

Studies on the Higher Oxides of the  
Alkali and Alkaline Earth Metals

by

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## Introduction

Of the higher oxides of the alkali and alkaline earth metals, only the peroxides of sodium and barium had any extensive use before World War II. Since the beginning of the war, however, potassium superoxide,  $\text{KO}_2$ , has been prepared for the Navy in large quantities and finds use as a source of oxygen in breathing apparatus for fire-fighting and rescue work aboard ship. The oxide is used in canisters in a closed system apparatus where its ready reaction with carbon dioxide and moisture from the breath releases sufficient oxygen to supply the wearer's needs. This development, borne of war time need, has pointed out the inadequacy of our knowledge of this type of compound which is suitable for air purification.

This study represents a two-fold purpose. The first is to summarize the work that has been done on these oxides and to evaluate it critically whenever possible. The second is to prepare and study the peroxides and superoxides of the alkali and alkaline earth metals which have not previously been investigated. These purposes have been only partially fulfilled.

### Historical Review

The oxides of the alkali and alkaline earth metals may be divided into three classes--namely, monoxides, peroxides, and superoxides. The "normal" oxides of the alkali and alkaline earth metals, of the general formulas  $M_2O$  and  $MO$ , respectively, may be considered to be salts of the weak acid water. These oxides react with water to give, in most cases, highly ionized hydroxides. The members of the second type of oxides, the peroxides, are derivatives of the weak acid hydrogen peroxide and contain the  $O_2^{--}$  ion, of the structure  $^-\ddot{O}:\ddot{O}^-$ . By definition, peroxides are compounds which give a solution of hydrogen peroxide when treated with a strong acid. Since they are salts of the weak acid hydrogen peroxide, the peroxides are extensively hydrolyzed; their strongly alkaline solutions are active oxidizing agents. The least familiar class is that group of oxides referred to in the recent literature as superoxides, a name suggested by Bray and Eastman (1). The superoxides are salts of the unstable acid  $HO_2$ , which decomposes into hydrogen peroxide and oxygen (2). The superoxide salts react similarly in water. This investigation is concerned primarily with the last two classes of oxides--the higher oxides.

#### The Alkali Metal Oxides

Numerous investigators have studied the oxides of the

alkali metals. Some of the first experiments were performed by such well known pioneers in chemistry as Berzelius (3) and Gay Lussac (4). As would be expected with the equipment available at that time and the techniques employed, this work was not extremely accurate but did serve as a basis for further research. The first reliable work was done by Harcourt (5) who found that the highest product of the direct oxidation of potassium is  $K_2O_4$ , but he could isolate no intermediate oxides. Sometime later Lupton (6) published data indicating that the peroxide,  $K_2O_2$ , is obtained by the continued action of dry air or oxygen on potassium. He also described the complex oxides  $K_8O_5$ ,  $K_6O_4$ ,  $K_4O_3$  (probably aggregates of the different oxides in varying proportions) which he obtained by analyzing different parts of the product showing different colors.

To clear up some of the earlier discrepancies, Holt and Sims (7) felt it desirable to repeat this work. Their work was by far the best, and incidentally the last reported in the literature on the direct oxidation of the alkali metals in absence of a solvent. A few years previous to their work it had been shown by Baker (8) that oxidation in certain cases proceeds with extreme difficulty in perfectly dry oxygen, and since Holt and Sims' work seemed to indicate this also, they carried out experiments to see whether potassium would react with extremely dry oxygen. In order to

test this a tube of thick glass was constricted to form two chambers. Into one end was placed a sealed tube of potassium and into the other some phosphorus pentoxide. After a time the tube was shaken, thus breaking the potassium tube and exposing the free metal. The bright surface remained unchanged for several days at room temperature, and even when the metal was heated until it vaporized, no evidence of oxidation could be seen. The same results were obtained with sodium.

In view of these findings, Holt and Sims dried the oxygen used in their experiments by passing it through about eight inches of calcium chloride. They found that when potassium (contained in a sheet-iron boat in glass tubing) is heated in a stream of oxygen, the oxidation proceeds without a break until  $K_2O_4$  is obtained as the final product. By using nitrous oxide as the oxidizing agent both  $K_2O_2$  and  $K_2O_3$  were prepared. This was accomplished by oxidizing the potassium in a small flask which was heated by a fusible metal bath and connected on either side by a cylindrical gas holder. By alternately raising and lowering the gas holders a known amount of gas could be passed over the metal sample and the oxidation stopped when the theoretical amount of gas had been absorbed to form the intermediate oxides. The  $K_2O_3$  so prepared was buff-colored and the  $K_2O_2$  sulfur-yellow in color. The  $K_2O_2$  upon exposure to the air slowly deliquesced without

further oxidation, but the  $K_2O_3$  was oxidized so violently that a red glow spread through the mass and the oxide became fused.

The same investigators prepared sodium for oxidation in the following manner. A small flask was filled about three-fourths full with toluene, and the air in the flask displaced by nitrogen; small lumps of sodium were then introduced, and the flask was heated on a sand bath until the metal melted, and then violently agitated until the mixture cooled. The toluene was then removed by washing, first with benzene, and then several times with pure dry ether, and finally heated in dry nitrogen. By this means the sodium was obtained in a very fine state of division, and with a bright surface. Some of this sodium was then heated in an iron boat in a stream of moderately dry oxygen; it was soon coated over with an oxide film but no definite oxide could be obtained below the melting point of sodium. If heated slightly above its melting point, it was found the sodium would catch fire, and if the temperature was kept below  $180^\circ$  and the supply of oxygen limited, the greyish-white  $Na_2O$  was formed. The latter also was formed when sodium was oxidized slowly with nitrous oxide at a temperature of  $180-200^\circ$ . By using larger quantities of sodium and by raising the temperature rapidly in an excess of oxygen, the yellow-white  $Na_2O_2$  was formed. Both sodium and potassium were found to form



mixtures of nitrites and nitrates with the red oxides of nitrogen.

An attempt was also made to prepare lithium peroxide. When the metal was heated to  $250^{\circ}$  in a stream of oxygen, it burned with a bright white flame, forming almost pure  $\text{Li}_2\text{O}$  with only traces of the peroxide in it.

In their work, Holts and Sims substantiated the composition of several higher oxides but were unable to prepare  $\text{K}_2\text{O}$ . Rengade (9) claimed to have obtained the monoxides  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ , and  $\text{Cs}_2\text{O}$  by direct oxidation in the presence of excess metal with subsequent removal of this excess by distillation in a vacuum.

So far only the direct methods of oxidizing the various metals have been considered. There are at least two other methods used to prepare alkali metal oxides. The first of these has been used only as a means of preparing  $\text{Li}_2\text{O}_2$ . In this method  $\text{LiOH}$  is dissolved in ethanol (95%) and upon the addition of 30%  $\text{H}_2\text{O}_2$  there is formed a precipitate of  $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$  which may be dehydrated to give pure  $\text{Li}_2\text{O}_2$ . This means of preparation has been used by Blumenthal (10) and a similar method by deForcrand (11). Lithium peroxide differs from the other alkali metal oxides in that it is not hygroscopic and has little tendency to react with carbon dioxide at room temperature. This technique is limited in its applications, but the second method, that of oxidizing a

solution of the metal in liquid ammonia, has been used to prepare a number of the oxides and probably its possibilities have not yet been fully explored.

One of the first investigators to use liquid ammonia as a solvent was Joannis who contributed much in this field. His work (12) on the oxidation of sodium and potassium in liquid ammonia deserves particular attention as the present investigation is an extension of this work and that of Kraus and Whyte (13). Joannis claims to have prepared  $K_2O_2$ ,  $K_2O_3$ ,  $K_2O_4$ ,  $Na_2O \cdot NH_3$  and  $Na_2O_3$ . Apparently he did prepare the three potassium compounds but probably, as will be shown later, did not prepare the two sodium compounds listed.

Joannis realized that the two compounds of sodium that he reported would sometimes form simultaneously. He found that by a controlled oxidation of sodium in liquid ammonia a pale rose colored compound corresponding to the formula  $Na_2O \cdot NH_3$  was formed. The method of analysis used in this investigation consisted of weighing the metal as such before the experiment was started and afterwards in the form of the sulfate. The amount of oxygen was taken as the increase in weight during the experiment; in some cases the amount of gas absorbed was measured. The ammonia was analyzed volumetrically after separation from the hydroxide by distillation.

The following is the only analysis given on this compound. No indication was given as to whether this amount of oxygen was

a measured volume or reported as a difference in weight.

	Calculated for <u><math>\text{Na}_2\text{O}\cdot\text{NH}_3</math></u>	<u>Found</u>
Na	58.23%	58.45%
$\text{NH}_3$	21.52	22.08
O	20.25	19.45

He further claimed that the compound  $\text{Na}_2\text{O}\cdot\text{NH}_3$  may take up two more equivalents of oxygen but no more ammonia to give the pale rose colored  $\text{Na}_2\text{O}_3$ . Upon treatment with water it supposedly liberated oxygen and was transformed into  $\text{Na}_2\text{O}_2\cdot 8\text{H}_2\text{O}$ . Following are the only analytical results given on this compound; no explanation is given as to what became of the ammonia molecule attached to the  $\text{Na}_2\text{O}$ .

	Calculated for <u><math>\text{Na}_2\text{O}_3</math></u>	I	<u>Found</u>	II
Na	48.94%	48.74	49.59	
O	51.06	51.26	50.41	

He does admit that the composition is variable if the oxidation is terminated at the moment of disappearance of the blue color. Due to lack of details these data are severely limited in their usefulness.

Rengade (9) made a study of the oxidation of potassium, cesium, and rubidium, in liquid ammonia, and established the existence of the oxides corresponding to the formulas  $\text{M}_2\text{O}_2$ ,  $\text{M}_2\text{O}_3$ , and  $\text{M}_2\text{O}_4$ . He also showed that in the case of cesium and

rubidium the product formed in liquid ammonia depends upon the rate of oxidation. With rapid oxidation the initial product corresponds to  $M_2O_2$  and the final product to  $M_2O_4$ . On slow oxidation the initial product is a mixture of the hydroxide,  $MOH$ , and the amide,  $MNH_2$ , which is further oxidized to the nitrite.

