A CONTRIBUTION TO THE CHEMISTRY OF THE "OZONATES"

by

Thomas Patrick Whaley

B. S., St. Benedict's College, 1943

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 Doctor of Philosophy.

Advisory Committee:

Redacted Signature

Redacted Signature

Redacted Signature

Redacted Signature

May, 1950

Acknowledgment

The author wishes to express his appreciation to Dr. L. W. Seagondollar for his generous assistance in dealing with the electrical problems of the ozonizers used in these investigations.

The author is particularly indebted to Dr. Jacob Kleinberg for his guidance, assistance and encouragement throughout the entire course of this study.

TABLE OF CONTENTS

Introduction

Chemists have known since 1868 that ozone-containing oxygen reacts with several of the alkali and alkaline earth metal hydroxides to from highly colored substances which are readily decomposed with the liberation of molecular oxygen upon addition of water or acid. Throughout the past half century several experimenters have conveyed to the scientific world the results of their investigations on this baffling laboratory curiosity, each giving an interpretation of the observations, but none producing conclusive proof as to the exact nature of the phenomena.

One of the first postulates concerning the identity of these colored, oxygen-liberating compounds, and the one which has been accepted by several authors, states that these so-called alkali "ozonates" are identical with the alkali superoxides. Another explanation proposed that the oxygen is bound to the hydroxide by means of a coordinate bond to form an addition compound, much in the same manner as in the hydration of molecules. A more recent proposal, supported by several different experimental data, attributes the observed phenomena to the formation of a new, higher oxide in which each oxygen atom has an effective oxidation state of -1/3.

The difficulties encountered in the investigation of these substances are many, but the one outstanding obstacle which has proved insurmountable to previous investigators is the problem of obtaining the "ozonates" in a reasonably purified form. The reaction between ozone and solid alkali metal hydroxides is a surface phenomenon, so that a quantitative reaction is quite impossible. Furthermore, the instability of the "ozonates" with respect to water and their insolubility in all of the common organic solvents has rendered the purification by solvent extraction inachievable. Recently, some success has been achieved in extracting the "ozonates" with liquid ammonia.

Due partly to this failure to purify them, and partly to their apparent lack of utility, the "ozonates" have remained little more than laboratory curiosities. A recent search for oxygen-liberating compounds has revived interest in them, however, and this study was originally undertaken in order to determine their utility as such compounds. Although their usefulness has proved questionable, this study was continued in an attempt to throw more light on an intriguing problem. The purpose of this study was essentially three-fold. First, all previous work on the subject was to be repeated, insofar as was possible, and the existing information critically evaluated. Second, further experimentation designed to produce data of significance to the problem was to be conducted. Third, these data were to be evaluated and utilized in determining the nature of these alkali metal "ozonates".

Historical Review

"L'ozone donne avec la potasse sèche du peroxide de potassium jaunebraun que se detruit très vite in dehors du contact de l'ozone."[1]

This sentence taken from Wurtz's Dictionnaire de Chimie pure et appliquée in 1868 was apparently the first published information on the alkali metal "ozonates". This information was written without further reference, so that the credit for the original discovery must remain temporarily unawarded.

Baeyer and Villiger[2] in 1902 published a short report of a phenomenon observed during their study of organic ozonides. They found that dry pulverized potash was immediately colored a deep orange when a stream of ozone-containing oxygen was passed through it. They reported that, when water was added to this orange colored substance, the color disappeared and a strong evolution of gas took place. The color was found to fade also when the source of ozone was removed. Strangely enough, the ozone-treated potassium hydroxide appeared to display no oxidizing action, but when it was dissolved (with evolution of oxygen) in water and the solution permitted to stand for a while, the solution was reported to contain hydrogen peroxide. Further investigation showed that the orange color could be produced by passing ozonated oxygen into a cold solution of 40% potassium hydroxide. In this case, however, the color disappeared when the cooling bath was removed, thus indicating that the substance could not exist in aqueous solution at ordinary temperatures. These qualitative observations were repeated in the case of rubidium hydroxide and sodium hydroxide; the latter became colored only a feeble yellow in the presence of the ozone-containing oxygen.

Although no quantitative determinations were made, Baeyer and Villiger assumed this orange substance to be identical with the K_2O_4* which had been reported by Erdman and Kothner[3] only a few years prior to that time. They reasoned that, if the ozone-treated potash were really K_2O_4, it might be considered as the potassium salt of a hypothetical "ozonic acid", or ozone hydrate, which would result from the action of ozone on water according to the equation:

$$O_3 + H_2O = H_2O_4$$

This "ozonic acid" could then react with potassium hydroxide in a typical acid-base neutralization reaction to give the salt, K_2O_4. In the light of these hypotheses, they termed the dolored products "ozonsauren Alkalien", i.e., "alkali ozonates", in much the same manner that one terms the alkali metal salts

---

* Now formulated as KO_2.

of sulfuric and nitric acid, sulfates and nitrates. The name "ozonate" has prevailed since that time.

No further information on the subject was published for several years, although Bach[4] suggested in 1902 that the "ozonates" would be more properly considered as acidic salts; he proposed the formula KHO_4. Some five years later, Manchot, a consistent contributer to the field of peroxide chemistry, and Kampschulte[5] undertook to investigate the acidic properties of ozone. During the course of their investigations, they had occasion to repeat and expand the work reported by Baeyer and Villiger while studying the reaction of ozone with both organic bases and such inorganic bases as ammonia and the hydroxides of the alkali and alkaline earth metals. They found that ozone imparted to liquid ammonia, at the temperature of solid carbon dioxide, a deep orange-red color which disappeared when the temperature was permitted to rise to the boiling point of liquid ammonia. They reported that addition of the ozone-treated ammonia to cold titanium(IV) sulfate solution showed the presence of hydrogen peroxide, even after the color had disappeared from the ammonia. (This is somewhat confusing since the formation of hydrogen peroxide could scarcely be attributed to the oxidation of ammonia by ozone.) They found that all of the alkali metal hydroxides, with the exception of lithium hydroxide, became colored in a stream of ozone-containing oxygen, and they reported positive peroxide tests with titanium(IV) sulfate solution for all of these "ozonates". In attempting to show quantitatively the relative stability of the alkali metal "ozonates", they heated them in a stream of ozone-containing oxygen; in this way they maintained an ozone pressure above the hydroxides and could obtain a more reliable determination of the decomposition temperature. The results of these experiments showed that ozone-treated sodium hydroxide lost its color at about 90°C, the potassium hydroxide "ozonate" became colorless at about 110°C, the corresponding rubidium compound was decolorized at about 140°C, and the color of the cesium hydroxide "ozonate" was preceptible even after fusion at 200-220°C. From these data, Manchot and Kampschulte concluded that the stability of the alkali metal "ozonates" increased with increasing atomic weight of the metal. They found also that fusion of the "ozonates" resulted in the liberation of oxygen but no ozone. (The very fact that the fusion temperature of cesium hydroxide was reported as being between 200° and 220° indicates that the authors must have been working with the hydrated material. Although cesium hydroxide monohydrate melts at 180°C[6], the anhydrous substance does not melt until 272°C.)

Manchot and Kampschulte also investigated the action of ozone on the oxides and hydroxides of the alkaline earth metals. They found that all of these substances decomposed ozone, but that only barium hydroxide became colored to any appreciable extent. At the temperature of solid carbon dioxide, barium hydroxide was colored strongly yellow by ozone but calcium hydroxide was colored only slightly; magnesium hydroxide remained colorless under these conditions. The decomposition of ozone by both alkali and alkaline earth hydroxides was accompanied by liberation of heat. The presence of water was found to hinder or prevent the formation of the "ozonates".

The first quantitative investigation of the nature of the alkali ozonates was undertaken by Wilhelm Traube[7] (not to be confused with Moritz Traube, who was quite active in the field of peroxide chemistry) about five years after Manchot and Kampschulte had published their work on the subject. Traube constructed an apparatus wherein pulverized potassium hydroxide could be exposed to a stream of ozone-containing oxygen and which could also serve as a decomposition chamber in the gasometric analysis of the resulting "ozonate". The entire apparatus was weighed before and after ozonization and, since the weight of the potassium hydroxide contained was known, the increase of weight due to ozonization of the hydroxide could be determined by difference. In order to eliminate all traces of residual ozone, the system was flushed with dry oxygen before the final weighing.

The apparatus was then connected to a gas burette and the "ozonate" decomposed by means of a known amount of water. The volume change in the burette minus the volume of the added water was assumed to be due to the oxygen liberated during the decomposition of the "ozonate". Thus, the weight of liberated oxygen could be compared with the weight of oxygen taken up during ozonization. Results of several experiments showed that the weight of collected gas was essentially equal to the increase of weight resulting from the attack of the potassium hydroxide by the ozone, the variation being only from 2 to 5 mg. per 50 mg. total.

Traube reported that the solution which remained after decomposition of the "ozonate" contained small amounts of hydrogen peroxide, the quantitative determination of which was accomplished by titration with standardized potassium permanganate solution. He found that the number of moles of liberated oxygen was many times greater than the number of moles of hydrogen peroxide produced by solution of the "ozonate"; he was thus led to the conclusion that two different products must have been formed during the ozonization, both of which liberated oxygen upon decomposition, but only one of which gave rise to hydrogen peroxide upon being dissolved. In order to further establish this last point, he prepared a sample of the "ozonate", divided it into two portions, analyzed one portion immediately after preparation and permitted the other portion to remain in a closed vessel for 2 to 4 days before analyzing. The results showed that, although the molar ratio of liberated oxygen to hydrogen peroxide was extremely large immediately after ozonization, after 2 to 4 days the molar ratio had decreased to almost exactly 1:1. This last fact was confirmed by at least five consecutive experiments.

Traube interpreted the analytical data as indicating the formation of two different higher oxides of potassium, one having the formula K_2O_7 and the other having the composition K_2O_4. The first product of the reaction between ozone and potassium hydroxide was assumed to be K_2O_7 and was formed according to the reaction:

$$K_2O + 2O_3 = K_2O_7$$

This potassium "heptoxide" was then assumed to decompose into oxygen and potassium "tetroxide" according to the equation:

$$K_2O_7 = K_2O_4 + 3/2O_2$$

He assumed that the potassium "tetroxide" would then decompose in water or acid solution to produce oxygen and hydrogen peroxide in equimolar quantities. This assumption was based on the analytical data which indicated a value of unity for the oxygen-peroxide ratio after 2 to 4 days standing.

Although these proposals explained rather well the reported data, at least two discrepancies are immediately obvious: (1) the formula for potassium superoxide is now known to be KO_2 rather than K_2O_4, and (2) if a compound K_2O_7 is to exist, either the potassium must exhibit a valence of +1 or a new oxide ion possessing a valence of -3.5 must exist. Temporarily minimizing these apparent discrepancies of formulation, however, one can scarcely disregard these hypotheses completely since they do explain the experimental observations and analytical data. Certainly the reported facts can be explained by the existence of more than one substance, and the change with time of the evolved oxygen-peroxide ratio could be properly attributed to the change from a non-peroxide-producing oxide to one which does give up molecular oxygen and peroxide oxygen in equimolar quantities. Nevertheless, the lack of magnetic data and neglect of many standard chemical tests prevent one from accepting Traube's arguments unhesitatingly.

Traube himself was apparently not completely convinced of the reliability of his original work, for he published in 1917[8] another article dealing with the alkali metal "ozonates". Using essentially the same type of apparatus and the same experimental procedure, he investigated the behavior of the "ozonates" of potassium, rubidium and cesium hydroxides and found results which agreed favorably with those of his earlier work. He reported that none of the alkali "ozonates" investigated gave more than a trace of hydrogen peroxide when decomposed by means of water or acid immediately after preparation; however, as before, he reported that the analyses of "ozonates" which had been permitted to remain in an ice box for several days indicated approximately equimolar quantities of liberated oxygen and hydrogen peroxide.

The results of eighteen experiments indicated that potassium, rubidium and cesium hydroxides were readily colored by oxygen containing 6 to 8% ozone, with corresponding changes in weight accompanying the coloration. The change in weight of cesium hydroxide as a result of ozonization was a maximum of 2.2%, that of rubidium hydroxide was 4.9%, whereas potassium hydroxide "ozonate" contained a maximum of 8%, by weight, of added oxygen. The color of the heavier alkali "ozonates" was much deeper than that of the potassium compound, the color of the former being compared to that of freshly precipitated antimony sulfide, while the color of the potassium compound was likened to that of potassium dichromate. All of these "ozonates" lost their color on standing and were decomposed, with oxygen evolution, when added to water or acid. Cesium "ozonate" was found to retain its color for several days when kept at 0°C.

In addition to repeating his earlier work on the determination of oxygen-peroxide ratios, Traube conducted several other experiments which were designed to substantiate his arguments. In two of the experiments the "ozonate" was divided into approximately half; one portion was acidified with cold sulfuric acid and titrated with standardized potassium permanganate solution, the other portion was also acidified with cold sulfuric acid, potassium iodide added, and the liberated iodine titrated with standardized sodium thiosulfate solution. The amounts of hydrogen peroxide indicated by each determination were essentially the same. Finally, a succession of ozonizations on the same sample was carried out; a sample was ozonated, its color permitted to fade, reozonated, and so forth for as many as five or six ozonizations on the same sample. Although the molar ratio of oxygen to peroxide was reported to be the same, the amount of each present was found to increase after several ozonizations.

Although Traube reported no specific tests for peroxide, the fact that the solutions remaining after decomposition of the "ozonate" showed both oxidizing power (in oxidizing potassium iodide) and reducing power (in reducing potassium permanganate) seems to bear out his contention that hydrogen peroxide must result from solution of the "ozonates". (It must be pointed out, however, that ozone also displays both reducing and oxidizing properties[9].) He concluded that, since the evolved oxygen and hydrogen peroxide were formed in approximately equimolar quantities after standing, the aged product must have been the "tetroxide" (i.e., the superoxide). Inasmuch as the amount of hydrogen peroxide per gram increased upon standing, he assumed that another oxygen-liberating substance, which in itself did not produce hydrogen peroxide upon solution, must have been present originally but must have rearranged to the "tetroxide" while standing at 0°C. In this manner, he accounted for both the increase of hydrogen peroxide with time and the extremely large oxygen-peroxide ratio immediately after formation of the "ozonate".

Up to this point, little was proposed by Traube that was not to be found in his earlier paper. However, his views on the nature of the non-peroxide-producing substance changed considerably. Werner[10] had proposed that the "tetroxide" be written as $K_2O \cdot O_3$, analogous to his formulation for the polyhalides and polysulfides. Traube perferred to write the "tetroxides" as $K\text{-}O\text{-}O\text{-}K \cdot O_2$, in order to explain the origin of both peroxide oxygen and molecular oxygen. He proposed a similar formulation for the "ozonate" - $(KOH)_2 \cdot O_2$ or $KOH \cdot O_2$ - with the oxygen being bound by means of "auxiliary valence" to the potassium hydroxide. Potassium "ozonate" would thus be termed potassium "oxyhydroxide", and would rearrange to the "tetroxide" according to one of the equations:

$$3(KOH)_2 \cdot O_2 = 2K_2O_2 \cdot O_2 + 2KOH + 2H_2O$$

$$\text{or,} \quad 4KOH \cdot O_2 = 2K_2O_2 \cdot O_2 + 2H_2O + O_2$$

Although the analytical data were far too inadequate to justify his hypotheses concerning the "oxyhydroxide", or to establish the exact oxygen-hydroxide ratio, Traube proposed the following decomposition reactions for both substances:

$$(1) \quad (KOH)_2 \cdot O_2 + H_2SO_4 = O_2 + K_2SO_4 + 2H_2O$$

$$(2) \quad K_2O_2 \cdot O_2 + H_2SO_4 = O_2 + K_2SO_4 + H_2O$$

He also supposed that if the original hydroxide contained water of hydration, the "ozonate" would decompose according to equation (1) above rather than rearrange to the "tetroxide". In this respect, he reported that the lack of complete dehydration was detrimental to the progress of the reaction and would cause the resulting "ozonate" to be less stable; he found that the same percentage of water was more detrimental to the formation and stability of rubidium and cesium "ozonates" than of the potassium compound.

A few years after Traube's second paper on the alkali "ozonates", Strecker and Thiëneman[11] investigated the action of ozone on solutions of alkali metals in liquid ammonia. They reported that the first action of ozone was to form the metal hydroxide, which appeared as a gelatinous mass. This precipitate dissolved upon continued ozone treatment and a deep orange liquid was formed. Finally, an orange precipitate formed. Sepia-brown precipitates were observed when solutions of calcium and barium in liquid ammonia were ozonated, but these precipitates decomposed as soon as the ammonia had evaporated. They reported that the orange colored "ozonates" of the alkali metals decomposed also upon complete evaporation of the ammonia, although decomposition was slower than in the case of calcium and barium. The final products were found to be mixtures of ammonium nitrate, ammonium nitrite, and the hydroxide of the alkali metal in question. The nitrate and nitrite result from the oxidation of the ammonia by ozone, a reaction reported by Manchot[12] in 1908.

The method of analyzing for oxygen and alkali metal consisted of permitting most of the liquid ammonia to evaporate, attaching the apparatus to a gas measuring device and simultaneously decomposing the "ozonate" and evaporating the remaining ammonia by heating the reaction vessel to 250-300° in an oil bath. The volume of the liberated gases, which consisted of oxygen and ammonia, was measured and the oxygen then determined by absorption in an alkaline solution of pyrogallol. The alkali was determined by neutralizing the residual hydroxide by means of dilute sulfuric acid, evaporating to dryness, and determining the alkali metal gravimetrically as the sulfate. Determinations were made for potassium, rubidium and cesium, with the mol ratio of liberated oxygen to alkali metal being about 0.7 to 1 for potassium and rubidium, and approximately 1 to 1 for cesium. No quantitative determinations were made on sodium.

Strecker and Thieneman reported that, using acidic titanium(IV) sulfate solution, they obtained positive peroxide tests on the solutions remaining after the decomposition of the "ozonates" in water or acid. They also reported that the ease of formation and the stability of the "ozonates" appeared to increase with increasing atomic weight of the metal, that of sodium being the least stable and most difficult to obtain, and that of cesium being the most stable and easiest to obtain. These results verified the observations reported by Manchot and Kampschulte[5].

Little more was published on the subject of the alkali metal "ozonates" until 1935, when Weiss reported the results of his investigations on the HO_2 radical in solution. Unfortunately, many of the conclusions reached by Weiss were based on insufficient experimental evidence and must be considered to be more speculation than acceptable conclusions based on experimental data. For the most part, his publication dealt with the existence and behavior of the HO_2 radical in solution, but his many references to the reaction between ozone and hydroxyl ion provide sufficient excuse for including it among the literature of the alkali metal "ozonates".

Weiss assumed, citing the original qualitative work of Baeyer and Villiger[2] as his authority, that the action of ozone on solid potassium hydroxide resulted in the production of potassium superoxide. He then postulated the formation of HO_2 from KO_2 according to the equation:

$$KO_2 + H_2SO_4 = KHSO_4 + HO_2$$

He proposed that either hydrogen peroxide or ozone would result from the decomposition of HO_2 according to one of the following equations:

$$2HO_2 = O_3 + H_2O + 35\text{Kcal}$$
$$2HO_2 = H_2O_2 + O_2 + 49\text{Kcal}$$

He did not propose a method for determining which of these reactions took place, nor, indeed, did he even suggest that one might take place in preference to the other. Nevertheless, he showed that ozone could be analytically determined in the presence of hydrogen peroxide according to methods based on the following equations:

Iodometric Titration

(ozone) $O_3 + 2I^- + H_2O = O_2 + I_2 + 2OH^-$ $(O_2/I_2 = 1)$

(H_2O_2) $H_2O_2 + 2I^- + 2H = I_2 + 2H_2O$ $(O_2/I_2 = 0)$

Permanganate Titration

(ozone) $2KMnO_4 + 5O_3 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 10O_2$
(ratio of O_2 to $KMnO_4$ is 5)

(H_2O_2) $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$
(ratio of O_2 to $KMnO_4$ is 2.5)

Weiss also assumed the correctness of Baeyer and Villiger's hypothesis that the yellow color resulting from the action of ozone on concentrated aqueous potassium hydroxide solutions at low temperatures was due to the formation of potassium superoxide. He then measured spectroscopically the absorption due to solutions of ozone in water, in acid, and in alkali solutions, and also determined the ozone content of such solutions. Gaseous ozone had a strong absorption in the ultra-violet, with a maximum at 2500A°; acidic solutions of ozone showed the same general characteristics, but with a more diffuse spectrum. As the alkalinity of the ozone solutions was increased, the absorption in the ultra-violet decreased until it completely disappeared in strongly alkaline solution. He obtained an absorption band in the blue region of the visible spectrum for solutions of ozone in 40% potassium hydroxide solution at a temperature of about -40°C, and assumed this absorption to be due to potassium superoxide and superoxide ion. However, he showed no direct evidence to substantiate his assumption, and one is forced to accept his claim as mere conjecture. Weiss's spectroscopic observation is really no more significant than saying that solutions of zone in strongly alkaline medium at low temperatures are colored yellow; this much has been known since 1902.

At the time that the present work was begun, all of the available information on the alkali metal "ozonates" was contained in the publications just described. Since that time, however, a new and more complete approach to the problem was described by Kazarnovskii, Nikolskii, and abletsova[14]. One must remember that, prior to 1949, all attempts to isolate the pure "ozonate" had been unsuccessful. Strecker and Thieneman[11] had shown that the ozonization of solutions of alkali metals in liquid ammonia gave first the metal hydroxide and then orange colored solutions. Although they were apparently unaware of their discovery, it has recently become obvious that they stood closer to a successful attempt at isolating the pure compound than any one prior to 1949. However, Kazarnovskii, Nikolskii, and Abletsova were the ones who produced the first reasonably pure potassium "ozonate" by utilizing a liquid ammonia extraction process.

