

The Determination of Superoxide Oxygen
and
The Attempted Preparation of Lithium and
Alkaline Earth Metal Superoxides

by

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Part I

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PART I

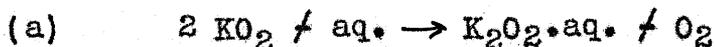
The Determination of Superoxide Oxygen

Introduction

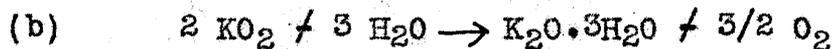
The commercial development of potassium superoxide, KO_2 , as a source of oxygen in breathing apparatus for fire-fighting and rescue work during World War II, has stimulated research in both the theoretical and practical aspects of superoxide chemistry. In practical application, the oxide is used in canisters in a closed-system apparatus because of its ability to absorb carbon dioxide and moisture from the breath and simultaneously release sufficient oxygen to supply the wearer's needs. The increased interest in superoxides has led to the discovery and preparation of sodium superoxide (1, 2) and to further investigations on the oxides of lithium and of the alkaline earth metals. In many cases, experimental work has been hampered by the lack of a suitable analytical method for the direct determination of superoxide in the presence of peroxide and other impurities. The need for an accurate analytical method became increasingly urgent when the mixed oxides containing both peroxide and superoxide ions which are discussed in Part II of this thesis could not be clearly characterized by the analytical methods available in the literature. The experimental work described in this section of the thesis records the development of a reasonably accurate method for the determination of superoxide ion. The nature of the method is such that neither the presence of peroxide nor of other impurities interferes with its accuracy.

Historical Review

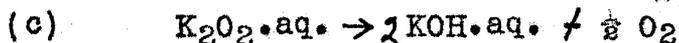
Holt and Sims (3) first showed that potassium superoxide reacts with water vapor in accordance with the equation



This reaction, if quantitative, should provide a method for determining the amount of superoxide present in a sample, since peroxide presumably is not decomposed. The peroxide could then be catalytically decomposed in a second step if its determination were also desired. In 1934, Kraus and Parmenter (4) stated that potassium superoxide reacts with water vapor according to the equation



Once the decomposition of some of the potassium superoxide has started, it continues until potassium hydroxide is formed, while the remaining superoxide remains intact. Kraus and Parmenter state that equation (a) is correct for the reaction between potassium superoxide and liquid water at 0°. From this reaction they developed a so-called "two-step" method of analysis whereby an oxide sample which is added to ice-cold water presumably decomposes according to equation (a) for the first step and then the resulting peroxide solution is decomposed catalytically to give a second volume of oxygen. The peroxide decomposes according to the equation



From the volumes of oxygen evolved in each step and the weight of the metal combined in the oxides (or the total weight of the oxides), the composition of the material can be calculated. This method of analysis was used by Kraus and Parmenter to determine the composition of various oxides and oxide hydrates of potassium. Occasionally, the analysis gave results which were too high in the superoxide step and the authors attributed this to partial decomposition of peroxide. The two-step method was used by George (5) in 1947, on one sample of mixed potassium oxides with apparent success. However, it has been the experience in this Laboratory that, although the theory of the method is sound, in practice it is impossible to add a mixed oxide sample to water without obtaining some decomposition of peroxide because of local heating during the solution process. Apparently, Kraus had this same difficulty to some extent in his experiments, since occasionally his superoxide results were high, a fact which was attributed to partial decomposition of some peroxide.

In 1949, Stephanou (6), working with sodium superoxide, also attempted to develop a method for the direct determination of peroxide and superoxide in a mixture of oxides. The method was based upon the same reaction (a), but instead of water, glacial acetic acid was used as the decomposing agent. Here the most serious objection to the ice water method (decomposition of peroxide because of local heating) was minimized by first covering the

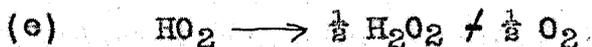
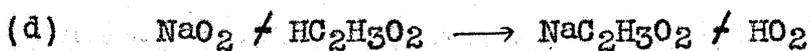
oxide sample with an inert organic diluent (carbon tetrachloride) and then slowly adding acetic acid at 0° with constant stirring. By this procedure, the oxide sample came in contact with acid slowly and local heating in large measure was prevented. Stephanou (6) was able to show quantitatively that peroxide, treated in this manner, decomposed only to the extent of 2%.

The details of the procedure were as follows:

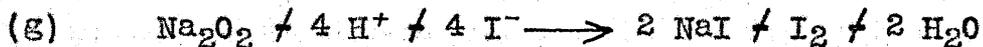
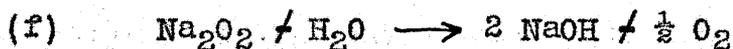
Approximately 5 cc. of dry carbon tetrachloride were added carefully to a mixed oxide sample in a reaction cell connected to a gas buret. The cell was cooled in an ice-water bath until the system attained equilibrium, and then the initial buret readings were taken. Exactly 10 cc. of acetic acid solution (20% by volume with respect to carbon tetrachloride) were added slowly into the cell with stirring. The stirring was continued and buret readings taken every five minutes until a fairly constant reading (within 0.2 cc.) was attained. Peroxide content was then determined in the following manner. Ten cc. of acidified potassium iodide solution was added and the solution was stirred until a constant buret reading was again obtained. The analysis cell was then removed from the gas buret system and the iodine liberated by the peroxide titrated with standard sodium thiosulfate solution. The oxygen released on treatment with acetic acid solution gave a measure of the superoxide content of the sample,

while the combined values of oxygen released by the acidified potassium iodide solution and the thiosulfate required, permitted calculation of the total peroxide content. The equations involved in the reactions are

superoxide step:



peroxide steps:



The data presented by Stephanou indicated that the superoxide determination under the most favorable conditions gave results on prepared sodium superoxide-sodium peroxide mixtures which checked to within 2% with the calculated values. The peroxide step was consistently low (about 8%), however, and Stephanou concluded that even with measurement of the oxygen evolved due to decomposition of a small portion of the peroxide during its reaction with potassium iodide, the peroxide is not quantitatively determined.