The only research on these oxides so far reported in the literature in this country was done under the direction of Dr. Charles Kraus, one of the pioneers in the liquid ammonia field. Two important investigations on the oxides of sodium and potassium were conducted under his direction.

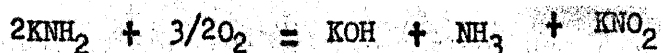
In the first paper (13) in agreement with Rengade's work, it was shown that upon slow oxidation of either sodium or potassium solutions the initial products are the hydroxide and amide, and upon further oxidation the amide is oxidized to the nitrite.

More complete data are given by Whyte (14) on the formation of the amide and its subsequent oxidation. In a study, first in the case of slow oxidation, he attempted to prepare  $K_2O$ . This may be accomplished either by carrying out the oxidation with extreme slowness or by admitting the calculated amount of oxygen necessary to form the monoxide. The latter method was adopted and gave a white, gelatinous precipitate and a rather yellowish liquid. The weight found was much greater than the theoretical value and the excess weight corresponded very

closely to that of one molecule of ammonia. He assumed that ammonolysis had taken place, yielding potassium hydroxide and potassium amide as indicated by the equation,



Since it was not certain whether a complex compound or a mixture of KOH and KNH<sub>2</sub> was produced a separation was attempted by means of a two-legged glass tube, such as that used by Peck (15). As potassium amide is very soluble and potassium hydroxide is insoluble in liquid ammonia it was established that these two compounds were formed and that the amide can be oxidized either in solution or in the dry state. Whyte's data indicated that the reaction is:



Upon rapid oxidation of the metal solution he was able to isolate both the peroxide and the superoxide but not the trioxide.

This investigator also studied the oxidation of solutions of sodium in liquid ammonia. He found that the initial product was always the monoxide and that this ammonolyzes with the formation of sodium amide and sodium hydroxide. The amide was converted to the nitrite upon further oxidation, this reaction appearing to be identical with the analogous reaction in the slow oxidation of potassium. The publication (13) based on this work stated that the peroxide is formed upon the rapid oxidation of sodium in liquid ammonia. This is

in contradiction to the findings reported in Whytes' thesis.

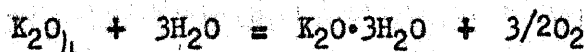
This first work of Kraus' was carried out at or near the boiling point of ammonia and  $\text{Na}_2\text{O}_2$  was reported as the highest oxidation product of sodium. Joannis claimed to have obtained  $\text{Na}_2\text{O}_3$  by working at  $-50^\circ$ . In Kraus' second paper (16) the oxidation of potassium was carried out at  $-50^\circ$  and very nearly pure samples of both  $\text{K}_2\text{O}_2$  and  $\text{K}_2\text{O}_4$  were obtained. By allowing oxygen at low pressure to react with  $\text{K}_2\text{O}_2$  at room temperature the unstable chocolate colored  $\text{K}_2\text{O}_3$  was prepared.

In Kraus' original work the procedure used consisted essentially in passing a controlled stream of oxygen through a solution of the metal in liquid ammonia contained in a weighed tube at liquid-ammonia temperatures. The volume of oxygen absorbed was measured and the weight of the products of reaction was determined by weighing the tube at the end of the reaction. The metal employed was melted in a vacuum and run into small sealed tubes of known weight. These tubes were broken just prior to introduction into the liquid ammonia. In Kraus' second paper (16) the same method of handling the metal was used, but the analysis consisted of decomposing the oxide and measuring the evolved oxygen as it was realized that the weight of the product formed was not a satisfactory criterion of purity. The oxygen evolved on treating the higher oxides with ice water serves to determine the amount of oxygen combined in excess of  $\text{K}_2\text{O}_2$ .



When  $\text{K}_2\text{O}_2$  is dissolved in ice cold water, no oxygen is evolved, at least theoretically. The oxygen evolved on heating the resulting solution indicates the amount of potassium present in the form of the peroxide,  $\text{K}_2\text{O}_2$ .

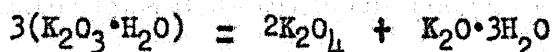
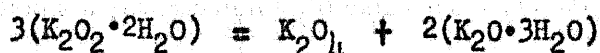
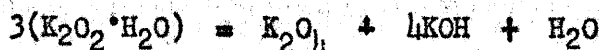
With water vapor,  $\text{K}_2\text{O}_4$  reacts according to the equation,



Once the breakdown of some of the  $\text{K}_2\text{O}_4$  is initiated, it decomposes completely to potassium hydroxide, while the remaining  $\text{K}_2\text{O}_4$  remains intact. This is indicated by the fact that on partially decomposed  $\text{K}_2\text{O}_4$ , the oxygen evolved in the second stage of the analysis is one-half that of the first stage (addition of ice water to the sample). Water added to  $\text{K}_2\text{O}_4$  suspended in liquid ammonia shows no indication of reaction so long as liquid ammonia or ammonia vapor is present.

Kraus also showed that  $\text{K}_2\text{O}_2$  and  $\text{K}_2\text{O}_3$  absorb definite quantities of water vapor without evolution of oxygen. However, this method of preparation of the hydrates was found to be unsatisfactory because of the rearrangement of the hydrates. A better method is to introduce the necessary quantity of water into a suspension of the oxides in liquid ammonia. By this method  $\text{K}_2\text{O}_2 \cdot \text{H}_2\text{O}$ ,  $\text{K}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{K}_2\text{O}_3 \cdot \text{H}_2\text{O}$  may be prepared. These hydrates rearrange slowly at room temperature in the dry state to give  $\text{K}_2\text{O}_4$  and KOH hydrates. By

the two stage analysis previously described the following rearrangements were studied:



The first rearrangement shown above goes rather fast and to completion, the second one goes a little slower, and the third much slower, but with definite indications of autooxidation.

According to deForcrand (17)  $\text{K}_2\text{O}_4$  loses oxygen above its melting point with the formation of  $\text{K}_2\text{O}_3$ . Holt and Sims (7) found that the final product, on heating  $\text{K}_2\text{O}_4$  in glass, corresponds to the formula  $\text{K}_2\text{O}$ , reaction presumably taking place between the oxide and the glass. Kraus (13) repeated this work and found that  $\text{K}_2\text{O}_4$ , when melted in pyrex or soft glass, gives a product which by analysis corresponds to  $\text{K}_2\text{O}$ . If heated in an aluminum boat, however, the final product is  $\text{K}_2\text{O}_3$ , which is in agreement with deForcrand's work. Kraus also observed that  $\text{K}_2\text{O}_4$ , after exposure to the action of moisture, loses oxygen irreversibly between  $100^\circ$  and  $200^\circ$ . At temperatures above  $300^\circ$  it dissociates reversibly but the equilibrium pressures appear to depend on the oxygen content of the solid phase.

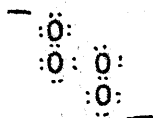
Previous to this work of Kraus, the dissociation of the peroxides of sodium and lithium, and the superoxide of potassium had been studied by Blumenthal (18). Shortly after this work



appeared Tzentnershver and Blumenthal (19) published data giving the melting points, dissociation temperatures at a pressure of one atmosphere, and the heats of formation of the known higher oxides of the alkali metals. Also, estimated melting points for the unknown oxides  $\text{Li}_2\text{O}_3$ ,  $\text{Na}_2\text{O}_3$ ,  $\text{Li}_2\text{O}_4$  and  $\text{Na}_2\text{O}_4$  were given.

Recently an attempt has been made (20) to prepare the higher oxides of sodium and potassium by thermal decomposition of the nitrates at temperatures ranging from  $750^\circ$  to  $1200^\circ$ . Sodium nitrate was found to decompose at  $800^\circ$  to form only a little peroxide. High peroxide content was obtained only by heating the salt rapidly to a high temperature. It was found necessary to heat the potassium salt to about  $1000^\circ$  where appreciable quantities of the stable black molten peroxide were obtained. Upon cooling, the melt was yellow to dark brown in color due to the presence of various oxides of potassium.

Alkali metal oxides of the general formula  $\text{M}_2\text{O}_4$  have until recently been called alkali tetroxides in the belief that the substances were analogous to the tetrasulfides and contained the  $\text{O}_4^{--}$  anion with the structure:



According to Pauling (1) the discovery of the three-electron bond suggested that these alkali oxides might contain the  $\text{O}_2^{--}$  ion with the structure  $\ddot{\text{O}} \text{---} \ddot{\text{O}}^{--}$  which involves a single bond and

a three-electron bond between the two identical atoms. This was proved by measuring the magnetic susceptibility of the potassium compound. The superoxide ion  $O_2^{\cdot -}$  contains one unpaired electron and therefore should be paramagnetic which was found to be the case, whereas the  $O_2^{2-}$  ion would be diamagnetic. The existence of the superoxide ion in crystalline potassium superoxide has also been verified by X-ray examination (22), and the crystal structure shows the potassium and superoxide ions to be arranged in a simple cubic array. Accordingly, the formula  $MO_2$  is indicated rather than  $M_2O_4$ . Several investigators have reported alkali metal oxides of the empirical formula  $M_2O_3$ . Magnetic and X-ray data on the rubidium and cesium compounds prove that these contain both the peroxide and the superoxide ion (22) and that their structures may therefore be represented by the formula  $M_2O_2 \cdot 2MO_2$ .

Kazarnovskii and Raikhstein (23) have shown by means of dissociation studies that  $K_2O_3$  is not a definite compound but a mixture of  $KO_2$  and  $K_2O_2$ . This is in agreement with the findings of Helms and Klemm (22).

The structure and properties of the univalent superoxide ion have been studied by Kasatochkin (24), who also gives an electronic scheme for oxidations which involves this ion. Attempts have also been made (25) (26) to study the reaction mechanism operative in the reaction of water with the superoxide ion to liberate oxygen. Supposedly the  $HO_2$  radical is involved in this

process.

