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The formation of ozone
at the
liquid-air temperature
by the
silent electric discharge

by

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THESIS

presented to the faculty of the Graduate School of the
University of Kansas in partial fulfilment of the re-
quirements for the degree of Master of Science.

H.P. Cady
Dept. of Chem.

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F O R E W O R D

This thesis embodies the results of an original investigation on ozone. The subject is so vast embracing the most perplexing problems in the domains of chemistry and modern physics that a few months' work could do hardly more than touch just the remotest corner of the whole theme; consequently in the following pages the writer has recorded the results of his own observations and the conclusions based thereon.

The short acquaintance with the subject has not enabled me to comprehend it in its entirety and much less does it authorise me to pronounce judgement upon the numerous questions connected with the nature, constitution and reactions of the same. Considering the fact that such divergent and conflicting views are held on these points I will be satisfied if my labours will help to clear the slightest obscurity.

The mechanism of the ozone action, its nature and constitution are questions which are far from being settled and will require the labors of some more generations of scientists before they are solved. The literature on the subject, voluminous as it is, contains a very small amount of purely scientific information scattered amongst a vast heap of commercial advertisements. There are for instance one hundred and twenty five American patents* alone and some one hundred and forty books and articles (one fifth of those actually in exis-

tence) dealing with the problem. I have not found it possible to go through all of them but I have tried to consult all the available information relating to my topic, namely the formation of ozone at the liquid-air temperature and the catalytic influence of nitrogen on the action. References to sources of such information have been made on occasions.

My thanks are due to Prof H.P. Cady for his assistance in the prosecution of the work. I am also obliged to Miss for her help in going through certain foreign publications in the original.

April 30, 1925.

Surain Singh

Chapter I

Review of the previous work

The history of ozone begins from 1785 when the Dutch philosopher Van Marum observed its smell in the air round his electrostatic machine. In 1801 Cruikshank drew attention to the fact that the oxygen gas produced by the electrolysis of dilute acids had an identical smell.

Schonbein in 1840 advanced the view that the smell of electrolytic oxygen and that of the air subjected to the action of electric spark was due to the presence of a new gas whom he gave the name ozone. He further showed that the same gas was produced in the autoxidation of phosphorus and certain other other substances. For every molecule of oxygen thus produced ^{or} rather consumed an equivalent amount was transformed to a more active state. He carried on an extended series of experimental researches to establish his hypothesis of positively and negatively charged oxygen atoms which he termed ozone and antozone respectively.*

The ozone and antozone hypothesis was at first advanced by C. Brodie in 1850 was further enlarged upon by Van't Hoff[#] in 1895. He concluded by his researches on the autoxidation of phosphorus that a definite equilibrium exists between the molecules and the charged atoms of gaseous oxygen.

Prof Nernst*working on the electromotive force of oxygen and ozone cells came to the conclusion that the concentration of atomic oxygen, assuming it to be uncharged, would be of the order of ten raised to the power minus five hence undetectable by chemical tests. This as we see amounts to an indirect confirmation of Van't Hoff's views to some extent. The fact remains then that active oxygen is only temporarily produced in some chemical reactions. This view is supported by the study of reactions like the decomposition of peroxides, autoxidation of metals and of phosphorus, the production of ozone by the action of fluorine on water and so on. The activity of chlorine and some other elements in the nascent state and the evidence regarding the existence of hydrogen in the atomic state give further support to the said view.

There were several other hypotheses made at this time regarding the composition of the substance. Williamson suggested that it might be hydrogen peroxide while Baumert said that it might be an oxidised form of hydrogen peroxide. The problem was elucidated by Becquerel and Fremy who by the measurements of changes of volume when ozonised oxygen was absorbed by turpentine came to the conclusion that the substance was an allotropic modification of oxygen.