The quantitative data given by Stephanou is the most extensive thus far presented in the literature for a series of superoxide-peroxide mixtures. Two objections are immediately apparent, however. The first objection is the indeterminacy of the end-point in the superoxide step, which practically necessitates the preparation of a graph to determine just when the gas evolution levels off, and

the second is the consistently low value obtained in the peroxide step. The first objection, although troublesome, still does not prevent obtaining reasonably good determination for superoxide oxygen, especially when the content of the latter is high, a condition under which the two-step method of Kraus is most weak.

The method for the determination of superoxide oxygen developed during the course of the present investigation is described below. This method overcomes the objections raised to the Stephanou procedure.

Experimental

Procedure. The system used in the analysis of superoxides (Fig. 1) consisted essentially of a reaction cell D-E of about 100 cc. capacity, connected to a water-jacketed buret G by means of capillary tubing. The reaction cell was composed of the cell-head D joined to the cell-body E by a ground glass joint. The various solutions used to decompose the superoxide samples were added through the dropping funnel B which was connected to the cell by means of a three-way stopcock C.

A weighed oxide sample (preferably 0.1 to 0.2 g.) was transferred to the cell-body in a dry-box which contained anhydrous magnesium perchlorate; the cell-body was connected to the cell-head. The system was then swept out with oxygen which was dried by passage through anhydrous magnesium perchlorate in A. The reaction cell was thermostated at 0° by means of an ice-water bath and buret readings taken until equilibrium had been established. The decomposing solution was added through the dropping funnel B and when the reaction was complete, the system was again brought to equilibrium at 0° and the final buret readings were taken.

Three methods of analysis were used in this investigation; (1) the total decomposition method in which a HCl-FeCl_3 catalyst was used to decompose both peroxide and superoxide quantitatively, (2) the direct determination of superoxide, involving conversion of superoxide to peroxide with acetic

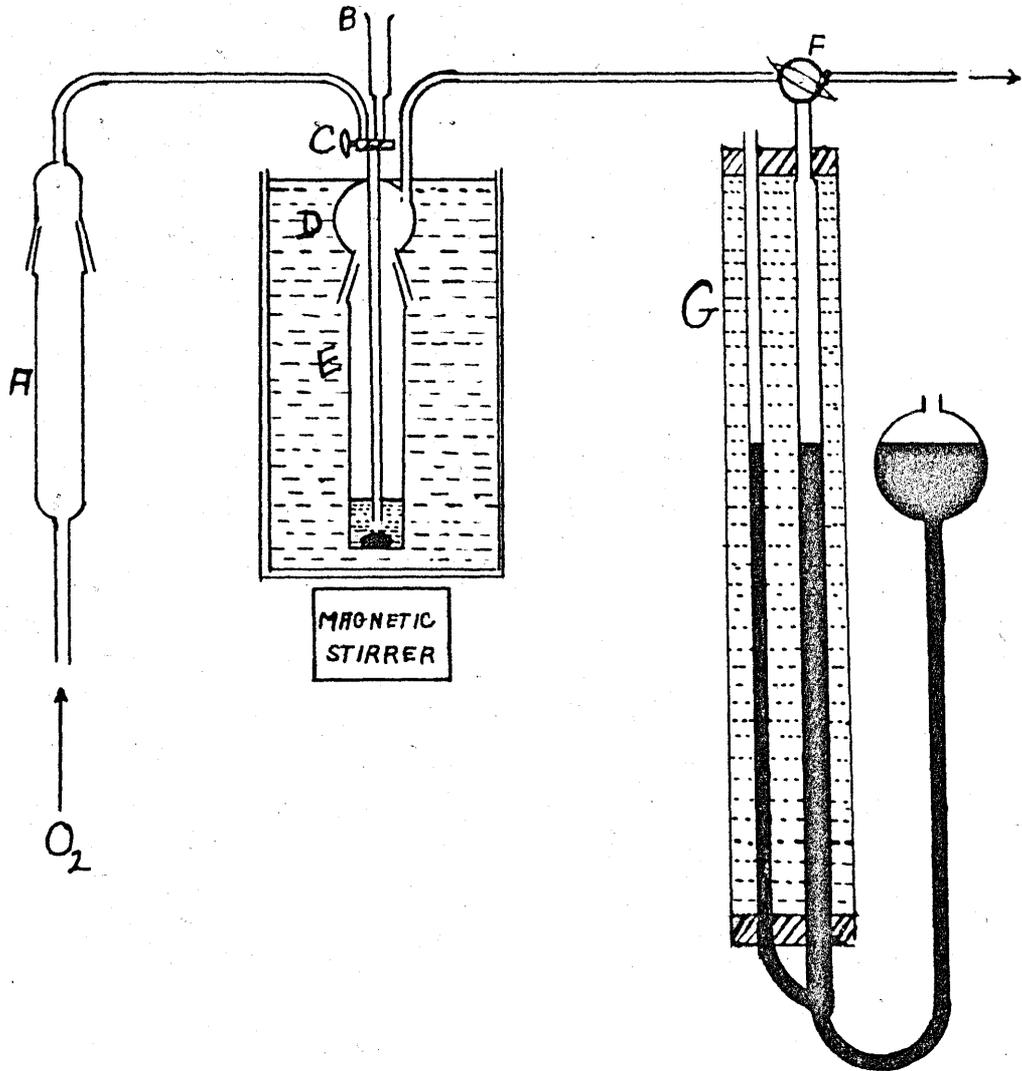


Fig. 1

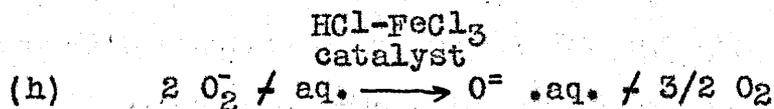
acid-diethyl phthalate solution, and (3) a two-step analysis on the same sample with first the superoxide being converted to peroxide, the oxygen evolved giving a measure of superoxide content, and then the peroxide formed being decomposed in a second step with HCl-FeCl₃ catalyst.