### The Alkaline Earth Metal Oxides

The literature on this group of compounds is somewhat more scanty than on the related alkali metal compounds. Like the alkali group, three types of oxides of the alkaline earth metals are known.

The monoxides are the most common type found in this family. These oxides are formed when the hydroxides, carbonates or nitrates are decomposed by heat, the stability of these compounds being roughly parallel to the strength of the oxides as bases. Whereas the hydroxides or carbonates of the alkalis cannot be appreciably decomposed by heating, those of this group are all decomposed at high temperatures. The nitrates of the alkali metals are decomposed to nitrites on heating, while those of the heavy metals give oxides without the nitrite stage. At moderate temperatures the nitrates of the alkaline earths give a mixture of oxide and nitrite, with complete decomposition to the oxide at very high temperatures. Barium is nearest to the alkali metals in this property—its carbonate is the most difficult to decompose—while magnesium (and beryllium) is most unlike them. As is in the case with lithium, the lightest member of the group approaches the elements of the next heavier group of the periodic system in its properties.

The method of production ordinarily used to prepare these oxides is that which involves the decomposition of the carbonates,

but owing to the high temperature of decomposition of barium carbonate the hydroxide is usually employed in this case. The oxides are crystalline when prepared at high temperature, but as ordinarily manufactured they are in the form of a loose powder. These oxides are very difficult to melt but are liquefied in the electric arc. Their refractory properties, combined with their inertness to many reagents after they have been ignited, makes them useful in the construction of furnace linings, etc. Ignited BeO, like alumina, is insoluble in all acids with the exception of concentrated sulphuric acid.

The peroxides of this group are not as easily prepared as are the alkali metal peroxides. The formation of stable peroxides at high temperatures is characteristic of the more electropositive alkaline earth metals. This property is not very pronounced in lithium and is entirely absent in beryllium, while of the alkaline earths, barium forms a peroxide most readily in the dry way. The oxidation of calcium monoxide with oxygen at high pressure and temperature produces no peroxide, and only a 15 per cent yield of strontium peroxide is obtained by the oxidation of the monoxide at  $400^{\circ}\text{C}$  and 98 atmospheres pressure (27). On the other hand, barium monoxide is readily converted to the peroxide by heating in air to  $400^{\circ}\text{C}$ . This peroxide is readily decomposed at low pressures or at temperatures above  $400^{\circ}$ , and before the advent of liquid oxygen, this reaction was the basis of the Brin process for the manufacture of

oxygen.

Attempts have been made to prepare the alkaline earth peroxides by oxidation of the liquid ammonia solution of the metal. Only a poor yield is obtainable by the action of oxygen on the calcium solution, although the preparation of the strontium compound has been reported (28) in liquid ammonia.

From the above discussion it is readily apparent that there is a direct relationship between the size of the ion of the alkaline earth metal and its ability to form a peroxide. The peroxide of the comparatively large barium ion is readily obtained, while those of the smaller strontium and calcium ions are less readily formed. Magnesium peroxide has been obtainable only in the form of the impure hydrate, whereas it has thus far proved impossible to make the peroxide of beryllium, the member of the group whose ion is smallest.

The reversible equilibrium between barium oxide and the peroxide indicates the great stability of this compound. The radius of the Ba ion (1.3-1.4 Å) is close to that of the potassium (1.33 Å) and rubidium (1.48 Å) ions, so that from the standpoint of crystal chemistry it is to be expected that  $\text{BaO}_2$  and  $\text{KO}_2$  should be comparable in stability, since both have the calcium carbide type of crystal lattice with anions of similar dimensions:  $\text{O-O} = 1.28$  Å in the  $\text{O}_2^{\bar{2}}$  anion, 1.31 Å in the  $\text{O}_2^{\bar{1}}$  anion. As the radius of the cation decreases, the stability of the peroxide falls relative to that of the monoxides (28), as was indicated above.

Hildebrand (29) has studied the dissociation of barium peroxide and found that the dissociation depends on the presence of small quantities of water and that a rather large solid solution range complicated the determination of the dissociation curve. Blumenthal (30) has studied the thermal decomposition of calcium peroxide and found it to be reversible; this is in disagreement with the work of Fischer and Ploetze (27) previously cited.

The alkaline earth peroxides show a decided tendency to form hydrates. These peroxide hydrates are formed from the hydroxides of the metals and hydrogen peroxide, by the addition of  $\text{Na}_2\text{O}_2$  to solutions of the salts of the metals, or by precipitation of solutions of the salts containing  $\text{H}_2\text{O}_2$  with ammonia (31). There are two distinct types of these compounds. The hydrates peroxides,  $\text{MO}_2 \cdot x\text{H}_2\text{O}$ , usually contain eight molecules of water of hydration. They form pearly scales which lose their water without decomposition if carefully heated and which are slightly more soluble than the metal hydroxides. A second series of compounds are formed containing hydrogen peroxide of crystallization with the type formula  $\text{MO}_2 \cdot x\text{H}_2\text{O}_2$ . Most of these contain two molecules of  $\text{H}_2\text{O}_2$ , though a barium compound containing one molecule is also known. They are formed in the cold when concentrated  $\text{H}_2\text{O}_2$  is used. At higher temperatures the peroxides are obtained free from both water and hydrogen peroxide.

It has been found that  $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$  deepens in color upon standing, especially when exposed to ultra-violet light, and then evolves oxygen upon treatment with water. The change is attributed to the formation of  $\text{BaO}_4$ , although the compound has not been isolated in the pure state. These colored compounds can best be made by the action of 30 percent  $\text{H}_2\text{O}_2$  on the hydrated peroxides. By this procedure Traube and Schulze (32) were able to prepare mixtures of about 8.7 per cent  $\text{CaO}_4$  in  $\text{CaO}_2$ , and about 8 per cent  $\text{BaO}_4$  in  $\text{BaO}_2$ . Presumably the low yields were due to the decomposing action of the water present during formation of the superoxide. Magnetic studies on impure  $\text{CaO}_4$  (33) demonstrate the existence of the  $\text{O}_2^-$  ion in this compound, thus proving the similarity of the highest oxides of the alkali and alkaline earth metals.

#### Discussion of Previous Work

It has been shown that Joannis (12) claimed to have prepared  $\text{Na}_2\text{O}_3$  by the oxidation of a solution of sodium in liquid ammonia at  $-50^\circ$ . Insufficient data were presented to substantiate this claim as is shown by the following. This author advanced two arguments in proof of his claim of preparing  $\text{Na}_2\text{O}_3$ . The first was that the product liberated oxygen upon treatment with water and was transformed into  $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ . No analytical proof of this was given. It must be remembered that it is almost impossible even to add water to  $\text{Na}_2\text{O}_2$  without the liberation of a noticeable amount of oxygen. The undecomposed

peroxide would presumably form the octahydrate.

The second point of proof was the analysis of the product; these analyses, however, depend upon the per cent by weight of sodium in the compound, as the percent of oxygen was calculated by difference. The slow oxidation of sodium in liquid ammonia gives NaOH and NaNO<sub>2</sub> in the ratio of 3 to 1 or a mixture of the empirical formula of Na<sub>11</sub>O<sub>5</sub>NH<sub>3</sub> which contains very nearly the same per cent of sodium on a weight basis as does Na<sub>2</sub>O<sub>3</sub>. Thus these analytical data are practically worthless. The claim is further invalidated by the author's statement that the initial compound (Na<sub>2</sub>O·NH<sub>3</sub>) may take up two more equivalents of oxygen to give the Na<sub>2</sub>O<sub>3</sub>. This is obviously impossible as undoubtedly the Na<sub>2</sub>O·NH<sub>3</sub> was in reality a 1 to 1 mixture of NaOH and NaNH<sub>2</sub> as was shown by Whyte (14).

Also there are reasonable grounds for doubting the claim by Kraus and Whyte (13) that Na<sub>2</sub>O<sub>2</sub> is the product formed by the rapid oxidation of sodium dissolved in liquid ammonia at -33°. The data given are rather scanty and the only proof of the composition of the product formed is the amount of oxygen absorbed by the sodium solution. Further, this claim is in disagreement with the findings reported by Whyte (14).

Because of these apparently conflicting data an investigation was begun (34) to determine the oxidation products of sodium in liquid ammonia. No single definite compound (or compounds) was found as the result of this work. It was found



though that by passing oxygen gas through solutions of sodium in liquid ammonia at about  $-77^{\circ}$  that a product was obtained, which upon analysis, was shown to be between  $\text{Na}_2\text{O}_2$  and  $\text{Na}_2\text{O}_3$  in composition. The results, however, were not consistent; hence the oxygen uptake of sodium in liquid ammonia at  $-77^{\circ}$  C was studied quantitatively. This in turn led to a series of attempts to form the higher oxide by burning the sodium in a spray of sodium-liquid ammonia solution. Finally from this developed rapid oxidation studies in which a solution of a metal in liquid ammonia is passed slowly into liquid ammonia through which a stream of oxygen is passing.

These last three phases of the investigation are the subject of this thesis and will be presented in chronological order.

## Experimental Methods and Results

Oxygen Absorption Studies--Experimental

The apparatus employed (Fig. 1) is suitable for use only at temperatures at which the vapor pressure of the solvent has a known, moderately low value. The volume of gas absorbed by the solution can be calculated from the observed change in volume in the gas buret C; if the reaction is not too rapid, it is possible to determine its rate.

A sample of sodium of the desired size is cut in a dry-box containing phosphorus pentoxide. The metal is placed in the tared sampling stopcock G and the plug is rotated. After the ground glass cap has been replaced over the male joint, the stopcock is removed from the dry-box and weighed. The sampling stopcock is then placed at the point shown (Fig. 1) in the system, which has been previously dried by flushing for a considerable time with anhydrous (dried over sodium) ammonia.