Kazarnovskii, Nikolskii, and Abletsova began by ozonating well-dehydrated, pulverized potassium hydroxide for 2 to 3 hours at -10 to -15°C with a carefully dried stream of 6-8% ozonated oxygen. This reaction was no different than the one noted by all previous investigators. However, they found that liquid ammonia did not decompose the "ozonate" and, furthermore, the "ozonate" was quite soluble in the ammonia. They found that when ammonia was condensed on the "ozonate" at the temperature of solid carbon dioxide, an orange-red solution came through the sintered-glass filter used in the process, leaving behind the unreacted hydroxide which was insoluble in the ammonia. Upon evaporation of the liquid ammonia, there were obtained reddish-brown crystals which, upon analysis, proved to consist mainly of a compound having the formula KO_3

The authors did not report their method of analysis, but gave the results of eight analyses which indicated between 41.9 and 43.5 weight percent of "active"* oxygen, and between 54.6 and 55.8 weight percent of potassium monoxide. The sum differs from 100 by only 2 to 3%; this deviation was explained by the presence of water as an impurity. The formula was achieved by determining the above-mentioned values for "active" oxygen and the alkali metal oxide, then determining theoretically the values for water, potassium monoxide, and active oxygen which would result from the decomposition of several possible types of compounds. The following theoretical calculations were made:

Compound	active oxygen*	K_2O	H_2O
$KOH{\cdot}O$	22.2%	65.3%	12.5%
$KOH{\cdot}O_2$	36.3%	53.5%	10.2%
$KOH{\cdot}O_3$	46.1%	45.3%	8.6%
KO_2	33.7%	66.3%	0.0%
KO_3	45.9%	54.1%	0.0%

It thus appeared that the analytical data fitted the formulation KO_3 better than any of the other possibilities and the authors concluded that potassium "ozonate" must be a new oxide of potassium, KO_3.

---

*The term "active oxygen" as used here refers to the oxygen liberated upon complete decomposition of the compound.

The authors reported that the new oxide decomposed slowly at room temperature, liberating oxygen, and giving potassium superoxide as the end product, according to the reaction:

$$KO_3 = KO_2 + 1/2O_2$$

However, no mention was made as to the experimental verification of the reaction, i.e., no specific chemical tests to substantiate the formation of potassium superoxide was offered. They were no more specific than to state that KO_3 possessed "highly reactive properties" and "appeared to be strongly acidic". They likewise reported that oxygen was given off vigorously when water was added to the "ozonate", according to the equation:

$$KO_3 + H_2O = K^+ + OH^- + O_2 + OH$$
$$2OH = H_2O + 1/2O_2$$

Thus, they assumed that hydrogen peroxide was not a product of the decomposition, unless they purport to indicate its existence by means of the OH radical.

The kinetics of the proposed decomposition of KO_3 to what was presumably potassium superoxide indicated that the time required for half-disintegration was 90 hours at 15-20°C, with complete decomposition taking place in 11 days. At a temperature of 50 to 60°C, the disintegration required only about 30 minutes, but at the temperature of solid carbon dioxide, no appreciable decomposition was observed. They reported that the initial substance contained 93.4% KO_3 and

5% KO_2; after decomposition, the product was reported to contain 89.8% KO_2 and 8.6% KOH. Again they failed to indicate how they arrived at these figures.

Magnetic measurements of a mixture presumably of 88% KO_3 and 4% KO_2 indicated a gram susceptibility at 20 degrees of 12.5×10^{-6} cgs. units. This gave a value of 13.6×10^{-6} cgs units for the gram susceptibility of pure KO_3, a molar susceptibility of 1185×10^{-6} cgs units, and, consequently, a magnetic moment of 1.67 Bohr magnetons. These magnetic data showed the KO_3 to be paramagnetic and to contain one unpaired electron per molecule, thus eliminating the possibilities of the formulae K_2O_6 and $KOH{\cdot}O_3$, both of which should be diamagnetic.

Electrical conductivity measurements on solutions of KO_3 in liquid ammonia (at $-50^{\circ}C$) indicated a value of 3.4 ohms^{-1} for the molecular electrical conductivity. As the authors pointed out, this value would seem to establish KO_3 as an electrolyte of "moderate strength" and give additional proof to the existence of an O_3^- ozonide ion. They suggested that the stability of the O_3^- ion could be explained on the basis of resonance hybridization between the regular two-electron bonds, and postulated the following resonance structures:

$$^{-}O{-}O{-}O{-} \qquad {-}O{-}O{-}O^{-}$$

In addition, resonance between a two-electron bond and a three-electron bond was assumed to be possible, with the following resonance structures:

$$^{-}O{-}O\overset{\cdot\cdot\cdot}{\text{—}}O \qquad O\overset{\cdot\cdot\cdot}{\text{—}}O{-}O^{-}$$

The bond distance was calculated to be 1.38Å, based on the expression:

$$d(KO_3) = 1/2(d(H_2O_2) + d(KO_2))$$

where d refers to the oxygen-oxygen distance.

Preliminary crystallographic studies indicated that the KO_3 molecule probably possesses a crystalline structure similar to KN_3. The O_3^- ion was found to be linear, as is the N_3^- ion.

The authors proposed the following chain mechanism for the ozonization reaction:

$$KOH + O_3 = KOH{\cdot}O_3$$

$$KOH{\cdot}O_3 + O_3 = KO_3 + HO_2 + O_2$$

$$HO_2 + O_3 = HO + 2O_2$$

$$HO + O_3 = HO_2 + O_2\text{, etc.}$$

The over-all reaction was written as:

$$3KOH + 2O_3 = 2KO_3 + OH \qquad \Delta F \text{ greater than zero.}$$

The electron affinity of the ozone molecule was calculated from bond energies and resonance energies to be between 60 and 70 Kcal, whereas the electron affinity of the oxygen molecule is only 22 ± 10 Kcal.

In attempting to evaluate the previous work, one can find many points of agreement among the various investigators. All apparently agree that the "ozonates" decompose in water and dilute acid to liberate oxygen. Most of the investigators reported positive tests for hydrogen peroxide on solutions resulting from the decomposition of the "ozonates", although Traube[7,8] reported only a trace of hydrogen peroxide immediately after preparation of the "ozonate". All of the authors who ventured opinions on the matter seemed to feel that the "ozonates" were either superoxides (Baeyer and Villiger[2], Weiss[13]) or were substances which formed superoxides upon standing (Kazarnovskii, Nikolskii, and Abletsova[14], Traube[7,8]); these proposals, if true, would explain the positive peroxide tests. However, Baeyer and Villiger[2] presented no quantitative data to support their proposal, so their opinion must be disregarded; Weiss merely accepted the views of Baeyer and Villiger; therefore, his opinion must be completely ignored; Kazarnovskii, Nikolskii, and Abletsova failed to mention their methods for determining potassium superoxide in the presence of KO_3, so one cannot properly evaluate their data; Traube appears to have the strongest case, with his quantitative determinations of the oxygen-peroxide ratios, and one can scarcely ignore the consistency of his analytical data.

The role of water in the formation and stability of the "ozonates" has been repeatedly mentioned by several authors, but no one has attempted to carry out experiments designed specifically to determine the exact role played by the water.

All of the authors who conducted experiments on several of the alkali metals agreed that the stability and ease of formation of the "ozonates" appear to increase in the order sodium, potassium, rubidium, cesium, but very little work has been reported on the action of ozone on sodium hydroxide. All of the quantative data has been for the "ozonates" of potassium, rubidium, and cesium; no investigator has yet reported quantitative studies of sodium hydroxide "ozonate".

The report by several of the authors of the exothermic nature of the reaction between ozone and the hydroxides of the alkali metals can hardly be considered as significant, since the catalytic decomposition of ozone to oxygen is highly exothermic. The enthalpy change of the reaction $2O_3 = 3O_2$ is given by Lewis and Randall[15] as $\Delta H = -34000$ cal.

The observations made by Strecker and Thieneman[11] were unquestionably the same as those made by Kazarnovskii, Nikolskii, and Abletsova[14]. After reading the paper of the latter group of authors, one can explain the observations of Strecker and Thieneman on the basis of the sequence: (1) formation of the hydroxide, (2) partial ozonization of both hydroxide and ammonia, and (3) extraction of the alkali metal "ozonate" by the ammonia to give the deep orange color. That the color was not due completely to ozonization of ammonia is evident from the report that the color did not disappear until the ammonia was almost completely evaporated. The fact that they did not obtain directly the colored crystals obtained by Kazarnovskii, Nikolskii, and Abletsova cannot be explained on the basis of published information, but this does not alter the fact that they were apparently the first to observe the solubility of the "ozonate" in liquid ammonia even though they were apparently unaware of this fact. Their value of unity for the O_2/CsOH ratio agrees approximately with the value of 1.25 reported by the Russian authors.

Nevertheless, the work of the latter investigators is by far the most complete investigation of the subject to date. Their kinetic and conductivity data, and particularly their magnetic data, coupled with their success in isolating a fairly pure product, leaves one with little doubt that theirs is the most readily acceptable explanation yet offered. Despite their reluctance to indicate their methods of analysis and the results of specific chemical tests, if any, one is almost forced by the preponderance of their experimental data to accept their formula for the potassium "ozonate" as being the most nearly correct formula that has been yet proposed.

EXPERIMENTAL

Sources of ozone

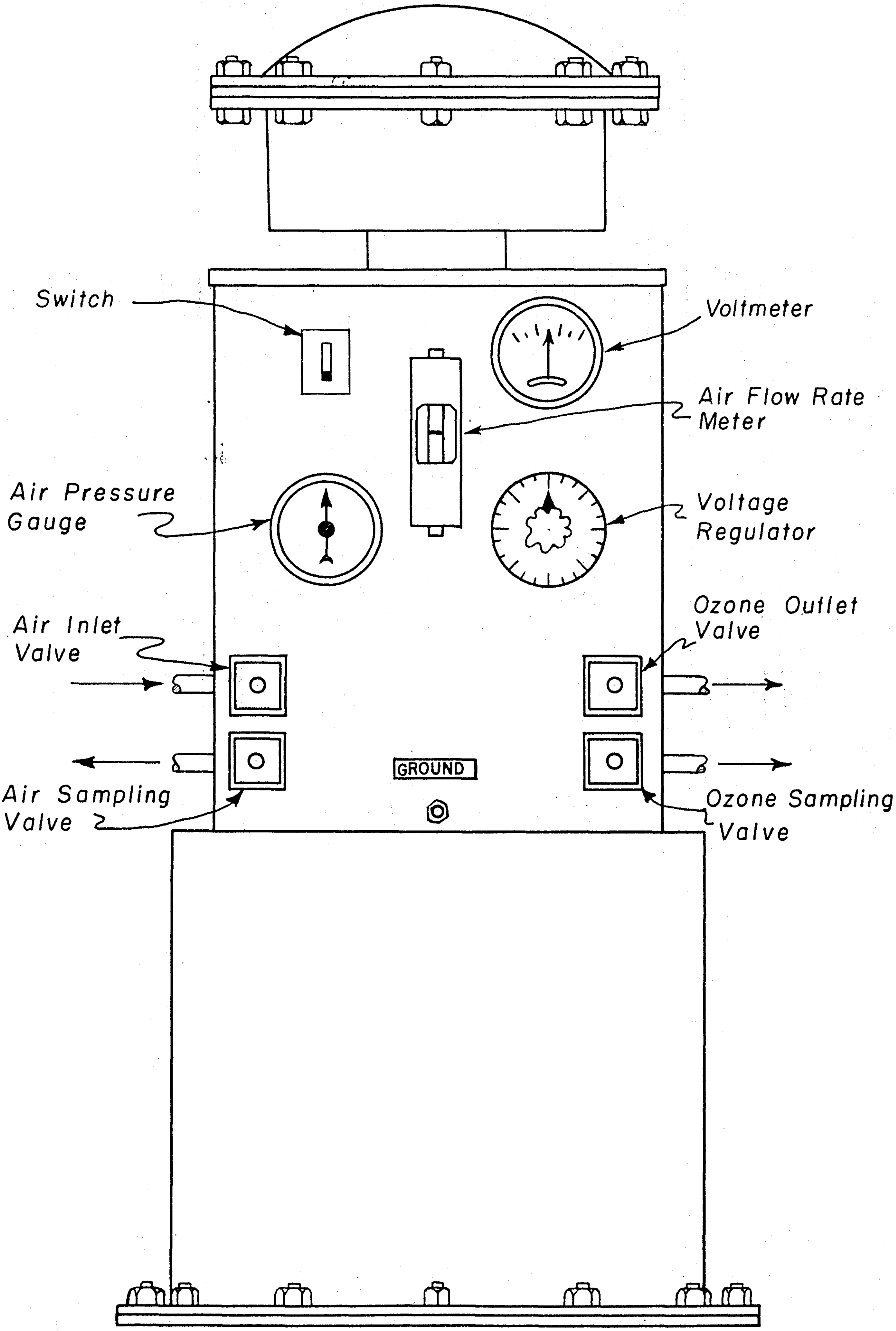
Ozone-containing oxygen was supplied at different times throughout the investigation by two ozonizers. The machine used throughout the greater portion of this study and the one used exclusively throughout the early phases of the work was a type T-12 "ozonator" (Fig. I) manufactured by Ozone Processes, Inc., Philadelphia, Pa. Ozone is produced in this machine by passing either air or oxygen through an electrical discharge between electrodes consisting of a graphite-coated glass tube and a steel jacket which surrounds the glass tube electrode concentrically. The glass tube electrode is sealed on both ends and is coated on the inside with graphite so that only the glass outer surface comes in contact with the oxygen and can thus catalyze the formation of ozone; it is connected by means of a steel rod on one end to a spring contact on a step-up transformer with a voltage ratio, primary to secondary, of 1:130 and with a maximum secondary voltage of approximately 16,000 volts. The voltage is regulated by means of a variable voltage transformer in the primary circuit and the voltage leading to the primary of the main transformer is indicated on a panel voltmeter. The "Ozonator" is designed for operation on a 115-volt, 60-cycle A.C. circuit; the primary voltage should not exceed 120 volts when the machine is operating on air and should not be greater than 110 volts when the machine is operating on oxygen. A steel case, as shown in Fig. I, encloses the transformer and electrodes and is maintained at ground potential. The steel jacket which surrounds the glass tube electrode concentrically is cooled by means of a flow of water through the surrounding cooling jacket.

Throughout this entire study, tank ozygen (Linde or Puritan) was used in operating the "Ozonator" and the laboratory ozonizer described later. The oxygen pressure in the "Ozonator" was maintained at 8 pounds per sq. in., as indicated by a pressure gauge on the panel board, by means of a reducing valve on the oxygen cylinder. (8 pounds per sq. in. is the pressure recommended by the manufacturer as optimum.) A safety pressure switch in series with the primary circuit of the "Ozonator" opens the circuit when the pressure inside the machine falls below 3 pounds per sq. in.

The flow of ozone-containing oxygen was controlled entirely by means of the ozone outlet valve; the oxygen inlet valve was left completely open throughout all ozonizations. A rotameter, calibrated at the optimum pressure of 8 pounds per square inch, has been placed on the panel board for the purpose of reading flow rate directly. This rotameter, however, was calibrated in cu. ft. per minute and was too insensitive for use in experiments that

Figure I

The Ozonator

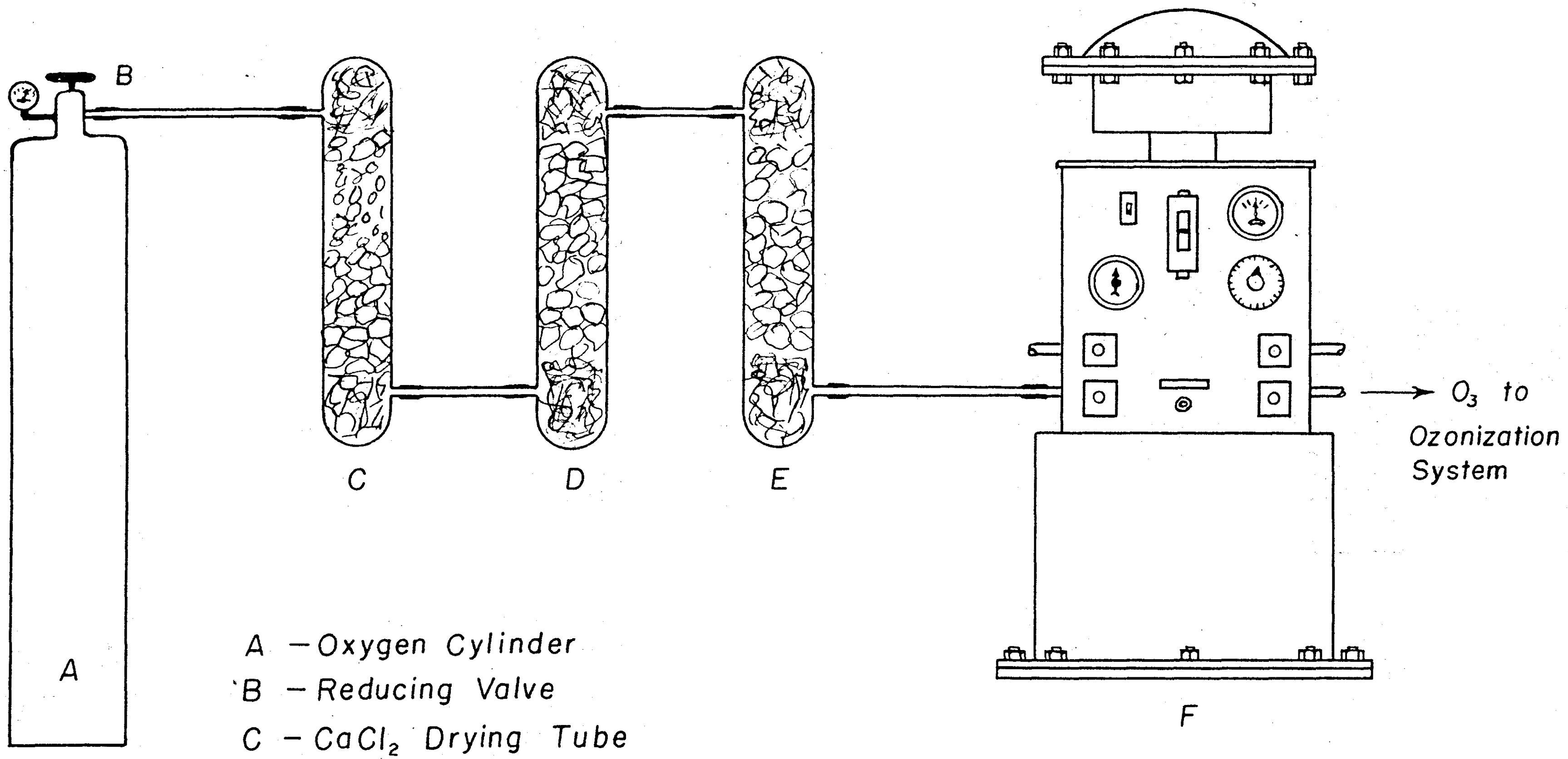


require precise knowledge of flow rate. For this reason, the flow rate was determined by means of a liquid-filled gas flowmeter filled with a light weight mineral oil, and calibrated against a "Wet Test Meter" (manufactured by Precision Scientific Co.) which was placed at the extreme end of the ozone destroying train (Fig. III), which will be described later.

Since the production of ozone is favored by a low moisture content, it is necessary to use oxygen which is as completely anhydrous as possible. Although very little moisture should be present in tank oxygen, rigidly anhydrous conditions were assured by first passing the oxygen through a purification and drying train consisting of two towers of anhydrous calcium chloride and one tower of anhydrous magnesium perchlorate, all towers being about 30 cm. in height (Fig. II). Traces of nitrogen in the oxygen do not apparently hinder the formation of ozone and no attempt to remove the nitrogen was made; however, traces of iron(II) nitrate and iron(III) nitrate along the steel walls of the "Ozonator" gave testimony to the fact that nitrogen was oxidized during the production of zone. If the glass tube inside the "Ozonator " is first exposed to insufficiently dried air or oxygen and then operated with dry oxygen, it takes 36 to 48 hours for the "Ozonator" to reach equilibrium conditions and maximum output.

Figure II

Purification Train



A – Oxygen Cylinder
B – Reducing Valve
C – $CaCl_2$ Drying Tube
D – $CaCl_2$ Drying Tube
E – $Mg(ClO_4)_2$ Drying Tube
F – Ozonator

Ozone Concentration

The production of ozone from oxygen is affected by many factors, the more outstanding of them being (a) moisture content (b) frequency of electrical discharge (c) voltage (d) type of glass used in constructing the ozonizer, and (e) temperature. In addition, the concentration of ozone in a gaseous mixture of oxygen and ozone is affected by the flow rate of the oxygen. The effect of moisture content has already been discussed, and the type of glass and the frequency of electrical discharge are constant factors determined by the construction of the apparatus and the source of A.C. current. If the voltage remains constant, the temperature and flow rate are factors which can be varied during the operation of the "Ozonator" in order to either increase or decrease the percentage ozone output.

The reaction $3O_2 = 2O_3$ is an endothermic one; hence, it is favored by high temperatures. For this reason, it should be possible to produce ozone from oxygen merely by heating the oxygen to a very high temperature. However, the decomposition of ozone is much slower at low temperatures, and for this reason, ozone production by the electrical discharge method is favored by low temperatures; the energy necessary for the reaction to proceed is provided by the electrical discharge. Low temperatures in the T-12 "Ozonator" are maintained by means of the previously mentioned cooling jacket which surrounds the outer (steel) electrode. Cold water is passed through this jacket during the operation of the machine and the concentration of zone is a function of the temperature of this cooling water; considerably higher concentrations are possible at lower cooling water temperatures.

The ozone concentration is also a function of the flow rate (cf. graph). At very high flow rates, the total ozone output is greater due to the greater total volume of gas; however, the concentration is quite small at very high flow rates and increases steadily as the flow rate decreases. At very low flow rates (less than 3 liters per hour) the concentration of ozone was found to decrease rapidly. This presumably is due to decomposition of the ozone between the time of formation and the time of reaction with the potassium iodide used in the analysis. It is not inconceivable that the manner in which the concentration varies with flow rate may be some function of the time of electrical discharge, i.e., some function of the frequency of discharge.

Measurement of Ozone Concentration

The concentration of the ozone-containing oxygen is measured by passing the mixture of gases into a dilute solution of potassium iodide, acidifying to decompose any iodates or periodates formed during ozonization, and titrating the liberated iodine with a suitable reducing agent such as sodium thiosulfate or arsenic(III) oxide.

In this study, the mixture of ozone and oxygen was led into a 10% solution of potassium iodide (iodate free), the solution acidified with cold, dilute hydrochloric or sulfuric acid before titrating, and the liberated iodine titrated with a standardized solution of sodium thiosulfate, using starch solution as an indicator. The total volume of gas was determined by means of the "Wet Test Meter" placed at the end of the ozonization train and the total weight determined from this volume and the known values of temperature and atmospheric pressure. The vessel containing the potassium iodide solution was kept at 0° in order to diminish, or eliminate completely if possible, the loss of free iodine by vaporization; since the vapor pressure of iodine is only 0.0299 at this temperature,[17] the loss of iodine by evaporation is not great, particularly if an excess of iodide ion is present to form the I_3^- complex ion.

