

the different runs, but during individual runs it never varied more than 1°, even when the ozonizer ran continuously for several hours.

It will be seen from the table that the concentration of ozone increases slowly with the rate at which the gas passes through the apparatus. This continues until a maximum of about 15% is reached at a rate of about 5 liters per hour. Then the concentration gradually decreases with increasing rate. The total amount of ozone produced in an hour, however, increases steadily with the rate, reaching 4.68 g. when the rate is 100 liters per hour.

Summary

This paper contains a description of a flexible, relatively inexpensive ozonizer for laboratory work, capable of producing concentrations of ozone in ozonized oxygen of about 15%, or of making over 4 g. of ozone per hour, depending upon the rate at which the gas is passed through the apparatus.

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THE ACTION OF CERTAIN REAGENTS UPON OZONE

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Preliminary to some work upon organic ozonides, it was desired to know the effect of various reagents upon the decomposition of ozone when ozonized oxygen was passed through them at various rates. Many qualitative statements dealing with this subject are to be found in the literature, but the quantitative data are comparatively rare. This paper reports the results of a series of investigations undertaken to obtain such quantitative data.

Apparatus and Method of Attack

The ozonizer used in these experiments is described in the preceding paper.¹ The oxygen was obtained from a cylinder, and was passed through sulfuric acid and phosphorus pentoxide before it was ozonized. The apparatus for containing the liquid reagents consisted of three types. (a) Ordinary gas washing bottles each with a small bulb blown on the end of the inlet tube and this bulb perforated several times. These were of two sizes, 500 cc. and 125 cc. (b) The same as (a), but with an "apron" over the small perforated bulb, and with a capacity of 125 cc. (c) Emmerling towers filled with glass pearls. These towers were made of soft glass and were 4 × 45 cm. in size.

Solid reagents were placed in U-tubes, each arm of the tube approximately 3 × 30 cm. and terminating in a stopcock. All pieces of apparatus

¹ Smith, THIS JOURNAL, 47, 1844 (1925).

were equipped with the "outside seals" (described in the preceding paper), and connections between the different parts of the apparatus were made by means of U-tubes made of two "inside seals" joined together.

The method of sampling, analyzing, etc., and the general set-up of the whole apparatus have been previously described.¹

The general procedure followed in all these experiments is as follows. The containers holding the reagents were connected, and the exit tube from the last piece of apparatus attached to the ozone destroyer through the three-way stopcock H (see Fig. 2 of the preceding paper). The ozonized oxygen was allowed to pass through the reagents for some time, and then the stopcock H was turned and a sample of 1416 cc. passed through the analysis bottle and the gas meter, the time being noted by means of a stopwatch. Two or more samples were analyzed in this way, after which stopcock G was turned and a sample direct from the ozonizer analyzed. The analyses of these samples direct from the ozonizer are designated as "crude" in the tables given later. The length of time for the preliminary sweeping out of the apparatus varied in the different runs, but was never less than 30 minutes.

Results

Blanks.—Since it is known that ozone decomposes on standing, some preliminary runs were made with empty apparatus to determine the difference in concentration of the ozone as it issues from the ozonizer and after passing through a train of apparatus containing no reagents. The results show that this difference in concentration is about 0.4%, which is about as close a check as can be expected from two successive samples taken anywhere in the line. A typical experiment is given in Table I.

The destruction of ozone by passing it through water, sulfuric acid (dil. and concd.), water followed by concd. sulfuric acid, and acid potassium permanganate was so slow as to be negligible; a typical experiment showing the effects of each of these reagents is given in Table I.

TABLE I
EFFECT OF WATER, SULFURIC ACID (DIL. AND CONCD.), WATER FOLLOWED BY SULFURIC ACID AND ACID POTASSIUM PERMANGANATE UPON OZONE

Preliminary sweeping Hours	Rate Liters per hour	Wt. of % O ₃ end of train	Wt. of % O ₃ crude	Apparatus
1	6.6	12.72	13.07	Empty train, 3 bubblers in series
...	7.3	13.7	13.95	2 bubblers, each cont. 100 cc. of H ₂ O
3	5.0	14.0	14.16	2 bubblers, each cont. 100 cc. of 5% H ₂ SO ₄
3	5.0	14.25	14.6	2 bubblers, each cont. 75 cc. of concd. H ₂ SO ₄
1	9.4	11.5	12.0	2 bubblers, each cont. 100 cc. of H ₂ O, followed by 2 bubblers each cont. 75 cc. of concd. H ₂ SO ₄
3	4.4	14.0	14.16	2 bubblers, each cont. 25 cc. of 0.5996 N KMnO ₄ and 75 cc. of 5% H ₂ SO ₄

The titer of the potassium permanganate was not affected by passing the ozonized oxygen through it.