The system is again flushed with ammonia, the stopcock J is closed, and the required volume of ammonia is condensed in the reaction cell F by means of the cold bath E, which consists of a mixture of equal volumes of carbon tetrachloride and chloroform to which dry ice has been added. The temperature of this mixture, with which the reaction cell is surrounded during the process of oxidation, as well, is between  $-77^{\circ}$  C and  $-79^{\circ}$  C.

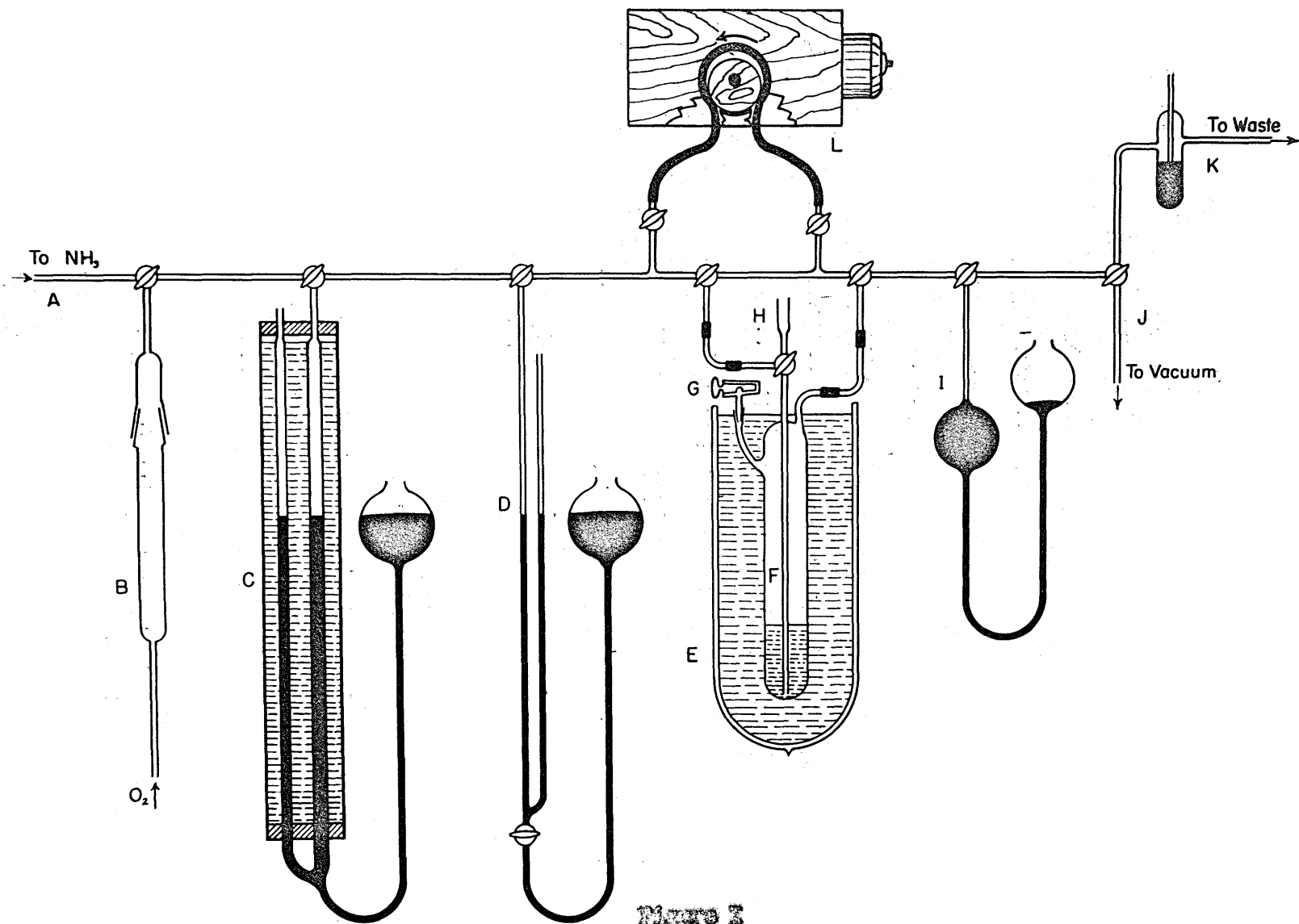


Figure 3

When the ammonia has been condensed, oxygen is permitted to enter through the drying tube B, which contains anhydrous magnesium perchlorate, until the buret C is almost filled. The system is then isolated by closing the stopcock above the drying tube. At this point, with the eccentric pump turned on, oxygen from the buret is forced through the reaction cell and is collected in the reservoir I. With the manipulation of the appropriate stopcocks the gas is returned to the buret, and the cycling process is then repeated until the oxygen and the liquid ammonia are mutually saturated. During the cycling process and throughout subsequent operations, the level of the cooling liquid on the reaction cell is kept as nearly constant as possible in order to avoid changes in oxygen volume. This is necessary because the sampling stopcock cannot be covered by the cooling bath.

Once the initial static volume in buret C has become constant, the pump L is turned on, and with the proper adjustment of stopcocks, oxygen at a rate of 850-900 cc. per min. is cycled through the reaction cell. (By regulated clamping of the rubber tubing leading to the pump, the rate of oxygen flow may be adjusted to any desired lower value.) By turning stopcock G the sodium sample is dropped into the liquid ammonia. The system is kept at approximately atmospheric pressure during the oxidation by raising the mercury leveling bulb of buret C to continually higher levels as the oxygen is consumed. When the oxidation has proceeded to the point where there is no

longer any noticeable change in the mercury level in the buret, the pump is turned off, the system permitted to come to apparent equilibrium, and the final static volume obtained. The change in volume is then corrected for temperature, pressure, and the vapor pressure of liquid ammonia to give the standard volume of oxygen absorbed by the known weight of sodium.

After the absorption data have been obtained, the cold bath is removed and ammonia allowed to boil off through the trap K to the waste jars. A slow flow of oxygen through the reaction cell is maintained during the removal of ammonia; this sweeps the last traces of ammonia from the system, thus preparing it for the analysis.

For the analysis, the cell, now cooled by an ice-water bath, is connected with the measuring buret only, and both the cell and the buret contain oxygen at atmospheric pressure. A 10 ml. portion of catalyst solution (to be described below) is added from H and the cell, which is connected to the rest of the system by means of Tygon tubing, is shaken to hasten the decomposition of the oxide (or oxides); the quantity of oxygen liberated is calculated from the volume change in the buret. The decomposition of the cold, dilute, acidic solutions of hydrogen peroxide, formed upon the addition of acid to peroxides and superoxides of the alkali metals, is catalyzed by a solution which is 0.6 molar with respect to hydrochloric acid and 2 molar with respect to ferric chloride. To correct for

the volume change due to the addition of the catalyst, a blank run is made with no oxide present.

### Absorption Studies -- Discussion of Results

Some twenty-seven runs were made on this apparatus of which twelve are reported in Table I. The runs not reported include the first dozen or so which were necessary to develop the apparatus in the form in which it is shown in Fig. I. The first run was made with no pump in the set up but the work involved in handling all the mercury necessary to cycle the oxygen was too great. A pump was designed and tried but was not satisfactory, then the model shown was built and proved to be adequate for the job.

The next problem encountered was that of getting a known weight of sodium into solution in the ammonia in a short length of time. In the first few runs a short length of glass tubing (4mm.) containing sodium was dropped into the ammonia at the appropriate time. This was found to be unsatisfactory as the sodium shows a decided tendency to form some sort of compound with the liquid ammonia at  $-77^{\circ}$ . Thus a dark blue insoluble precipitate would form in the glass tubing and was found to be most difficult to remove. As a result of this difficulty the sampling stopcock G was designed and proved to be quite satisfactory.

Another source of difficulty was the rubber tubing in the pump. Gum rubber tubing was found to be the most satisfactory

Table I

The Oxygen Uptake of Sodium in Liquid Ammonia at  $-77^{\circ}\text{C}$ 

<u>Na, g.</u>	<u>Dilution, cc. NH<sub>3</sub>/g. Na</u>	<u>O<sub>2</sub> flow, cc./min.</u>	<u>Uptake, cc. (STP)</u>		<u>% of theoretical uptake</u>	<u>Analyses cc. O<sub>2</sub> (STP) liber- ated</u>	
			<u>Calcd. for NaO<sub>2</sub></u>	<u>Obs.</u>		<u>Calcd. for NaO<sub>2</sub></u>	<u>Obs.</u>
0.0266	380	850-900	25.9	23.3	90	19.4	10.8
.0235	380	850-900	22.9	21.0	92	17.1	9.3
.0428	430	850-900	41.7	35.8	86	31.2	15.9
.0616	680	700-750	59.9	51.3	86	45.0	22.3
.0317	760	ca. 150	30.8	26.2	85	23.1	12.1
.0343	770	ca. 150	33.4	30.9	93	25.0	12.0
.0279	810	850-900	27.1	24.3	90	20.3	10.1
.0183	1200	850-900	17.8	16.0	90	13.4	7.3
.0213	1240		20.7	18.7	90	15.5	8.9
.0163	1780	850-900	15.8	14.4	91	11.9	5.6
.0293	1830	850-900	28.5	24.9	87	21.4	11.9
.0191	2490	850-900	18.6	16.8	90	13.9	6.9

for this use, but it had to be replaced frequently due to excessive wear caused by imperfections in the construction of the pump. After each change of tubing the first run made was found to be below average. Apparently this was due to insufficient drying or removal of organic vapors from the rubber before use.

After these and other minor problems had been worked out the data given in Table I were collected.

These data show that the sodium-ammonia solutions pick up nearly the quantity of oxygen needed to form  $\text{NaO}_2$ . When these data were published (35) it was concluded that  $\text{NaO}_2$  was formed at  $-77^\circ$  but that it decomposed in the process of boiling off the ammonia at  $-33^\circ$ . This was assumed to be the case as Kraus and Whyte (13) had stated that only slightly impure  $\text{Na}_2\text{O}_2$  is formed in the rapid oxidation of sodium at  $-33^\circ$ . By comparison with the potassium oxidation then, one would expect to get a more nearly pure oxide at the lower temperature; thus the possible ammonolysis of the oxide at the lower temperature was not taken into account. This assumption of the validity of Kraus' work was not justified as will be shown later and leads to the incorrect interpretation of the absorption data.