The number of equivalents of iodine is determined from the titration by the sodium thiosulfate solution according to the equation:

$$I_2 + 2S_2O_3^{=} = S_4O_6^{=} + 2I^-$$

Thus, the volume of sodium thiosulfate solution used, multiplied by its normality and divided by 500, gives the number of moles of liberated iodine. Since the iodine is formed according to the equation

$$H_2O + 2KI + O_3 = 2KOH + O_2 + I_2,$$

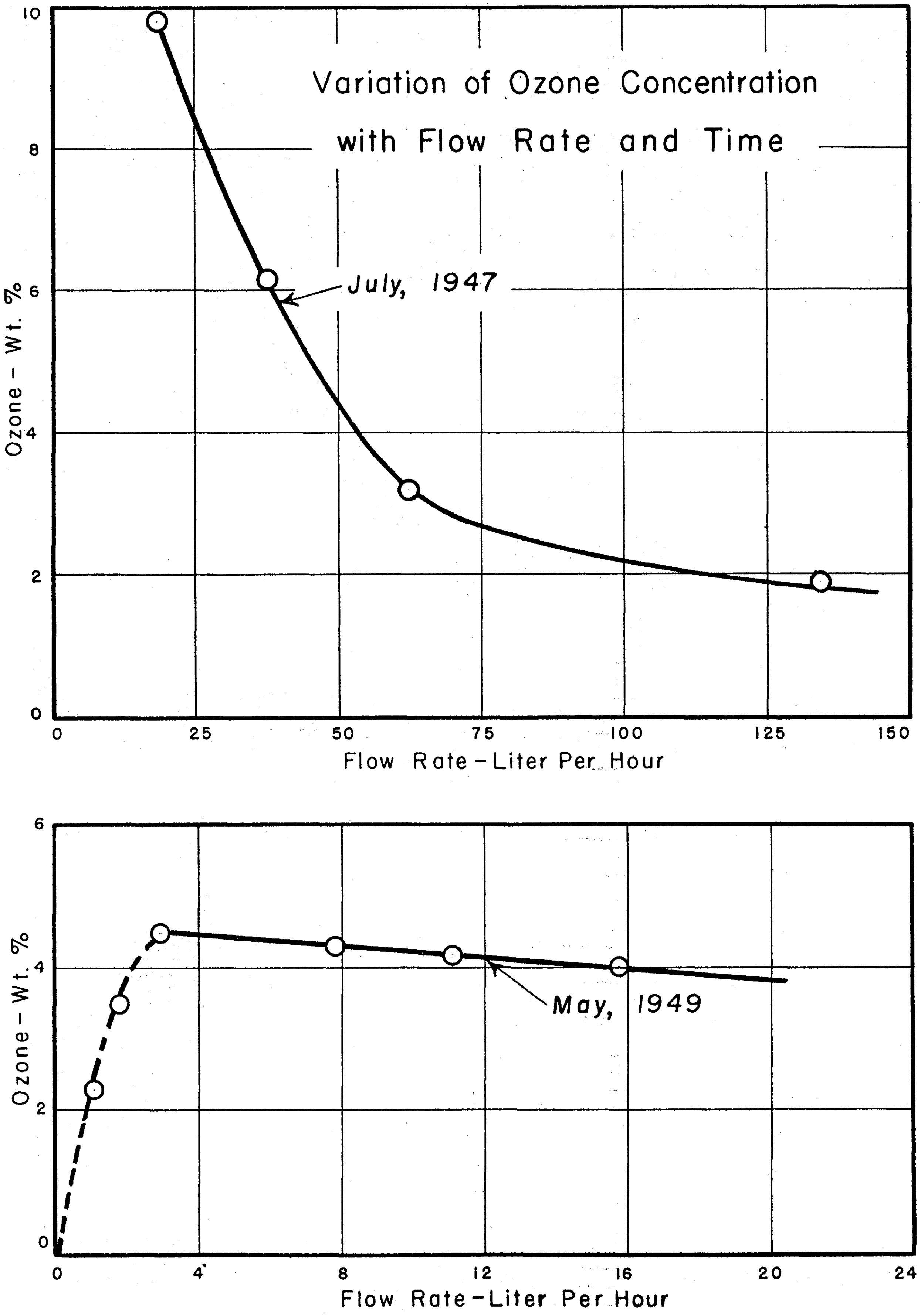
the number of moles of iodine is also the number of moles of ozone used to produce it, and multiplication by the molecular weight of ozone (48) gives the number of grams of ozone. The total weight of the mixture of ozone and oxygen is determined by reducing the volume of oxygen measured by the "Wet Test Meter" to standard conditions of temperature and pressure, dividing by the gram molecular volume, multiplying by the molecular weight of oxygen (32) and adding one third the weight of the measured ozone. From the weight of ozone and the total weight, one can readily determine the weight percent of ozone in the gaseous mixture.

In determining the concentration of the ozone output by the T-12 "Ozonator," one must bear in mind that the ozone concentration increases with time until an equilibrium condition is reached. If the apparatus has been completely dried, the time required for equilibrium to be established is only about 6 hours, but if the "Ozonator" has been exposed to insufficiently dried air or oxygen, as stated previously, the time required for an equilibrium concentration to be reached may be as long as 36-48 hours. Concentration determinations may be made during the course of a reaction, without disturbing the reaction itself, by use of a "bleeder valve" on the "Ozonator."

When air is the source of oxygen, the exit gases from the ozonizer contain lower percentages of ozone than when the pure oxygen is used. The gases also contain small amounts of nitric anhydride or nitrogen pentoxide, depending on the voltage used. A decrease in the rate of flow increases the amount of nitrogen pentoxide, but such amounts are relatively low and need be considered only when examining a reaction mixture for small amounts of by-products, or when the presence of such oxides causes a catalytic effect on the oxidation of the compounds in the reaction.

Ozone concentration determinations on the T-12 "Ozonator" used in this work were first made in July, 1947[16] at a voltage of 110 volts, the maximum specified for the use of oxygen, and with varying rates of flow. The pressure was maintained constant at 8 pounds per square inch and the temperature of the cooling water remained about 15°C. The ozone concentrations were as indicated by the graph. Ozone concentrations determined in May, 1949 at lower flow rates were much lower (cf. graph).

In addition, a considerable amount of moisture was found to be coming from the "Ozonator". This was determined by passing the ozone-containing oxygen through anhydrous (white) copper(II) sulfate and noting the change in color to the hydrated (blue) sulfate. Passage of the ozone-containing oxygen through a trap immersed in a bath of acetone and solid carbon dioxide resulted in a considerable amount of water in the bottom of the trap after several hours operation of the "Ozonator". Since the presence of large amounts of moisture was very undesirable in this study, this trap was used for removing the water from the mixture of ozone and oxygen during ozonization



Variation of Ozone Concentration with Flow Rate and Time reactions. However, the low concentration of ozone produced by the T-12 "Ozonator" even at optimum flow rates was undesirable, and the latter portions of this study were conducted with the aid of a laboratory ozonizer which produced ozone concentrations of 7 to 8 percent.

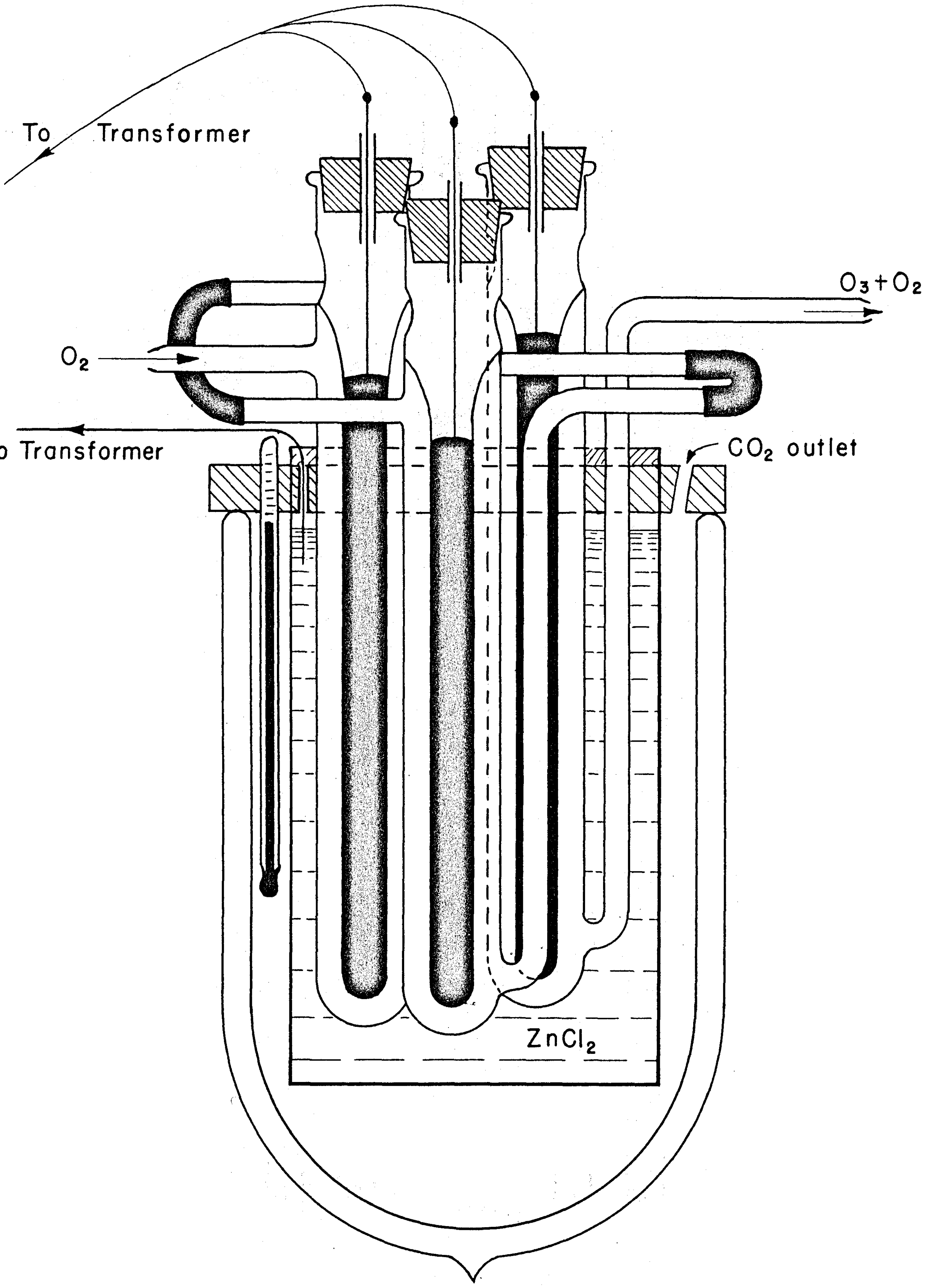
Laboratory Ozonizer

The laboratory ozonizer used during the latter phases of this work was a small, compact ozonizer constructed for the purpose of producing a large concentration of ozone and designed so as to take up very little space since it was to be used inside the hood.* The essential features of this ozonizer were patterned after the designs suggested by many previous investigators[18,19] but all of the factors conducive to a large percentage ozone output have been incorporated into a slightly new design in order that a maximum output could be obtained with the use of minimum amount of space.

Since ozone production in a silent-electrical-discharge type ozonizer is greatly affected by the type of glass which comes in contact with the oxygen, the temperature at which the discharge takes place, and the extent of the electrode area, these factors were taken into account in the construction of the ozonizer. Whether due to a negative catalytic action of

---

*An excellent review of laboratory ozonizers may be found in <u>Organic Syntheses</u>, <u>26</u>, 63-76 (1946).



Laboratory Ozonizer

Pyrex type glass, or to a positive catalytic effect of soft glass, it has been found by earlier investigators[20] that use of soft glass in ozonizer construction greatly enhances the conversion of oxygen into its more active allotropic form. Greater conversion is obtained by cooling the glass through which the oxygen passes: investigators have found that the output at -50°C is approximately three times that obtained at room temperature.[21] Many experimenters[18,19] have increased the percentage output by connecting several ozonizer tubes in series. All three of these effects were considered in the construction of the ozonizer described below.

The individual ozonizer tubes were constructed of soft glass tubing, the inner tubes of 12 mm. O.D.* tubing and the outer tubes of 22 mm. O.D. tubing. The inlets and outlets were 8 mm. O.D. soft glass tubing. (A somewhat larger size tubing should be used for the inner tubes if the secondary voltage of the transformer is less than 8000 volts.) Any conventional ring type seal may be used to seal the inner tube to the outer, since the only function of the part above the seal is to provide some means of support for the copper wire leading to the transformer. Although the extension shown in Fig. IV is the same size diameter as the outer tubing, with a length of 3 mm. O.D. Pyrex tubing in a No. 2 one-hole rubber

---

* outside diameter

stopper used to support the copper wire, the extension may be any size consistent with the amount of insulation of the wire and with the type of seal used. The seal should be as close to the inlet as possible so that maximum electrode area may be obtained.

The container which holds the ozonizer tubes was constructed of 74 mm. O.D. Pyrex tubing, 21 cm. in length and slightly flared at the top. (A 600 ml. Berzelius beaker is quite adequate for this purpose, but permits a smaller electrode area.) The three ozonizer tubes were held in place by a support on the bottom of this container, cut to size from a piece of clay plate and containing three holes slightly smaller than the diameter of the outer ozonizer tubes. (If a non-corrosive material is to be used as the outer electrode, this support may be conveniently constructed from a large rubber stopper.) The support at the top was made of thin, plywood, cut to fit the flared top of the container, with openings to permit passage of both the outer tubes and outlets, and arranged so as to be coincident with the holes on the bottom support. An opening in the top support provided for the passage of the copper wire leading from the transformer to the solution in the container that served as the outer electrode.

When the ozonizer tubes were in place, the top support was firmly fastened to the Pyrex container by means of rubber tape which was then covered with friction tape to guard against attack of ozone. The tubes were constructed by means of Tygon tubing; both Pyrex container and inner tubes were filled with 7.7 M zinc chloride solution and copper wires leading from the secondary of the transformer were permitted to dip into the electrode solutions. (The inner electrode may also be mercury or any type of electrolytic conductor which will not freeze at the temperature of the cooling bath.) The ozonizer was then placed in a large Dewar vessel containing a suitable cooling bath, supported at the top by a medium-size cork ring. The cork ring was fitted with an opening to permit addition of solid carbon dioxide if the temperature of the bath became too high, and with another opening to permit passage of a low-temperature thermometer to check on the temperature of the bath.

The transformer used was a war surplus Navy transformer, capable of 10,800 volts at 115 volts primary and rated at 0.095 amps on the secondary. (A lower voltage may be used if the distance between electrodes is decreased accordingly; with the distance described above, however, no discharge took place at secondary voltages less than 8000 volts.) A "Powerstat" was used to regulate the voltage and the lines leading from the "Powerstat" to the primary of the transformer were fused at 2 amps. The fact that these fuses were quite adequate indicates that the amount of current drawn by the ozonizer must have been less than 0.02 amps. This ozonizer, while taking up no more space than the Dewar vessel used for cooling purposes, consistently produced between 7.5 and 8 per-cent, by weight, of ozone at a temperature of -40°C and a 60 cycle secondary voltage of about 10,500 volts. The method used to determine the concentration was the same as that used to determine the ozone output of the T-12 "Ozonator."

Tank oxygen, carefully dried by passage through the previously mentioned drying and purification train, was passed through the apparatus at a flow rate of 5 to 6 liters per hour, as indicated by the "Wet Test Meter." Lower percentage conversion was obtained at faster flow rates. Since the production of ozone is enhanced by high pressures, a somewhat greater conversion was obtained by creating a pressure differential across the ozonizer by placing an adjustable clamp on the tubing leading from the ozonizer outlet. (This pressure dependence is clearly indicated by an application of the principle of Le Chatelier to the equation $3O_2 = 2O_3$.)

Chemical and Biological Effects of Ozone

Ozone is one of the most powerful oxidants known, and its use does not entail the removal of contaminating reduction products which so often accompany the use of other oxidants. For this reason, it has found increasingly greater popularity in oxidation studies. However, the very attributes which make it desirable cause it to be a rather dangerous and somewhat aggravating tool.

Because of its great reactivity, ozone is also a very toxic substance, and concentrations in excess of 0.15 to 1.0 part per million of air are extremely harmful to the human body. For this reason, all reactions were carried out in an efficient hood so that no ozone was permitted to enter the laboratory proper. The ozone outlet of the T-12 "Ozonator" led directly into the hood through a small hole in the side of the hood; the entire assembly of the laboratory ozonizer was placed and was operated in this hood.

To further insure an ozone-free atmosphere in the laboratory proper, the effluent gases from the reaction vessel were passed through several ozone destroyer tubes before being permitted to enter the atmosphere of the hood. Several good ozone destroyers were used at various times throughout this study; solid manganese dioxide, or a suspension of manganese dioxide in water, was found to be a good ozone destroyer. (The action is presumably catalytic, but a purple color was imparted to the suspension of manganese dioxide in water after several hours of ozone passage; this would seem to indicate oxidation of manganese dioxide to the permanganate.) Calcium oxide was also used at times, but the most satisfactory method of destroying ozone and the one used throughout the major portion of this study consisted of passing the effluent gases through two 30-inch towers of concentrated sodium hydroxide (or potassium hydroxide) solution connected in series, and then into a bubbling tower of potassium iodide solution as a final indication of complete ozone decomposition. Since ozone reacts quantitatively with potassium iodide, this last tower served admirably as an indicator of ozone destruction as well as an additional destroyer of the ozone.

Ozone reacts quantitatively with the double bonds in unsaturated organic compounds; therefore, any rubber exposed to ozone-containing oxygen is quickly attacked. For this reason, it was found necessary to replace all rubber tubing and rubber stoppers in any equipment inside (or immediately adjacent to) the hood. (This is an additional reason for destroying all of the ozone before permitting the effluent gases to enter the atmosphere of the laboratory.) Tygon tubing was found to be quite resistant to attack by ozone, and was therefore used for all connections. Ground glass stoppered vessels, lubricated by ozone-resistant lubricants, were used throughout all operations. Silicone stop cock grease, manufactured by Dow, was found to be an excellent ozone-resistant lubricant.

Ozonization of the Alkali and Alkaline Earth Metal Hydroxides

As has already been mentioned, one purpose of this study was to repeat, insofar as possible, the previous experimental work of earlier investigators. Ozone-containing oxygen was passed through columns of the solid hydroxides of lithium, sodium, potassium, cesium, magnesium, calcium, and barium; the oxides of magnesium and calcium were already powder-like, but all of the other hydroxides were pulverized by means of an agate mortar and pestle in a moisture-free atmosphere. (Rubidium hydroxide was not used in this study; it was felt that its behavior should be quite similar to that of potassium and cesium, and little more would be gained from the investigation of rubidium "ozonate".)

The hydroxides of the alkali and alkaline earth metals are hygroscopic, those of sodium, potassium, rubidium, and cesium being particularly so. For this reason, the hydroxides of these metals were pulverized within an air-tight "dry box" which contained phosphorus pentoxide and magnesium perchlorate as drying agents, and which was fitted with two rubber gloves sealed to openings in the sides of the box by which manual operations inside the box could be completed; an electric light inside the box provided the necessary light for manipulations. This "dry box" was also equipped with an inlet and outlet for passage of dry nitrogen or some other unreactive gas in order to maintain an inert atmosphere inside the box. In addition to using the "dry box" for pulverizing the hydroxides, all operations involving the handling of any of the samples, such as transferring samples, removing products, preparing samples for magnetic or gasometric analyses, etc., were carried out in the moisture-free atmosphere inside.

The cells used for the ozonization of the solid hydroxides were of two different types, depending on the intended purpose (Fig. III). The cell in which hydroxide pellets or flakes were ozonated consisted merely of a fairly large diameter tube (25 to 20 mm. O.D.) of Pyrex brand glass, fitted at one end with a 29/42 or 24/40 ground glass male joint and sealed at the other end to a length of capillary bore (1 to 2 mm. I.D.*) Pyrex tubing that was bent upwards in

---

*inside diameter

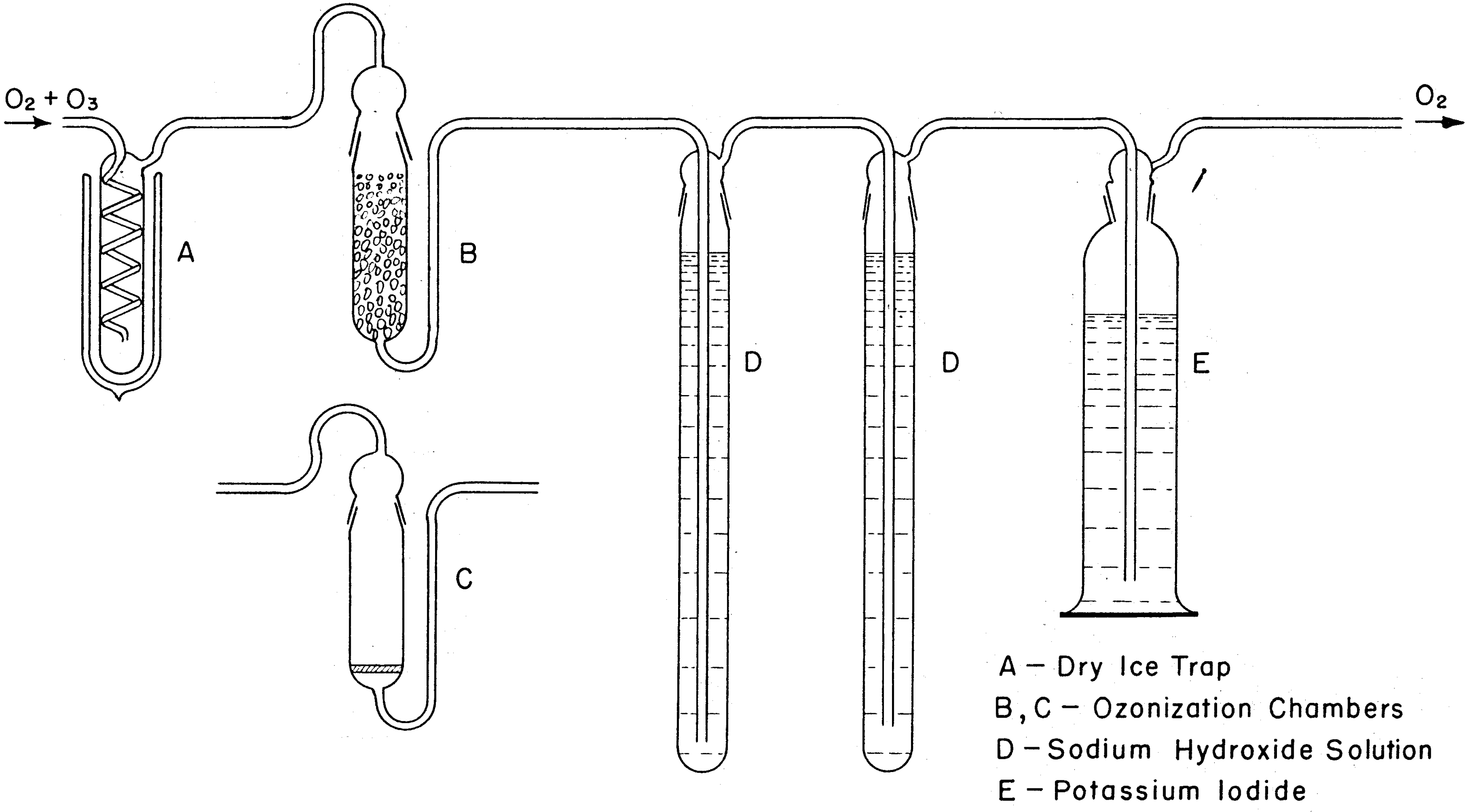


Figure III Ozonization Apparatus with Ozone Destroying Train.

a U-shape (B of Fig. III). To the male joint on this tube was fitted a cap consisting of a ground glass female joint of the size and taper corresponding to the male joint, and sealed to a short length of 8 mm. O.D. Pyrex tubing. With this apparatus it was possible to have the ozone-containing oxygen pass through the hydroxide pellets or flakes from either the top or bottom of the column. The shape of this ozonization vessel was so designed in order that ozonizations in a bath of any desired temperature could be performed. In all cases, glass wool was placed at the bottom and top of the hydroxide column in order to prevent clogging of the gas inlet or outlet.

