THE CONVERSION OF LIQUID OXYGEN INTO OZONE.

By

Lanning Rankin.
A. B. Kansas University, 1924.

Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of MASTER OF ARTS.

Approved by: J. P. Cady
Chairman of Department.

July, 1925.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION AND HISTORY</td>
<td>1</td>
</tr>
<tr>
<td>PROBLEM</td>
<td>2</td>
</tr>
<tr>
<td>APPARATUS</td>
<td>3</td>
</tr>
<tr>
<td>EXPERIMENTAL WORK</td>
<td>8</td>
</tr>
<tr>
<td>CONCLUSION</td>
<td>12</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>13</td>
</tr>
</tbody>
</table>
The author of this thesis is indebted to Dr. H. P. Cady for his ever helpful suggestions and continuous aid in the course of the experimentation. Also, he wishes to thank Dr. H. M. Elsey for his skillful work in the preparation of the apparatus.
INTRODUCTION AND HISTORY.

Ozone, an allotropic form of oxygen, was first observed and recorded by Van Marum in 1785. He noticed the peculiar smell that accompanied the operation of a static machine and found that oxygen gas, through which a stream of sparks had been passed, would tarnish mercury.

C. F. Schonbein¹ in 1840 showed that this substance was present in the oxygen liberated during electrolysis of acidulated water and gave it the name "ozone" from the Greek, meaning "to smell".

In 1899, H. Moissan² obtained it by the action of fluorine on water at 0°C. A. v. Baeyer and V. Villegier³ obtained it in 1901 by treating BaO₂ or certain other peroxides with concentrated H₂SO₄. Ozone is produced by the action of cathode rays and ultra-violet rays on oxygen. E. Briner and E. Durand⁴, in 1907, submitted oxygen at the temperature of boiling oxygen to the silent electrical discharge and obtained a ninety per cent. yield.

The constitution of ozone was determined by J. F. Soret⁵ in 1866 and shown to be O₃. More recently (1901), H. Ladenburg⁶ has obtained the molecular weight, 47.78, which corresponds with the above molecular formula.

Ozone is a light blue gas which condenses to an indigo blue liquid at -119°C. At this temperature it is exceedingly explosive. At still lower temperatures, it is more
stable. If heated to 300° C or brought into contact with platinum black or some metallic oxides, gaseous ozone decomposes instantly into oxygen. It is a most powerful oxidizing agent attacking most metals, rubber, and any organic matter. It liberates iodine quantitatively from solutions of potassium iodide, the course of the reaction depending on whether the solution is neutral or acid. If the latter, hydrogen peroxide is produced as well as oxygen and iodine.

Ozone is used mostly for sterilizing water, it having no other practical use at present. Various types of ozonizers are now on the market, all of which use the silent electrical discharge for the production of the ozone.

The work which has been done on ozone is rather limited in quantity, due perhaps to the nature of the substance it being unstable and having so few practical uses.

In this problem, the author was interested in seeing whether or not oxygen in the liquid state could be converted into ozone. As radium has well known ionizing effects on gases, it was thought that it might ionize liquid oxygen and thus assist in the transformation and in the course of the experiment give an index to the ionization effect of radium on liquids.

Problem.

(a) To determine whether or not liquid oxygen can be converted into its allotropic form ozone, O₃, under the ef-
effects of the silent electrical discharge, both with and without the influence of radium.

(b) Also, to determine not only by virtue of the above problem, but directly, the extent to which liquid oxygen is ionized by radium.

**Apparatus.**

In order to make the first determination, an apparatus was designed and constructed with the following points in mind:

First, it must be of such a size as to go into a Dewar bulb and thus be completely surrounded by liquid air when wished. Otherwise, it would be impossible to keep the oxygen in the interior of the vessel in the liquid state.

Second, it must be a double walled chamber so arranged that the electrodes could be placed on the exterior surface of each wall, this, in order to obtain the silent discharge.

Third, the apparatus must be shaped so that a quantity of radium can act on the liquid oxygen with the maximum intensity.

Fourth, the oxygen chamber must be designed so as to facilitate the admittance and removal of the gases with ease.

In Figure 1, page 4, the interior chamber \( B \) was filled with iron filings in lieu of an electrode and the outside of "C" was coated with tinfoil for the other electrode. The stopcocks "D" allowed the entrance and removal of the gases.
FIGURE I.
As a source of pure oxygen, an electrolysis apparatus was constructed using a twenty per cent. solution of pure NaOH as the electrolyte. Four cells of the type shown in Figure II, page 6, were used — all of them being connected in series electrically and the oxygen from all four generators being directed into one tube. The electrodes were of nickel metal, the inner electrode being riveted to a piece of iron rod and set in the bent glass tube. In order to make an electrical contact with the inner electrode, the glass tube was partly filled with mercury — the mercury making the connection between the iron rod and a wire in the other arm of the glass tube.