In the total decomposition procedure, the sample was introduced, the system swept with dry oxygen and brought to temperature equilibrium in the ice-water bath, the initial buret readings taken, and then exactly 10 cc. of HCl-FeCl₃ solution was added. The ice-water bath was removed, the catalyst solution brought to boiling and the ice bath replaced around the cell body. This treatment was repeated several times until the reaction was complete. Then temperature equilibrium was again attained and the final buret readings were taken. The HCl-FeCl₃ solution was 1 M in HCl and 3 M in FeCl₃.

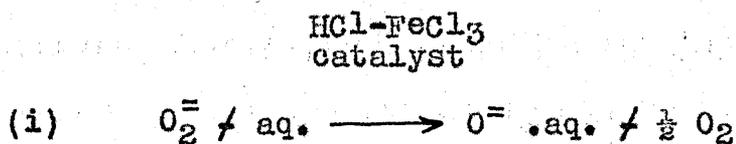
The procedure for the direct determination of superoxide included the same introduction of the sample and the taking of initial buret readings at 0°. Then exactly 5 cc. of diethyl phthalate (Eastman) was introduced in the cell. This was followed by the slow addition (10-15 minutes) of exactly 10 cc. of a mixture of acetic acid and diethyl phthalate (8 volumes to 2 volumes, respectively). Throughout the addition of the acetic acid solution the contents of the cell, which were kept at 0°, were stirred by means of the

magnetic stirrer shown in Fig. 1; this permitted gradual contact between the oxide sample and the acetic acid, and therefore, a slow release of superoxide oxygen. Buret readings were taken at five minute intervals until a constant value had been attained. The volume of gas liberated, when corrected for the volumes of the added decomposant solutions, gave a measure of the oxygen evolved in the conversion of superoxide to peroxide. It is noted that the sample, when decomposed as described above, no longer contains the yellow color characteristic of superoxides. The two-step method combines the first two procedures for use on the same sample of oxide when insufficient material is available for two separate analyses. The oxide was analyzed in the same manner as described above for superoxide alone, and then HCl-FeCl₃ catalyst was added to cause decomposition of peroxide. When the volume changes in the two stages were corrected for the volumes of the decomposant solutions, a measure of both the superoxide and peroxide content could be calculated.

Calculations. The stoichiometry for the total decomposition reaction is shown in the following reactions:



Any peroxide originally present will also be decomposed.

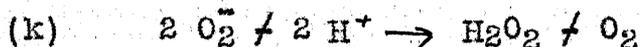


If only superoxide and peroxide are present in the oxide sample, the per cent peroxide can be calculated from the algebraic relationships involved. This calculation is shown in equation form:

$$(j) \quad \frac{\text{obs'd cc. (STP) O}_2 \text{ per g. material} - \text{theor. cc. (STP) O}_2 \text{ per g. peroxide}}{\text{theor. cc. (STP) O}_2 \text{ per g. superoxide} - \text{theor. cc. (STP) O}_2 \text{ per g. peroxide}} \times 100 = \% \text{ superoxide}$$

where the numerator represents the cc. of oxygen evolved per gram of sample beyond that required for pure peroxide and the denominator represents the difference in cc. of oxygen evolved per gram between pure superoxide and peroxide.

The stoichiometry for the direct superoxide determination reaction is



It is seen that a half mole of oxygen is released for each mole of superoxide involved in the reaction. The equation for per cent superoxide in the sample from the direct determination is

$$(l) \quad \frac{\text{obs'd cc. (STP) O}_2 \text{ evolved / g. material}}{\text{theor. cc. (STP) O}_2 \text{ evolved / g. superoxide}} \times 100 = \% \text{ superoxide}$$

If it is desired to obtain both peroxide and superoxide content separately for the mixed oxide sample, a combination of the results of the first two types of analyses will give the quantity of superoxide and the quantity of peroxide in the sample. Or if preferred, the two-step

method may be used. In either case the method of calculation is the same. The superoxide content is calculated as shown above. An examination of equations (i) and (k) shows that for a sample of pure superoxide twice as much oxygen is liberated in conversion to peroxide as is formed in decomposition of the latter to hydroxide. Thus, the amount of oxygen liberated from peroxide, originally present as such in the sample, is given by the equation,

$$(m) \quad \begin{array}{l} \text{total cc. (STP) O}_2 \\ \text{evolved per gram} \end{array} - \frac{1}{2} \text{ cc. (STP) O}_2/\text{g.} = \begin{array}{l} \text{cc. O}_2 \text{ (STP)} \\ \text{/g. due to} \\ \text{peroxide} \\ \text{originally} \\ \text{present} \end{array}$$

and the per cent of peroxide present is

$$(n) \quad \frac{\text{obs'd cc. (STP)/g. peroxide}}{\text{theor. cc. (STP)/g. peroxide}} \times 100 = \% \text{ peroxide}$$

Results. Initial experiments on samples of higher oxides of sodium in which the ice-water method of Kraus and Parmenter was used gave results for superoxide content which were usually high and variable. Table I gives typical data.