This type of ozonization vessel was also used for ozonization of the pulverized hydroxides. When used for this purpose, it was found to be expedient to have the afore-mentioned glass wool traps so that the hydroxides could not be carried mechanically from the cell by the issuing gases. Ozonization of pulverized hydroxides in such a vessel was found to acquire the problem of "channeling" when the flow of ozone-containing oxygen was in the direction of gravity, i.e., from the top to the bottom of the column. The incoming gases picked certain "channels" of least resistance in going through the powder column, and many areas were not able to come in contact with the ozone. This difficulty was partially overcome by periodically reversing the gas flow and permitting the gases to go up through the column from bottom to top. This method overcame the difficulty of "channeling", but presented the additional problem of mechanically carrying of the hydroxide from the cell by the effluent gases unless the glass wool plug was of sufficient size to trap the hydroxide.

Another type of vessel used in ozonating pulverized material is shown in C of Fig. III. The construction of this vessel was quite similar to the one mentioned above; however, this cell was fitted with a coarse fritted glass filter at the bottom of the cell which was of sufficient porosity to permit the rapid passage of the issuing gases. The problem of "channeling" was also encountered with this cell but to a lesser extent than in the other; the method of reversing the flow of ozone-containing oxygen was not feasible with this cell because of the catalytic decomposition of the ozone by the sharp edges of the sintered glass filter. However, the flow was often reversed in order to destroy the "channels" created by the gases in flowing in the direction of gravity. This type of vessel was used primarily in the phase involving the extraction of the "ozonates" with liquid ammonia, and its use will be more fully described in a later section.

Ozone-containing oxygen was found to color the hydrated hydroxides of sodium, potassium, and cesium at room temperature as well as at temperatures as low as -50 to -60°C. Sodium hydroxide was colored yellow, with occasional patches of orange; potassium hydroxide was colored a deep orange; and cesium hydroxide was colored a dark orange-red or deep red, depending upon the degree of hydration of the hydroxide and extent of ozonization. Barium hydroxide hydrate was colored a pale yellow-pink under the same conditions, but the hydroxide of lithium, calcium and magnesium apparently remained uncolored by the ozone, even though they decomposed the ozone into oxygen. Magnesium oxide and calcium oxide were impervious to attack by ozone.

The effect of water on the reaction was quite pronounced. All of the hydroxides that were colored by ozone were first utilized in hydrated form. Sodium hydroxide, both in pellet and flake form, was found to contain between 5 and 10 percent water, by weight, presumably in the form of the monohydrate. The potassium hydroxide which was originally used was found to contain between 15 and 20 weight percent water, and the cesium hydroxide was present entirely as the monohydrate, containing between 10 and 15 percent, by weight, of water. The hydrated hydroxides were even more readily attacked by ozone than the anhydrous hydroxides. In fact, the dehydrated barium hydroxide was not colored by the ozone stream at room temperature; only the hydrated form was affected. The water of hydration was apparently released during the reactions of the various hydroxide hydrates with ozone. In all cases where the hydrated materials were used, drops of water appeared along the walls of the vessel nearest the points of greatest color. That this moisture must have come from the starting material was shown by removing all other possible sources of moisture, e.g., the Dry Ice trap removed all moisture coming from the "Ozonator". When the dehydrated hydroxides were used as starting materials, the droplets of water were not in evidence. This fact would lend weight to the theory that the moisture was due to water of hydration being liberated during the course of the reaction. Barium hydroxide octahydrate was dehydrated by the ozone-containing oxygen during the course of the reaction; this was indicated by a change from a crystalline form to a powder.

Although hydration did not appear to unfavorably influence the course of the reaction, excessive moisture caused the resulting potassium and cesium "ozonates" to be quite unstable, with the result that their colorations soon vanished after the source of ozone was removed; sodium hydroxide "ozonate", on the other hand, appeared to be comparatively stable even in the presence of a considerable amount of moisture. However, when strictly anhydrous conditions were maintained by passing the ozone-containing oxygen through a column of magnesium perchlorate before permitting it to reach the hydrated hydroxides, no reaction took place, or at least it took place so slowly as to be unobservable. This experiment was repeated several times, using the hydroxides of sodium, potassium and cesium, and in every case the complete drying of the ozone stream resulted in a lack of coloration of the hydroxides. In order to establish that this lack of coloration was not due to the decomposition of the ozone by magnesium perchlorate, the issuing gases were passed over a moist sample of the corresponding hydroxide, or into a solution of potassium iodide, after leaving the ozonization vessel; that these effluent gases contained ozone was definitely indicated by the coloration of the moist hydroxide or by liberation of iodine from the potassium iodide solution, depending upon the test used. These observations can only be explained on the assumption that a trace of moisture is necessary to catalyze the reaction between ozone and the hydroxide hydrates of sodium, potassium, and cesium. No reaction was noted when particular care was taken to exclude moisture, particularly when the hydroxide was "sandwiched" between layers of magnesium perchlorate, even after a period of ozonization time of 4 to 5 hours.

The stability of the hydrated alkali metal "ozonates" was found to decrease, surprisingly enough, in the order sodium, cesium, potassium. The color of the potassium "ozonate" was found to disappear within a few hours after ozonization at room temperature, even when kept in a closed vessel, leaving only a pale yellow color after 4 to 12 hours, and this color also disappeared after two or three days. The orange-red color of ozonated cesium hydroxide monohydrate disappeared within a few days of standing at room temperature, leaving only a yellow-orange color. The corresponding sodium compound, on the other hand, remained apparently unchanged for a period of at least a year and a half; ozonated sodium hydroxide which had been standing at room temperature in a closed vessel for 18 months showed no apparent loss in color over that period of time. The decomposition of the cesium and potassium compounds was retarded by lower temperatures.

The rate at which ozonization of the anhydrous hydroxides proceeded was quite different from the rate at which the reaction of ozone with the hydrated materials took place. As has been mentioned earlier, the hydrated hydroxides of sodium, potassium, and cesium were colored almost immediately by a stream of ozone-containing oxygen, provided that the incoming gases were not first passed through a dehydrating agent such as magnesium perchlorate. Barium hydroxide octahydrate was colored faintly under these conditions, although not so rapidly. The dehydrated materials, on the other hand, reacted with ozone at a much slower rate; in fact, anhydrous barium hydroxide gave no evidence of chemical reaction when the ozone-containing stream was passed through it. Dehydrated sodium hydroxide was colored only faintly by the ozone after an exposure of five hours. Potassium hydroxide, after dehydration in a stream of dry nitrogen at 300°C*, was colored slowly but to a lesser extent than the hydrated material. Cesium hydroxide, after being heated in a nickel crucible in an inert atmosphere at 450°C and then pulverized, was colored quite rapidly by the ozone, but at a perceptibly slower rate than was the monohydrate. These observations lend added weight to the postulate that the ozonization reaction is catalyzed by water.

---

*The hydroxides of sodium, potassium, and cesium were dehydrated in a muffle furnace at 250°, 300°, and 450°C, respectively. Continued passage of dry nitrogen during the dehydration process prevented both absorption of atmospheric carbon dioxide as well as attack of the containing vessel by air. A nickel crucible was used to contain the hydroxides, although it was attacked to some extent. Cesium hydroxide, although heated in the inert atmosphere, attacked Pyrex glass and silver at 400-500°C to such an extent that these materials could not be used for containers.

An excessive amount of moisture proved to be as detrimental to the production of alkali metal "ozonates" as was the complete absence of water. Although the sodium compound did not readily lose its color in the presence of a slight excess of moisture, a large excess decolorized it quite rapidly; the corresponding potassium and cesium compounds decomposed rather quickly in the presence of even a slight excess of water. The extent to which the reverse approach, i.e., ozonization of concentrated hydroxide solutions, took place was quite different, however. Highly concentrated (12M) solutions of cesium and potassium were colored yellow by ozone-containing oxygen at temperatures of -40 to -50°C, but sodium hydroxide solutions containing 20 per cent solute remained uncolored at even lower temperatures.* 12M potassium hydroxide solutions were colored yellow by the ozone-containing stream at temperatures as high as -35°C, but the corresponding cesium solutions were not colored until a temperature of -51.5°C was reached. The color of these solutions disappeared when the temperature was permitted to rise above these values; when the temperature was maintained below these values, the color of the solutions persisted for 20 to 30 minutes after removal of the source of ozone. In every case, the coloration was preceded by a partial

---

*Pickering[22] has reported the lowest eutectic temperature of a sodium hydroxide-water system as being -32°C at a concentration of 20 per cent sodium hydroxide. However, a 20 per cent solution of sodium hydroxide was made to exist as low as -60°C, without freezing, by cooling the solution gradually while ozone-containing oxygen was passed into the solution.

crystallization of the solute out of the solution as a result of the decreased solubility at these low temperatures. This indicates that the coloration may possibly have been due to a reaction between ozone and the suspended (solid) particles. Quantitative magnetic studies of these phenomena were made, and will be described in the section dealing with the quantitative aspects of this problem.

The effect of temperature on both the formation and decomposition of the "ozonates" was found to be quite consistent with the expected kinetic aspects of the problem. All of the alkali metal "ozonates" decomposed at higher temperatures, with the decomposition temperature increasing roughly in the same order as the atomic weight of the metal. In other words, the cesium compound was only slowly decomposed with evolution of oxygen at the temperature of boiling water, whereas the sodium compound decomposed much faster at this temperature. The formation of the "ozonates" appeared to go faster at room temperature than at lower temperatures, even though the color disappeared faster when the ozone source was removed. At temperatures below -70°C, the reaction was so slow as to be almost unobservable, but very little decomposition was noted in the compounds that were formed at these temperatures. This must mean that the formation and decomposition of the "ozonates" are competing reactions, the extent or velocity of each being determined to a large extent by the temperature at which the reaction was permitted to proceed.

Chemical Reactions of the "Ozonates"

The ozonated hydroxides of sodium, potassium, cesium and barium showed very little chemical activity; their chemical activity appeared to be confined largely to decomposition reactions or to reactions involving the unreacted hydroxides. They did not react with pyridine, carbon tetrachloride, benzene, or dioxane; a color reaction between nitrobenzene and sodium "ozonate" was proved to be merely the reaction between nitrobenzene and sodium hydroxide. Similarly, a color reaction with ethyl alcohol proved to be due to aldol condensation with aldehyde impurities in the alcohol. The "ozonates" decomposed with evolution of oxygen when heated to high temperatures or when added to water or acid, the rate of decomposition in water being inversely proportional to the solubility of the hydroxide, i.e., the sodium compound decomposed the slowest of all, and the cesium "ozonate" decomposed the most rapidly. (The glowing splint test was used to detect the liberated oxygen; tests with starch-iodide paper showed that the liberated gases did not contain ozone.) The reaction with acidified potassium iodide solution differed with the different "ozonates"; cesium hydroxide monohydrate which had been ozonated at room temperature liberated a small amount of free iodine when added to acidified potassium iodide solution, but a somewhat larger amount of iodine was obtained when the test was run on cesium hydroxide which had been ozonated at about -30° to -40°C, and an even smaller amount of iodine was formed when the test was run on cesium "ozonate" which had been prepared at 60°C. In each case, the "ozonate" was washed well with dry oxygen in order to make certain that no residual ozone remained. Potassium hydroxide which had been treated with ozone-containing oxygen at room temperature liberated a very small, barely perceptible, amount of iodine under the same conditions; in fact the iodine liberated was detected only by comparing the resultant color with the color of a blank consisting of an equivalent amount of non-ozonated potassium hydroxide in an identical amount of acidified potassium iodide solution. (A similar blank was used in every case where the amount of iodine liberated was small.) Potassium hydroxide which had been ozonated at about -50°C liberated a considerably larger amount of iodine, but sodium "ozonate" failed completely to oxidize acidified potassium iodide; this observation was repeated with different samples on at least twenty occasions in order to definitely establish this fact. Only a very faint trace of iodine was noted after addition to acidified potassium iodide solution of sodium hydroxide which had been exposed to ozone-containing oxygen at -50° to -60°C. (In every case, the resulting solution was tested with litmus paper to make certain that the solution was acidic.) Sodium "ozonate" which had apparently remained stable for at least a year and a half liberated no iodine from acidified potassium iodide solution.

In almost every instance where the action of the ozonated hydroxides on acidified potassium iodide solution was investigated, a specific test for peroxide was conducted on another portion of the sample. At no time was a positive peroxide test observed on samples of sodium hydroxide "ozonate", either on samples which had stood for over a year at room temperature or on freshly prepared samples. Partially hydrated potassium hydroxide which had been ozonated at room temperature gave a negative peroxide test immediately after preparation; the potassium compound decolorized so rapidly upon standing, however, that the results of peroxide tests were not considered representative. Ozonated cesium hydroxide monohydrate gave a negative peroxide test after standing for a week, as well as immediately after preparation. (Somewhat different behavior was noted in the liquid ammonia extraction studies; these observations are described in the following section.)

Again, as was the case with the iodide tests, these observations were repeated well over twenty times, using two different peroxide tests, in order to definitely establish the absence of peroxide. That the tests themselves were not in error was established by adding one or two small granules of sodium peroxide to the solutions which remained after running the peroxide tests on the "ozonates"; in every case, this tiny amount of peroxide was sufficient to produce the positive color tests that a very large sample of "ozonate" could not produce. (The resulting solutions were always tested with litmus because the tests will not work on alkaline or neutral solutions.)

Two specific tests for peroxides were used throughout this study; (1) the perchromic acid test, capable of detecting 0.2 mg. of peroxide in concentrations of about 0.001 per cent,[23] consisted of dissolving the "ozonate" in an excess of ice-cold sulfuric acid, adding one drop of 5 to 10 per cent potassium chromate solution and adding ether to extract any perchromic acid* that might be formed, and (2) the pertitanic acid test, capable of detecting one part of peroxide in 1,800,000,[23] involved merely the addition of a small amount of a solution of titanium(IV) sulfate** in dilute sulfuric acid to a cold solution of the "ozonate" in an excess of dilute sulfuric acid. The perchromic acid ether solution has a blue color which is visible in dilutions of 1 in 40,000[24]; however, the perchromic acid is quite unstable and decomposes quickly in aqueous solution, whereas the pertitanic acid is a yellow-orange compound which is insoluble in ether but is much more stable in aqueous solution than is the perchromic acid. Both tests are specific for peroxide since they involve the replacing of an oxygen atom in the respective acids by a peroxide group[25], rather than any increase in oxidation state of the metal.

---

*The formula for perchromic acid is uncertain, but the most commonly accepted formula is H_2CrO_5.[24]

**Prepared by fusing titanium(IV) oxide with potassium pyrosulfate and dissolving the melt in cold sulfuric acid.

Since no peroxide was formed when the freshly prepared "ozonates" were dissolved in cold, dilute sulfuric acid, the hypothesis of Baeyer and Villiger[2], that the direct products of ozonization of alkali metal hydroxides are superoxides, is open to question. Furthermore, samples of sodium "ozonate" which had stood in tightly stoppered vessels at room temperature for over a year did not give positive peroxide tests; therefore, these substances could not have rearranged (or decomposed), on standing at room temperature, to sodium superoxide. The negative peroxide tests observed on samples of ozonated potassium and cesium hydroxides which had stood at room temperature for several days indicate that any superoxide must have been present in very minute amounts, since one or two small granules of sodium peroxide is sufficient to give a yellow coloration with a solution of titanium(IV) sulfate in dilute sulfuric acid.

Comparing the results of the pertitanic acid (and perchromic acid) tests and the acidified potassium iodide tests, one is immediately struck by the fact that the ozonated hydroxides of cesium and potassium contain a compound which is of sufficient strength to oxidize hydriodic acid, but which is neither peroxide nor superoxide. Some additional information was derived from the already mentioned experimental observations that ozone-treated sodium hydroxide evolved molecular oxygen upon decomposition, but did not oxidize hydriodic acid and gave negative peroxide tests; although potassium and cesium "ozonates" which had been prepared at room temperature liberated small quantities of iodine under the same conditions, low temperature ozonization of these hydroxides produced compounds which appeared to be richer in a substance which oxidized iodide ion. In addition to these observations, it was found that the solutions which remained after dissolving ozonated cesium and potassium hydroxides in water or acid solution were themselves capable of oxidizing acidified potassium iodide solution, even though the corresponding sodium solutions did not show this type of behavior. Solutions of the freshly prepared ozonates, when tested immediately after the solute had dissolved, did not contain hydrogen peroxide. When the residue remaining after several repeated ozonizations and liquid ammonia extractions of partially dehydrated cesium hydroxide "ozonate", covering a period of about five days, was dissolved in water and tested with a solution of titanium(IV) sulfate in sulfuric acid, traces of hydrogen peroxide were indicated (cf. following section).

These observations can best be explained on the assumption that at least two different compounds are formed as a result of the action of ozone of the alkali metal hydroxides, one of which evolves molecular oxygen upon decomposition but which does not liberate iodine from acidified potassium iodide solution, and the other which does oxidize iodide ion. These observations also indicate that the compound which liberates iodine from hydriodic acid is formed in larger amounts at lower temperatures. Furthermore, the oxidizing power of the solutions remaining after addition of cesium or potassium "ozonates" to water or acid solution seems to indicate that the compound which has the power to oxidize iodide ion is somewhat stable in solution. Quantitative experiments to determine the nature of these compounds were conducted and will be described in a later section.

Solubility of the "Ozonates"

Inasmuch as the reaction between ozone and the alkali metal hydroxides is a surface phenomenon, the only hope for obtaining reasonably pure compounds was to find a solvent which would either (1) extract the colored product but not the unreacted portions of the ozonated mixture, or (2) dissolve the unreacted portions of the mixture and leave behind the colored products. It was hoped that perhaps alcohol would serve in the latter capacity, but it was found that, although sodium "ozonate" did not decompose nor dissolve in anhydrous ethyl alcohol, the extent to which the unreacted hydroxide dissolved was not sufficient to render this method a feasible one. Furthermore, the various "ozonates" were found to be insoluble in anhydrous pyridine, dioxane, carbon tetrachloride, benzene, and ethyl ether. When ozone-treated sodium hydroxide which had been prepared at room temperature was added to liquid ammonia, no color was extracted. However, when liquid ammonia was added to a sample of ozone-treated potassium hydroxide which had been freshly prepared at room temperature, a definite orange-red coloration was imparted to the liquid ammonia, thus indicating either a reaction of ammonia with the "ozonate" or extraction of part of the colored portion by the ammonia. When this red solution was filtered from the insoluble material* and evaporated to dryness, a red crystalline solid was obtained. This was apparently the same product reported by Kazarnovskii, Nikolskii, and Abletsova[14] as having the formula KO_3. Addition of acidified potassium iodide solution to this solid resulted in the liberation of a considerable amount of free iodine; when a portion of this sample was added to cold dilute sulfuric acid and 1 ml. of a solution of titanium(IV) sulfate in sulfuric acid added, no coloration was observed. This indicated that the red product did not contain potassium superoxide or potassium peroxide immediately after preparation. It decomposed rapidly with liberation of oxygen in the presence of water or acid, and the resulting acidic solution was found to contain a substance which oxidized hydriodic acid to free iodine. These observations agreed with those reported earlier in this study on the ozonated mixtures.

In order to establish whether or not the red solution was due to the reaction between ammonia and any residual ozone that

---

*The extraction studies were carried out in an apparatus such as is shown in Fig. V. A detailed description of the techniques involved is included in the section dealing with the quantitative aspects of the problem.

may have remained on the ozonated hydroxide, a stream of ozone-containing oxygen was bubbled through liquid ammonia at -70°C. The liquid ammonia was soon colored a bright orange-red by the ozone, but the color soon disappeared when the temperature was permitted to rise above -55°C. The red solution resulting from extraction of potassium "ozonate" with liquid ammonia, on the other hand, retained its color throughout the entire process of evaporation (-33°C). This indicates that the two solutions were not the same. Furthermore, evaporation to dryness of the ozonated ammonia produced a white substance which gave a positive "brown ring" test for nitrate ion and which proved to be primarily ammonium nitrate. This observation agrees with the observations of Manchot[12] and of Strecker and Thieneman[11]. One must conclude, then, that the red solid was extracted from the "ozonate" by the liquid ammonia and was presumably the potassium "ozonide" reported by Kazarnovskii, Nikolskii, and Abletsova[14]. A rather rough quantitative determination on this red solid, which appears to confirm their hypotheses, will be described in the section on the quantitative aspects of the problem.