In order to be sure that the oxygen gas was perfectly dry, it was run first over solid potassium hydroxide and then through phosphorus pentoxide — each of the drying agents being in tall towers.

A high tension induction coil was used to obtain the silent discharge.

In order to detect any ozone formed, the gases were run through a neutral solution of potassium iodide containing a little starch solution. Ozone liberates iodine from potassium iodide quantitatively and this, of course, gives a deep blue color with the starch. The iodine may then be titrated with Na2S2O3, if desired. The tower containing the potassium iodide solution is shown in Figure III, page 7. "A" is the tube which connects the tower to ozonizing
apparatus. A pump is attached to "B" to decrease the pressure and thus draw the ozone through the potassium iodide solution. "C" is the potassium iodide starch solution and "D" shows small holes to produce small bubbles and promote absorption.

**EXPERIMENTAL WORK.**

The apparatus was then ready for a test run which consisted in running pure oxygen through the ozonizer bulb until assured that it contained only oxygen - closing the stopcocks - and applying the high tension electric current. After a short time, the gas in the ozonizer was drawn in through the potassium iodide tower and the presence of ozone was shown very plainly by the intense blue color appearing in the potassium iodide tower. Thus, the apparatus was able to produce ozone under ordinary conditions which it should do and was pronounced ready for further experimentation.

Before working with the oxygen in the liquid state, the experimenter determined whether or not oxygen in the gaseous state, at a temperature in the neighborhood of its boiling point, could be changed into ozone with the silent discharge. To determine this, the whole ozonizer was placed in a Dewar bulb containing liquid oxygen, the ozonizer filled with pure oxygen and the current applied. As the gas, oxygen, in the interior of the vessel contracted greatly, due to the intense cold, a mercury manometer was connected to the ozonizer and a run made at three different pres-
sures, namely, 735 m.m., 450 m.m., and 30 m.m. In each case ozone was obtained, the change in pressure apparently not affecting the transformation. This confirms the work of E. Briner and E. Durand in 1907.

As soon as ozone is formed in the apparatus, it liquifies as it's boiling point, -119° C, is considerably higher than that of oxygen, -183° C. In pumping it off, caution must be used for it explodes with extreme violence when it warms up to its boiling point. Thus, it must be pumped off at a somewhat lower temperature and pressure. Everything was then ready for the first determination.

The ozonizer was surrounded by new liquid air and oxygen run in until liquid oxygen had collected above the top of both electrodes, this latter precaution being necessary in order to be sure that no oxygen in the gaseous phase was acted upon by the silent discharge. After acting upon the liquid oxygen, with the silent electrical discharge for fifteen minutes, it was then pumped through the potassium iodide starch solution. The solution remained perfectly colorless indicating that no ozone was formed.

The experiment was then repeated in entirety with the radium in the center of the ozonizer and with several milligrams of radium placed around the ozonizer. In neither case was any ozone produced.

The last two experiments were then repeated, using oxygen that contained nitrogen to see whether nitrogen catalyz-
ed the reaction or not. No ozone was obtained in either of these cases. With the exception of the very first test run, (at ordinary temperature and pressure), all of the runs were repeated at least three times in order to check the results. They correlated in all cases.

In order to make a more radical test, a small bulb as shown in Figure IV, page 11, was constructed. "A" is a Dewar bulb filled with liquid air. "B" is a pair of aluminum electrodes, one millimeter apart. "C" is a glass bulb. This was filled with liquid oxygen (containing nitrogen) and the electric spark directly applied — both with and without radium. No ozone was produced in these two cases, likewise.

To determine the second problem, i.e., the ionizing effect of radium on liquid oxygen, a small electroscope, as shown in Figure V, page 11, was constructed. This consists of a small glass bulb "A", with amber bead "B" through which a copper wire, "C", passes. "D" is a piece of aluminum foil. The electroscope was of small size so as to be able to be placed in a Dewar bulb.

The electroscope was charged and placed in a transparent Dewar bulb and a quantity of radium brought near. It fell instantly. It, then, was recharged while in the Dewar bulb and completely surrounded with oxygen-rich liquid air. Now, the radium was brought very close to the Dewar bulb and no falling of the foil could be observed. All these
readings were made with a reading telescope. To be sure that the rays from the radium were penetrating the liquid oxygen, an electroscope was charged and the radium, completely surrounded by liquid oxygen, was brought near the electroscope. The electroscope normally fell one division in fifteen seconds. Upon the approach of the radium, it fell eight divisions in eighteen seconds, showing that the rays had no difficulty in penetrating the liquid oxygen.

CONCLUSION.

Liquid oxygen cannot be converted into ozone with the silent electrical discharge either with or without the influence of radium.

Radium exerts no ionizing influence upon liquid oxygen. This latter being shown not only by direct test but being indicated by the first statement.

Nitrogen apparently exerts no catalyzing influence upon the conversion of liquid oxygen into ozone.