Preliminary work with acetic acid-carbon tetrachloride solutions indicated that the indeterminate end-point for the superoxide determination mentioned by Stephanou might be attributed to the high vapor pressure of carbon tetrachloride. An organic diluent, which would be inert to superoxides, would not absorb oxygen, and would have a low vapor pressure, was required; diethyl phthalate,

Table IReaction of Ice-Water with Higher Oxides of Sodium

<u>Sample</u>	<u>Wt.</u>	<u>cc.(STP) O₂ liberated</u>	<u>cc.(STP) O₂ per gram</u>	<u>theo'l cc. O₂/g. (STP)</u>
Pure	0.0644	0.5	7.7	0
Na ₂ O ₂ *	.0615	0.7	12.0	
NaO ₂ ,	0.0503	10.2	203	192
94.5%	.0627	14.85	245	
pure				

* Supplied by Mine Safety Appliances Co., Pittsburgh, Pa.

a compound occasionally used as a manometer fluid, satisfied these requirements. When diethyl phthalate was substituted for carbon tetrachloride the superoxide end-point was quite sharp and remained constant for at least half an hour.

The acetic acid concentration in diethyl phthalate was varied in a number of runs to determine the optimum concentration for obtaining the most accurate results. Potassium superoxide, which was finely ground, gave good results with 20% acetic acid by volume in diethyl phthalate, but sodium superoxide samples, not so finely ground, required too long a time to decompose in this medium. It was found that the best solution contained 8 parts acetic acid and 2 parts diethyl phthalate by volume, but extreme caution was required in adding this solution, particularly at the beginning of the reaction. Ten to fifteen minutes for the addition of 10 cc. of 80% acetic acid in diethyl phthalate was found to be satisfactory. Pure white sodium peroxide (Mine Safety Appliances Co.) when treated with acetic acid-diethyl phthalate solution in the manner previously described did not evolve oxygen. This demonstrates that there is little, if any, release of oxygen by the secondary decomposition of hydrogen peroxide in solution, and indicates that the method is applicable to superoxide mixtures containing peroxide and other impurities.

The reliability of the method was tested in a series of analyses on potassium superoxide samples of relatively high purity, and also on mixtures of sodium peroxide and sodium superoxide. The potassium superoxide samples were analyzed by the two-step method of analysis already described. The data obtained are shown in Table II. It is evident that the agreement with the theoretical values is good and the conclusion must be reached that there is little if any decomposition of the peroxide which is formed from the superoxide.

Another test of the method was provided by the analysis of a series of sodium peroxide-sodium superoxide mixtures prepared in a stainless steel bomb. These mixtures were prepared as described previously by Stephanou, et al. (2). Since such mixtures contain only superoxide and peroxide oxygen, an accurate estimate of the superoxide content was obtained from the quantity of oxygen released on total catalytic decomposition by the use of equation (j). The data presented in Table III represent the results obtained on the direct determination of superoxide oxygen in a series of samples containing widely varying percentages of superoxide. The experimental values for superoxide content were found by the use of equation (1). An examination of the data shows that they are accurate to approximately 2%. It is believed that this is within

Table IIThe Liberation of Superoxide oxygen by KO₂

<u>Wt. of sample, g.</u>	<u>Total oxygen liberated, cc./g.</u>	<u>Calc'd superoxide oxygen, cc./g.*</u>	<u>Obs'd superoxide oxygen cc./g.</u>
0.1672	227	151	154
.1492	227	151	155
.0901	233	155	155
.1035	228	152	151
.1361	233	155	155
.1104	230	153	152
.1031	233	155	159

* The stoichiometry of the reactions involved in the decomposition of superoxides, which have already been discussed, shows that $2/3$ of the total oxygen liberated from a sample which contains no peroxide impurity comes from the conversion of superoxide to peroxide.

Table IIIThe Determination of Superoxide Oxygen in NaO₂-Na₂O₂ Mixtures

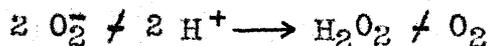
Weight of sample, g.	Oxygen liberated on total decomposition. cc./g. (STP)	Percent superoxide Calc'd.*	Superoxide oxygen liberated cc./g.**	Percent superoxide obs'd
0.8956	170	16.1	30.9	15.2
.0603			30.7	15.1
.3121	174	18.6	37.4	18.4
.2204			35.9	17.7
.0983	191	28.5	56.0	27.6
.1556			58.5	28.8
.1617	234	56.0	114	56.0
.1647			113	55.8
.0694	273	80.2	159	78.4
.0397			161	79.4
.1253	296	94.5	188	92.6
.1178			192	94.5

* calculated by the use of equation (j).

** calculated by the use of equation (l). Theoretical superoxide oxygen for sodium superoxide is 203 cc./g.

the accuracy of the gasometric method employed in these analyses.

summary. Superoxide oxygen has been determined with reasonable accuracy in samples of potassium superoxide and in mixtures of sodium superoxide-sodium peroxide by the employment of a solution of glacial acetic acid in diethyl phthalate as the decomposant. The reaction involves the conversion of superoxide ion to peroxide ion according to the equation



There is little, if any, release of oxygen by the secondary decomposition of the hydrogen peroxide formed. Thus, the method would appear to be applicable to mixtures containing superoxide ion.

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PART II

The Attempted Preparation of Lithium and
Alkaline Earth Metal Superoxides

Introduction

The most useful method for the preparation of higher oxides of the alkali and alkaline earth metals has been the direct treatment of the metal or lower oxide with oxygen. This reaction occurs at atmospheric pressure and at various temperatures to form peroxides in the cases of elementary barium and sodium, and the superoxides with potassium, rubidium, and cesium. At higher oxygen pressures, either the speed of the desired reaction is increased, e. g., the conversion of barium monoxide to the peroxide, or the course of the reaction is altered, e. g., the conversion of sodium to the superoxide.

The recent study which has resulted in the successful preparation of sodium superoxide (1), by the treatment of sodium peroxide with oxygen at high temperatures and pressures emphasized the need for a similar investigation for lithium and the alkaline earth metals. Thus, one purpose of the present investigation has been to explore the possibility of preparing the superoxides of lithium and of the alkaline earth metals by reaction of oxygen with the metal or some lower oxide at high temperatures and pressures. No higher oxide, not already well known, was formed under the conditions of the experiments to be described.

