°, when the air contained 1 mgrm. ozone in the liter, or about one-half cubic centimeter.

In the second series of experiments, the water was replaced by a solution, containing to the liter of saturated solution potassium bichromate, 150 cc. H_2SO_4. In each experiment, 8½ liters air were drawn over. The results were as follows :

Temperature.	Time.	Hyposulphite.
7°		0.40 c.c.
13°—14°	70 minutes	4.25
17°—20°	56 "	6.77
21°—22°		7.10
24°	60 "	8.35
30°—31°.5	60 "	7.13
31°—32	60 "	7.18

From which it would appear that at a temperature of about 6° no ozone is given off, and from this point the percentage rises, until the temperature attains about 24°, the percentage falling off quite evenly on both sides of the maximum. The maximum production was 1.86 mgrm. per liter air, corresponding to 0.87 cubic centimeter.

II.—OZONE FROM PHOSPHORUS IN BICHROMATE (ONE BELL-JAR).

T	Mgrm. per Liter air.	Wpc.	cc per Liter.	Volume Ratio.	Wpc. of O.	Vpc. of O.
7°	0.089	0.0069	0.042	0.8	0.0298	0.020
13°.5	0.945	0.0730	0.441	8.8	0.3154	0.210
20°	1.505	0.1163	0.705	14.1	0.5011	0.336
21°.5	1.580	0.1221	0.741	14.8	0.5270	0.353
24°	1.857	0.1438	0.870	17.4	0.6221	0.415
31°.5	1.590	0.1229	0.745	14.9	0.5314	0.355

A third series of experiments was instituted to determine whether the air which had been ozonized in this manner, could receive an increment of ozone by being again subjected to the influence of phosphorus in a second bell-jar. The liquid contained to each liter of saturated solution of bichromate, 250 c.c. H_2SO_4.

Temperature.	Amount of Air.	Time.	Hyposulphite.
13°	2 liters.		1.20 c.c.
19°	2 "	12 minutes.	2.00 "
21°	2 "		2.1 "
23°	3 "		3.0 "
24°	3.5 "	20 minutes.	4.0 "
24°	2 "		2.6 "
27°	2 "		2.25 "

III.—OZONE FROM PHOSPHORUS IN BICHROMATE (TWO BELLS).

T	Mgrm. per Liter air.	Wpc.	cc per Liter.	Volume Ratio.	Wpc. of O.	Vpc. of O.
13°	1.134	0.0877	0.531	10.6	0.3789	0.255
19°	1.890	0.1460	0.885	17.7	0.6307	0.425
21°	1.985	0.1546	0.929	18.6	0.6696	0.446
23°	1.890	0.1460	0.885	17.7	0.6307	0.425
24°	2.155	0.1701	1.009	20.2	0.7344	0.489
24°	2.457	0.1933	1.151	23.0	0.8338	0.552
27°	2.127	0.1643	0.996	19.8	0.7098	0.478

It will be seen that the air ozonized in two bells, likewise contains a maximum percentage at 24°, but this maximum is 25 per cent. higher than the corresponding amount obtained with one bell; and, in general, the percentage obtained by two bells is 25 per cent. greater than that with one bell at any given temperature.

Before proceeding further, it appeared advisable to determine whether some other liquid might be substituted for the bichromate with advantage. Alkaline liquids seemed inapplicable, owing to the danger of formation of alkaline hypophosphites, and the evolution of hydrogen phosphide. Of the acids, sulphuric appeared the most suitable, although even this was attended with the disadvantage of the probable formation of some sulphurous anhydride at the same time. Mixtures of potassium permanganate, and similar salts with dilute acid, have not as yet been tried. The permanganate would have the disadvantage of being expensive, and even when sold as chemically pure, is usually contaminated with much potassium chlorate. The results obtained with a bath containing 250 c.c. H_2SO_4 to the liter of water, were as follows, two liters of air aspirated in each experiment, the interval varying from 12 to 25 minutes :

Temperature, 25° Sodium Hyposulphite, 1.60 c.c.
" 26° " " 2.90 "
" 25° " " 1.06 "
" 26° " " 1.30 "
" 26° " " 1.35 "

These low results made it appear probable that the phosphorus had become oxidized. It was, therefore, allowed to stand for some time in the bichromate mixture, and the experiment repeated:—

Temperature, 27° Sodium Hyposulphite, 1.70 c.c.

