

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY]

PREPARATION OF PURE OZONE AND DETERMINATION OF ITS MOLECULAR WEIGHT

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In connection with its study of the arc process of nitrogen fixation, the Fixed Nitrogen Research Laboratory has initiated a series of general investigations on the nature of the chemical reactions in gases which take place in the path of an electric discharge. This work has led, among other things, to a study of the preparation and properties of ozone.

In the present paper we shall describe the preparation of practically pure ozone and a determination of its molecular formula from a direct measurement of the density of the gas. These are matters of some interest, since pure ozone apparently has not hitherto been investigated, and since there has been much doubt as to whether *concentrated* ozone has the formula O_3 , or is a mixture of such polymers as O_3 , O_4 and O_6 .¹ Our results show that even completely pure ozone can be prepared which has the formula O_3 , that of dilute ozone. We believe that the results of previous investigators, indicating higher molecular weights, are to be accounted for by the fact that the potassium iodide method of analyzing for ozone fails at high concentrations.¹ Our method of attack, by working with pure ozone, eliminates the necessity for analysis and thus leads to a solution of this important problem.² Owing to the considerable experimental difficulty, the method is described in some detail for the benefit of others working in this field.

Apparatus and Method

As the boiling point of oxygen is -182.7° and that of ozone is about 63° higher,³ the 2 substances should be separable by fractional distillation⁴ provided the ozone does not decompose too rapidly. This method of separation has actually proved feasible, primarily because the system behaves as though the 2 liquids were immiscible, and because the ozone decomposes only slowly under favorable conditions. Thus, a single fractionation removes all the oxygen from the ozone except a small amount which may be actually dissolved in the liquid. A considerable amount

¹ For a summary and critical review of the work indicating higher polymers than O_3 , and a discussion of methods of analyzing ozone, see E. H. Riesenfeld and F. Bencker, *Z. anorg. Chem.*, **98**, 167 (1916).

² It should be noted that though our work shows that pure ozone will not combine to form higher polymers, it does not preclude the possibility of forming higher polymers in some other way. If they are formed, however, in the ordinary corona discharge, our work shows that they must either be very unstable or be formed in very small quantities.

³ M. L. Troost, *Compt. rend.*, **126**, 1751 (1896).

⁴ Ladenberg, *Ber.*, **31**, 2508 (1898).

of pure ozone has been prepared according to this scheme, and the work demonstrates that ozone of high purity can be isolated from oxygen or any substances other than ozone which may be produced in the electric discharge through oxygen, and that if the substance be properly handled some of the properties of pure ozone can be studied in a very direct manner.

Apparatus and Procedure.—The apparatus used for the production of the gaseous mixture and for its condensation, and fractional distillation is represented in detail in Fig. 1.

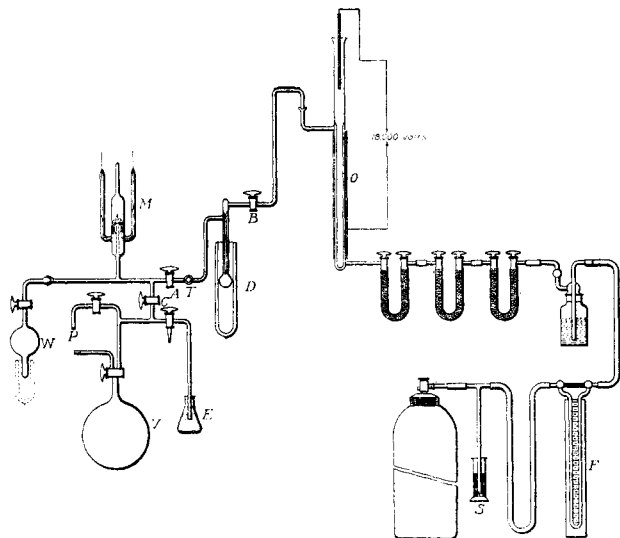


Fig. 1.

The ozonizer, O, was of the familiar type consisting of 2 concentric Pyrex glass tubes with tin-foil around the outer one and a conducting solution in the inner one. It was joined to the remainder of the apparatus, which was constructed of soft glass, by means of a rubber tube at the lower end where the pure oxygen enters, and a special paraffin joint at the upper end where the ozone-oxygen leaves. Ordinary commercial electrolytic oxygen, purified and dried by passing through conc. sulfuric acid and phosphorus pentoxide, was used in the preparation of the ozone-oxygen mixture. The electrical discharge in the ozonizer was produced by an alternating potential difference of 18,000 volts with a frequency of 60 cycles per second. When the gas flowed through the system at a rate of 0.2 liters per minute as indicated by the capillary tube flowmeter, F, the concentration of the ozone produced in the gas was from 3 to 4% by volume. These conditions were kept practically constant throughout all the work.