The above conclusion was confirmed by the work of Andrew, Soret and Tait in 1876. They submitted oxygen gas to the action of spark discharge and absorbed the ozone thus formed in turpentine. The change of volume was measured with a sulphuric acid manometer. From these observations Soret came to the conclusion that the molecule of ozone consisted of

three atoms of oxygen.

Goldenstein working with oxygen gas at the temperature of liquid air showed that a hundred percent transformation into ozone could be effected that way. He also arrived at a very important conclusion regarding the vapour pressure of the substance which he gave equal to one tenth of a millimeter. This result has not been varified by any other investigator and my own experience does not confirmed (that result) it.

Prof Shenstone has experimented with perfectly dry oxygen. His results indicate the catalytic effect of nitrogen on ozonisation and exhibit a close similarity between ozone and higher oxides of nitrogen, atleast so far as their unsta- bility is concerned. He says that the presence of at least 7% nitrogen is necessary for catalytic effect.

The recent investigations of Prof Warburg and Kabak- jian deserve a special mention. The former has made exhaustive

Page 1

* Henry Roscoe's treatise on chem V:I

E.K. Rideal "Ozone"

Page 2

*E.K. Rideal "Ozone"

@The whole of oxygen was gradually converted into ozone

researches on the efficiency of brush discharge, on the laboratory scale. He holds the view that negative discharge is more effective than the positive one. Vosmaer and others hold the opposite opinion. He has observed that the yield of ozone is proportional to the pressure which I think must be true within very narrow limits. Working at the liquid-air temperature I found that for ozonisation of pure oxygen a vacuum of about 72 cms is necessary. Warburg worked between the temperatures of -71 and 90 degrees centigrades. I also worked with commercial oxygen at the ordinary temperature and marked that ozone was formed under about 70 cms vacuum with some difficulty. As I did not repeat the experiment at different pressures so very reliable comparison can-not be made.

On the strength of evidence obtained from this investigation Warburg has advanced the theory that the formation of ozone is a photochemical reaction. It will be mentioned in some detail in connection with the work of Kabakjian in the next paragraph.

Kabakjian* carried an extended series of researches on the subject between 1908-1910. Some of his conclusions are:-
 1. "A silent discharge obtained by an alternating E.M.F. and an insulating dielectric between the electrodes separated by an air space is, under certain conditions, oscillatory in character."

2. Greater yield is obtained by the use of a dielectric between the electrodes.
3. Quantity of ozone produced is directly proportional to the

current, after a full steady discharge is obtained. With the same current the yield is different in different ozonisers.

4. No definite voltage is necessary for the transformation of oxygen into ozone.

Kabakjian offers the following observations on the photochemical theory of Warburg:-

1. The transformation of certain elementary substances like that of yellow into red P or monoclinic into rhombic sulphur takes place with the evolution of heat, giving rise to more stable forms.
2. The ozone action is endothermic hence can-not be classed with the above reactions.
3. The formation of ozone from molecular oxygen necessitates the dissociation of these molecules into atoms which cannot be brought about by the direct action of ultraviolet light to any great extent. Prof J. J. Thomson has found that such ionisation in air is very small.* E. Bloch says that ionisation is produced by light waves striking the solid particles in suspension@.
4. Dissociation is produced by ions or electrons carrying the discharge. This explains the fact observed by him that the quantity of ozone produced is a function both of the current and E.M.F. within certain limits. When the voltage exceeds this limit a part of the energy of the ions ^{used} is in producing dissociation and a part is wasted in the form of he

-at at the opposite plates. This conclusion is confirmed by more or less rapid ^{rise} of his curves with voltage before the critical point is reached.

5. The increase of efficiency with the increase of capacity is also accounted for by this theory. With small capacity the discharge curves are like that of a long period spark discharge but with large capacity the curves are smoother. The sparks produce little ozone hence smoother discharges give higher efficiency through increased dissociation.

This brief review I think sums up so far as possible our present position with regard to the subject. The history of the determination of certain constants, the development of certain tests and certain other details relating to ozonators have been omitted; because of the uncertainty that attaches to them. The large volume of such information also makes a complete treatment within a short space impossible.