The solid material remaining on the sintered glass filter after extraction of the potassium compound with liquid ammonia was not uncolored. The extraction process was continued until the ammonia came through the filter uncolored, i.e., until the extraction was apparently complete; the non-extractable material remaining on the filter was colored a faint yellow-orange. Addition of this residue to acidified potassium iodide solution resulted in the liberation of a trace of iodine, but a perchromic acid test failed to indicate the presence of superoxide or peroxide. This material was then placed in a closed vessel and was permitted to stand at room temperature for about two weeks. Portions were withdrawn periodically and tested for oxidizing power and for peroxide. In every case tested, the sample liberated iodine from acidified potassium iodide solution, but in no case was a positive peroxide test observed; this includes the test made on a rather large portion which had stood for two weeks; therefore, any amount of superoxide present must have been extremely small.* These observations appear to substantiate the suggestion made earlier that at least two products are formed when alkali metal hydroxides are submitted to attack by ozone-containing oxygen. At any rate, the yellow-orange coloration of the residue reamining on the filter can best be explained on the assumption that both a liquid-ammonia-soluble and a liquid-ammonia-insoluble compound are formed during the ozonization process. If two such substances do exist, the nature of the liquid-ammonia-soluble compound is presumably that reported by Kazarnovskii, Nikolskii, and Abletsova[14]; the nature of any other products must be determined by quantitative experimentation.

---

*Kazarnovskii, Nikolskii, and Abletsova[14] reported that the liquid-ammonia-extractable material decomposed to potassium superoxide completely in eleven days.

In order to further establish the existence of at least two products of ozonization, reactions were carried out at various temperatures in the hope that the relative amounts of the products formed might be a function of the reaction temperature. When the potassium hydroxide was ozonated at room temperature, a relatively small amount of red material was extracted by the liquid ammonia; when the ozonization was carried out at -30°C, however, a much greater amount of extractable product was formed. Although the observation was only qualitative, it seemed to bear out the contention that the formation of the liquid-ammonia-extractable substance was a function of the reaction temperature. At temperatures below -65°C, the reaction proceeded so slowly that it was impractical to attempt extraction studies at these temperatures. Nevertheless, the observations which were noted when extraction studies were made on sodium and cesium "ozonates" substantiated the findings made during the study of the potassium compound.

When pulverized sodium hydroxide was ozonated at room temperature, a yellow color developed,* but when liquid ammonia was condensed on top the "ozonate" and filtered, no coloration

---

*As was mentioned earlier, the reaction between ozone and anhydrous sodium hydroxide proceeded to such a small extent that the production of sodium "ozonate" from the dehydrated material was impractical. In the extraction studies as well as in the quantitative determinations of sodium "ozonate", it was found expedient to use sodium hydroxide which contained 5 to 10 per cent H_2O of hydration.

in the liquid ammonia was noted. When the reaction was carried out at -40°C and extraction attempts were made, the liquid ammonia filtrate was colored a very faint yellow. Evaporation of this yellow solution to dryness produced a very small amount of yellow solid, scarcely enough to use for quantitative determinations, but enough to show the temperature dependence of the liquid-ammonia-extractable product. The residue on the sintered glass filter was colored quite yellow and reacted in the same manner as the ozonated mixtures which had been prepared at room temperature. No colored product was extractable by the liquid ammonia from the sodium "ozonates" which had been prepared at room temperature and which had been standing for several months.

Liquid-ammonia-extraction studies made on the cesium "ozonate" were more successful than were those made on the corresponding sodium and potassium compounds. Extraction with liquid ammonia of the cesium "ozonate" which had been prepared at room temperature, followed by filtration, produced a relatively large quantity of red solution; upon evaporation of this solution to dryness, a red crystalline solid, similar in appearance to that obtained from the potassium "ozonate", was obtained. At the same time, the color of the residue on the filter seemed to indicate that a larger percentage of the "ozonate" had been extracted by the ammonia than was the case with the potassium compound. No apparent increase was noted in the amount of extractable material obtained from cesium "ozonates" which had been prepared at 0° and at -30°C, respectively; however, when the ozonization was carried out at 60°C, no color was noted in the liquid ammonia extract, although the material remaining on the filter was colored a deep orange-red. The chemical behavior of both extracted material and residue agreed with that found for the corresponding potassium compounds when only a single ozonization had been performed; however, when a series of ozonizations and extractions was carried out on a sample of cesium hydroxide (covering a period of five days), the residue gave positive peroxide tests.

As was the case with the ozonated mixtures, the role of water in these extraction studies was quite important. The absence of any reaction between ozone and the alkali metal hydroxides under strictly anhydrous conditions has already been mentioned; it was necessary, therefore, to avoid complete exclusion of water during the ozonizations. On the other hand, if the extent of hydration was too great, part of the water liberated during the reaction was carried over by the liquid ammonia solution and, when the ammonia evaporated, no solid product was obtained. This was particularly true in the case of the cesium hydroxide, which was completely in the form of the monohydrate. This difficulty was overcome by partially dehydrating the cesium hydroxide monohydrate and then using a relatively high (2 to 3 cm.) column of starting material. Under these circumstances the water liberated during the course of the reaction was absorbed by the anhydrous hydroxide in the lower portion of the column to form a stable hydrate, and was not available for extraction by the liquid ammonia. In other words, the hydroxide column served also as an absorbent for the moisture produced in the reaction. This method seemed to work quite well, and dry products were obtained by utilizing these principles, provided that the remainder of the apparatus was dry.

The red solid material obtained from the liquid ammonia extraction of cesium hydroxide "ozonate" was quite stable at room temperature, in the absence of moisture. No apparent decomposition took place when it was kept in an air-tight vessel for seven days. When added to acidified potassium iodide solution immediately after preparation, as well as after standing for seven days, large amounts of iodine were liberated. When added to cold dilute acid, oxygen was liberated, and the resulting solution retained sufficient oxidizing power to oxidize iodide ion to free iodine. When the freshly prepared product was tested with cold titanium(IV) sulfate solution in dilute sulfuric acid, no coloration was observed; after standing in a closed vessel at room temperature for seven days, it still gave a negative peroxide test. However, when the red solid was heated to 100-150^{o}C in an oil bath for two to three hours, the red color disappeared and, although most of the remaining product was white, a portion of the red product decomposed to a yellow substance. When tested with titanium(IV) sulfate solution in dilute sulfuric acid, this yellow product gave a positive peroxide test. It must be emphasized that the major portion of the red solid decomposed at 100°C to a white product, while only a relatively small portion of the red solid decomposed to the yellow compound. This latter substance gave no evidence of decomposition when heated for about two hours at 170°C. This observation and the positive pertitanic acid test are those which would be expected if the yellow material were cesium superoxide.* The white decomposition product was assumed to have been hydroxide although no specific analysis for substantiating this assumption was performed. One would expect the final decomposition product of a higher oxide of cesium, in the absence of water, to be cesium monoxide;** however, a trace of moisture may have been present, so that the hydroxide rather than the monoxide may have been formed.

If the assumption that the yellow decomposition product of the red solid is cesium superoxide is correct - and the experimental observations seem to bear out this contention - the behavior of at least a portion of the red solid is analogous to that reported for the corresponding potassium compound

---

* Cesium superoxide melts at 432°C; the dissociation temperature (p = 1 atm.) is reported as being 1265°C[26].

** Cesium monoxide is described in the literature[27] as being an orange-red solid.

by Kazarnovskii, Nikolskii, and Abletsova[14]. If the two compounds are analogous, a portion of the red solid must be a substance having the formula CsO_3 and which decomposes to the superoxide at higher temperatures. The experimental evidence which has previously been mentioned shows that this red solid, however, does not decompose to the superoxide or peroxide when added to water or acid; it presumably passes directly to the hydroxide under such circumstances, without passing through the intermediate oxidation states. The quantitative determinations described in the following sections were designed to determine the validity of the conclusions based on qualitative observations and to arrive at a more definite concept of the nature of these alkali metal "ozonates."

Quantitative Aspects of the Problem

Inasmuch as qualitative observations can, at best, serve only to substantiate the findings of quantitative investigations, the true picture of the nature of any compound must be founded on the results of chemical analyses. The alkali metal "ozonates" are oxygen-liberating substances, therefore quantitative oxygen determinations were deemed to be of utmost importance; since the "ozonates" produce the corresponding hydroxides upon decomposition, a measure of the alkali content was also considered to be expedient. In addition to the oxygen and alkali analyses, the amount of oxidizing power displayed by the "ozonates" should indicate the proportion of the "active" component present. Finally, magnetic measurements of these substances should establish the number of unpaired electrons per molecule, if the compound is paramagnetic, and serve to eliminate from consideration those formulas which do not meet the magnetic requirements.

Two avenues of approach to the quantitative investigation of the "ozonates" were open: (1) the solubility in liquid ammonia of the cesium and potassium compounds pointed the way for a direct analysis of the purified substances, but (2) the insolubility in liquid ammonia of the sodium compound forced the utilization of the more indirect method of analyzing for this compound in a mixture of several chemical species. This latter method was found to be applicable to analyses of all of the ozonated hydroxides, and was so utilized in order to more completely coordinate the results obtained by both types of analyses.

Of the three alkali metal "ozonates" that were investigated, the sodium and cesium compounds were the most thoroughly studied. Little quantitative work was done on ozonated potassium hydroxide because of the rapidity with which the ozonated potassium hydroxide lost its color when not in contact with the ozone stream, thus rendering it less suitable for analysis in the unpurified form. Nevertheless, a few determinations were made on the potassium "ozonate" and these determinations are included in a later section.

Ozonated sodium hydroxide appeared to be, by far, the most stable of the unpurified compounds; hence, this substance was investigated first. Since it could not be purified by solvent extraction, the sodium "ozonate" was investigated completely in the form of a mixture containing the "ozonate", unreacted sodium hydroxide, sodium carbonate, and water of hydration. Two methods for obtaining mixtures with maximum amounts of the "ozonate" were utilized: (1) ozonization of the pulverized hydroxide, with constant agitation of the sample in order to present the maximum amount of surface to the attacking ozone, and (2) ozonization of sodium hydroxide pellets (or flakes), followed by removal of the ozonated surface of the pellets. The latter method, while presenting the problem of dealing with increased carbonate and water content, produced mixtures which contained relatively larger percentages of the oxygen-liberating component. This was presumably due to the fact that the surface of the hydroxide pellets was more vulnerable (than the inner part of the pellets) to attack by not only the ozone during ozonization, but also by atmospheric water and carbon dioxide during handling operations.

Sodium hydroxide pellets were ozonated at room temperature in the vessel shown in Fig. III (C). When ozonization of the surface of the pellets appeared to be as complete as possible, the contents of the ozonization vessel were transferred to another vessel, tightly stoppered, and shaken vigorously. The vigorous shaking jarred loose the ozonated surface from the main body of the pellets; this surface was then separated from the major portion of the material by means of a fine (50 to 60 mesh per sq. in.) seive, and put in a stoppered vessel.* All operations involving handling and transfer of this ozonated surface were carried out in a "dry box" in which the moisture content was kept at a minimum by means of powerful dehydrating agents such as phosphorus pentoxide and magnesium perchlorate. The ozonated hydroxide was then weighed on a Gouy-type magnetic balance[28] in order to determine its magnetic susceptibility and ascertain the presence of any paramagnetic material.

---

*Ground glass stoppered vessels were found to be less suited for storage of the ozonated hydroxides than were vessels equipped for screw-type caps or rubber stoppers, provided that the latter were air-tight, since the ground glass joints showed a great tendency to "freeze" if they were not completely cleaned of alkali.

Determination of Magnetic Susceptibility

When a substance with a magnetic susceptibility different from zero is placed in an inhomogeneous parallel magnetic field, it is subject to a displacing force proportional to its magnetic susceptibility. This displacing force is also a function of the magnetic field intensity and the cross-sectional area of the substance. The Gouy method utilizes an analytical balance to measure this force as a change in weight of the sample when placed in a magnetic field. The sample, in the form of a homogeneous cylinder, is suspended from a balance arm so that one end hangs in the region of maximum strength of the magnetic field and the other end is essentially out of the field. The weight of the sample when it is suspended in the field, subtracted from the weight of the sample in field-free space, gives a measure of the displacing force of the field and, consequently, a measure of the magnetic susceptibility of the sample.

The procedure for determining magnetic susceptibility that was followed throughout this study was as follows: the calibration of the field strength was first accomplished by weighing a known volume of distilled (and deaerated) water, in a weighing tube, both in and out of the magnetic field, then the weight of the same volume of the sample both in and out of the field was determined - in the same weighing tube that was used to calibrate the field strength. The weighing tube was merely a flat-bottomed piece of 8 mm. O.D. Pyrex tubing (larger tubing was used for samples of low "ozonate" content); the tube was about 12 cm. in length with a ground glass female joint on the open end and with an index mark on the side to provide for uniform filling depth. A male joint of the same size and taper fitted into the female joint; it was sealed at the top and fitted with a small glass ring for attaching to a wire suspended from the left hand pan of a semi-micro analytical balance. The weighing tube was suspended so that the flat bottom was exactly in the center of the magnetic field and the index mark was placed 7 cm. from the bottom of the tube (the magnetic field was found to extend radially only about 7 cm. from the center). In order that no error would be introduced by the use of varying amounts of lubricant from time to time, the ground glass joint of the weighing tube was not lubricated. The weighing tube was first cleaned, dried well, and weighed both in and out of the field. It was then filled with water to the 7 cm. mark and weighed both in and out of the field. (Water was used as a calibrating liquid since its susceptibility has been accurately determined by several independent methods.) The difference between the change in weight of the empty tube and the change in weight of the water-filled tube was taken as the change in weight due to the water. The weight of the water was taken as the volume of the tube to the 7 cm. mark, assuming the density of water to be unity. The cross-sectional area of the tube was readily determined from the volume and the height of the index mark. From these data, the magnetic field strength, H, was determined by means of the formula:

$$H^2 = \frac{2\,\Delta w\ (\text{water})}{1.019 \times \text{area} \times (k_w - k_a)}$$

where k_w, the volume susceptibility of water = -0.72×10^{-6}cgsu. and k_a, the volume susceptibility of air = $+0.03 \times 10^{-6}$cgsu. The figure 1.019 is a conversion factor.

The weighing tube was then dried well and filled to the index mark with the sodium "ozonate", particular care being taken to insure a homogeneous sample. The difference between the change in weight (due to the magnetic field) of the sample-filled tube and the change in weight of the empty tube was taken as the change in weight due to the sample. The volume susceptibility, in cgs. units per ml., of the sample was then calculated by means of the equation:

$$(2) \quad k = k_a + \frac{2\Delta w\ (\text{sample})}{1.019 \times \text{area} \times H^2}$$

where H is the (apparent) magnetic field intensity calculated from equation (1) for the particular weighing tube used, and varies with different weighing tubes. By substituting expression (1) for H^2 in expression (2), a simpler expression for the volume susceptibility is obtained:

$$(3) \quad k = k_a + \frac{\Delta w\ (\text{sample})}{\Delta w\ (\text{water})}\ (k_w - k_a)$$

or, substituting the numerical values of k_w and k_a,

$$(4) \quad k = 0.03 - 0.75\ \frac{\Delta w(\text{sample})}{\Delta w(\text{water})} \times 10^{-6}\ \text{cgsu./ml.}$$

The gram susceptibility is readily determined by dividing the volume susceptibility by the apparent desity of the sample, i.e., by the weight of the sample divided by the volume of the tube to the index mark. (Since the apparent density approaches the value of the true density as the packing increases, the sample was packed in the weighing tube as much as possible). The simplified expression for the gram susceptibility can be written:

$$(5)\ \chi_g = 0.03 - 0.75\ \frac{\Delta w(\text{sample})}{\Delta w(\text{water})} \times 10^{-6} \times \frac{\text{vol.}}{\text{wt.}}\ \text{cgsu./g.}$$

Inasmuch as the magnetic field strength and, consequently, the change in weight varies with the square of the current that passes through the coils of the magnet, all magnetic measurements were reduced to an arbitrarily chosen reference value of the current. Measurements taken at any other current reading were first reduced to an arbitrarily chosen "standardized" condition, based on a coil current of 6.30 amperes, by means of the expression:

$$\frac{\Delta w_1}{\Delta w_{6.30}} = \frac{I^2}{(6.30)^2}$$

$$\text{or, (6)}\quad \Delta w_{6.30} = \Delta w_1 \times \frac{(6.30)^2}{I^2}$$

where Δw_1 is the observed change in weight at a coil current of I amperes, and $\Delta w_{6.30}$ is the change in weight at a coil current of 6.30 amperes. It was found that, since the changes of weight observed during a large portion of this study were of the order of a few milligrams, a variation in the coil current of a few hundredths of an ampere was sufficient to appreciably alter the final results; therefore, a Weston Precision Ammeter,* which could be read to 0.01 ampere, was used for current readings throughout all magnetic measurements. Errors due to fluctuations in line voltage and, consequently, in coil current were reduced by taking several current readings during each measurement and recording the average value as the value of the current.

Chemical Analysis of the Sample - Method of Mixtures

The ozonated alkali metal hydroxides used in this study contained, in addition to the "ozonate", varying proporations of unreacted hydroxide, water of hydration, and (except for a few of the cesium samples) alkali metal carbonate. No other compounds were found to be present, therefore the ozonated hydroxides were treated as four-component mixtures. The few cesium samples which were found to contain no carbonate were treated as three-component mixtures. The amounts of "ozonate"** and carbonate were determined gasometrically,

---

*This ammeter is recognized by the U.S. Bureau of Standards as a secondary standard for reading current, a silver coulometer being the only recognized primary standard.

**The amount of "ozonate" was determined gasometrically by the method described later in this section. The description of the analytical procedure in this section is that used for sodium "ozonate", although the same method was also applied to analyses of the cesium and potassium compounds.

the amount of unreacted hydroxide was obtained titrimetrically, and the water content was determined by difference.

After magnetic measurements had been taken on a sample, a portion was transferred (in the "dry box") to a small flat-bottomed glass insert which was of sufficient size to fit into a standard weighing bottle and small enough to fit into the decomposition chamber (B of Fig. IV) used in the gasometric analysis; a small glass hook on the inside of the insert permitted the lowering of the sample-filled insert into the weighing bottle or decomposition chamber by means of a long, hooked wire. This method of transferring the sample was used so that none of the sample would be lost during transfer to the decomposition chamber.

The weight of the sample was then determined, by means of an analytical balance, from the difference of the weight of the sample-insert-weighing bottle system and the weight of the previously weighed insert-weighing bottle system. The sample-filled insert was then transferred (in the "dry box") to the decomposition chamber (B).

Before connecting the decomposition chamber to the main body of the analytical system (Fig. IV), the capillary tubing leading from the decomposant reservoir (C) into the decomposition chamber was filled with the decomposant to a reference mark on the side of the reservoir. The decomposition chamber containing the sample was then attached to the main body of the system, the ground glass joints maintained air-tight by

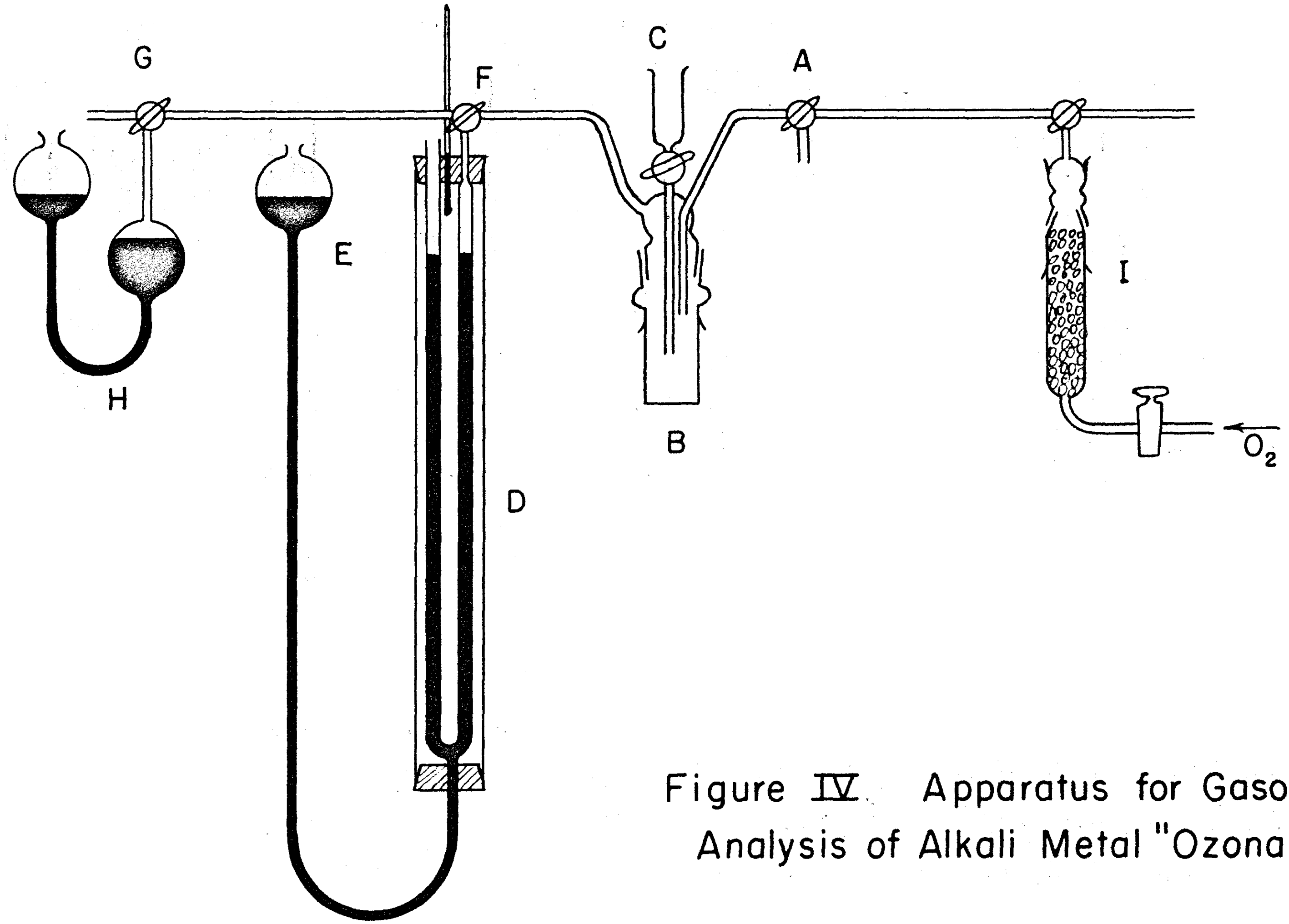


Figure IV. Apparatus for Gasometric Analysis of Alkali Metal "Ozonates" means of silicone lubricant, and held tightly by means of rubber bands. The entire system was then flushed well with dry oxygen from a tank of oxygen that was passed through a column of magnesium perchlorate (I of Fig. IV) and the system then closed by means of stopcocks (A and F). The levels of the two mercury columns in the gas-collecting apparatus (D) were equalized by lowering the mercury reservoir (E) and the reading of the burette taken as the initial volume. A known volume of standardized hydrochloric acid was added to the decomposant reservoir by means of a calibrated pipette; the volume of acid to be used was chosen so that the resulting solution would be acidic.