From the work reported later in this thesis it is apparent that  $\text{NaOH}$  and  $\text{NaNO}_2$  were formed even at the low temperature. Nevertheless  $\text{NaO}_2$  must have also been formed and it accounts for the analytical data given on the final product, as appreciably



more oxygen was liberated than can be accounted for otherwise.

#### Spray and Evaporation Studies -- Experimental

With the completion of the absorption studies on sodium some exploratory experiments were begun in an effort to devise new ways to make the superoxides. One method in particular was thought to have exceptionally good possibilities; in this process a metal-ammonia solution is sprayed into an oxygen atmosphere. Essentially, this should give a low temperature burning of the metal which is desirable as it is thought that burning of the metal vapors directly heats the products above the decomposition temperature of the superoxide. Further, by this method, it should be possible to control the temperature of burning to a certain extent by varying the ratio of metal to liquid ammonia.

Attempts were also made to oxidize the metal ammoniates by a mixture of oxygen diluted with gaseous ammonia. A few milliliters of liquid ammonia were condensed in a cell similar to that shown in Figure I; next the metal sample was added and the excess ammonia boiled off leaving a gold colored product which was presumably the ammoniate of the metal. Then a mixture of air and ammonia or oxygen and ammonia was passed over this and the ammonia thus removed and the metal oxidized. Of course this procedure can only be used with the metals that form ammoniates -- the alkaline earth metals and lithium.

Several runs were made using calcium but the product obtained

was usually blue to pink in color. In some of the runs hydrogen was known to have been evolved during the analyses due to the presence of unoxidized metal. In four runs which yielded a pink colored material the analyses indicated products which liberated 6, 8, 9, and 10% as much oxygen as theoretically should have been liberated for the known weight of calcium in the form of  $\text{CaO}_2$ .

Only one run was made using lithium as during the oxidation process a rather sharp explosion occurred which shattered the reaction cell. It is probably that this was an ammonia-oxygen explosion initiated by the burning lithium. Later experiments with sodium showed this to be quite a common occurrence unless the composition of the oxygen-ammonia mixture is kept outside the explosive limits.

As this line of investigation did not appear very promising, attempts were made to perfect the spray process previously described. Because of the nature of this process, it was found most difficult to work with on a laboratory scale. The oxide formed by this method would be expected to be light, and in the gas volumes necessitated, would be very hard to collect. Because of the characteristics of the oxide all moisture must be excluded, not only during the synthesis of the product, but during any subsequent handling necessary before analysis.

First an attempt was made to spray the metal-ammonia solution into a small reaction cell in which the oxide could afterwards be analyzed. The initial trials were made with a

hypodermic syringe which was thrust through a rubber cap and by means of which the solution was sprayed into the reaction cell through which a stream of oxygen flowed. This experiment was not completely successful, however, since the spray was too coarse and the ammonia did not evaporate quickly enough; the liquid struck the opposite side of the cell where the ammonia evaporated and allowed the sodium to oxidize. Nevertheless this gave promise of yielding the superoxide because a yellow color was shown by the oxide so produced.

In an effort to obtain a finer spray of liquid a Kantleek medical atomizer, such as is sold at drug stores for nose and throat medication, was obtained. This was mounted through a rubber stopper in a small Dewar flask with the jet end in a four liter three necked flask through which oxygen was passing. By means of the atomizer bulb sodium-ammonia solution from the Dewar was sprayed into the oxygen atmosphere in the flask. In the initial attempt the spray became clogged and it was impossible to get even spraying; in spite of this difficulty some yellow product was obtained. In the next attempt oxygen was passed through the atomizer and although some plugging of the atomizer occurred a good yellow product was obtained. Finally the tip became plugged, was removed, cleaned and replaced, and after starting the atomizer again an exceedingly sharp explosion occurred. No glassware was broken but the operator's hands were burned. Apparently the oxygen-ammonia

was caused to explode by burning metal as had happened before.

Here again the oxidation did not take place in the vapor phase, but the spray struck the side of the flask where the ammonia evaporated and the metal was oxidized. Although the experiments were not completely successful, the yellow color of the product indicated that this method was worth investigating further.

Next a piece of glass tubing two inches in diameter and sixteen inches in length was adapted as a burning chamber. The atomizer was fitted into one end and was operated with oxygen pressure. The attempts using this apparatus were unsuccessful as the tip became plugged with sodium and the runs had to be discontinued. The oxygen flow reduced the pressure and thus pulled the solution up to the nozzle, as was necessary, but the pressure reduction caused such rapid evaporation of the ammonia from the solution that the inlet slots became plugged with sodium.

Therefore, the atomizer was replaced by two hypodermic needles which were used to atomize the solution. A small (#27) needle was placed vertically in the tube and conducted the solution from below. This needle opened beneath and in the center of the opening of a larger (#20) needle placed horizontally in the center of the glass burning chamber previously described. This latter needle was pressurized with 15 cm of mercury back pressure of air. By regulating the

nitrogen pressure on the metal solution the flow up through the needle could be controlled. This worked fairly well and an orange-yellow product was obtained which was later lost when the ammonia gas burned and its oxidation products destroyed the oxide. No explosions were experienced in this run but at three different times during the run flashes could be seen in the tube--twice they were small and barely noticeable but the third time the yellow product was destroyed.

The sodium solution used in the above run contained less than one-tenth of a gram of sodium dissolved in 40-45 milliliters of liquid ammonia. The flow of solution was intermittent due to heating up of the solution in the capillary tubing and needle.

Two runs were made pressurizing the large needle with oxygen but in both cases explosions occurred. In an attempt to prevent such explosions the oxygen was diluted with gaseous ammonia. Trouble was also experienced with plugging of the lower needle.

In using this apparatus it was observed that the yellow product formed when drops of the solution hit the walls of the burning chamber allowing the ammonia to evaporate with simultaneous oxidation of the sodium. It was originally hoped and thought that the evaporation and oxidation would all take place before the solution hit the walls of the burning chamber but in such a small-scale apparatus this was found to be quite difficult to accomplish. From the color of the product so far

obtained this vapor phase oxidation does not seem necessary although in the case of lithium and the alkaline earths it would be desirable because of the formation of ammoniates by these metals. It is possible that the stability of the ammoniates would prevent the dropwise oxidation of these compounds.

Due to the manner in which the sodium was oxidized in the above experiments it was decided to make the metal-ammonia solution in one cell and to run it slowly into a second cell through which oxygen was passing so that the solution would evaporate and the metal be oxidized. The reaction cell could then be disconnected from the solution cell and the resulting product analyzed in the conventional way. The method of analysis had to be modified slightly, however, as a known weight of sodium could not be used. A water-MnO<sub>2</sub> suspension was used to catalyze the oxide decomposition and subsequent titration with standard acid was used as a measure of the amount of sodium in the product. Thus the composition of the oxide could be ascertained. Using the acid titration as an indication of the amount of metal in the sample, the assumption is made that all the metal is present in the form of the hydroxide, some one (or more) of the oxides, or possibly the amide. In at least one run the final residue gave a positive qualitative test for nitrite. In several of the runs the color of the product might have been due to amide. It is seen that the oxidation products of the amide may be present and

would affect the accuracy of the analyses, as any nitrite or nitrate present would not be titratable with acid and thus the apparent yields would be high. With an increase in purity of the oxide, the analytical accuracy would increase proportionally.

Several runs were made in working out the details of this evaporation process. In the first few runs it was thought that the sodium-ammonia solution should be kept at about  $-78^{\circ}$  so the solution would be reasonably cold during the evaporation. Eventually it was realized that it made no difference whether the solution was kept at  $-78^{\circ}$  or at the boiling point as it was warmed up to the boiling point while being forced into the reaction cell in both cases. Therefore in the later runs the metal solution was kept near its boiling point; the temperature was so adjusted as to just force the liquid over by means of its vapor pressure when it was so desired.

Another reason for keeping the solution at  $-33^{\circ}$  or thereabouts was that at  $-78^{\circ}$  and even at  $-55^{\circ}$  the sodium metal showed a definite tendency to form a compound with the liquid ammonia. At both these temperatures a blue precipitate was formed and stuck to the sides of the solution cell as the solution was being removed during the course of a run. At  $-33^{\circ}$  this was not observed.

A number of runs were required to determine the best temperature at which to keep the reaction cell. No bath at all was tried, as well as a room temperature water bath, an ice bath,

and an ice-salt bath. It was finally decided that a room temperature water bath was at least as good as any other. With such a bath the ammonia was evaporated quickly, thus giving a rather rapid oxidation which seemed desirable. All the later runs were made using a room temperature water bath on the reaction cell.

It was also thought that the design of the reaction cell determined, to certain extent at least, the yield of the higher oxide. In some runs the solution was sprayed into the cell through a restricted nozzle. Later it was decided that a better product was obtained by allowing the solution to trickle down the side of the cell. This allowed the sodium to remain in solution while being oxidized and then the ammonia would vaporize leaving the yellow to deep orange colored product behind.

In this series of runs, trouble was experienced periodically with explosions, or burning of ammonia in the reaction cell, which ruined the product. Air-ammonia mixtures were used part of the time with some success, but eventually it was found more convenient to use oxygen-ammonia mixtures of known concentrations. Two orifice flowmeters were calibrated by means of a wet test meter and these were used to adjust the ratio of gases and the volumes necessary for the satisfactory oxidation of the ammonia solutions. In a series of runs it was found necessary to use less than four per cent oxygen in ammonia to obviate any



possibilities of the ammonia exploding or burning. In the later runs a three per cent mixture was used with a total flow of gas of about two to two and one-half liters per minute passing through the reaction cell.