Chapter II

Experimental research

Object-This investigation was undertaken with the object of finding out the lowest temperature at which oxygen begins to form ozone. In 1906 F. Fischer and E. Brahmmer burned hydrogen and certain other substances beneath the surface of liquid air. The authors failed to detect any ozone with the tetramethyl P-phenylene diamene test-paper*.

E. Warburg and his coworkers worked at the ^{or} rather between the temperature interval -71 and 93 degrees centigrade, using silent electric discharge as the source of energy. The investigator finds that the rate of decomposition of ozone increases with the temperature and that the yield is greater, the greater is the pressure. The purity of the gas which has a very marked effect on ozonisation due especially to the presence of nitrogen is not known. @

* Ber 35, 1324, 2902.

A# Ann Physik 8, 781, 1900.

@ E. P. Perman and R. H. Greaves hold that water vapour accelerates the decomposition of ozone. W. J. Mellor's inorg chem Prof Shenstone says that no nitrogen oxides are formed when oxygen is mixed with 7 % nitrogen; hence the format-

E. Goldenstein* worked on the formation of ozone under conditions comparable to ours but his results differ from ours in certain respects as will be shown later on. It may be mentioned here that the steps which he took to purify the oxygen gas are perhaps not recorded.

The next investigator who worked on the problem of ozone formation took a very great trouble in drying the gas thoroughly for months. But by working at 0 degree centigrade he did not very well succeed in detecting ozone. The problem of extreme purification and drying of oxygen is important from two points of view:

First. On account of our lack of understanding regarding the nature of the ozone action it is one of our chief points of attack to study the comparative ease with which the substance is formed under varying conditions of temperature, pressure, purity and so on. The ascertainment of the conditions and the agents which promote the action means an advance in

 ion of ozone may be accelerated by nitrogen without the formation of its oxides. J.C.S. 1898, P*246.

* Henry Roscoe's treatise on chemistry V:I

Prof. Shenstone J.C.S. 1897, 1898.

in its manufacture and stability on the commercial scale and is very likely to give us some clue as to the mechanism of the change. The researches of Sir J.J. Thomson* have shown us that hydrogen and other elements can exist in the form of allotropes as well as allotropic modifications possessing electrical charges. The polyoxides of nitrogen having been shown to be very similar to ozone in properties by Prof Shenstone#. Hence the importance of purification and drying of oxygen.

Second. To some minds the idea of looking for any further proof for the fact that ozone is only an allotropic modification of oxygen and nothing else as we go along in our research work might seem only a running after the first principles but so far as my knowledge of the literature on the subject goes I think there is still a need for experimenting, so far as possible, with pure oxygen, at least with one free from nitrogen. By so doing we will be moving along the way pointed out to us by the most recent researches in the field of electric discharges through gases. In my opinion the attempt to approximate the conditions for facilitating ozone formation and increasing the yield is not more promising than the idea of following the path of systematically restricting the formation if the use of pure oxygen and working at abnormally low or high temperatures leads to that.

* "Ozone" by E.K. Rideal

"J.C.S. 1898."

The attempts to form ozone out of pure oxygen at the liquid-air temperature having failed for some time in the past in this laboratory the work was again taken up in the winter of 1924. On account of the fact ^{that} commercial oxygen will form ozone at the ordinary temperature whereas pure oxygen will not it was suspected that nitrogen acts as a catalytic agent. Having got that idea from our previous experience this work was undertaken on Prof Cady's suggestion.

Our object being to ^{see} the effects of the varying amounts of nitrogen on the formation of ozone as well as the lowest temperature at which the formation occurs the experiment was begun with air at the ordinary temperature and pressure. Two concentric glass test-tubes, the outer one much wider than the inner one, were taken. Their outer surfaces near the bottoms were coated with two pieces of tin-foil about half an inch wide. The silent electric discharge was passed between them with a small induction coil. There was no ozone detected with starch-iodide solution. Then a bigger coil was used and the smell of ozone was detected near the induction coil in a very short time.