The hydrochloric acid was then added slowly to the decomposition chamber through the stopcock which separated it from the decomposant reservoir, and at the same time, the levels of the mercury columns were kept equal by lowering the mercury reservoir. When the "ozonate" had completely decomposed, the system was permitted to stand for 20 to 30 minutes so that it would be at room temperature. The liberated gases were mixed well by first forcing the gas in the burette back into the decomposition chamber (by means of the mercury reservoir) and then permitting it to return; this maneuver was repeated for several times in order to insure complete mixing of the gases, which were oxygen, carbon dioxide, and water vapor. The mercury levels were then equalized and the volume of collected gases in the burette recorded as the total volume of gases, less the blank. The stopcock (G) on the potassium hydroxide-filled absorption bulb (H) was closed to the atmosphere and the three-way stopcock at the top of the burette turned so that the gases in the burette were free to come in contact with the concentrated potassium hydroxide solution, but were closed to the main body of the gas in the decomposition chamber. The gases were then forced into the alkali solution, by means of the mercury reservoir, where the carbon dioxide was absorbed in the formation of potassium carbonate. The gas was then permitted to return to the burette by again lowering the mercury bulb until the mercury levels were equal. This maneuver was repeated until no volume decrease was noted after passage of gas into the alkali solution, i.e., until no more carbon dioxide was removed. The total volume decrease in the burette was recorded as the volume of carbon dioxide absorbed by the alkali, and the percentage of carbon dioxide in the system calculated by dividing this volume decrease by the total volume of gas in the burette before absorption of the carbon dioxide by the alkali. The number of mols of carbon dioxide in the liberated gases was determined by multiplying the volume of the system (less the volume due to the decomposant) by the percentage of carbon dioxide originally in the burette and reducing the volume of the carbon dioxide to standard conditions of temperature and pressure. The amount of sodium carbonate present in the sample of ozonated sodium hydroxide was then obtained from the equation:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

and the percentage of sodium carbonate in the sample calculated from this value and the weight of the sample. It was assumed that the carbon dioxide resulted entirely from the reaction of the carbonate with hydrochloric acid, rather than from any bicarbonate.

A blank, i.e., the volume due to the added volume of the decomposant, had been previously determined by adding to the decomposition cell the same amount of hydrochloric acid used in the analysis. All of the experimental details of the analysis were rigidly adhered to in the determination of the blank. The volume of this blank was reduced to standard conditions of temperature and pressure, and re-adjusted to the experimental conditions of temperature and pressure of the various analyses.

The volume of oxygen liberated from the "ozonate" was determined by subtracting from the volume in the burette the volume due to both the blank and the carbon dioxide. The number of mols of oxygen was determined by reducing this volume to standard conditions of temperature and pressure and dividing by 22,400. From this number of mols of oxygen and the following equations, the amount of NaO_3, NaO_2, $NaOH \cdot O_2$, or $(NaOH)_2 \cdot O_2$, respectively, was determined:

$$4NaO_3 + 2H_2O = 4NaOH + 5O_2$$

$$4NaO_2 + 2H_2O = 4NaOH + 3O_2$$

$$NaOH \cdot O_2 = NaOH + O_2$$

$$(NaOH)_2 \cdot O_2 = 2NaOH + O_2$$

These formulas are the sodium analogs of postulated formulas for potassium "ozonate". The first of these was suggested by Kazarnovskii, Nikolskii, and Abletsova[14], the second by Baeyer and Villiger[2], and the last two by W. Traube[7,8]. Since the "method of mixtures" used in this study was necessarily an indirect approach, all of these possibilities were considered, in order to determine which best fitted the experimental data.

The acidic solution remaining in the decomposition chamber was then titrated to the phenolphthalein end point with standardized sodium hydroxide solution. From the known amount of hydrochloric acid which was originally added, the amount of base used in the back-titration, and the amounts of carbonate and "ozonate" present in the sample, the amount of unreacted hydroxide originally present was calculated. The latter was determined by subtracting from the number of equivalents of acid added, the number of equivalents of base used in the back-titration, and the number of equivalents of acid used to decompose both carbonate and "ozonate", and multiplying by the equivalent weight of sodium hydroxide. The weight of water in the sample was obtained by subtracting from the total weight of the sample the weight of the three analytically determined components.

From the total weight of the sample and the amounts of each of the four components, the percentage or weight fraction of each component was determined. The percentage of water and carbonate present was invariable, i.e., did not depend on the assumed formula for the "ozonate". However, the relative percentages of "ozonate" and unreacted hydroxide differed with the formula which was assumed, even though their sum remained constant.

Once the proportions of each component was known, the gram susceptibility of the "ozonate" could be calculated from the gram susceptibility of the mixture and the known susceptibilities of the other three components, using the Wiedemann law for the additivity of susceptibilities[29]. This law, which states that the magnetic susceptibility of a mixture of two or more components is equal to the sum of the susceptibilities of the components, each multiplied by its weight fraction in the mixture, can be formulated:

$$\chi_{mix} = \sum_{i}^{n} \chi_i p_i,$$

where p_i is the weight fraction of component i in a mixture of n components and χ_i is its magnetic susceptibility; χ_{mix} is the gram susceptibility of the mixture. For the four-component mixtures analyzed in this study, the mathematical formulation of the Wiedemann additivity law assumed the form:

$$\chi_{mix} = \chi_{oz}\, p_{oz}^{*} + \chi_{NaOH}\, p_{NaOH} + \chi_{Na_2CO_3}\, p_{Na_2CO_3} + \chi_{H_2O}\, p_{H_2O}$$

---

*The subscript oz refers to "ozonate".

or, solving for χ_{oz}, which is the gram susceptibility of the "ozonate",

$$\chi_{oz} = \frac{\chi_{mix} - (\chi_{NaOH}\, p_{NaOH} + \chi_{Na_2CO_3} p_{Na_2CO_3} + \chi_{H_2O}\, p_{H_2O})}{p_{oz}}$$

The values of χ_{NaOH}, $\chi_{Na_2CO_3}$, and χ_{H_2O} were obtained from the literature[30], the value of χ_{mix} was determined from magnetic measurements of the sample, and the values of p_{oz}, p_{H_2O}, $p_{Na_2CO_3}$, and p_{NaOH} were determined analytically by the methods just described. Four determinations were made on each sample, each determination based on a different formula for the "ozonate".

The water contained in the ozonated sodium hydroxide was unquestionably present in the form of water of hydration. The assumption was made throughout this study that the hydrated hydroxides (or carbonates) could be treated in magnetic studies as mixtures of water and the anhydrous material, i.e., that the magnetic susceptibilities of water and the anhydrous material were additive and could be so utilized in the use of the Wiedemann additivity law. This assumption was based on susceptibility data[30] which showed, without exception, that the values of magnetic susceptibilities of hydrates were weighted averages of susceptibility values for water and the anhydrous materials. Recently, Prasad, Dharmatti, Kanakar, and Biradar[31] have reported that hydration does cause some deviation from linearity; however, their data indicate a maximum deviation of only about 8 per cent, with an average deviation of about 4 per cent. It was felt that a deviation of even 8 per cent would not appreciably alter the results obtained in the analyses.

The molar susceptibility of the "ozonate" was obtained by multiplying the gram susceptibility by the molecular weight corresponding to the assumed formula. The magnetic moment was then obtained by use of the formula:

$$\mu^2 = 8\chi_m T,$$

where T is the temperature, in degrees Kelvin, at which the magnetic measurement was made, μ is the magnetic moment, and χ_m is the molar susceptibility. μ is given by this formula in Bohr magnetons, i.e., in units of $\frac{eh}{4\pi mc}$, the natural quantum mechanical unit for magnetic moment. The number of unpaired electrons per molecule was obtained by use of the expression:

$$\mu^2 = n(n + 2),$$

where n is the number of unpaired electrons per molecule. From the obtained value of the magnetic moment for each assumed formula for the "ozonate", the formula could be critically evaluated, and either accepted or rejected.

Example of Calculations Involved in "Method of Mixtures"

In order to more clearly illustrate the use of the "method of mixtures" in investigating ozonated alkali hydroxides, a sample calculation, based on an actual analysis of a sample of ozonated sodium hydroxide, is hereby described.

Sodium hydroxide pellets were ozonated at room temperature for several hours, at the end of which time the ozonated pellets were transferred to another vessel, tightly stoppered, and vigorously shaken. The yellow (ozonated) surface of the pellets was jarred loose as a free powder from the main body of the pellets and was separated (in the "dry box") by means of a fine seive. It was then added to a ground glass-stoppered weighing tube for magnetic measurements.

The weighing tube had previously been weighed on the magnetic balance. Data are as follows:

(1) Empty tube:

(a)

weight with current off	23.74173 g.
weight with current on (6.41 amps.)	23.72773 g.
change in weight, Δw	-0.01400 g.

$$\Delta w_{6.30} = -0.01400 \times \frac{(6.30)^2}{(6.41)^2} = -0.01359 \text{ g.}$$

(b)

weight with current off	23.74208 g.
weight with current on (6.25 amps.)	23.72870 g.
change in weight, Δw	-0.01338 g.

$$\Delta w_{6.30} = -0.01338 \times \frac{(6.30)^2}{(6.25)^2} = -0.01351 \text{ g.}$$

average $\Delta w_{6.30}$ = -13.55 mg.

average weight of weighing tube = 23.74190 g.

(2) Tube filled with distilled water to index (7 cm) mark:

(a) weight with current off 27.57285 g.
weight with current on (6.22 amps) 27.54278 g.
change in weight, Δw -0.03007 g.

$$\Delta w_{6.30} = -0.03007 \times \frac{(6.30)^2}{(6.22)^2} = -0.03085 \text{ g.}$$

(b) weight with current off 27.57262 g.
weight with current on (6.36 amps) 27.54154 g.
change in weight, Δw -0.03108 g.

$$\Delta w_{6.30} = -0.03108 \times \frac{(6.30)^2}{(6.36)^2} = -0.03060 \text{ g.}$$

average $\Delta w_{6.30}$ = -30.72 mg.

average weight of water-filled tube = 27.57273 g.

average volume to index (7 cm.) mark= 3.83083 ml.

average cross-sectional area = 0.5473 cm.^{2}

average Δw(water) = -30.72 -(-13.55)= -17.17 mg.

The weighing tube was then filled with ozonated sodium hydroxide and weighed on the magnetic balance, both in and out of the magnetic field. Data are:

(3) Tube filled with ozonated hydroxide:

(a) weight with current off = 28.03278 g.
weight with current on (6.38 amps) = 28.01392 g.
change in weight, Δw = -0.01886 g.

$$\Delta w_{6.30} = -0.01886 \times \frac{(6.30)^2}{(6.38)^2} = -0.01886 \text{ g.}$$

temperature = 24°C

(b) weight with current off = 28.03322 g.
weight with current on (6.38 amps) = 28.01410 g.
change in weight, Δw = -0.01912 g.

$$\Delta w_{6.30} = -0.01912 \times \frac{(6.30)^2}{(6.38)^2} = -0.01866 \text{ g.}$$

temperature = 24°C

average $\Delta w_{6.30} = -18.52$ mg.

average $\Delta w(\text{sample}) = -18.52 - (-13.55) = -4.97$ mg.

average weight of sample = 4.29110 g.

$$\chi_g = (0.03 - 0.75 \times (\frac{-4.97}{-17.17})) \times 10^{-6} \times \frac{3.831}{4.291}$$

$$\chi_g = -0.168 \times 10^{-6} \text{ cgsu./g.}$$

The sample was then transferred to the "dry box" and a portion added to the glass insert, which was placed in a ground glass-stoppered weighing bottle. The entire system was then weighed on an analytical balance. Data are:

weight of weighing bottle + insert + sample = 19.5972 g.
weight of weighing bottle + insert = 19.0744 g.
weight of sample = 0.5228 g.

Prior to filling the decomposition chamber with the "ozonate", it had been connected in place and the system filled with water from (A) to (F), through (B), in order to determine the volume of the system. The weight of the water was then determined, and the weight taken as the volume of the system, the density of water being taken as unity. The volume of the system with the decomposition chamber used throughout most of this study was found to be 89.0 ml.

In addition to determining the volume of the system, a blank, <u>i.e.</u>, the volume change due to the addition of decomposant, was determined prior to the analysis of the sample. The decomposition chamber was secured in place, with the capillary leading to the decomposant reservoir (C) filled to the reference mark with 1.4720 N hydrochloric acid. The system was first flushed with dry oxygen to simulate experimental conditions, then closed by means of stopcocks (F) and (A), and the pressure inside the apparatus equilibrated with atmospheric pressure by means of the mercury bulb. Ten ml. of 1.4720 N hydrochloric acid was added to the decomposant reservoir by means of a pipette, and this volume of acid was slowly added to the empty decomposition chamber through the stopcock separating the two containers. The pressure was once more equilibrated and the final volume read.

Data are:

temperature = 26.5°C
pressure = 734 mm. (corr.)
final burette reading = 12.90 ml.
initial burette reading = 0.50 ml.
change in volume (blank) = 12.40 ml.
change in volume (blank), STP = 10.90 ml.

The decomposition chamber containing the previously weighed sample-filled insert was then connected to the analytical system (Fig. IV). Ten ml. of 1.4720 N hydrochloric acid was then added to the sample in the decomposition chamber, the mercury levels being kept as even as possible during the decomposition of the sample by lowering the mercury bulb at approximately the same rate as that at which the volume of gas in the burette increased. When the evolution of gas was complete, the gases were mixed well and the final volume read. Data are:

temperature = 29.0°C
pressure (uncorrected) = 731.5 mm.
pressure (corrected) = 728.3 mm.
final burette reading = 18.90 ml.
initial burette reading = 0.00 ml.
change in volume = 18.90 ml.
blank, experimental conditions = 12.55 ml.
volume of liberated gases = 6.35 ml.

The stopcock (G) at the top of the carbon dioxide absorption bulb (H) was turned so that the potassium hydroxide solution was open only to the burette. Then, the stopcock (F) at the top of the burette was turned so that the gases in the burette were free to pass over into the potassium hydroxide solution. At this point, the gases in the burette consisted mainly of oxygen and carbon dioxide, and occupied a volume extending from the stopcock (F) to the top of the mercury column; since the volume from this stopcock to the zero mark of the burette was found to be 2.0 ml., the total volume of gases was 18.90 + 2.0 = 20.9 ml. The gases in the burette were then forced over into the bulb containing the potassium hydroxide solution (H) by raising the mercury bulb in order to remove carbon dioxide; the gas was then forced back into the burette by lowering the mercury bulb until the mercury columns were level, and the new burette reading taken. (The decrease in volume was due to absorption of the carbon dioxide.) This maneuver was repeated until no further decrease in volume was noted upon further transfer of gas. Data are:

volume of gases in burette = 20.9 ml.
volume after absorption of carbon dioxide = 20.7 ml.
volume of carbon dioxide absorbed = 0.2 ml.

The percentage of carbon dioxide originally present in the burette was calculated by dividing the volume decrease by the total volume of gases originally in the burette. Since the gases in the system had been well mixed prior to the absorption of the carbon dioxide, this percentage was also the percentage of carbon dioxide in the system. The volume of carbon dioxide in the system was then calculated by multiplying the total volume, less the blank, by the percentage of carbon dioxide. The number of mols of carbon dioxide was determined by reducing this volume to STP and dividing by 22,4000, the gram molecular volume. The amount of sodium carbonate in the sample was then determined from the equation:

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

by multiplying the number of mols of carbon dioxide (which is also the number of mols of sodium carbonate) by the formula weight of sodium carbonate, roughly 106. Data are:

per cent of carbon dioxide = 0.20 x 100/20.9 = 0.96%
volume of carbon dioxide in system = 0.0096 (89+20.9+12.6) = 0.93ml.
volume of carbon dioxide at STP (in entire system = 0.81ml.
mols of carbon dioxide (and sodium carbonate) = 3.6 x 10^{-5} mols.
weight of sodium carbonate = 106 x 3.6 x 10^{-5} = 0.0038 g.
weight per cent of sodium carbonate = 0.0038/0.5228 = 0.73%

The volume of oxygen liberated was then determined by subtracting the volume of carbon dioxide from the total volume of collected gases, and this volume then reduced to STP. From this last value, the volume of oxygen (at STP) per gram of sample was calculated. Data Are:

volume of oxygen = 6.35 - 0.93 = 5.42 ml.
volume of oxygen at STP = 4.70 ml.
volume of oxygen (at STP) per gram = 4.70/0.5228
volume of oxygen (at STP) per gram = 8.98 ml./g.

The per cent of NaO_3, $NaOH \cdot O_2$, NaO_2, or $(NaOH)_2 \cdot O_2$, respectively, was then calculated by dividing the volume of oxygen liberated per gram of sample by the volume of oxygen which would be liberated per gram of the pure substances, assuming the following reactions:

(1) $4NaO_3 + 2H_2O = 4NaOH + 5O_2$; 393 ml./g.

(2) $NaOH \cdot O_2 = NaOH + O_2$; 311 ml./g.

(3) $4NaO_2 + 2H_2O = 4NaOH + 3O_2$; 305 ml./g.

(4) $(NaOH)_2 \cdot O_2 = 2NaOH + O_2$; 200 ml./g.

Multiplication of the total weight of the sample by the calculated percentages of each of these compounds gave the weight of each substance which would be present. Division of these weights by the corresponding formula weights gave the number of mols of each substance. Data are:

per cent NaO_3 = $8.98 \times 100/394 = 2.28\%$
per cent $NaOH \cdot O_2$ = $8.98 \times 100/311 = 2.89\%$
per cent NaO_2 = $8.98 \times 100/305 = 2.95\%$
per cent $(NaOH)_2 \cdot O_2$ = $8.98 \times 100/200 = 4.49\%$
weight of NaO_3 = $0.0228 \times 0.05228 = 0.0119$ g.
weight of $NaOH \cdot O_2$ = $0.0289 \times 0.05228 = 0.0151$ g.
weight of NaO_2 = $0.0295 \times 0.05228 = 0.0154$ g.
weight of $(NaOH)_2 \cdot O_2$ = $0.0449 \times 0.05228 = 0.0235$ g.
mols of NaO_3 = $0.0119 \div 71 = 1.68 \times 10^{-4}$ mols.
mols of $NaOH \cdot O_2$ = $0.0151 \div 72 = 2.09 \times 10^{-4}$ mols.
mols of NaO_2 = $0.0154 \div 55 = 2.80 \times 10^{-4}$ mols.
mols of $(NaOH)_2 \cdot O_2$ = $0.0235 \div 112 = 2.10 \times 10^{-4}$ mols.

It can be readily shown that the number of mols of $(NaOH)_n \cdot O_2$ will always be the same, irrespective of the value of <u>n</u>.

The acidic solution remaining in the decomposition chamber was then titrated with 0.0986 N sodium hydroxide solution, using phenolphthalein as an indicator. From the amount of hydrochloric acid added as decomposant there was subtracted the amount of sodium hydroxide used for titration, the amount of acid used to neutralize the sodium carbonate, and the amount of acid used to decompose the "ozonate", in order to determine the amount of unreacted sodium hydroxide in the sample. Data are:

volume of 0.0986 N sodium hydroxide solution = 24.50 ml.
equiv. of sodium hydroxide used in titration = 0.00242
equiv. of sodium carbonate = 0.00007
equiv. of acid if "ozonate" is NaO_3 = 0.00017
equiv. of acid if "ozonate" is $NaOH \cdot O_2$ = 0.00021
equiv. of acid if "ozonate" is NaO_2 = 0.00028
equiv. of acid if "ozonate" is $(NaOH)_2 \cdot O_2$ = 0.00042

From these values the number of equivalents of unreacted sodium hydroxide in the sample can be calculated. Calculations are:

equiv. of hydroxide if "ozonate" is NaO_3 = 0.01206
equiv. of hydroxide if "ozonate" is $NaOH \cdot O_2$ = 0.01202
equiv. of hydroxide if "ozonate" is NaO_2 = 0.01195
equiv. of hydroxide if "ozonate" is $(NaOH)_2 \cdot O_2$ = 0.01181

The weight and weight per cent of unreacted sodium hydroxide is readily determined from these values by multiplying by the formula weight of sodium hydroxide and then dividing by the total weight of the sample. Data are:

per cent hydroxide if "ozonate" is NaO_3 = 92.2%
per cent hydroxide if "ozonate" is $NaOH \cdot O_2$ = 92.0%
per cent hydroxide if "ozonate" is NaO_2 = 91.4%
per cent hydroxide if "ozonate" is $(NaOH)_2 \cdot O_2$ = 90.3%

The weight per cent of water was determined by subtracting from 100 per cent the sum of the weight per cents of unreacted sodium hydroxide, sodium carbonate, and sodium "ozonate". In most cases, the per cent of water was not appreciably dependent on the assumed formula for the "ozonate" and an average value was used. In this particular determination, the weight per cent of water was calculated to be 4.6 per cent.