The condenser, D, was constructed in such a way that the gases coming from the ozonizer entered it through the inner tube, and emerged through the outer tube. A flask containing liquid air surrounded the spherical bulb of the condenser. This made it possible to control the temperature of the condenser by raising or lowering the liquid air level so that complete or partial condensation of the gases from the ozonizer could be effected. The progress and nature of the condensation could be observed through the liquid-air flask, which was left unsilvered for this purpose. The excess of gas during a condensation or an evaporation always contained some ozone and was passed through a solution of potassium iodide at E, before entering the room.

T was a horizontal tube about 30 cm. long which served as a means for estimating the concentration of the ozone in the gas. The intense blue color of the ozone makes it possible to detect a relatively small variation in the concentration of the gas by this method.

Gas pressures were measured with the glass pressure gage, M, which is a modification of the gage used by Daniels and Bright⁵ which will be described in a later report from this Laboratory.

It was often necessary to evacuate the system when it contained considerable ozone. This could not be done with a metal pump on account of corrosion of the pump, and explosion of the gas which was found to occur as soon as the ozone reached the pump. A glass water aspirator at P served to reduce the pressure to about 30 mm. and the large evacuated flask, V, could produce a further decrease in the pressure when it was opened to the system. Then this vessel could be washed with air and again evacuated by the aspirator and finally by an oil pump, so that any desired number of expansions could be carried out after the aspirator had produced its lowest pressure. When no ozone was present in the gas the whole system was exhausted directly by means of a 3-stage oil pump.

The bulb, W, after being filled to a measured pressure with ozone, could be removed at the ground joint and weighed. All ground joints were lubricated with a very small amount of vaseline.

Method of Concentrating the Ozone.—After the gas flow and electrical discharge were adjusted, the gas was allowed to stream through the system for a few moments. Then the flask containing liquid air was placed around the condenser, D, in such a manner as to immerse the bulb completely in the liquid air. This caused all of the gas to condense, and the flow at E to stop, and at this instant the stopcock A was closed. The mercury level in the tube projecting into a beaker of mercury, S, indicated the pressure of the gas in the system. The temperature of the condenser was controlled by raising or lowering the liquid air in such a way as to maintain a constant gas flow of 0.2 liters per minute.

After the bulb was about $\frac{1}{2}$ to $\frac{3}{4}$ full of the blue liquid mixture of oxygen and ozone, the liquid air level was lowered so that only a partial condensation of the gases resulted, the stopcock A was opened and the excess gases allowed to flow out at E. This fractional condensation removed most of the ozone from the gas, but condensed very little oxygen.

When sufficient ozone had been collected, the stopcock at B was closed and the distillation begun. The distillation proceeded as though oxygen and ozone were immiscible. Over a long period of time, oxygen with about 0.8% ozone came off steadily without much change in the temperature of the liquid.

It should be mentioned that from this datum a rough calculation of the vapor pressure of ozone at approximately -182° can be made. This was done several times during preliminary work, the most reliable result giving a vapor pressure of 6 mm. of mercury.

As the distillation was continued, a point was finally reached when only a small portion of the original liquid remained, all boiling ceased and the temperature began to rise. When the temperature reached about -119° , the boiling point of ozone, a very blue gas began to come off. At this point, the greatest precautions were necessary to prevent superheating and explosion. It was a portion of the dark blue liquid which remained in the condenser and which boiled at about -119° , that was used in our experiments.

A few minutes after the first gas from this fraction with high boiling point started to come off, the gas passing through the observation tube developed a blue color which became deeper as time went on. At this instant, in order to avoid explosion, it was

⁵ Daniels and Bright, *THIS JOURNAL*, 42, 1131 (1920).

necessary to close Stopcock A, and immediately immerse the condenser bulb in liquid air. This condensed all the vaporized ozone, as shown by the disappearance of the blue color in the observation tubes.