#### Spray and Evaporation Studies--Discussion of Results

A total of twenty-two runs were made by the evaporation process using sodium metal. Seven of these runs were completed successfully and analyses on the product obtained. The accuracy of these runs is probably not very great but the yields, reported as per cent  $\text{NaO}_2$ , are given below. The only significance to be attached to these yield values is that they represent the percentage of the theoretical amount of oxygen calculated for pure superoxide actually obtained from each product. As indicated above, any sodium present as nitrate or nitrite would not be titratable and would give abnormally high percentage yields. As  $\text{Na}_2\text{O}_2$  gives off one third as much oxygen as  $\text{NaO}_2$  for equal amounts of sodium, it is seen that any yield below 33% indicates that the average composition is less than the peroxide so far as available oxygen is concerned.

Run No.	Yield (as NaO <sub>2</sub> )
3	49%
4	20
7	19
8	12
14	24
19	23
22	19

By the same procedure one run each was made with lithium, calcium, barium and strontium. The lithium and barium runs were completed successfully and analyzed; the analyses indicated 9% Li<sub>2</sub>O<sub>2</sub> and 25% BaO<sub>2</sub>, and in both cases the product was white in color. In the calcium run a white product was formed at first but toward the end of the run the ammoniate, which had concentrated in the bottom of the solution cell, came over too fast and was not completely oxidized, thus spoiling the run. In the strontium run some of the ammonia vaporized off the solution in the capillary tubing thus plugging it with a golden colored product. It was found impossible to force this out of the capillary at moderate pressures so the run was discontinued.

From the above data it seems probable that the product in each case was a mixture. The yellow color indicates that appreciable quantities of the superoxide were present. The analysis of Run #3 also indicated superoxide. Mixed with this

superoxide one would expect some nitrite, hydroxide, and in some cases possibly peroxide and perhaps even some amide.

Thus the indications are that some of the same products were obtained in this series of runs that have been previously reported by the slow (and fast) oxidation of the metal ammonia solutions. This suggested a reinvestigation of these studies, the results of which are given in the next section.

Rapid Oxidation in Solution

The early work on the rapid oxidation of sodium in liquid ammonia supposedly proved that  $\text{Na}_2\text{O}_2$  was the highest oxide formed under such conditions. The experiments indicated in the above sections seemed to show that this might not be true.

With the absorption apparatus it was impossible to study the oxygen absorption at the boiling point of ammonia due to interference of the ammonia vapor. This apparatus (without the pump) was, however, used to make a series of runs in which the sodium-ammonia solution was kept at  $-30^\circ$  to  $-35^\circ$  with a dry ice-solvent bath. Oxygen was passed through the solution at a rate of about 60 cc/min. in this series of runs. From the known weight of sodium and the amount of oxygen liberated upon adding a catalyst solution (1 M in HCl, 2 M in  $\text{FeCl}_3$ ) an indication was given of the composition of the product. In such a manner the following data were collected.

Run No.	Wt. of Na (grams)	NH <sub>3</sub> vol. ml. at -33°	Dilution ml. NH <sub>3</sub> /g. Na	Analyses O <sub>2</sub> Evolved (ml)		% Na <sub>2</sub> O <sub>2</sub> Indicated
				Calc. for Na <sub>2</sub> O <sub>2</sub>	Obs.	
27	.0498	9	180	12.1	7.4	61
28	.0664	13	190	16.1	13.2	82
29	.0669	17	250	16.3	14.4	88
30	.0755	14	180	18.5	13.6	74
31	.0593	14	240	14.4	11.4	79
32	.0529	28	530	15.1	12.9	117
33	.0820	33	400	19.9	20.3	102
34	.0272	29	1100	6.6	8.0	121
35	.0342	33	970	8.3	11.5	139
36	.0427	58	1350	10.4	11.9	115

Although these data are not very consistent they do definitely show that Kraus was wrong in his claim that Na<sub>2</sub>O<sub>2</sub> is the highest oxidation product of sodium at -33°. This is indicated by the color of the product (mixed white and yellow) as well as by the analyses, since in one-half of the above runs more oxygen was evolved than could possibly have been liberated by the peroxide. Thus formation of the superoxide is indicated.

The above data also seem to indicate that the superoxide reaction is favored by increased dilution of the sodium. The larger the volume of ammonia that one starts with the more oxygen is immediately available for oxidation. As oxygen is quite soluble in liquid ammonia, it is seen that this might

account for the greater tendency of the superoxide to be formed in more dilute solutions. As was shown previously there are undoubtedly two competing reactions in such a system. On the one hand there is the oxide formation and on the other the amide formation; the latter eventually gives nitrite and hydroxide under oxidizing conditions.

It would seem then that the best way to insure the oxide reaction would be to oxidize the sodium by dropping it in a sufficiently large volume of liquid ammonia, saturated with oxygen, so that the reaction would be essentially instantaneous. This is not a practicable method but the same effect is obtained by means of the apparatus shown in Figure II.

This apparatus is used by condensing ammonia in both the reaction cell F (which may be thermostated at any desired temperature between  $-33^{\circ}$  and  $-78^{\circ}$ ) and in the solution cell K. The latter, in this series of runs, was maintained at about the boiling point of liquid ammonia throughout the run. By adjusting the temperature of the bath, M, the desired pressure, as indicated by the manometer shown as N, can be maintained above the solution. With the reaction cell at the desired temperature and oxygen bubbling through it the metal sample is added to the solution cell by turning J. By controlling the pinch clamp L the resulting solution can be added at the desired rate to the oxidizing solution in the reaction cell F.

With this method it was found possible to add the solution

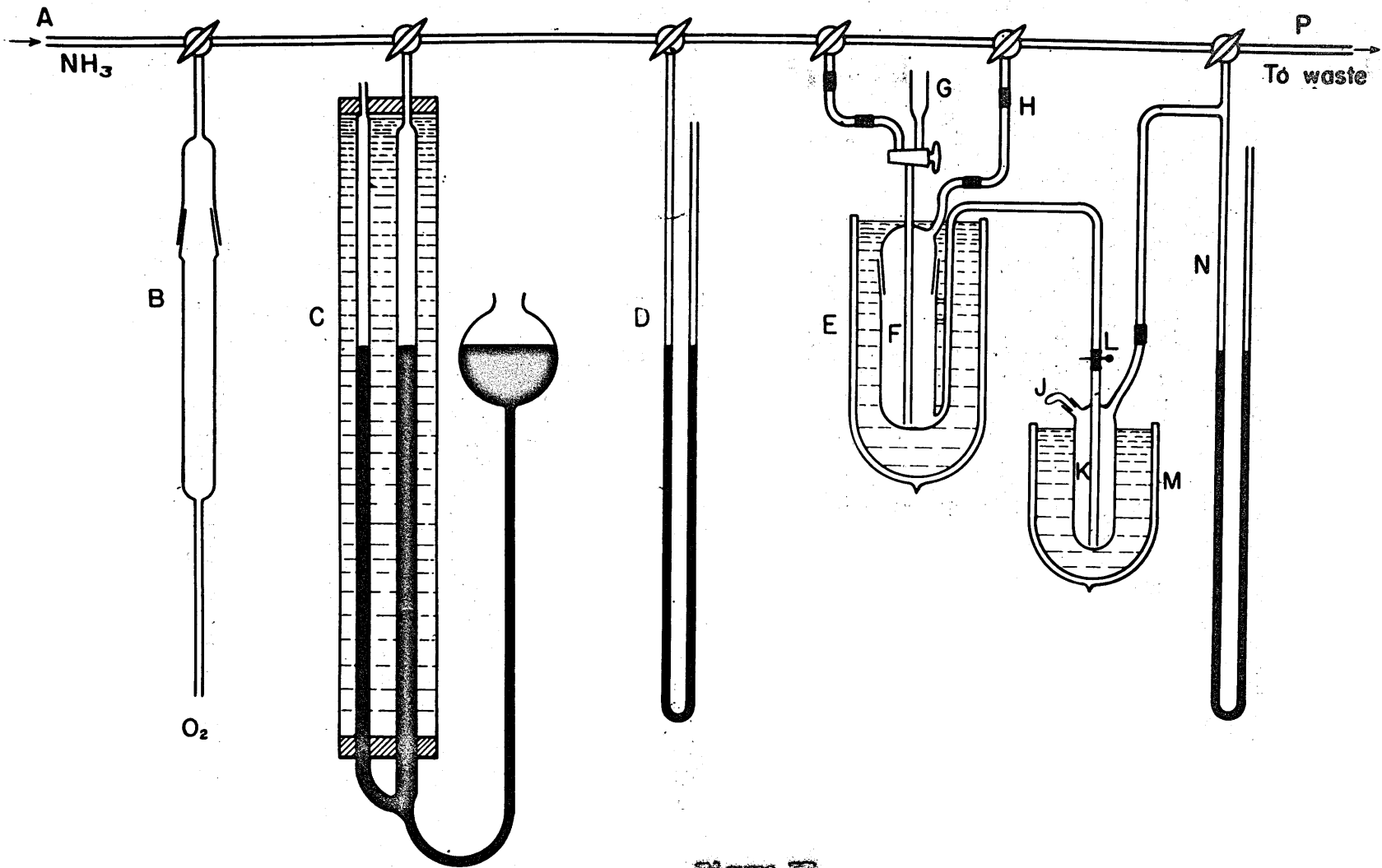


Figure 31

slowly enough so that the liquid ammonia in F retained its colorless appearance except for the "fugitive" blue color seen at the inlet. As a rule this color persisted for only a very short time as the metal was oxidized almost immediately under such conditions. When the addition got out of control, and the reaction cell solution turned blue for any appreciable length of time, the resulting product showed a smaller oxygen content and the final solution gave a positive (qualitative) test for the nitrite ion. Thus the amide reaction was indicated.