Another useful method for the preparation of the alkali metal higher oxides, at least on a laboratory scale, involves the oxidation of liquid ammonia solutions of the metals.

This method has yielded superoxides in the cases of cesium, rubidium, and potassium, and has also resulted in partial conversion of sodium to the superoxide. No superoxides have been obtained with the alkaline earth metals. One phase of the investigation to be described has involved a new approach to the problem in that liquid ammonia was used as the medium for attempted double decomposition reactions between superoxides of alkali metals and liquid ammonia soluble salts of alkaline earth metals. In the cases of barium and strontium the salt employed was the nitrate and in the case of calcium the iodide. It was hoped that superoxides of the alkaline earth metals would be isolated. This was not realized. However, in at least one case, a mixed superoxide-peroxide was obtained. In other cases only the alkaline earth metal peroxide was isolated.

Review of Direct Oxidation Studies

Alkali Metal Oxides. The end-products of the combustion of the alkali metals in an excess of oxygen are the oxides, Li_2O , Na_2O_2 , KO_2 , RbO_2 , and CsO_2^* , respectively. The formation of these products indicates the dependence of the nature of the product on cationic size.

Holt and Sims (2) obtained almost pure Li_2O with only traces of the peroxide by the combustion of the metal at 250° in a stream of oxygen. Attempts by Fischer and ploetze (3) to convert lithium hydroxide to the peroxide by treatment with oxygen at 1000° and 100 atmospheres pressure were unsuccessful. Stephanou (4) found no evidence for superoxide formation when lithium peroxide of 96 per cent purity was treated with oxygen in a stainless steel bomb at temperatures as high as 220° and pressures up to 255 atmospheres.

The reaction of oxygen with sodium has been studied extensively. prior to 1860, Gay Lussac and Thenard (5) studied the reaction, and in 1894, Holt and Sims (2) made an outstanding contribution in the field. The latter investigators found that sodium could be distilled in dry air without oxidation occurring. When heated below its

* The alkali metal oxides of the formula MO_2 are called superoxides. Early workers believed the correct formula for these substances to be M_2O_4 , and this formula, therefore, is frequently used in the historical section of the thesis.

melting point in a sheet-iron boat in a stream of moderately dry oxygen, the metal was soon coated over with an oxide film of no definite composition. When heated above its melting point, the metal caught fire and burned vigorously. In a limited supply of oxygen and at temperatures below 180° , the grayish white Na_2O was formed; with an excess of oxygen and at higher temperatures, the yellow-white sodium peroxide was obtained. Oxygen at atmospheric pressure was passed over sodium peroxide at 300° - 350° for six hours, but no evidence of oxygen absorption was found.

In 1906, Rengade (6) prepared Na_2O by bringing slightly less than the required quantity of oxygen in contact with the pure metal and distilling off the excess metal, after the oxygen had been absorbed. A year later, the same investigator (7) corroborated the findings of Holt and Sims that sodium undergoes no oxidation when kept in contact with perfectly dry oxygen at room temperature. In 1912, Fischer and ploetze (3) attempted, without success, to make sodium peroxide from sodium hydroxide and oxygen at temperatures up to 1000° and pressures to 100 atmospheres.

In a recent investigation on higher oxides of sodium, Stephanou et al. (1) prepared sodium superoxide of 92 per cent purity by the treatment of sodium peroxide with oxygen at temperatures of 450° - 500° and pressures of 280 - 300 atmospheres.

The first reliable work on the higher oxides of potassium was that of Harcourt (8) who found that the

highest product of the direct oxidation of potassium is K_2O_4 . He was unable to isolate any lower oxides. Holt and Sims (2) obtained products with chemical compositions of K_2O_2 and K_2O_3 from the oxidation of potassium with limited quantities of oxygen. K_2O_2 exposed to air, absorbed moisture slowly, while K_2O_3 was converted to $K_2O_4(KO_2)$ with the evolution of sufficient heat to cause the oxide to fuse. Holt and Sims also found that potassium, like sodium, was not oxidized during distillation in dry air. Rengade (6) made K_2O from the metal by using less than the theoretical quantity of oxygen and distilling off the excess metal. He also showed that with dry oxygen potassium underwent no change at room temperature. One of the earliest workers to make dissociation pressure measurements on alkali metal oxides was de Forcrand (9) who found that at 480° an oxygen pressure of 155 mm. was sufficient to prevent the dissociation of K_2O_4 . Kraus and Whyte (10) investigated the dissociation of K_2O_4 and found that the reaction, $K_2O_4 \longrightarrow K_2O + 3/2 O_2$, is reversible. Although the process is reversible, Kraus and Whyte found that the pressures at various temperatures appear to depend upon the oxygen content of the solid phase. Fischer and Ploetze (3) obtained a 70% yield of K_2O_2 from potassium hydroxide at 375° and 100 atmospheres oxygen pressure.

Much less work in the oxide field has been carried

out with rubidium and cesium than with the other alkali metals. The most stable oxide in either case is the superoxide, and is the product ordinarily obtained on direct oxidation. Rengade (7) claimed to have obtained the monoxides, Rb_2O and Cs_2O , by the same method used for preparation of Li_2O , Na_2O , and K_2O , i. e., by heating the metal in the presence of a limited supply of oxygen and distilling off excess metal.

Alkaline Earth Metal Oxides. The literature dealing with alkaline earth metal oxides is much less abundant than that of the corresponding alkali metal compounds. The final product on free combustion of the metal is in every case the monoxide, MO . Only barium monoxide is readily converted to the peroxide by heating in air to 400° at atmospheric pressure. This peroxide is readily decomposed at low pressures or at temperatures above 400° , and before the use of liquid oxygen, this reaction was the basis of the Brin process for the manufacture of oxygen. All the evidence which indicates the possible existence of superoxides of the alkaline earth metals comes from studies of the "wet method" (11,12) of preparation, which involves action of hydrogen peroxide on the metal hydroxide and the subsequent precipitation of the metal peroxide formed with alcohol.