Method of Filling Molecular-weight Bulb.—The system containing the molecular-weight bulb was now evacuated by means of the aspirator and finally by a 3-stage oil pump to a pressure below 1 mm. The system was then shut off from the pump and opened to the condenser. By carefully lowering the liquid air from around the condenser bulb, the liquid ozone was distilled over into the molecular-weight bulb at a rate which was not allowed to exceed about 20 mm. pressure increase per minute, since more rapid distillation was liable to lead to explosion. This method of procedure was finally perfected only after considerable experience and several damaging explosions.

When the pressure in the bulb W had reached the desired value, Stopcock A was closed and Stopcock B opened, and the remainder of the liquid ozone in the condenser allowed to evaporate slowly and escape back through the ozonizer into the atmosphere, the rubber tube connection to the ozonizer being removed for this purpose. The liquid thus discarded would contain any substances of higher boiling point than -119° .

At the moment when Stopcock A was closed, the lower end of the molecular-weight bulb W was immersed in liquid air, in order to condense ozone from the mixture, and after a definite time interval the uncondensed gas over the liquid, which contained practically all of the oxygen, was pumped off by means of the aspirator and the large evacuated bulb to a pressure of about 2 mm. The system was now closed at Stopcock C and the blue liquid again slowly evaporated into the bulb by lowering the liquid air. The progress of the process was accurately watched by reading the pressure of the gas.

After this evaporation the molecular-weight bulb was thermostated by immersing it in a large volume of water at room temperature, and the gradual rise of pressure of the decomposing gas measured regularly every 2 minutes for a period of 30 minutes. This observation on the rate of decomposition of the gas made it possible to determine what the pressure of ozone would have been if no decomposition had taken place. The mass of gas in the bulb was then determined by weighing it after all necessary precautions of cleaning and drying had been observed. The pressure, volume, temperature and mass of the gas were thus determined so that the molecular weight was calculable from the formula, $M = mRT/PV$.

After this determination the bulb was again placed upon the apparatus at the ground joint, and its tip immersed in liquid air. When condensation had thus proceeded for a considerable time and a large part of the ozone had been condensed, the system up to the stopcock of the bulb W was evacuated and the uncondensed portion of the gas pumped off. A molecular-weight determination similar to the previous one was then made with this condensed portion.

Example of Data and Method of Calculation of Results.—As an example of the data obtained and method of calculation employed, the results for our last experiment, No. 13, Table III, are given in considerable detail in Tables I and II.

Table I gives values of the time and corresponding gas pressures during the transfer of gas from the condenser bulb to the molecular weight bulb, during the condensation of the gas in the lower end of the molecular weight bulb, during the removal of residual gas over the condensate, and during the re-evaporation of the liquid ozone and its subsequent decomposition. Readings were actually taken throughout this whole series of operations at 2-minute intervals.

It will be noted that the decomposition proceeded very regularly and slowly. The small variations from a smooth pressure-time curve are largely due to error in reading the mercury manometer and slight irregularity in the action of the electrical contact of the pressure gage.

TABLE I
PART 1 OF EXPT. 13

Time Min.	Pressure Mm.		Time Min.	Pressure Mm.	
		Transfer of gas to mol.-wt. bulb			Evaporation of ozone together with decomposition
0	28	Closed B and C, lowered liquid air at D	84	2	Lowered liquid air at W
..	..		86	7	
10	47		88	18	
20	127		90	51	
30	285		92	92	
40	475		94	155	
50	664		96	218	
52	701	Closed A	98	256	
		Condensation of gas in mol.-wt. bulb	100	270	
54	...	Opened B, raised liquid air at D and W	102	276	Evaporation complete
					Decomposition of ozone
56	595		104	278.1	
58	579		106	278.1	
60	555		108	278.3	
62	540		110	278.9	
80	437		112	280.1	
..	...		114	280.1	Temp. 28.2°
		Removal of residual gas	116	280.5	
80	437	Applied aspirator	118	281.3	Wt. of bulb and gas 6.7624 g.
82 ¹ / ₂	25	Applied evacuated bulb			Wt. of bulb <u>6.5998</u>
83	2		120	282.7	
84	2	Closed evacuated bulb	122	283.1	
			124	284.0	Wt. of gas 0.1626
			126	284.3	
			128	284.7	Extrapolated pressure 274.4 mm.
			130	285.9	
			132	286.1	
			134	286.1	Vol. of bulb 235.67 cc.
			136	286.7	
			138	287.3	

Table II gives data for the second part of the experiment.