After all the solution is added the solution cell is disconnected, the ammonia allowed to evaporate off and the final product analyzed by the method previously described. Here again it was found necessary to decompose the product with an aqueous  $\text{MnO}_2$  suspension, and to titrate the resulting solution with standard acid in order to obtain the data necessary to calculate the composition of the oxide obtained. After titrating the solution it is boiled nearly to dryness and a qualitative nitrite test made using sulfuric acid to acidify the solution and then adding ferrous sulfate solution. A green to brown color indicates the presence of the nitrite ion. The series of runs tabulated below were the first ones made by this method; these results justified the building of a larger apparatus which proved more satisfactory.



Run No.	Wt. of Na (grams) (from titration)	Temp. of Reaction Cell Bath	Analyses		% NaO <sub>2</sub> Indicated
			O <sub>2</sub> Evolved Calc. for NaO <sub>2</sub>	(ml) Obs.	
1	.0096	Unthermostated	6.9	2.7	39
2	.0303	"	22.2	12.6	57
3	.0335	"	24.3	13.1	54
4	.0503	"	36.6	18.3	50
5	.0612	-30° to -35°	44.6	28.8	65
6	.0414	-30° to -35°	30.3	14.2	47
7	.0522	-30° to -35°	38.1	19.6	51
8	.0245	-30° to -35°	18.0	13.1	73
9	.0276	-30° to -35°	20.1	14.5	72

As 33% NaO<sub>2</sub> corresponds to the composition Na<sub>2</sub>O<sub>2</sub> (as far as O<sub>2</sub> liberation is concerned) it is seen that all nine of these runs yielded a product with more available oxygen than is found in the peroxide. Furthermore the last two runs indicate a product containing more oxygen than is available in Na<sub>2</sub>O<sub>3</sub>. Thus it seems likely that NaO<sub>2</sub> may be prepared by this method. No tests for nitrite were made on these runs.

In an attempt to improve the product this apparatus was rebuilt with a reaction cell of 140 ml. capacity; the volume of the solution cell was about 90 ml. With this apparatus more dilute solutions could be used thus favoring the oxide reaction. With the larger volume of ammonia possible in the reaction cell it was hoped that the metal solution could be added without

coloring the reaction solution. In most of the runs this was found possible. The following data were obtained with this modified apparatus.

Run No.	Wt. of Na (grams) (from titration)	Temp. of Reaction Cell Bath	Analyses		% NaO <sub>2</sub> Indicated
			O <sub>2</sub> Evolved (ml) Calc. for NaO <sub>2</sub>	Obs.	
1	.0478	Unthermostated	34.8	20.5	59
2	.0591	"	43.0	34.0	79
3	.0492	ca. -75°	35.9	27.8	78
4	.0453	"	33.0	25.7	78
5	.0412	Unthermostated	29.6	23.3	79
6	.0580	"	42.3	28.5	67

In this series of runs the first and last runs yielded a product with appreciably less available oxygen than was found in the other runs. In both these cases trouble was experienced in the addition of the metal solution to the reaction cell; this poor control resulted in the appearance of blue color throughout the reaction cell liquid for appreciable lengths of time. This difference in reaction rate is definitely reflected in the yield values. Attempts were made to get nitrite tests on the final solutions in these runs but because the solutions were so dilute the results were meaningless. In later runs the solutions were evaporated nearly to dryness and then satisfactory tests were found possible.

The product from the above runs was predominantly yellow

in color with small but definite amounts of white material visible.

In the next series of runs lithium and calcium metal were used as it was thought that at least the pure peroxides of these metals should be formed by the rapid oxidation method. The following data were collected.

Run No.	Wt. of Metal (grams) (from titration)	Temp. of Reaction Cell Bath	Analyses		% Peroxide Indicated
			O <sub>2</sub> Evolved Calc. for Peroxide	(ml.) Obs.	
7	.0301 g. Li	Unthermostated	24.3	2.2	9
8	.0128 g. Li	"	10.3	1.3	13
9	.0112 g. Li	ca. -75°	9.0	2.8	31
10	.0396 g. Ca	Unthermostated	11.1	.2	2
11	.0128 g. Li	ca. -75°	10.3	1.7	17

From the above it is seen that there is a decided tendency for Li<sub>2</sub>O<sub>2</sub> to be formed under such circumstances. The nitrite tests on the first two runs were unreliable but runs #9 and #11 gave positive tests for the nitrite ion in spite of the fact that the solution was added to the reaction cell with good control. This might indicate that the amide reaction took place in the solution cell. In these runs the metal was dropped into the cell and the ammonia condensed on it because these metals readily pick up ammonia gas and go into solution; therefore they can not be added after the NH<sub>3</sub> is condensed as is possible with sodium.

In the calcium run no definite indication was given of the

formation of  $\text{CaO}_2$  as the volume of oxygen liberated (.2 cc) may well be within the experimental error of the apparatus. The nitrite test was negative thus showing that the amide reaction did not take place to any great extent either in the solution cell or during the oxidation process.

The sodium runs checked so consistently it was thought desirable to try a few runs using potassium metal because the oxidation products of this metal in liquid ammonia are well known. These runs were to be used as a check on the system to see if everything was working right as it was somewhat puzzling that consistent results could be obtained with a composition less than that of  $\text{NaO}_2$ . The following data were obtained.

Run No.	Wt. of K (grams)	Analyses		% $\text{KO}_2$ Indicated
		$\text{O}_2$ Evolved (ml) Calc. for $\text{KO}_2$	Obs.	
12	.0413	17.8	13.8	78
13	.0517	22.2	19.8	89
14	.0422	20.3	16.9	83
15	.0497	20.8	19.2	92
16	Checked purity of K by adding it to isopropyl alcohol and titrating with standard acid (99.5% K indicated)			
17	.0562	24.2	19.2	79
18	.0653	28.1	24.6	88
19	.0492	21.1	18.1	86
20	.0500	21.5	12.5	58
21	.0460	19.8	12.1	61
22	Checked for reaction of K with the gaseous impurity in liquid ammonia solution.			

All the runs of the above series were made with the reaction cell thermostated at about  $-75^{\circ}$ . In the first three runs a liquid ammonia solution of potassium was added to liquid ammonia saturated with oxygen. Beginning with run number fifteen the potassium was added, by means of the sampling stopcock, directly to liquid ammonia in the reaction cell. By this means it was hoped to duplicate Kraus' results on the rapid oxidation of potassium. The color of the product in all cases was yellow and appeared to be homogeneous throughout and in all cases the qualitative nitrite tests proved to be negative. But in spite of the good appearance of the product and the absence of any nitrite, the yields were found to be discouragingly low. Finally after eight runs had been made with no marked degree of success it was decided to dry some ammonia over sodium and use it. Such ammonia had been used in the absorption runs but commercial anhydrous ammonia was used in the later runs as no advantage could be observed in using the dried ammonia during the earlier experiments.

Runs number twenty and twenty-one were markedly lower in yield than the previous ones. It had been noticed that a considerable quantity of a gas (presumably hydrogen from the reaction of sodium in the liquid ammonia cylinder) was present in the ammonia used in these runs. A definite but lesser amount of gas had been noticed in the ammonia from the commercial cylinder. As this increase in gaseous impurities apparently

resulted in a lower yield of  $KO_2$  it was decided to make a run (#22) to determine whether potassium would react (decolorize in solution) with the impurities in the ammonia.

To study this about 30-35 ml. of liquid ammonia was condensed in the reaction cell and a potassium sample was added to it. The cold bath ( $-75^\circ$ ) was kept on the cell and more ammonia condensed until 65-70 ml. was present; then the cold bath was removed and the ammonia was allowed to boil off. The blue color persisted until all the ammonia had evaporated off thus showing that the major portion of the potassium did not react. The residue showed that some reaction had taken place as a definite area of reaction was visible immediately below the inlet tube to the cell. Whether the reaction was sufficient to account for the low yields in the other runs is not known.

This posed a difficult problem since no way is known whereby hydrogen can be satisfactorily removed from liquid ammonia. Apparently the hydrogen (if hydrogen is the impurity) is not easily separated by fractionation or it would be removed with the first ammonia used from a cylinder. Such is not the case however, as the commercial cylinder had been in use for several months but still gave off a gaseous impurity that was detected by passing the gas through water. The ammonia was rapidly absorbed but fine bubbles of the impurity would pass up through the water.

As no solution to this problem was immediately available

it was decided to try oxidation of sodium again to see if the consistent results could again be obtained. Thus eight runs were made with the following results.

Run No.	Wt. of Na (grams) (from titration)	Analyses		% NaO <sub>2</sub> Indicated
		O <sub>2</sub> Evolved (ml.) Calc. for NaO <sub>2</sub>	Obs.	
23	.0634	46.3	17.1	37
24	.0372	27.2	19.6	72
25	Run was ruined.			
26	.0270	19.7	12.3	62
27	.0403	29.5	22.9	78
28	.0536	39.1	31.4	80
29	.0635	46.3	36.2	78
30	.0324	23.7	18.7	79

In the first four runs of this series the ammonia used had been dried over sodium, in the last four runs it was condensed directly from the commercial cylinder previously mentioned. In the first run the solution was added to the reaction cell with poor control, thus coloring the solution. As a consequence the yield was very poor and the resulting solution, after analysis, when boiled nearly to dryness gave a positive nitrite test. In the remaining runs the solution was added under control and the qualitative nitrite tests on the final solution were found to be negative.

It is seen that the yields (in the above table) in runs twenty-four and twenty-six were low, presumably for the same reason as in the potassium runs. In the last four runs using

the commercial ammonia the yields were consistent with each other and with the previous runs made in a like manner.

By calculation it may be shown that a product which releases 78 per cent as much oxygen as does  $\text{NaO}_2$  corresponds almost exactly to the empirical formula  $\text{NaO}_{1.67}$ , or in integral numbers to  $\text{Na}_3\text{O}_5$ . Eight runs have been made that indicate such a compound. Four of these showed 78 per cent, three showed 79 per cent and one showed 80 per cent  $\text{NaO}_2$ . These values check within the assumed accuracy of this type of apparatus, and being the only set of values checking so well in this investigation, seem to point to a definite (molecular) compound.