Fischer and Ploetze (3) attempted, without success, to prepare calcium peroxide from calcium monoxide and oxygen at temperatures up to 1000° and pressures to 100 atmospheres.

Holtermann (13, 14) more recently verified the inert character of calcium monoxide toward oxygen when he subjected it to oxygen pressures up to 300 atmospheres and temperatures as high as 600° . The samples were contained in porcelain, aluminum, or nickel crucibles.

Bergius (15) made peroxides of the alkaline earth metals by heating the corresponding monoxides with sodium hydroxide or potassium hydroxide until fusion occurred and then passing air or oxygen through the fused mass. After cooling, the alkali was removed by solution in alcohol, leaving the undissolved peroxide behind. Calcium peroxide was prepared by heating a mixture of calcium monoxide and alkali ($\text{NaOH} \neq \text{KOH}$) with oxygen at 350° and approximately 124 atmospheres pressure for several days.

Stephanou (4) treated dry commercial grade calcium peroxide (du pont and Buffalo Electro-Chemical Co.) at temperatures to 400° and oxygen pressures to 320 atmospheres without obtaining any evidence for the formation of a superoxide. The same investigator treated calcium monoxide with oxygen at $450^{\circ} - 480^{\circ}$ and 288 - 221 atmospheres for forty hours and obtained no evidence for peroxide formation.

Strontium does not form the peroxide readily. Fischer and ploetze (3) were able to obtain a 15% yield of the peroxide by the oxidation of the monoxide at 400° and 98 atmospheres pressure. Holtermann (13, 14) verified this result and also obtained strontium peroxide of 99% purity by the action of

dry oxygen on strontium monoxide (free from the hydroxide and carbonate) at 350° - 400° and 200 - 250 atmospheres pressure.

Barium is the only alkaline earth metal which readily forms the peroxide by direct reaction with oxygen. Barium monoxide is converted to the peroxide by combination with atmospheric oxygen at temperatures below 400° at atmospheric pressure; the peroxide is decomposed at temperatures above 400° or at low pressures. Hildebrand (16) has studied the dissociation of barium peroxide and found that dissociation occurs only with the presence of small quantities of water and that a rather large solid solution range complicates the determination of the dissociation curve. Holtermann (13, 14) also studies the system BaO_2 - BaO - O_2 up to pressures of 220 atmospheres and temperatures of 520° . He obtained no product containing more than 86% BaO_2 . Stephanou (4) attempted without success to prepare a higher oxide by treating commercial grade barium peroxide (Merk) with oxygen at a temperature of 450° and a pressure of 314 atmospheres for thirty hours.

Oxidations in Liquid Ammonia

Although the action of oxygen on solutions of the metals in liquid ammonia is not important commercially for the production of higher oxides of the alkali metals, nevertheless, it proved of great interest and value to the inorganic chemist.

The best summary of the work done in liquid ammonia on the oxidation of metal solutions has been compiled by Watt (17). The following data were taken from his review.

<u>Metal</u>	<u>Products</u>	<u>Notes</u>
Li	Li_2O , Li_2O_2	
Na	NaOH , NaNH_2 , NaNO_2	Slow reaction
	Na_2O_2	Rapid reaction
	Na_2O_3	Not confirmed
	NaO_2	At -77°
K	KOH , KNH_2 , KNO_2	Slow reaction
	K_2O_2 , $\text{K}_2\text{O}_4(\text{KO}_2)$	Rapid reaction
	K_2O_3	Not confirmed
Rb	Rb_2O	
	Rb_2O_2 , $\text{Rb}_2\text{O}_4(\text{RbO}_2)$	-60° (?)
Cs	Cs_2O	
	Cs_2O_2 , CSNH_2 , CSOH CSNO_2 , CSNO_3	Slow reaction at -60°
	Cs_2O_2 , Cs_2O_3 , Cs_2O_4	Rapid reaction
Ba	BaO , BaO_2	Gelatinous ppt.

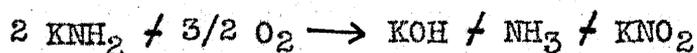
Alkali Metal Oxides. Joannis (18) was one of the first investigators to use liquid ammonia as a solvent for the oxidation of the alkali metals. Joannis claimed to have prepared K_2O_2 , K_2O_3 , $K_2O_4(KO_2)$, $Na_2O \cdot NH_3$ and Na_2O_3 by the oxidation of the appropriate metals. The lower oxides of potassium were presumably prepared by oxidation with limited supplies of oxygen; their existence has been questioned by some later workers and apparently confirmed by others. The formation of the two compounds of sodium shown above has been even more seriously questioned by more recent investigators (19,20), who have challenged the analytical proof for the products in the light of later knowledge of the course of the reaction of sodium in liquid ammonia. In 1907, Rengade (21) repeated the study of the oxidation of potassium in liquid ammonia and extended the method to rubidium and cesium. The existence of oxides corresponding to the formulas M_2O_2 , M_2O_3 and $M_2O_4 (MO_2)$ was further established. Rengade was the first to make the important observation that different products were formed upon slow and rapid oxidation. He showed that with rubidium and cesium the rate of oxidation determined the product formed. Thus on slow oxidation the initial product is a mixture of the hydroxide, MOH , and the amide, MNH_2 . Upon rapid oxidation the initial product corresponds to M_2O_3 and the final product to $M_2O_4 (MO_2)$.