The magnetic susceptibilities of water, sodium hydroxide, and sodium carbonate were found from the literature[30] to be -0.72×10^{-6} cgsu./g., -0.59×10^{-6} cgsu./g., and -0.25×10^{-6} cgsu./g., respectively. Using these values, the value for the magnetic susceptibility of the mixture as determined experimentally, and the analytically determined weight fractions of the four components, the magnetic susceptibility of the sodium "ozonate" was determined by the use of the Wiedemann additivity law. Multiplication of the gram susceptibility by the (assumed) formula weight gave the molar susceptibility for the "ozonate", from which the magnetic moment was readily determined by means of the equation; $\mu^2 = 8\chi_m T$. Data are:

NaO_3

$$\chi_g = \frac{10^{-6}\,(-0.17 + (0.007 \times 0.25)+(0.046 \times 0.72)+(0.92 \times 0.59))}{0.023}$$

$$\chi_g = 18.0 \times 10^{-6} \text{ cgsu./g.}$$

$$\chi_m = 18.0 \times 10^{-6} \times 71 = 1280 \times 10^{-6} \text{ cgsu./mol.}$$

μ = 1.74 Bohr magnetons

$NaOH \cdot O_2$

$$\chi_g = \frac{10^{-6}\,(-0.17 + (0.007 \times 0.25)+(0.046 \times 0.72)+(0.92 \times 0.59))}{0.029}$$

$$\chi_g = 14.2 \times 10^{-6} \text{ cgsu./g.}$$

$$\chi_m = 14.2 \times 10^{-6} \times 72 = 1023 \times 10^{-6} \text{ cgsu./mol.}$$

μ = 1.56 Bohr magnetons

NaO_2

$$\chi_g = \frac{10^{-6}\,(-0.17 + (0.007 \times 0.25)+(0.046 \times 0.72)+(0.91 \times 0.59))}{0.030}$$

$$\chi_g = 13.8 \times 10^{-6} \text{ cgsu./g.}$$

$$\chi_m = 13.8 \times 10^{-6} \times 55 = 758 \times 10^{-6} \text{ cgsu./mol.}$$

μ = 1.34 Bohr magnetons

$$(NaOH)_2 \cdot O_2$$

$$\chi_g = \frac{10^{-6}\,(-0.17 + (0.007 \times 0.25) + (0.046 \times 0.72) + (0.90 \times 0.59))}{0.045}$$

$$\chi_g = 8.90 \times 10^{-6} \text{ cgsu./g.}$$

$$\chi_m = 8.90 \times 10^{-6} \times 112 = 997 \times 10^{-6} \text{ cgsu./mol.}$$

$$\mu = 1.54 \text{ Bohr magnetons}$$

The results of six determinations are listed in Table I, all determinations being made in a manner analogous to that used for illustration. Throughout the entire study the practice of disregarding all data on samples containing less than 1.5 per cent NaO_3 (or KO_3 or CsO_3, as determined in a later paragraph) was followed, since the limit of accuracy of the least reliable analysis was estimated to be this value. Values of magnetic moment are reported only to the nearest tenth of a Bohr magneton.

The values shown in Table I are, admittedly, not sufficiently precise to warrant a definite formulation for the sodium "ozonate" based on these data alone. However, since the magnetic moment corresponding to one unpaired electron per molecule is, roughly, 1.7, the statement can be made that the experimental data are best fitted to a compound having the formula NaO_3. Since the formulas $NaOH \cdot O_2$ and $(NaOH)_2 \cdot O_2$ (or, in general, $(NaOH)_n \cdot O_2$) would require two unpaired electrons per molecule, the magnetic moments calculated on the bases of these formulas indicate that these formulations are not substantiated by the experimental data. Aside from the fact that the magnetic data is not well fitted to a formulation of NaO_2, negative peroxide tests and lack of oxidizing power displayed by the sodium "ozonate" indicate that it is not sodium superoxide. Furthermore, these sodium compounds have been found to contain paramagnetic material, hence, the formulas Na_2O_2, $NaHO_2$, $(NaOH)_n \cdot O_3$ and Na_4O_6 must be discounted, since compounds such as these would be diamagnetic.

<u>"Method of Mixtures" Applied to Potassium and Cesium Compounds</u>

The "method of mixtures" was also applied to samples of ozonated potassium and cesium hydroxides. All experimental details were the same as those applied in the investigation of the sodium compounds, although the only method used for the preparation of the samples was the ozonization of the finely pulverized materials. The samples were constantly agitated during ozonization in order to insure maximum exposure to the ozone. The potassium compound was found to decolorize considerably during the time required for the complete analysis, with the result that relatively small percentages, <u>i.e.</u>, low oxygen content per gram of sample, were obtained in the analyses. For this reason, the majority of the determinations were rejected on the basis of insufficient oxygen content - less than 1.5 per cent of KO_3 - of the samples. Only two determinations of the potassium compounds are reported in Table III.

Table I - Data on Analyses of Ozonated Sodium Hydroxide

			for NaO_3				for $NaOH \cdot O_2$			
	10^6 χmix	$\%Na_2CO_3$	%NaOH	$\%H_2O$	$\%NaO_3$*	μ	%NaOH	$\%H_2O$	$\%NaOH \cdot O_2$*	μ
Na I	+0.54	9.8	58.8	26.7	4.5	2.0	58.2	26.7	5.7	1.8
Na II‡	+0.44									
Na III‡	+0.37									
Na IV	-0.01	9.2	74.7	12.5	3.6	1.6	74.0	12.5	4.6	1.4
Na V	-0.17	0.7	92.2	4.6	2.3	1.7	92.0	4.6	2.9	1.6
Na VI	+0.85	21.8	46.4	20.9	10.2	1.5	45.1	20.9	13.0	1.3
Na VII‡	-0.20									
Na VIII	+0.45	32.2	47.0	8.8	11.0	1.2	45.5	8.8	14.0	1.0
Na IX	-0.03	10.0	80.5	8.0	3.2	1.7	77.6	8.0	4.1	1.5

---

*As calculated from oxygen evolution

‡See Table II.

Table I (Continued)

	for NaO_2				for $(NaOH)_2\cdot O_2$			
	% NaOH	$\%H_2O$	$\%NaO_2$*	μ	%NaOH	$\%H_2O$	$\%(NaOH)_2\cdot O_2$*	μ
Na I	57.4	26.7	5.83	1.6	55.0	26.7	8.90	1.8
Na II‡								
Na III‡								
Na IV	73.2	12.5	4.8	1.2	71.3	12.5	7.2	1.4
Na V	91.4	4.6	3.0	1.3	90.3	4.6	4.5	1.5
Na VI	42.6	20.9	13.5	1.1	37.9	20.9	20.2	1.3
Na VII‡								
Na VIII	43.7	8.8	14.5	0.9	38.5	8.8	21.7	1.0
Na IX	76.8	8.0	4.2	1.3	75.3	8.0	6.3	1.4

*As calculated from oxygen evolution.

‡ See Table II.

Table II

Sodium "Ozonate"-Summary of Magnetic Moments

	$\mu(NaO_3)$	$\mu(NaOH \cdot O_2)$	$\mu(NaO_2)$	$\mu((NaOH)_2 \cdot O_2)$
Na I	2.0	1.8	1.6	1.8
Na II*				
Na III*				
Na IV	1.6	1.4	1.2	1.4
Na V	1.7	1.6	1.3	1.5
Na VI	1.5	1.3	1.1	1.3
Na VII*				
Na VIII	1.2	1.0	0.9	1.0
Na IX	1.7	1.5	1.3	1.4

---

* Na II, III, and VII were used up in utilizing faulty analytical methods, so that analytical data are not available. However, values of magnetic susceptibilities for these samples indicate the presence of a paramagnetic material in the mixtures.

The cesium compounds, although retaining their coloration fairly well during the handling operations, liberated much less oxygen per gram of sample than did the corresponding sodium compounds. This corresponds to the observations reported by Manchot and Kampschulte[5], that ozonated cesium hydroxide contained less available oxygen (per cent by weight) than did the ozonated hydroxides of the other alkali metals. Therefore, in order to minimize the errors due to insufficient mixing (non-homogeneity) of the sample, the entire weight of product used for the individual magnetic measurements was used in the analyses. The entire contents of the weighing tube were added to the decomposition chamber after magnetic measurements had been taken. The percentages of cesium "ozonate", calculated on the basis of CsO_3, varied between 1.6 per cent and 2.5 per cent. These percentages are, admittedly, quite low and precariously close to the limit of accuracy of the analytical method; however, the consistency of the results shown in Table III can scarcely be denied.

The magnetic susceptibility of cesium hydroxide has not been reported in the literature; it was therefore necessary to determine this quantity before final calculations could be made. This was accomplished by determining the susceptibility of the cesium hydroxide (monohydrate) used in the ozonization studies, weighing out samples for analysis, and titrating the samples with 0.0915 N hydrochloric acid, using the phenolphthalein end point for the determination of the hydroxide content and the methyl orange end point to determine the carbonate content. The amount of water was determined by difference. The values so obtained were then used to determine the susceptibility of the pure cesium hydroxide, utilizing the Wiedemann additivity law. Data obtained follow;

(1) Magnetic data: (average of three determinations)

weight of sample-filled tube = 31.31410 g.
weight of empty tube = 23.74190 g.
weight of sample = 7.57220 g.
Δw(tube), at 6.30 amps. = -13.54 mg.
Δw(water), at 6.30 amps. = -30.72 mg.
Δw(sample), at 6.30 amps. = -31.10 mg.
volume of tube to index mark = 3.8308 ml.

$$\chi_{mix} = ((0.03 - 0.75 \times (\frac{-17.6}{-17.2})) \times \frac{3.8308}{7.5722} \times 10^{-6}$$

$$\chi_{mix} = -0.254 \times 10^{-6} \text{ cgsu./g.}$$

Three samples were then analyzed titrimetrically for cesium hydroxide and cesium carbonate with 0.0915 N hydrochloric acid solution, using phenolphthalein and methyl orange as indicators; water was determined by difference, and the weight percentages of the constituents were calculated. The average values of the percentages of the three constituents were found to be: CsOH, 86.6%; Cs_2CO_3, 1.8%; H_2O, 11.6%. Qualitative tests indicated the absence of other contaminants, such as halides, nitrate, sulfate, etc.

The susceptibility of cesium hydroxide was then calculated from these data, using the Wiedemann additivity law. This value was found to be:

$$\chi_g \text{ (CsOH)} = -0.203 \times 10^{-6} \text{ cgsu./g.}$$

From this value, the gram susceptibility of the mixture, the analytically determined fractions of the constituents, and the values for $X_g(Cs_2CO_3)$ and $X_g(H_2O)$ reported in the literature[30], the gram susceptibility of cesium "ozonate" was determined by utilizing the additivity law. Subsequent calculations for magnetic moments produced the data tabulated in Table III.

Oxidizing Power of Cesium "Ozonate" Solutions

The application of the "method of mixtures" to samples of ozonated cesium hydroxide involved the assumption that these samples were mixtures of only four components (hydroxide, carbonate, water, and "ozonate"). The presence of an appreciable amount of fifth constituent, not considered in the calculations, would alter considerably the calculated results. The solutions resulting from the acidic decomposition of samples of ozonated cesium hydroxide were found to liberate iodine from acidified potassium iodide solution. Since ozonated sodium hydroxide was found to evolve oxygen, upon decomposition with hydriodic acid, without a concomitant oxidation of iodide ion, it is not inconceivable that the oxidizing power displayed by cesium "ozonate" solutions is due to the presence of a compound other than cesium "ozonate." If such were the case, the data shown in Table III would be valid only if the resulting solutions displayed an inappreciable amount of oxidizing power in comparison with the amount of oxygen liberated. In order to establish this point, acidified potassium iodide solution was used as a decomposant in the "method of mixtures" and the iodine liberated was determined by titration with arsenic(III) oxide, after the volume of evolved oxygen had been measured. In this manner both the amount of oxygen liberated and the amount of oxidizing power remaining in

Table III

Analyses of Potassium and Cesium "Ozonate" Mixtures

Potassium "Ozonate"

	χ_{mix}	%KOH	%K_2CO_3	% H_2O	%KO_3*	μ
K I	-0.23×10^{-6}	73.8	2.2	22.3	1.8	1.5
K II	-0.24×10^{-6}	80.0	0.7	17.6	1.8	1.4

Cesium "Ozonate"

	χ_{mix}	%CsOH	%Cs_2CO_3	%H_2O	%CsO_3*	μ
Cs I	-0.075×10^{-6}	87.8	0.0**	9.9	2.3	1.8
Cs II	-0.039×10^{-6}	84.3	0.4	12.8	2.5	2.0
Cs III	-0.153×10^{-6}	84.4	0.0**	13.4	2.2	1.5
Cs IV	-0.226×10^{-6}	85.1	0.0**	13.3	1.6	1.2
Cs V	-0.107×10^{-6}	83.8	1.5	13.2	1.5	1.7

*As calculated from oxygen evolution. Only values calculated for KO_3 and CsO_3 are shown here inasmuch as the other three suggested formulas for the "ozonates" would give lower values than the values shown here.

**The absence of cesium carbonate is attributable to the extreme care taken in preventing exposure of these samples to atmospheric carbon dioxide. Samples taken from freshly opened bottles of the cesium hydroxide were found to be essentially carbonate-free.

solution could be determined from the same sample.

The experimental technique involved in these determinations was exactly analogous to that involved in the "method of mixtures". The decomposant consisted of 10 ml. of 1.2287 N hydrochloric acid solution and 5 ml. of 0.1 N potassium iodide solution, all quantities measured by means of pipettes and mixed well before adding to the decomposant reservoir. A blank was first determined under simulated experimental conditions in order to establish the change in volume due to the addition of the decomposant as well as the amount of hydriodic acid oxidized by the oxygen in the system. The acidified iodide solution was permitted to stand in the oxygen-filled atmosphere of the decomposition chamber for 30 minutes, the average time required for an analysis. The change in volume due to addition of the decomposant was determined, and the iodine liberated by the oxygen was then determined by titrating with 0.05048 N arsenic(III) oxide solution, using starch solution as an indicator. A semi-micro burette was used in all iodine titrations. Data on the blank are:

temperature = 25.5°C
pressure (corrected) = 731 mm.
change in volume due to decomposant = 16.30 ml.
blank, at STP = 14.25 ml.
volume 0.05048 N As_2O_3 solution to titrate I_2 = 0.075 ml.

were then ozonated at room temperature, weighed, and added to the decomposition chamber in the same manner as was used in the "method of mixtures". The "ozonate" was then decomposed by means of the decomposant (5 ml. of 0.1 N Potassium iodide solution and 10 ml. of 1.2287 N hydrochloric acid solution) and the volume of liberated gases determined. After the analysis of the gases for carbon dioxide (by absorption in concentrated alkali solution), the solution remaining in the decomposition chamber was neutralized with sodium bicarbonate and the iodine which was liberated during the decomposition of the "ozonate" was titrated with 0.05048 arsenic(III) oxide solution, using starch solution as an indicator. From these data the amount of liberated iodine as well as the amount of evolved oxygen was determined. A sample calculation follows:

weight of sample = 1.0296 g.
temperature = 28.5°C
pressure (corrected) = 729 mm.
change in volume = 18.60 ml.
volume change, at STP = 17.05 ml.
volume decrease due to CO_2 absorption = 0.00 ml.
volume of carbon dioxide = 0.00 ml.
volume of oxygen, at STP = 2.70 ml.
mols of oxygen = 1.2×10^{-4}
volume of 0.05048 N As_2O_3 used to titrate I_2 = 0.280 ml.
volume of As_2O_3 blank = 0.075 ml.
mols I_2 liberated during decomposition = 0.52×10^{-5}
mols O_2/mols I_2 = $1.20 \times 10^{-4}/0.52 \times 10^{-5} = 23 : 1$

The results of five such determinations are tabulated in Table IV. These data show that the amount of oxidizing power remaining in solution after decomposition of cesium "ozonates" is very small in comparison with the amount of oxygen evolved. Such being the case, the results based on the data tabulated in Table III would appear to be completely valid.

FIG. IV.

Comparison of Liberated Oxygen With
Residual Oxidizing Power

	weight sample	mols of O_2	mols of I_2	O_2/I_2
(1)	1.8274 g.	2.92×10^{-4}	5.6×10^{-6}	52 : 1
(2)	0.4911 g.	6.02×10^{-5}	3.2×10^{-6}	19 : 1
(3)	1.0296 g.	1.20×10^{-4}	5.2×10^{-6}	23 : 1
(4)	0.7930 g.	6.92×10^{-5}	2.3×10^{-6}	32 : 1
(5)	0.6489 g.	4.02×10^{-5}	6.3×10^{-7}	64 : 1

Quantitative Studies on the Extracted "Ozonates"

As has already been mentioned, potassium and cesium "ozonates" are apparently quite soluble in liquid ammonia, for they are readily extracted from the unreacted hydroxides by this solvent. Evaporation of the resulting solutions produces red solids which are decomposed by water or acid with a concomitant evolution of gas. In order to establish the nature of these substances, several quantitative determinations were made on both the potassium and cesium materials extracted by liquid ammonia.

This work on the extract of ozonated potassium hydroxide which was reported by Kazarnovskii, Nikolskii, and Abletsova[14] (reported by them to be KO_3) was first repeated insofar as was possible, and then similar studies were conducted on the corresponding cesium compounds. The experimental technique involved in the ozonization of the hydroxides were similar to those which have been already mentioned. A sample of pulverized dehydrated potassium hydroxide was placed in the ozonization chamber (K) shown in Fig. V. Ozone-containing oxygen* was then passed through the sample and permitted to pass through the stopcock (G) into the calcium oxide tower (C), and then into the solution of potassium iodide (D). (The latter two substances were utilized to decompose any effluent ozone.) During the ozonization process, the sample was periodically agitated in order to expose the maximum surface to the ozone; this was accomplished by tapping the reaction vessel gently with the fingers, or by periodically opening the stopcock (F) and permitting the pressure in the calcium oxide tower to force the gases back through the sintered glass filter and up through the pulverized sample. When the sample appeared to be well-ozonated, the current passing through the laboratory ozonizer was turned off, and dry oxygen was passed through the sample in order to remove all traces of residual ozone that might oxidize the ammonia to be used for extraction of the "ozonate". After washing the sample with dry oxygen for about 20 minutes, the oxygen was turned off and the stopcock (G) was turned so that the system was opened to the ammonia cylinder. Cooling baths

---

*The laboratory ozonizer which was described earlier was utilized in all of the studies on the liquid ammonia extraction of the "ozonates".

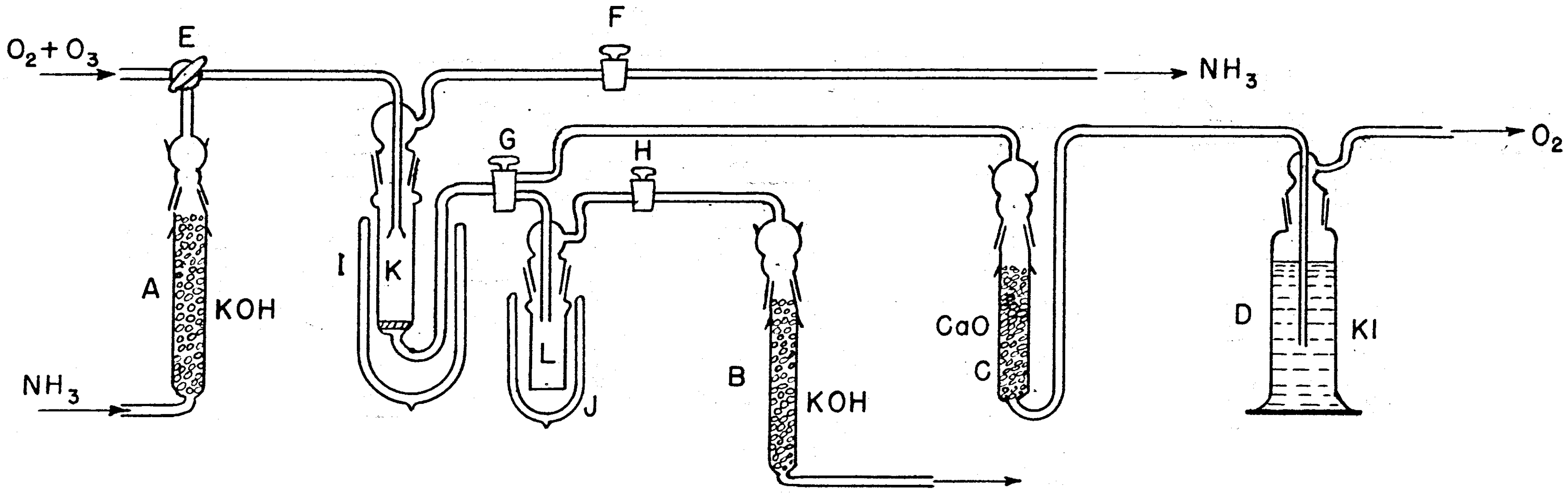


Figure V Apparatus Used for Liquid Ammonia Extraction of Alkali Metal "Ozonates" of cellosolve and solid carbon dioxide were prepared in Dewar flasks (I and J) and these baths were then placed around the chambers (K and L) as shown in Fig. V. Stopcocks (G) and (H) were closed so that the collection vessel (L) was completely closed to the atmosphere and to the remainder of the system. When the "ozonate" was cooled to the temperature of the cooling bath, stopcock (F) was opened, and tank ammonia was passed through the potassium hydroxide drying tower (A) and into the ozonization vessel where it condensed on top of the ozonated hydroxide and extracted the "ozonate". After approximately 10 ml. of liquid ammonia had been collected in the ozonization vessel, stopcocks (H) and (G) were opened so that the solution was free to pass into the collection flask (L), stopcock (F) was closed, and the cooling bath (I) surrounding the solution was removed. The pressure of the ammonia from the tank forced the solution into the collection vessel, where it was permitted to evaporate to dryness by removing the cooling bath (J) and passing dry oxygen through the system.

It was found necessary to dry the system well before any extraction was undertaken, particularly the collection vessel, since liquid ammonia readily absorbs moisture. Potassium hydroxide towers were used for dehydrating purposes since magnesium perchlorate readily absorbs ammonia; the dehydrating tower (B) leading to the collection apparatus was utilized so that atmospheric moisture could not diffuse into the collection flask after evaporation of the liquid ammonia.