Dilute Sodium Hydroxide.—Harries² has shown that upon bubbling ozonized oxygen through 5% sodium hydroxide solution the concentration of the ozone is reduced considerably, depending upon the rate at which the gas is passed through. Although Harries believed that most of the decrease in concentration was due to the destruction of "oxozone" by the alkali, he stated that ozone, too, was decomposed at the same time. In many of his experiments he reduced the concentration of ozone by passing it through 5% sodium hydroxide and then through concd. sulfuric acid, in this way destroying about half the ozone (from 14% to 6 or 7%).

Using Emmerling towers as containers for the alkali, practically all of the ozone is destroyed, even when the rate at which the gas passes is as high as 53 liters per hour. Table II shows the results obtained in this way.

TABLE II
EFFECT OF SODIUM HYDROXIDE UPON OZONE

Preliminary sweeping Hours	Rate Liters per hour	Wt. % of O ₃ , end of train	Wt. % of O ₃ , crude	Apparatus
3	3.4	None	12.3	2 Emmerling towers, filled with glass pearls, each cont. 150 cc. of 5% NaOH
4	10.3	trace	11.8	
4	20.0	0.15	9.5	
...	53.0	0.5	5.7	

Phosphorus Pentoxide.—Harries, in his papers, has mentioned several times that moist ozone cannot be dried with phosphorus pentoxide without considerable decomposition³ and in one case^{3b} he reduced the concentration of ozone from 14 to 1% by passing it successively through 5% sodium hydroxide, sulfuric acid and phosphorus pentoxide.

The results given in Table III show that commercial phosphorus pentoxide is very effective in decomposing ozone. The phosphorus pentoxide used was a sample of Merck's, marked "perfectly white."

TABLE III
EFFECT OF COMMERCIAL PHOSPHORUS PENTOXIDE UPON OZONE

Preliminary sweeping Hours	Rate Liters per hour	Wt. % of O ₃ , end of train	Wt. % of O ₃ , crude	Apparatus
3.5	2.1	0.90	14.7	2 U-tubes filled with P ₂ O ₅ and glass wool
3	5.0	3.1	15.7	
1	9.2	3.8	13.0	
...	17.7	1.67	10.8	
2	28.2	1.48	8.65	

From Table III it will be seen that ozone is rather quickly decomposed in contact with commercial phosphorus pentoxide. The rate at which the

² Harries, *Z. Elektrochem.*, **13**, 129 (1912).

³ Harries, (a) *Ber.*, **42**, 3305 (1909); (b) **43**, 32 (1915).

gas passes through the U-tubes determines how much of the ozone will be destroyed, but with a solid reagent it is difficult to avoid the formation of channels, so that the results when plotted show considerable deviation from a smooth curve.

The same phosphorus pentoxide was used for many more runs than those given in Table III. These runs, together with the preliminary sweeping out of the tubes, represent a considerable amount of ozone, and yet the phosphorus pentoxide was as efficient during the last run as during the first. It is thus improbable that the effect of the phosphorus pentoxide was due to oxidation of lower oxides by the ozone, nor is it likely that a peroxide of phosphorus is formed, for Schmidlin and Massini⁴ attempted to make perphosphoric acid by passing ozone over phosphorus pentoxide, with no success.

In order to eliminate any lower oxides of phosphorus, some phosphorus pentoxide was resublimed in a current of oxygen, and the effect of this resublimed material upon ozone was determined. The results are given in Table IV, and they show that on resublimation in a current of oxygen, phosphorus pentoxide loses most of its ability to destroy ozone. Hence, whatever causes the decomposition of the ozone, it is not phosphorus pentoxide but something present in the phosphorus pentoxide which is removed by sublimation in a current of oxygen. The investigation of this effect will be continued and the results reported in a later paper.

TABLE IV

EFFECT OF RESUBLIMED PHOSPHORUS PENTOXIDE UPON OZONE				
Preliminary sweeping Hours	Rate Liters per hour	Wt. % of O ₃ end of train	Wt. % of O ₃ crude	Apparatus
3	0.8	11.2	13.3	2 U-tubes filled with resublimed P ₂ O and glass wool
1	7.1	9.7	10.6	
1	18.0	9.46	9.57	

Summary

This paper describes the results obtained by determining the effect of various reagents upon the decomposition of ozone, when the gas is passed at various rates through apparatus containing these reagents. The reagents investigated fall into two classes with respect to their effect upon ozone: (1) those having a very small effect; to this group belong water, concd. sulfuric acid, 5% sulfuric acid, water followed by concd. sulfuric acid, acidified potassium permanganate solution and phosphorus pentoxide which has been resublimed in a current of oxygen; (2) those having a great effect, and destroying much or all of the ozone; to this group belong 5% sodium hydroxide solution and ordinary phosphorus pentoxide.

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⁴ Schmidlin and Massini, *Ber.*, **43**, 1162 (1910).