The inner tube was next replaced by a long glass tube bent nearly at the upper end which was connected to a test-tube containing starch-iodide solution. The latter was connected to a water pump. The discharge was passed through as before. The ozonised air was passed through the starch iodide solution. It was turned blue, thus indicating the presence of ozone or

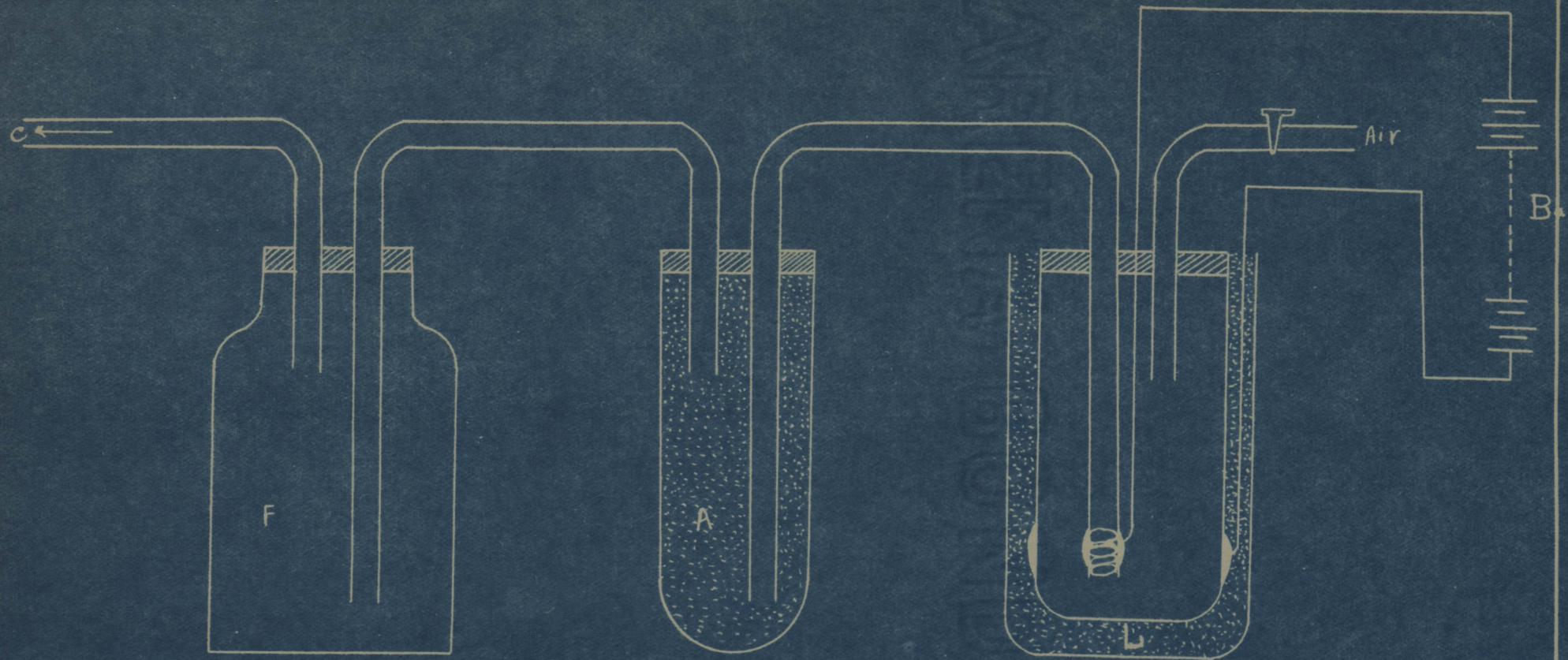


Fig. 1

- Ba - battery
- F - empty Wolff's bottle
- L - liquid air
- A - Starch and potassium iodide solution
- C to suction pump

nitrogen oxides. But as our later experience showed that the passage of the silent electric discharge is more favourable for the formation of ozone than that of nitrogen oxides therefore there seems to be no hesitation whatsoever in saying that the reaction was due to the formation of ozone which was almost instantaneous.