Table V. Analyses of Extracted Materials (Cesium and Potassium)

"ozonate"		decomposant	mols O_2	mols MOH	% O_2	%M_2O	mols I_2	O_2/I_2
1)	Cs	HI	0.00017	-	-	-	0.00085	2.0 : 1
2)	Cs	HI	0.00023	-	-	-	0.000079	2.9 : 1
3)	Cs	H_2O	0.00016	-	-	-	0.000062	2.5 : 1
4)	Cs	H_2O† (MnO_2)	0.00015	0.00035	-	-	0.000044	2.9 : 1
5)	Cs	H_2O* (MnO_2)	0.00018	0.00028	-	-	-	-
6)	K	H_2O	0.00029	0.00024	44.5‡	55.5‡	-	-
7)	K	H_2O	0.00026	0.00018	48.8‡	51.2‡	-	-
8)	K	50°	0.00016	-	16.0	-	-	-

---

*Acidified potassium iodide solution was added to the solution remaining after decomposition. No additional evolution of oxygen.

† Acidified potassium iodide solution was added to the solution remaining after titration with 0.0915 N hydrochloric acid; the iodine liberated was then titrated with 0.05048 N arsenic(III) oxide solution.

‡ These values are calculated on the assumption that the only products of reaction with water are O_2 and KOH. This assumption would appear valid in the light of the fact that the solutions left after decomposition liberated only traces of iodine from acidified potassium iodide.

When the liquid ammonia solution had evaporated to dryness and all residual ammonia had been swept out by the stream of dry oxygen, the collection flask (which was not lubricated) was removed, quickly stoppered, and weighed on an analytical balance. After the weight had been determined, the collection flask was fastened to the analytical apparatus (Fig. IV), where it served as the decomposition chamber. The red solid was then analyzed gasometrically by the previously described methods, and the resulting solution analyzed titrimetrically for alkali content. Similar analyses were performed on samples of extracted cesium "ozonate", and results for both the potassium and cesium compounds are tabulated in Table V. Inasmuch as the weight of the collection flasks used in these studies were approximately 50 grams, weights of samples of only 50 to 100 mg. were not considered sufficiently accurate to warrant inclusion in this table.

Several different decomposants were used in the analyses of the cesium and potassium materials, and the results of these various analyses are shown in Table V. Results of two analyses on the cesium compound, shown in the first two rows of the table are based on the use of acidified potassium iodide solution as a decomposant; the resulting solutions were neutralized with sodium bicarbonate and the iodine liberated was titrated with 0.05048 N arsenic(III) oxide solution, using starch solution as an indicator. The following row in the table shows the results obtained from the use of distilled water as a decomposant; after measurement of the evolved gas, acidified potassium iodide solution was added to the resulting solution and the iodine liberated was determined titrimetrically. The fourth and fifth rows in the table show data obtained from the use of an aqueous suspension of manganese dioxide as a decomposant; the resulting solutions were titrated with 0.0915 N hydrochloric acid solution to determine the alkali content. In one of these determinations, acidified potassium iodide solution was added to the solution remaining after titration with acid, and the iodine liberated was determined by use of arsenic(III) oxide solution. These data show that treatment of the solid "ozonate" with water or acid does not appreciably affect the inherent oxidizing power of the solids. The amount of cesium hydroxide impurity in these (fourth and fifth rows) cesium "ozonate" samples was such as to render the percentages of cesium monoxide and oxygen not very significant.

The sixth and seventh rows of Table V give the results obtained by decomposing samples of the potassium compound with water, measuring the evolved gas, and titrating the resulting solutions with 0.0915 N hydrochloric acid solution. Addition of acidified potassium iodide to these solutions after neutralization by the hydrochloric acid resulted in the liberation of only faint traces of iodine. (This behavior is to be contrasted to that shown by the cesium compound.) However, it must be stated that considerable quantities of iodine are liberated if the solid extract is decomposed by acidified potassium iodide. The calculated percentages of oxygen and potassium monoxide agree favorably with those calculated for the complete decomposition of material of gross composition KO_3. The last row in Table V shows the amount of oxygen liberated by heating a 0.0319 g. sample of the potassium compound for one hour at 50°C. The percentage of oxygen, calculated on the basis of the total weight of the compound, is very roughly equivalent to that calculated for the oxygen liberated in the decomposition of KO_3 to KO_2. (Observed, 16.0%; calculated, 18.4%).

A few interesting observations were made during the study of the extracted materials. When water is added to either the potassium or cesium material, the decomposition takes place with almost explosive violence and is accompanied by a bright flash of light. The brilliance of this flash seems to depend on the purity and quantity of the sample. The flashes are accompanied by sudden evolution of gas. When the extracted materials are added to water immediately after preparation and tested with a solution of titanium(IV) sulfate solution in dilute sulfuric acid, no test for peroxide is obtained. The cesium solid material gave no test for peroxide after standing in a stoppered vessel at room temperature for seven days. When the substances are heated (to 50°C for the potassium material and 100-150°C for the cesium material), the red coloration gives way to a mixture of white and yellow and positive peroxide tests are obtained on these substances.

The residue remaining on the filter after extraction with liquid ammonia gives positive peroxide tests after several successive ozonizations and extractions, the residue from the potassium material giving only an exceedingly faint test, but the residue reamining after extraction of cesium "ozonate" giving a fairly good peroxide test.

These observations can be interpreted to mean that the extracted materials do not decompose to the corresponding superoxides (or peroxides) when added to water or acid, but that they do decompose to these substances at higher temperatures in the absence of moisture. The positive peroxide tests obtained on the residue remaining on the filter after extraction with liquid ammonia probably indicates that a very small amount of superoxide (or peroxide) is formed during the reaction with ozone. The failure to observe positive peroxide tests on small quantities of non-extracted potassium and cesium "ozonates" is probably attributable to the extremely small amount of superoxide formed. The flashes of light obtained when the extracted materials are added to water probably indicates merely that a very large amount of energy is released in the decomposition process. If the red solids contain materials possessing the formulas KO_3 and CsO_3 - and the analytical data would seem to bear out this contention - this liberation of energy should not be unexpected, since ozone itself decomposes (when present in high concentrations) to oxygen with explosive violence.

Ozonization of Concentrated Alkali Solutions

As was stated previously, passage of ozone-containing oxygen into concentrated (12 m) solutions of potassium hydroxide (and cesium hydroxide) results in the formation of a yellow color if the temperature of the reaction is kept below -35°C. (Sodium hydroxide does not show this behavior). This yellow color is presumably due to the formation of the "ozonate". An attempt to gather some quantitative information concerning the nature of these yellow solutions was made by taking magnetic measurements on them at low temperatures (-35°to -50°C).

Since the color of the potassium solutions disappeared when the temperature rose above -35°C, it was necessary to devise a scheme for ozonating the solutions at the required low temperatures and obtaining magnetic measurements without permitting the temperature to rise above this value at any time. In order to accomplish this purpose, it was necessary to so adjust the magnetic balance that it could be used for low temperature measurements. This was accomplished by separating the pole pieces of the magnet so that an unsilvered Dewar flask of approximately 60 mm. O.D. could be placed between them. A clamp (of a non-magnetic material) was fastened to a brass rod extending vertically through the supporting table, and so arranged that it held in a vertical position a Pyrex restraining tube (open at the top end) which dipped into the Dewar flask. This tube, which was about 30 mm. O.D., was of sufficient length that it extended from the balance pan to a point about two inches below the center of the magnetic field. When clamped in a vertical position and permitted to dip into a cooling bath in the Dewar flask, this tube permitted a weighing tube (suspended from the balance pan) to hang freely between the pole pieces of the magnet inside the cooling apparatus without touching the cooling bath itself. Since the Dewar flask was unsilvered, an observer could readily see into the suspended weighing tube during the course of a magnetic measurement. The Dewar flask was merely permitted to stand on the floor of the magnet, since it was sufficiently long to extend between the pole pieces to a height about 3 in. above the center of the magnetic field. The cabinet which supported the magnetic balance was enclosed so that the atmosphere in which the measurements were to be taken could be kept relatively free of moisture by means of containers of dehydrating agents such as calcium chloride, etc. This was necessary in order to minimize the amount of moisture condensing on the weighing tube during the course of a weighing at low temperatures.

The weight and magnetic susceptibility of the empty tube was determined under the same conditions of temperature and humidity that would prevail during magnetic measurements of the ozonated solutions. This was necessary so that the gain in weight due to condensed water vapor would not constitute an error during susceptibility determinations. In addition, susceptibility measurements on 12 m potassium hydroxide solution, saturated with oxygen, were made under the same conditions.

Since diamagnetism is supposedly temperature-independent, the calibration of field strength was determined by weighing the tube filled with water at room temperature. The Dewar vessel, filled with cellosolve, and the restraining tube were also in position so that experimental conditions might be simulated. When the field strength and both the weight and Δw of the empty tube had been determined, the entire cooling apparatus was transferred to the hood for use in the ozonization reaction.

The weighing tube (22 mm. O.D.) was then filled with 12 m. potassium hydroxide solution and placed in the restraining tube which rested in the cooling bath (-50°C). Ozone-containing oxygen was slowly bubbled through the solution by means of a small (3 mm. O.D.) Pyrex tube until a definite yellow color was imparted to the solution. The bubbling tube was then removed, the cap placed on the weighing tube, and the entire ensemble transferred to the magnetic balance. The solution-filled weighing tube was suspended from the balance pan, the restraining tube clamped into position, and the magnetic measurements quickly taken before the yellow color faded. At no time was the solution-filled weighing tube permitted to leave the confines of the restraining tube, which was suspended in the cooling bath. Since the Dewar flask was unsilvered, the color of the solution could be noted throughout all operations. A thermometer, which was placed

Table VI. Magnetic Data on Ozonated Solutions

(Density of potassium hydroxide solutions = 1.265 g./ml.

	k*	χ*
1) Non-ozonated, unsaturated with oxygen (28°C)	-0.720	-0.569
2) Non-ozonated, saturated with oxygen (-50°C)	-0.451	-0.357
3) Non-ozonated, saturated with oxygen (-50°C)	-0.504	-0.398
4) Ozonated solution (-40° to -50°C)	-0.202	-0.159
5) Ozonated solution (-40° to -50°C)	-0.095	-0.075
6) Ozonated solution (-40° to -50°C)	-0.190	-0.150
7) Ozonated solution (-40° to -50°C)	-0.202	-0.159
8) Ozonated solution (-40° to -50°C)	-0.020	-0.016
9) Ozonated solution (-40° to -50°C)	-0.141	-0.111
10) Ozonated solution (-40° to -50°C)	-0.263	-0.208

---

*Values of k are given in 10^{-6} cgsu./ml. Values of χ are given in 10^{-6} cgsu./g.

Note: The lack of precision in the values (4) through (10) is attributable to the difference in the time involved in the various measurements. Since the yellow color faded slowly with time, even when the temperature was kept constant, a greater time required for magnetic measurements would permit greater decomposition of the paramagnetic material.

in the cooling bath, provided temperature readings throughout all operations; solid carbon dioxide was added to the Dewar vessel periodically so that the temperature was never allowed to rise above -40°C.

The volume susceptibilities for seven samples of potassium hydroxide solution (of the same concentration) which had been ozonated at -40° to -50°C, are included in Table VI. By dividing these values by the density of the solutions (1.265 g./ml.), the gram susceptibilities were also determined. As a standard for comparison, the susceptibility values for potassium hydroxide solution (of the same concentration), which had been saturated with oxygen under the same conditions, are also shown. The data do little to establish the nature of the yellow substance in solution, but they do indicate that a paramagnetic substance must be present. Weiss[13] has suggested that the yellow substance is potassium superoxide. However, the data in the following section would seem to refute this hypothesis.

Stability of Potassium Superoxide in Alkaline Solution

If Weiss's hypothesis, that the yellow color of the ozonated potassium hydroxide solutions is potassium superoxide, is correct, then the superoxide ion must be somewhat stable in strongly alkaline solution at low temperatures. If superoxide ion is stable in strongly alkaline medium at low temperatures, addition of such a solution to solid superoxide at -40° to -50°C should not result in complete decomposition of the superoxide. An attempt to either verify or disprove this hypothesis was made by adding concentrated potassium hydroxide solution to weighed samples of potassium superoxide at low temperatures, and measuring the evolution of oxygen.

A sample of potassium superoxide (98 per cent purity) was weighed on an analytical balance and placed in a vessel for attaching to an analytical apparatus analogous to the one shown in Fig. IV. (In this case, however, the decomposition cell was so constructed that the entire cell - including the decomposant reservoir - could be thermostatted at -50°C, or lower, in a large Dewar flask.) The vessel was attached to the remainder of the apparatus and held in place by means of rubber bands. Ten ml. of 11 m potassium hydroxide solution were added to the decomposant reservoir and both the decomposant and superoxide were thermostatted at -40° to -50°C, in order to minimize any decomposition due to local heating. When the system had reached thermal equilibrium, the solution was added to the decomposition chamber through the stopcock separating the two chambers, and the volume of oxygen evolved was measured, due account for the volume due to the decomposant being taken. From this volume and the weight of the superoxide sample, the volume of liberated oxygen per gram of sample was calculated. A sample calculation follows:

temperature of decomposition cell = -45°C
temperature of burette = 30.0°C
pressure (corrected) = 725 mm.
weight of superoxide = 0.0570 g.
volume of oxygen liberated = 14.80 ml.
volume of oxygen at STP = 12.73 ml.
volume of oxygen (STP) per gram = 223 ml./g.

The results of four such determinations are shown in Table VII. The potassium superoxide used in these experiments was found to give up 237 ml. oxygen per gram of material upon complete decomposition. The values shown in Table VII can scarcely be attributed to anything other than decomposition of the superoxide. Even the value of 175 ml./g. is much greater than the volume of oxygen which would be evolved when one gram of potassium superoxide decomposes to potassium peroxide. Furthermore, the solutions remaining in the decomposition chamber were tested with

Table VII

Data on Stability of Superoxide in Alkaline Medium

	wt. sample	temp. (bath)	vol. O_2 (STP)	vol. O_2/g. (STP)*
1)	0.0369 g.	-48°C	8.73 ml.	236 ml.
2)	0.0570 g.	-45°C	12.73 ml.	223 ml.
3)	0.0813 g.	-48°C	14.20 ml.	175 ml.
4)	0.1395 g.	-49°C	33.00 ml.	236 ml.

*Complete decomposition of the potassium superoxide utilized in these studies gave 237 ml. O_2 (STP)/g. One gram of pure potassium superoxide would give 158 ml. O_2 (STP)/g. upon decomposition to potassium peroxide.

acidified potassium iodide solution within 20 minutes after decomposition and, in every case, no liberation of iodine was noted. From these observations, one can conclude that potassium superoxide, and also the peroxide, are not stable in concentrated potassium hydroxide solution, even at temperatures as low as -49°C, and that Weiss's[13] hypothesis concerning the nature of ozonated potassium hydroxide solutions is extremely questionable.

Ozonization of Sodium and Barium Peroxides

Very little work was done on the ozonization of peroxides. Only qualitative observations on this subject have been noted, with no quantitative investigations being made. However, it has been observed that when ozone-containing oxygen was passed through sodium peroxide at room temperature for several hours, a considerable portion of the peroxide was colored a definite orange. The color could conceivably be due to a reaction between ozone and hydroxide impurities in the peroxide, although the extent of the orange color would seem to indicate that this is not the case. No evidence is available which would indicate that a reaction does not take place between ozone and peroxide. As was noted in the ozonization studies of the hydroxides, no reaction between ozone and the peroxide samples took place under strictly anhydrous conditions.

When a stream of ozone-bearing oxygen was passed through barium peroxide at room temperature for several hours, a light brown color was imparted to the peroxide. This change in coloration was not great, but was quite evident when the color of the ozonated peroxide was compared with that of the strating material. Again, no quantitative work was done on this compound. However, magnetic measurements were taken on samples of ozonated sodium and barium peroxides. In every case, the ozonated peroxides were appreciably less diamagnetic than the starting materials; in some cases they were actually paramagnetic.

Summary

Ozone-treated sodium hydroxide contains a yellow material which is not soluble in liquid ammonia or any of the common solvents, and which decomposes in water or acid with a concomitant liberation of oxygen. Neither the ozonated material nor the solution remaining after decomposition liberates iodine from acidified potassium iodide solution. One can conclude, therefore, that the yellow material is neither sodium superoxide nor sodium peroxide. The data obtained from magnetic measurements and chemical analyses are most reasonably interpreted by assigning the formula NaO_3 to the yellow material.

The products obtained from the ozonization of potassium and cesium hydroxides are colored orange and orange-red, respectively. They also give up oxygen upon treatment with water or acid. The ozonated hydroxides of potassium and cesium hydroxide, however, contain material which oxidizes iodide ion, but which gives observable tests for peroxide only after several successive treatments with ozone-containing oxygen. Furthermore, the data obtained from chemical analyses and magnetic measurements of the ozonated hydroxides are also most reasonably interpreted by assigning the formulas KO_3 and CsO_3, respectively, to the colored materials.

The solid red materials extracted by liquid ammonia from ozone-treated potassium and cesium hydroxides decompose with almost explosive violence when added to water, with a

concomitant liberation of gas, and of energy in the form of light. Analyses of the extracted potassium material indicate a gross composition corresponding essentially to the formula KO_3. Similar analyses on the extracted cesium containing products cannot be so simply interpreted. When the extracted materials are added to acidified potassium iodide solution, considerable quantities of iodine are liberated, the molar ratio of evolved oxygen to liberated iodine being approximately 2.5 : 1 in the case of the cesium material. If the material extracted from ozone-treated cesium hydroxide is first dissolved in water or acid and the resulting solution is then treated with acidified potassium iodide, the ratio of evolved oxygen to liberated iodine is essentially that found as a result of primary decomposition with acidified potassium iodide. However, when the extracted potassium material is added to water, the resulting solution liberates only faint traces of iodine under the same conditions. This would seem to indicate that the substance which is responsible for the oxidation of iodide ion is more stable in solution in the case of the cesium material than in the case of the potassium material. The gradation of oxidizing power displayed by solutions of sodium, potassium, and cesium "ozonates" would argue against the hypothesis that the oxidizing action is due to an O_3^- ion, since the behavior of this ion in solution should be independent of the nature of the cation.

The red materials extracted from ozonated potassium and cesium hydroxides do not give positive peroxide tests when decomposed immediately after preparation. This would indicate that the solid materials decompose directly to the corresponding hydroxides when added to water. When thermally decomposed at 50° to 100°C, the red solids decompose to a mixture of white and yellow substances which exhibits the behavior expected of superoxides.

Ozonization of concentrated potassium hydroxide solutions at -40° to -50°C produces unstable yellow solutions which contain paramagnetic material. That this paramagnetic material is not superoxide was established by proving that potassium superoxide decomposes completely in strongly alkaline solution at -40° to -50°C, and that the resulting solutions do not contain peroxide. Therefore, Weiss's[13] postulate that the yellow solutions are alkaline solutions of superoxide cannot be correct. The yellow coloration is presumably due to an O_3^- ion.

Suggestions for Future Work

Many points must be established before the complete nature of the alkali metal "ozonates" can be definitely established. Certainly a more thorough study of the behavior of the red materials extracted by liquid ammonia from ozone-treated potassium and cesium hydroxides would give a more complete picture of the nature of these substances. Magnetic studies of the extracted materials, supplemented by more precise analytical data, should be performed. The solubility of cesium hydroxide in liquid ammonia should be determined in order to establish whether hydroxide impurities are carried into the collection flask by the extracting solvent.

The reaction between ozone and the peroxides of the alkali and alkaline earth metals should be more fully investigated in order to determine whether the reaction is analogous to that between ozone and the hydroxides.

Perhaps oxygen-rich precipitates may be obtained by addition of a liquid ammonia solution of the extractable materials to a liquid ammonia solution of barium nitrate or certain other of the liquid-ammonia-soluble salts of the alkaline earth metals.

These are but a few of the investigations that would add considerably to our understanding of the nature and behavior of the "ozonates".

References

1. Wurtz, Dictionnaire de Chimie pure et appliquée, 11, 721 (1868).
2. Baeyer and Villiger, Ber., 35, 3038 (1902).
3. Erdman and Kothner, Ann. 193, 241 (1878).
4. Bach, Ber., 35, 3424 (1902).
5. Manchot and Kampschulte, Ber., 40, 4984 (1907).
6. deForcrand, Compt. rend., 142, 1254 (1906).
7. Traube, Ber., 45, 2201 (1912).
8. Traube, Ber., 49, 1670 (1917).
9. Rothmund and Burgstaller, Monatshefte Chem., 34, 693 (1913).
10. Werner, "Neuere Andschauungen and dem Geniete der anorganischen Chemie", 3rd. ed., pp. 121-122.
11. Strecker and Thieneman, Ber., 53, 2096 (1920).
12. Manchot, Ber., 41, 471 (1908); 46, 1089 (1913).
13. Weiss, Trans. Farad. Soc., 31, 668 (1935).
14. Kazarnovskii, Nikolskii, and Abletsova, Doklady Akad. Nauk. S.S.S.R., 64, 69-72 (1949).
15. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances", McGraw-Hill Book Co. Inc., New York, 1923, p. 476.
16. Lindenstruth, Ph.D. Thesis, University of Kansas, Lawrence, Kansas, 1950.
17. Lange, "Handbock of Chemistry", Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1413.
18. Smith, J. Am. Chem. Soc., 47, 1850 (1925).
19. Henne, J. Am. Chem. Soc., 51, 2676 (1929).
20. Smith and Ullyot, J. Am. Chem. Soc., 55, 4327 (1933).

21. Thorp and Armstrong, The Frontier, 9, No. 2, 3-5, 16-17 (1946).

22. Pickering, J. Chem. Soc., 63, 890 (1893).

23. Machu, "Das Wasserstoffperoxyd und die Perverbindungen", Julius Springer, Wien, 1937, p. 332.

24. Ephraim, "Inorganic Chemistry", Gurney and Jackson, London, 1948, pp. 524-6.

25. Ibid., p. 527.

26. Kleinberg, "Unfamiliar Oxidation States and Their Stabilization", University of Kansas Press, Lawrence, Kansas, 1950, p. 24.

27. Mellor, "A Comprehensive Treatise on Inorganic Chemistry", vol. II, Longmans, Green, and Co., London, 1922, pp. 485-6.

28. Thompson, Master's Thesis, University of Kansas, Lawrence, Kansas, 1949.

29. Selwood, "Magnetochemistry", Interstate Publishers, Inc., New York, 1943, p. 231.

30. Hodgman (Editor), "Handbook of Chemistry and Physics", 25th Ed., Chemical Rubber Publishing Co., Cleveland, 1941, pp. 1873-83.

31. Prasad, Charmatti, Kanekar, and Biradar, J. Chem. Phys., 17, 813 (1949).