Kraus and co-workers (10, 22) began a series of investigations in 1923, extending to sodium and potassium

Rengade's observations on the dependence of the course of the reaction upon the rate of oxidation. Here, again, slow oxidation of the metal solutions in liquid ammonia gave initial products of hydroxide and amide, with the latter then being oxidized to the nitrite. The course of the reaction (10) was studied by attempting to prepare K_2O by slow oxidation of the metal with the calculated quantity of oxygen. The weight of the white gelatinous precipitate was much greater than the theoretical value for K_2O and this excess weight corresponded closely to that for one mole of ammonia. This illustrated that ammonolysis was occurring,

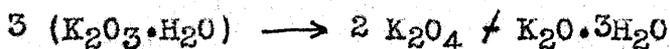
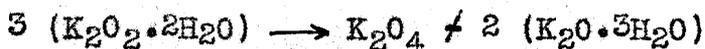
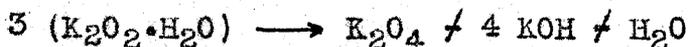


Since the amide is soluble in liquid ammonia while the hydroxide is not, these workers were able to separate the two products and to show that the amide was further oxidized to nitrite,



Upon rapid oxidation of the monoxide they were able to isolate the peroxide and on further oxidation the superoxide. Their work with sodium gave the peroxide as the highest oxidation product. Kraus and Parmenter (22) oxidized potassium at -50° and obtained very nearly pure samples of K_2O_2 and K_2O_4 (KO_2). By permitting oxygen at low pressure to react with K_2O_2 at room temperature, the unstable chocolate colored K_2O_3 was prepared. It was also shown that oxide hydrates could be prepared by intro-

ducing the necessary quantity of water into suspensions of the various oxides in liquid ammonia. By this method $K_2O_2 \cdot H_2O$, $K_2O_2 \cdot 2H_2O$ and $K_2O_3 \cdot H_2O$ were prepared. These hydrates rearrange slowly at room temperature in the dry state to form K_2O_4 (KO_2) and KOH hydrates.



The first reaction shown above goes relatively rapidly to completion, the second goes somewhat slower, and the third is much slower still.

By the very rapid oxidation of sodium under carefully controlled conditions in liquid ammonia solutions, Schechter et al. (19) were able to obtain a product of the empirical formula $NaO_{1.67}$. This formula corresponds to a mixture of superoxide and peroxide in the ratio of four to one. Sodium was shown to possess a strong tendency to undergo the nitrite reaction already discussed for potassium, rubidium, and cesium unless the oxidation was very rapid.

The oxidation of lithium in liquid ammonia gives chiefly the monoxide and some peroxide according to Pierron (23).

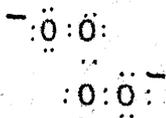
Alkaline Earth Metal oxides. A few relatively unsuccessful attempts have been made to prepare the alkaline earth peroxides by oxidation of liquid ammonia solutions of the metals. A poor yield of the peroxide is obtained by the

action of oxygen on the calcium solution; a somewhat higher percentage has been reported in the case of the strontium compound (24). The formation of barium peroxide in poor yield has also been reported (25, 26).

Pertinent Miscellaneous Topics

Indication of the formation of the superoxides of barium and calcium has been reported by Traube and Schulze (11). Calcium or barium peroxide octahydrate treated with 30% hydrogen peroxide at about 100° forms a yellow precipitate which retains its color when dry and liberates more gaseous oxygen on decomposition than can be obtained from peroxide alone. The phenomenon is regarded as evidence for the partial rearrangement of the alkaline earth peroxide peroxyhydrate, e. g., $\text{CaO}_2 \cdot \text{H}_2\text{O}_2$ or $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$, to the superoxide $\text{Ca}(\text{O}_2)_2$ or $\text{Ba}(\text{O}_2)_2$. Traube and Schulze reported mixtures containing about 8 per cent $\text{Ba}(\text{O}_2)_2$ and 8.7 per cent $\text{Ca}(\text{O}_2)_2$ in the respective peroxides, with the calcium superoxide being more stable than the barium compound. Erhlich (12) has demonstrated the existence of calcium superoxide by magnetic susceptibility studies of the product formed by this method, but was unable to obtain the barium compound.

The structures of superoxides and "sesquioxides". Until recently, the alkali metal superoxides have been called tetroxides and were believed to contain the O_4^- ion of the structure



After the discovery of the three electron bond, it was

suggested that these alkali metal oxides might contain the O_2^- ion with the three electron bond of the structure (27)



In 1934, Neuman (28) prepared potassium superoxide, measured its magnetic susceptibility, and showed it to possess a paramagnetism corresponding to one unpaired electron, a fact which supported the O_2^- structure. The existence of the superoxide ion has been verified by X-ray examination of the crystals (29). The X-ray crystal study shows potassium and superoxide ions to be arranged in a simple cubic array. Thus, the formula MO_2 has been adopted rather than M_2O_4 . Further verification has been provided in the case of sodium by Stephanou (1), who measured the magnetic susceptibility of NaO_2 and by Templeton and Dauben (30), who obtained X-ray data on the crystal structure of NaO_2 .

It has been mentioned in this review that several investigators have reported the existence of alkali metal "sesquioxides" of the empirical formula, M_2O_3 . Helms and Klemm (29) showed from magnetic and X-ray data that the rubidium and cesium compounds contained both the peroxide and superoxide ions and, therefore, their structures may be represented by the general formula, $M_2O_2 \cdot 2MO_2$.

Kazarnovskii and Raikhstein (31) have shown by means of dissociation studies that K_2O_3 is not a definite compound but rather a mixture of KO_2 and K_2O_2 .