The next step in the experiment was to draw the fresh air for the purpose from out of doors. The experiment was repeated this way and the result was the same as before.

For the purpose of carrying on the experiment with air at the temperature of the liquid air the apparatus shown in the diagram on the opposite page was used. The discharge was passed through for a long time and then the air was drawn through the apparatus in order to test for ozone. There was no effect on starch-iodide solution.

The liquid air was then removed and the contents of the ozoniser tube allowed to warm up a little. There was some dark blue liquid in the tube. On drawing air through the apparatus the solution was turned blue.

Instead of air commercial oxygen was used. The experiment was performed at the ordinary temperature. After passing the discharge the ozonised oxygen was tested with starch-iodide solution. It was turned blue. It may be due to the formation of ozone or nitrogen oxides.

In order to distinguish between ozone and nitrogen

oxides the following test was applied. The solutions of sulphanic acid and alpha naphthyl-amine were prepared in the following way.

Sulphanilic acid	.5 grs
Acetic acid(galacial)	30 c.cs
Distilled water	120 c.cs

The sulphanilic acid solution was made by dissolving it in galacial acetic acid and then diluting it with water.

Alpha naphthyl-amine	.1 gr
Acetic acid(galacial)	30 c.cs.
Distilled water	120 c.cs.

The amine was dissolved by ^{or} rather in water heated to boiling. It was cooled and then acetic acid added to it.

For the purpose of making a test two cubic centimeters of each solution were taken out of the stoppered bottles and mixed with fifty c.cs. of distilled water. The solution was put into a large test-tube which was interposed between the starch-iodide solution and the ozoniser. The apparatus was

The apparatus was washed for sometime by drawing oxygen through it. The discharge was then passed through for a short time. On drawing oxygen through the apparatus there was

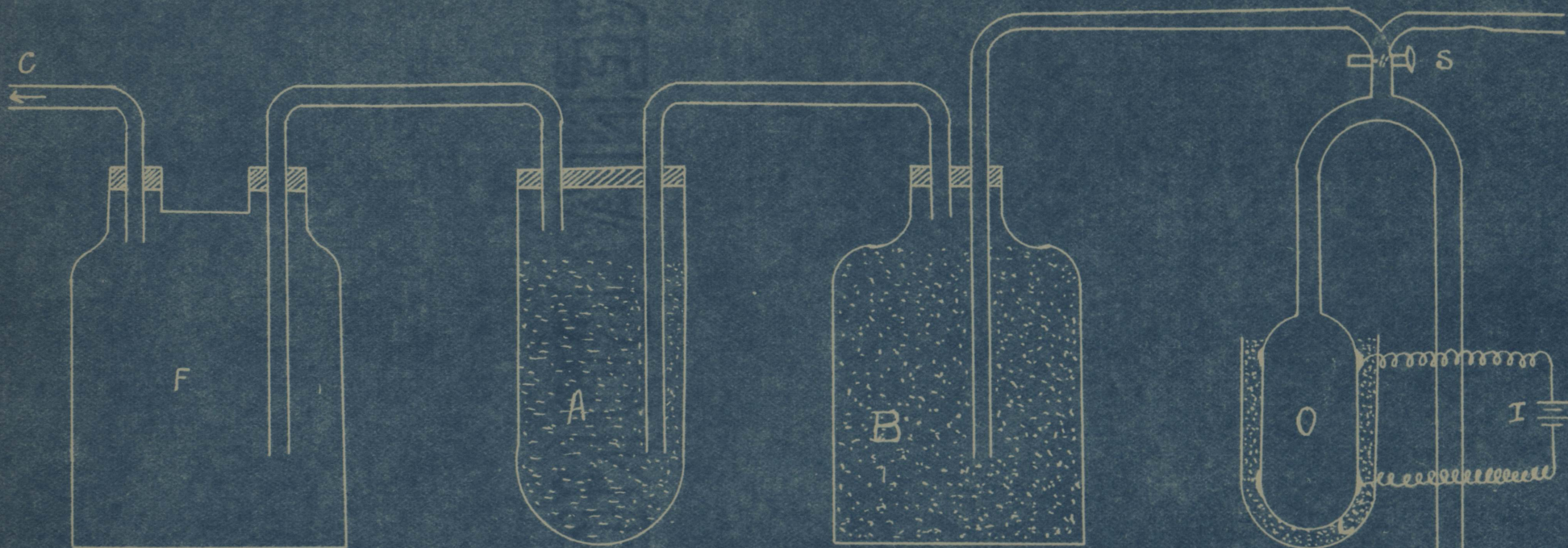
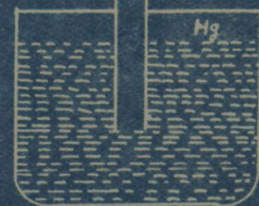