Although even this amount was not so high as that previously obtained under similar circumstances, at the same temperature, when the bichromate was employed, yet it confirmed the justness of the above supposition, and caused the use of the acid alone, as a bath, to be definitely abandoned. In the following table, the trials are given in the order as made, with the view of showing the gradual deterioration. The abnormally high result obtained for the first 26°, was due to the phosphorus having been kept for an unusual length of time in contact with the air in the bells, before aspiration was begun.

IV.—OZONE FROM PHOSPHORUS IN SULPHURIC ACID (TWO BELLS).

T	Mgrm. per Liter air.	Wpc.	cc per Liter.	Volume Ratio.	Wpc. of O.	Vpc. of O.
25°	1.512	0.1169	0.708	14.2	0.5011	0.340
26°	2.741	0.2119	1.283	25.7	0.9154	0.616
25°	1.002	0.0775	0.469	9.4	0.3347	0.225
26°	1.229	0.095	0.575	10.5	0.4104	0.276
26°	1.276	0.0986	0.597	11.9	0.4259	0.287
27°	1.607	0.1242	0.752	15.0	0.5365	0.361

Another related query was, whether so concentrated a bath was essential. To settle this point, a solution was made containing to each 1250 c.c. H_2O, 150 c.c. H_2SO_4, and 25 grms. $K_2Cr_2O_7$. The determinations were purposely made at about the maximum temperature:

Temperature, 26°5 Sodium Hyposulphite, 2.00 c.c.
" 26°5 " " 2.18 "

V.—OZONE FROM PHOSPHORUS IN DILUTE BICHROMATE (TWO BELLS).

T	Mgrm. per Liter air.	Wpc.	cc per Liter	Volume Ratio.	Wpc. of O.	Vpc. of O.
26°.5	1.890	0.1460	0.885	17.7	0.6307	0.425
26°.5	2.060	0.1592	0.965	19.3	0.6868	0.461

These results, though inferior to those obtained with the more concentrated solution, were nevertheless so satisfactory and constant, that this mixture was adopted, and used during the subsequent work.

The results arrived at on increasing the number of bells to two had been so gratifying, that it was thought advisible to employ three, and to combine them in an arrangement which would permit them to be easily handled, the form finally adopted being that figured in the text. The temperatures given are those read from the thermometers in the three bells, a reading being taken from each at the beginning, middle and end of every experiment, and the average result stated. After the apparatus and bath had arrived at temperature desired, the stages were raised by one motion of crank, to height proper to expose a uniform surface of phosphorus, eight liters of air aspirated, and then one, two or more liters, drawn over, and the ozonized air titrated by solution of potassium iodide. All the figures obtained are given, although they are not so uniformly progressive as was hoped for, a result due perhaps in part to the difficulty of completely changing the atmosphere in three six-liter bells by a slow current of air, without an expenditure of an amount of time which other duties would not permit.

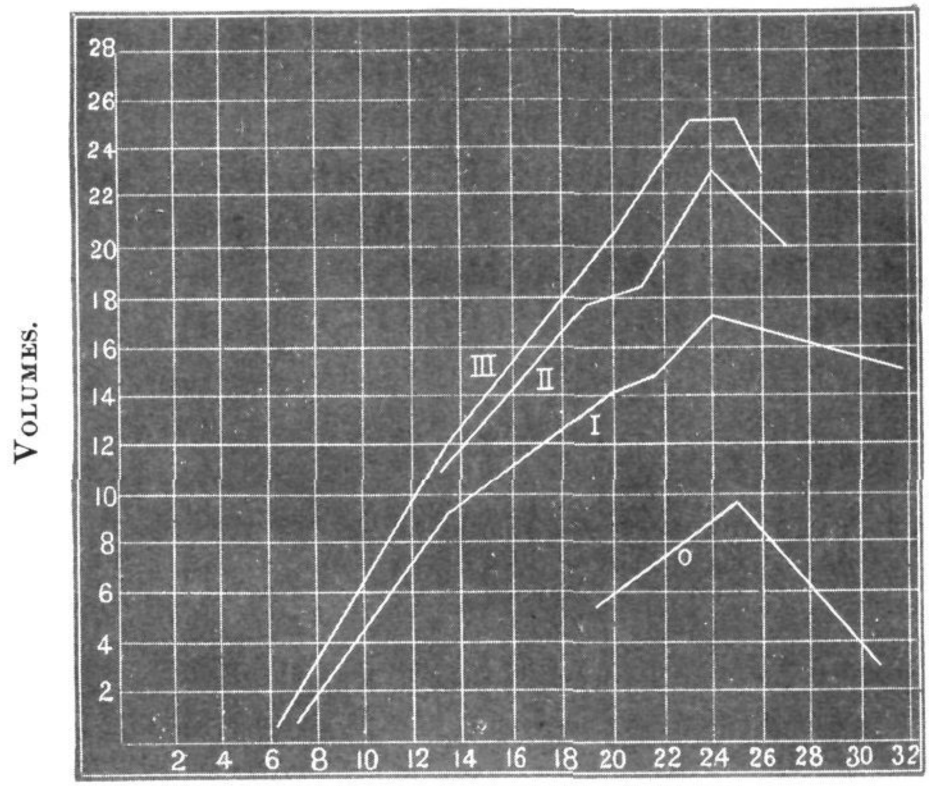
Temperature.	Amount of Air.	Time.	Hyposulphite per Liter.
6°.3	3 liters.	15 minutes.	0.033 cc.
6°.3	4 "	20 "	0.033 "
10°.63	2 "	15 "	0.08 "
11°.1	2 "	13 "	0.10 "
11°.21	2 "	15 "	0.20 "
12°.22	2 "	15 "	0.225 "
12°.22	2 "	13 "	0.215 "
13°.33	2 "	20 "	0.68 "
13°.33	2 "	10 "	0.60 "
14°.99	2 "	15 "	0.40 "
14°.99	2 "	15 "	0.40 "