In order to determine the pressure of the ozone which must be used in the calculations of its molecular weight from the observed values of time and pressure, a pressure-time curve of the evaporation and decomposition was plotted for each determination. At a point far enough along this curve so that it was certain that all the ozone had evaporated and that temperature equilibrium had been reached, as indicated by preliminary experiments performed with a thermocouple, a tangent to the curve was

constructed. The slope of this tangent gave the rate of decomposition used in the evaluation of the desired ozone pressure. It is obvious that some gas decomposed during the time required for the evaporation and it is this which must be determined by some method of extrapolation. It was found by experiment that ozone in the liquid state did not decompose to any measurable extent. In order to correct for the somewhat uncertain decomposition during evaporation, the tangent was extended backwards and the correct ozone pressure was taken as given by a point

TABLE II
PART 2 OF EXPT. 13

Time Pressure		Time Pressure			
Min.	Mm.	Min.	Mm.		
Second condensation		Decomposition of ozone			
0	...	Reconnected mol. wt. bulb	48	208.3	
		and applied liquid air	50	208.9	
30	56		52	209.4	
		Removal of residual gas	54	209.8	
30	56	Applied aspirator	56	210.2	
32	25	Applied evacuated bulb	58	210.8	Temp. 27.4°
32 ¹ / ₂	2		60	211.2	
34	2	Closed evacuated bulb	62	211.6	Wt. of bulb and gas 6.7232 g.
Evaporation of ozone					
34	2	Lowered liquid air at W	64	212.2	Wt. of bulb 6.5998
36	4		66	212.5	
38	6		68	213.0	Wt. of gas 0.1234
40	32		70	213.4	
42	122		72	213.9	Extrapolated
44	187	Evaporation complete	74	214.1	pressure 206.4 mm.
46	206		76	214.3	
			78	214.9	Vol. of bulb 235.67
			80	215.47	
			82	215.73	

on the tangent corresponding to the time at which the pressure during evaporation had its average value over the whole period of pressure change due to the evaporation. It is evident that there is a certain amount of arbitrariness in this method of extrapolation which assumes that the rate of decomposition is always proportional to the pressure of the ozone which has evaporated and that the proportionality factor is determined by the slope of the tangent to the curve at the particular point used. Nevertheless, the correction to be made is small (less than 2% in Expt. 13) and a slight error in the method of extrapolation has no appreciable effect.

Results

Following this method of procedure, 17 experiments for the determination of the molecular weight of ozone were made. However, only the last 14 are included in this report, since the first 3 were concerned with the

perfection of the operations involved in the experiment. Table III gives a summary of the results. P_1 and P_2 are the pressures of ozone in the first and second parts of each experiment as calculated from the data on the decomposition and evaporation of the gas.

The mean value of the molecular weight as determined from the first condensations is 47.3, with a maximum of 48.7 and a minimum of 46.5. The mean value of the molecular weight as determined from the second condensations is 47.3, maximum 48.1 and minimum 46.5, showing a slightly smaller variation from the mean value than in the previous case. The fact that these values are slightly lower than 48 is presumably due to the difficulty of removing all traces of oxygen. The identity of the values obtained in the first and second condensations indicates that we really obtained a practically pure substance.

TABLE III
MOLECULAR WEIGHT OF OZONE

Expt.	Mol. wt. from first condensation	Ozone pressure		Mol. wt. from second condensation	Ozone pressure
		Mm. Hg.	P_1		
1	47.4	426
2	47.1	332.0	46.5	46.5	146.5
3	46.5	135.5	46.7	46.7	82.4
4	46.7	161.4	47.8	47.8	87.75
5	47.7	268.7	47.5	47.5	166.5
6	48.7	174.7	48.1	48.1	96.7
7	47.7	131.2	47.6	47.6	90.5
8	47.2	173.25	46.9	46.9	118.2
9	47.9	203.8	47.7	47.7	141.8
10	46.6	232.8	47.3	47.3	158.1
11	46.9	282.75	46.6	46.6	179.4
12	47.4	297.4	47.3	47.3	211.9
13	47.2	274.4	47.5	47.5	206.4
14	47.3	47.3	227.8

Summary

A method for the preparation of ozone of high purity has been developed.

A determination of the molecular weight of the gas so obtained has been made by a method *independent of any chemical analysis*.

The mean value of this molecular weight is 47.3.

We are greatly indebted to Dr. Richard C. Tolman, former Director of the Laboratory, for the help which he has given us in this work.

WASHINGTON, D. C.