Fig. 2

- I - induction coil
- S - two-way glass stopper
- O - oval tube
- Hg- mercury
- F - empty Wolff's bottle
- L - liquid air
- A starch and potassium iodide solution
- B sulphuric and acetic acids
- C to suction pump



no effect on the sulphanic acid and the alpha naphthylamine solutions. The nitrogen oxides were therefore absent. But the starch-iodide solution was turned blue, indicating the presence of ozone.

The apparatus was not perfectly air-tight due to so many cork-joints therefore a modified form of the above was used. The modification was based on the fact that there is a change of volume when oxygen changes into ozone. Thus it afforded a check on the starch-iodide solution test for ozone.

The apparatus used is shown in the diagram on the opposite page. A is an ozoniser tube having two pieces of tin-foil attached to it near the top and the bottom. C is a double-way cork ^{or} rather a glass stopper and M is a mercury cup. The commercial oxygen enters at D and the end S of the tube from the glass stopper was connected with the test mixtures, using very short rubber connections because they are very easily attacked by ozone.

The apparatus was cleaned and thoroughly dried by passing air through it. Then the discharge was passed through it for a very long time. A slow but steady decrease in volume was observed. The loss of mobility of mercury in the column was noted. After the discharge was passed through the ozonised oxygen gave a clear test for ozone by turning starch-iodide solution blue but the other reagents were not affected thus indicating the absence of nitrogen oxides. The exp-