Temperature.	Amount of Air.	Time.	Hyposulphite per Liter.
15°.88	2 liters.	15 minutes.	0.42 cc.
16°.11	1 "	10 "	0.66 "
16°.11	1 "	10 "	0.68 "
17°	2 "	15 "	0.84 "
17°.5	3 "	18 "	0.61 "
20°	2 "	18 "	1.15 "
22°.78	2 "	15 "	1.52 "
22°.78	2 "	10 "	1.32 "
25°	2 "	15 "	1.42 "
26°.11	2 "	13 "	1.30 "
26°.11	2 "	10 "	1.20 "

VI.—OZONE FROM PHOSPHORUS IN DILUTE BICHROMATE (THREE BELLS).

T	Mgrm. per Liter air.	Wpc.	cc per Liter.	Volume Ratio.	Wpc. of O.	Vpc. of O.
6°.3	0.0624	0.0048	0.029	0.6	0.0208	0.014
10°.63	0.1512	0.0116	0.071	1.4	0.0501	0.034
11°.1	0.1890	0.0146	0.089	1.8	0.0631	0.043
11°.21	0.378	0.0292	0.177	3.5	0.1262	0.085
12°.22	0.416	0.0321	0.195	3.9	0.1391	0.093
13°.33	1.285	0.0993	0.602	12.0	0.4290	0.289
13°.33	1.134	0.0876	0.531	10.6	0.3784	0.255
14°.99	0.756	0.0587	0.354	7.1	0.2536	0.170
15°.88	0.794	0.0618	0.372	7.4	0.2678	0.179
16°.11	1.285	0.0993	0.602	12.0	0.4290	0.289
17°	1.588	0.1229	0.745	14.9	0.5309	0.355
17°.5	1.153	0.0889	0.540	10.8	0.3840	0.259
20°	2.170	0.1677	1.018	20.4	0.7245	0.486
22°.78	2.684	0.2075	1.257	25.1	0.8964	0.603
25°	2.684	0.2075	1.257	25.1	0.8964	0.603
26°.11	2.457	0.1902	1.151	23.0	0.8212	0.552
26°.11	2.268	0.1778	1.062	21.2	0.7690	0.510

It will be seen from the above, and from the accompanying diagram which graphically represents the relations between the tem-



TEMPERATURES.

peratures and the corresponding volumes, that in each case the maximum volume was obtained at about 24° C. While there is a general similarity in the curves, yet it will be noted that III does not fall relatively so far beyond *II*, as *II* beyond *I*, and there would accordingly be little advantage in increasing the number of bells beyond three. Below 6° C. no ozone appears to be generated, and probably little or none beyond 38°, phosphoric oxide being formed in increasing quantities as the temperature approaches 44°, the melting-point of phosphorus, and the danger of inflammation correspondingly increasing. On substituting certain of the values determined for curve I, in the general formula, it was found that they satisfied the equation for the oblique hyperbola of the primary order. This curious coincidence is noted, although we are not able to attach to it a meaning of scientific import. But the practical value of these curves has been constantly tested in the course of protracted experiments, and it has been possible to determine in each case to what extent the substance under examination has been subjected to the action of ozone. And while there is little over 2½ mgrms. of ozone in the liter of air drawn 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