The empirical formula  $\text{Na}_3\text{O}_5$  suggests a mixture of superoxide to peroxide in the ratio of four to one. The molecular compound  $\text{M}_2\text{O}_3$ , where M represents either rubidium or cesium, has been shown to contain both the peroxide and the superoxide ion and the structure may be represented as  $\text{M}_2\text{O}_2 \cdot 2\text{MO}_2$ . In a like manner one would expect  $\text{Na}_3\text{O}_5$  to contain both the peroxide and superoxide ion; its structure might be represented as  $\text{Na}_2\text{O}_2 \cdot 4\text{NaO}_2$ .

Although these results seem to indicate the formation of  $\text{Na}_3\text{O}_5$  there are reasons for questioning this conclusion. For one thing the color of the product was not homogeneous in these runs. In all the runs but one a small but definite amount of white color could be seen along with the yellow. If the white material indicated impurities then one would expect the analyses



to show slightly less oxygen than is available from  $\text{Na}_3\text{O}_5$ . Instead of this the correct amount of oxygen or slightly more than the theoretical quantity was liberated. Of course this might be accounted for as "experimental error" but the positive deviations may be indicative of some other product than that suggested by the formula  $\text{Na}_3\text{O}_5$ .

Two pieces of data seemed necessary to substantiate this formula. First ammonia would have to be obtained of sufficient purity so that pure  $\text{KO}_2$  might be prepared. Then by use of similarly treated ammonia the rapid oxidation studies with sodium should be repeated. If  $\text{Na}_3\text{O}_5$  were still indicated a sufficient quantity of the material should be prepared on which to make magnetic measurements. These data with X-ray diffraction measurements, should prove conclusively the composition of the oxide.

Preliminary experiments were made toward this end; several runs were made in an attempt to obtain pure ammonia and with it to prepare pure  $\text{KO}_2$ . The following data were collected.

Run No.	Wt. of K (grams)	Analyses		%K <sub>2</sub> O Indicated
		O <sub>2</sub> Evolved (ml) Calc. for K <sub>2</sub> O	Obs.	
31	The NH <sub>3</sub> , produced from NH <sub>4</sub> Cl and CaO, contained water and no superoxide was obtained.			
32	.0681	29.3	21.2	72
33	.0470	20.2	16.5	82
34	.0469	20.2	16.7	83
35	.0558	24.0	18.3	76
36	.0504	21.7	17.3	80
37	.0517	22.2	17.5	79

In the first run (#31) of this series a mixture of NH<sub>4</sub>Cl and CaO was heated together and the resulting gases passed through a drying tower, packed with soda lime and quicklime, which was expected to remove the water vapor. Apparently the drying tower was not very effective in drying the gas as the liquid ammonia that was condensed in the reaction cell contained water. Therefore no superoxide was formed and only a white precipitate was visible after the ammonia had evaporated.

In two more runs (#35 and #36) the ammonia was made in the same way but better means of drying the gas were used. In these runs the gas was passed through a glass trap immersed in an ice-salt bath at about -15 to -17° C. This removed the major portion of the water vapor. Next the gas was passed through a 10 to 12 inch bed of soda lime pellets that had been heated to 500-600° C in a muffle furnace. It was expected that

the soda lime would remove the remaining traces of water. As shown by the results this expectation was apparently not realized as the yields remained low.

It was also thought that possibly the gaseous impurities could be flushed from the liquid ammonia by bubbling oxygen through it for a period of time. The remaining runs of this series were made to test this hypothesis.

In run number thirty-two about 75 ml. of ammonia was condensed in the reaction cell, the ammonia was allowed to warm up till it started to boil and then oxygen was bubbled through it for fifteen minutes. The ammonia was then cooled to about  $-75^{\circ}$  and oxygen passed through it for an additional forty-five minutes. After this treatment the potassium sample was added to the ammonia and the run made in the usual manner. In run number thirty-three the flushing time was extended to an hour and in the other two runs (#34 and #37) to over three hours. As is evidenced by the yields of these runs, this method of ammonia purification seems ineffective.

## Suggestions for Future Research

The attempts to make pure  $KO_2$  have so far been unsuccessful. Efforts should be made to prepare pure ammonia or to purify the commercially available ammonia and with it make pure  $KO_2$ . There is a possibility that the trouble may not be in the ammonia but in the potassium metal used. When this difficulty has been removed the rapid oxidation studies of sodium should be repeated using ammonia of proved purity.

Next, gram quantities of the  $Na_3O_5$ , or of any higher oxide found, should be prepared and magnetic measurements made on the product. Thus the ratio of superoxide to peroxide ion can be established and with powder diffraction data the formula and structure of the oxide can be definitely established.

The preliminary runs in which lithium metal was oxidized by the rapid oxidation method showed promise of yielding  $Li_2O_2$ . It is likely that the addition of lithium metal from the sampling stopcock, after ammonia is condensed in both the solution and reaction cells, may lead to a higher yield of  $Li_2O_2$  and that the amide reaction may be eliminated.

The alkaline earth metals should be studied by the same method as outlined for lithium. Although the first run on calcium by the rapid oxidation method gave no indication of forming the peroxide, the suggested change of method in handling the metal may well make a difference in the product obtained. The more electropositive metals, strontium and barium,

should show greater tendencies to form the higher oxides under these conditions.

If future work shows that the poor  $KO_2$  yields were due to hydrogen (or nitrogen) impurities in the liquid ammonia, the possible reactions of hydrogen (and nitrogen) with solutions of the alkali metals in liquid ammonia should be investigated. Should hydrogen prove to be the impurity responsible for the low yields then these studies should include the effect of such hydrogenation catalysts as may be used with liquid ammonia solutions of the alkali and alkaline earth metals.

## Summary

It has been shown, contrary to Kraus' statement, that  $\text{Na}_2\text{O}_2$  is not the highest oxide of sodium formed by the oxidation of sodium in liquid ammonia. At least one higher oxide is formed, at  $-33^\circ$  or at  $-77^\circ$ , as is shown by the results of three different methods of investigation. The composition of the product has been found to be more dependent on the method of oxidation than upon the temperature at which the oxidation takes place.

Sodium, unlike potassium, undergoes the amide reaction even at  $-77^\circ$ . A method of oxidation has been developed that eliminates this reaction almost entirely over the entire liquid ammonia range—from  $-33^\circ$  to  $-77^\circ$ . With this method a solution of the metal in liquid ammonia is added slowly to liquid ammonia through which oxygen is being passed.

Evidence is presented which indicates the formation of a sodium-oxygen compound of the empirical formula  $\text{Na}_3\text{O}_5$ . This molecular compound is probably made up of a mixture of sodium superoxide and peroxide in the ratio of four to one ( $\text{Na}_2\text{O}_2 \cdot 4\text{NaO}_2$ ).

Lithium metal, when oxidized by the rapid oxidation method, shows a definite tendency to form the peroxide,  $\text{Li}_2\text{O}_2$ .

Suggestions have been offered for future work to complete this investigation.

## Bibliography

- (1) Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, 1940, p. 272.
- (2) Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, 1940, p.34.
- (3) Berzelius, Traite de Chimie (1846).
- (4) Gay Lussac and Thenard, Recherches Physiocochimiques, 1, 132.
- (5) Harcourt, J. Chem. Soc., 14, 267 (1862).
- (6) Lupton, J. Chem. Soc., 30, 565 (1876).
- (7) Holt and Sims, J. Chem. Soc., 65, 432 (1894).
- (8) Baker, Trans. Roy. Soc. (London) (1888).
- (9) Rengade, Ann. chim. phys., (8) 11, 348 (1907).
- (10) Blumenthal, Roczniki Chemji, 12, 119 (1932).
- (11) deForcrand, Compt. rend., 130, 1465 (1900).
- (12) Joannis, Compt. rend., 116, 1370 (1893).
- (13) Kraus and Whyte, J. Am. Chem. Soc., 48, 1781 (1926).
- (14) Whyte, Doctoral Thesis, Clark University, Worchester Mass., (1923).
- (15) Peck, J. Am. Chem. Soc., 40, 339 (1918).
- (16) Kraus and Parmenter, J. Am. Chem. Soc., 56, 2384 (1934).
- (17) deForcrand, Compt. rend., 158, 991 (1914).
- (18) Blumenthal, Roczniki Chemji, 11, 865-9 (1931); 12, 119-34, (1932).
- (19) Tzentnershver and Blumenthal, Bull. intern. acad. polon., Classe sci. math. nat., 1933A, 499-522.

- (20) Leschewski and Zulla, Ber. Ges. Freunden tech. Hochschule Berlin, 1, 168-70 (1942); Chem. Zentr., 1944, I, 743-4.
- (21) Neuman, J. Chem. Phys., 2, 31 (1934).
- (22) Helms and Klemm, Z. anorg. Chem., 241, 97 (1939); 242, 201 (1939).
- (23) Kazarnovskii and Raikhstein, J. Phys. Chem. (USSR), 21, 245-55 (1947).
- (24) Kasatochkin, Compt. rend. acad. sci., (URSS), 47, 193-6 (1945); Doklady Akad. Nauk. (SSSR), 47, 199-202 (1945).
- (25) Weiss, Trans. Faraday Society, 31, 668 (1935).
- (26) George, Trans. Faraday Society, to be published in 1948.
- (27) Fischer and Ploetze, Z. anorg. Chem., 75, 10 (1912); 75, 30 (1912).
- (28) Emelius and Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., 1938, p. 341.
- (29) Hildebrand, J. Am. Chem. Soc., 34, 246 (1912).
- (30) Blumenthal, Roczniki Chemji, 12, 232-240 (1932).
- (31) Reisenfeld and Nottebohm, Z. anorg. Chem., 89, 405 (1914).
- (32) Traube and Schulze, Ber., 54, 1626 (1921).
- (33) Ehrlich, Z. anorg. Chem., 252, 370 (1944).
- (34) Schechter, Masters Thesis, University of Kansas, Lawrence, Kansas, (1947).
- (35) Schechter, Sisler, Kleinberg, J. Am. Chem. Soc., 70, 267 (1948).