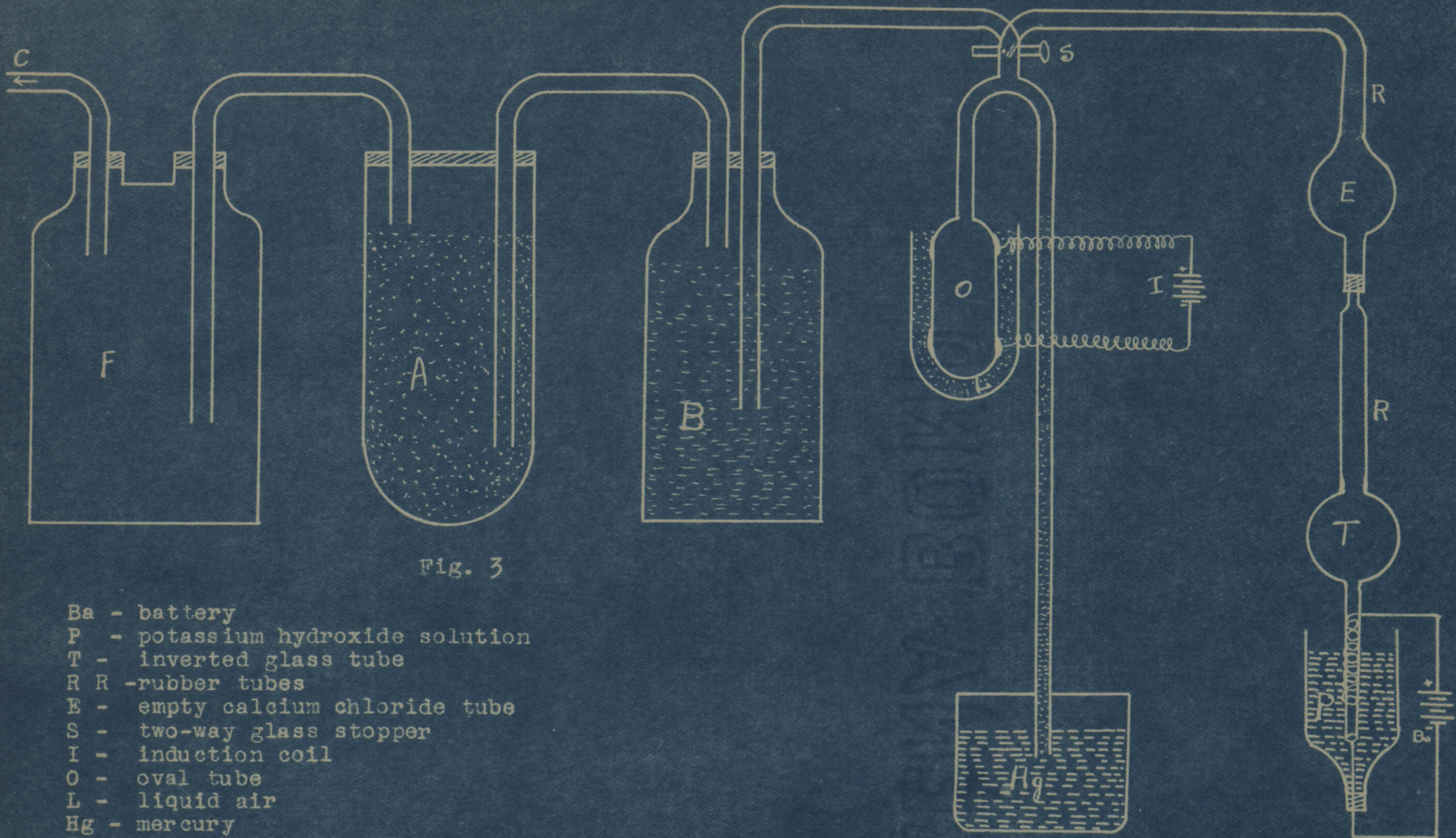


Fig. 3

- Ba - battery
- P - potassium hydroxide solution
- T - inverted glass tube
- R R -rubber tubes
- E - empty calcium chloride tube
- S - two-way glass stopper
- I - induction coil
- O - oval tube
- L - liquid air
- Hg - mercury
- F - empty Wolff's bottle
- A starch and potassium iodide solution
- B sulphuric and acetic acids
- C to suction pump

eriment was performed at the ordinary temperature and 734 mm pressure. The gas was under 70 cms vacuum.

The experiment was repeated at the liquid-air temperature. The ozoniser tube was surrounded by liquid air and after washing the apparatus with commercial oxygen for about an hour the discharge was passed through for a long time. Then the rather more oxygen was passed through the apparatus while the ozoniser tube was still surrounded by liquid air. The issuing gas gave no test for ozone. On removing the liquid air the dark blue liquid evaporated and gave a clear test for ozone. No test for nitrogen oxides was obtained with the other solution.

The next step in the investigation was the preparation of pure oxygen gas electrolytically. A fifteen percent solution of potassium hydroxide recommended by M. W. Travers was used. The arrangement of the whole apparatus is shown in the diagram on the opposite page. Nickel wire spirals were used as electrodes and the anode was placed inside an empty calcium chloride tube. The cathode was placed above above the mouth of the same.

The whole apparatus was washed with the electrolytic oxygen but since some foam and solution were eventually carried over to the stopper and ozoniser an empty calcium chloride tube was interposed between the ozoniser and the electrolyser.

The whole apparatus was washed with dis

-tilled water and dried with compressed air. It was washed a
-gain with oxygen for about an hour and then the supply of
oxygen was shut off and the hole connecting the gas in the
ozoniser and the mercury in the column was left open as bef
-ore.

The suction pump was constantly working to mainta
-in the vac^uum. A slight change in volume was observed and
there was a loss in the mobility of the mercury too ^{but} no test
for ozone was obtained with the starch-iodide solution. The
sides of the ozoniser tube were wet and greasy----

The sides of the ozoniser tube were wet and gre
asy and it was suspected that there might be some alkali st
-icking to the sides of the tube which allowed the discharge
to pass through easily thus prevented ozonisation. The whole
apparatus was therefore thoroughly cleaned with distilled
water, alcohol, ether, benzene and the washing was finished wi
th acetone. The tube was thoroughly dried by passing compres
-sed air through it.

The experiment was performed at the liquid-air te
-mperature and 734 mms pressure. Instead of using suction
pump as mentioned before a motor driven vac^uum pump was used
and a 73 cms vac^uum created with it. To begin with the appar-
atus was thoroughly washed with oxygen for about an hour and
then the discharge was passed through for about forty minutes.
There was some decrease in volume and also the loss of mobili
-ty by mercury but the rate of formation was extremely slow
not comparable with the ease with which air or even commerc-

ial oxygen was ozonised. A little oxygen was let in so as to lower the vacuum by about half a centimeter. The formation of ozone was again indicated by the decrease in volume but after sometime some more oxygen was let in so as to lower the vacuum by about one centimeter there was no change of volume for a considerable time showing that it is extremely difficult to form ozone out of pure oxygen under a vacuum lower than 72 cms or thereabout. After that oxygen was drawn through the apparatus and a clear test for ozone but none for nitrogen oxides was obtained.

Air at the ordinary as well as at the liquid-air temperature forms ozone more readily than commercial oxygen and commercial oxygen forms ozone more readily than pure oxygen. From these observations I conclude that nitrogen acts as a catalytic agent* in the ozonisation of oxygen. Moreover it seems evident that in order that the yield may be greatly increased nitrogen must be present in proportions considerably larger than those in which it is found in commercial oxygen. #

Up to so far more interest has been taken in the technical side of the subject but the question of determining the most favourable temperature and other conditions for the manufacture of ozone is very far from being settled as yet. As far as the silent electric discharge method is concerned it seems that the use of pure oxygen is out of the question since only traces of ozone are formed under about 73 cms vacuum and the rate of formation is very very slow.

The exact determination of the temperature at which the formation occurs is difficult since it is not that of the liquid air or ~~that of~~ that of any other medium surrounding the ozoniser tube. The liquid air simply condenses the ozone for med.

E. Warburg finds that the yield of ozone is proportional to the pressure of oxygen which I think can only be true when oxygen is mixed with some nitrogen, since pure oxygen forms ozone in a very attenuated state. This is borne out by the fact that pure oxygen forms ozone under about 73 cms vac^uuum. Moreover since there was no sudden drop p^u of pressure equal to one-tenth of a millimeter as observed by Goldstein# hence I do not accept that value as the vapour pressure of the substance, at the liquid-air temperature. The ozonisation does occur even^{when} the vac^uuum is reduced a little but if the vacuum is reduced by about a centimeter no formation occurs for a considerable time.

 * Modern inorg chem by W. J. Mellor V: I

H. Roscoe's "Treatise on inorg chem V: I

 Refs P I6.

*# Both these conclusions happen to be in agreement with Prof Shenstone. He says that the % of nitroge should be greater than 7%. See J. C. S. London, 1898.