High Temperature-pressure Studies

Apparatus and Procedure. The system for high pressure studies (Fig. 1) consisted of a stainless steel bomb A of about 180 cc. capacity, fitted in a heating jacket B, and equipped with tubing and needle valves in such a manner that the system could be completely evacuated or filled with oxygen under pressure. The bomb, furnace, tubing and valves* were obtained from the American Instrument Company, Inc., of Silver Spring, Maryland, as a hydrogenation apparatus and was adapted for use with oxygen by the removal of oil and grease with carbon tetrachloride and acetone, and replacement of valve packing with a special oil-free packing obtained from the Puritan Compressed Gas Corporation, Kansas City, Kansas. The heating jacket B of the bomb was insulated against heat loss with magnesia. A chromel-alumel thermocouple H, inserted in the wall of the bomb and connected to a Brown Electronik Recorder and Regulator C, provided temperature control. The voltage across the elements of the heating jacket B was adjusted by means of the Powerstat D.

*This is the same apparatus previously used and described by Stephanou (1,4).

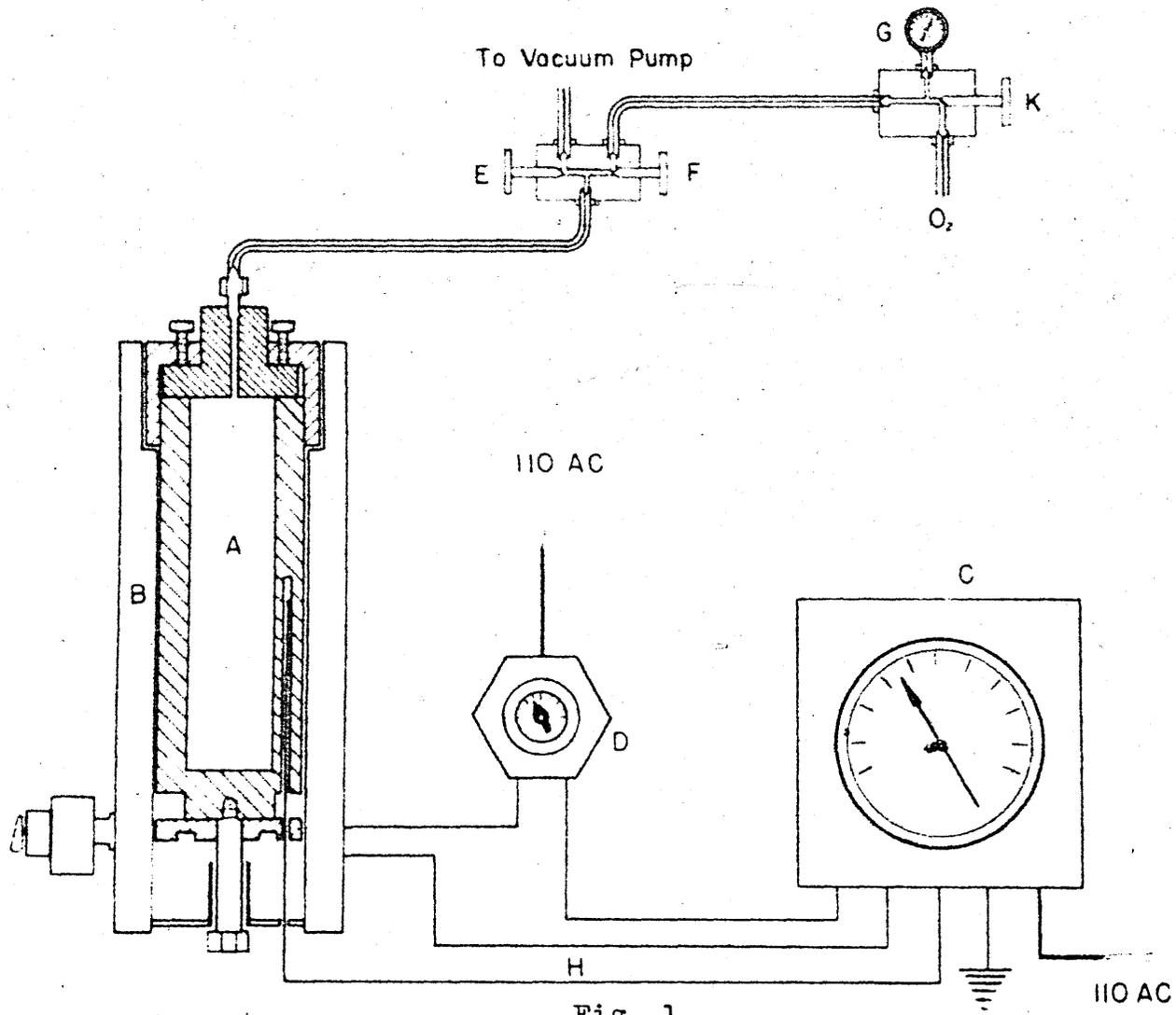


Fig. 1

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A sample of the metal or oxide was transferred to a suitable crucible in a dry box containing magnesium perchlorate and was then placed in either a glass-stoppered Pyrex liner or an alundum liner which was then fitted into the bomb. The system was evacuated to 1-3 mm. of mercury pressure, valve E closed, and oxygen from a cylinder added slowly through valves F and K until the desired initial pressure was obtained. Valve K was then closed and the bomb heated to the desired temperature. The absorption of oxygen was followed by reading the pressure gage G at frequent intervals. When the experiment was completed, the bomb was cooled to room temperature and the oxygen bled slowly from the system through valve E until atmospheric pressure was reached. The bomb was then opened, the liner containing the sample removed and placed in the dry box.

Results. Since barium is the alkaline earth metal which most readily forms the peroxide and which also might be expected to form the superoxide most readily, it was tested more extensively than the other alkaline earth metals. Experiments on the treatment of barium metal with oxygen gave no product which could be analyzed because the various crucibles used (porcelain, stainless steel, and alundum) were severely attacked at the high temperatures of reaction.

The oxidation of barium monoxide was also attempted in porcelain, stainless steel, and alundum crucibles; these crucibles again proved unsatisfactory. It was found, however, that beryllium oxide crucibles would "take" the high temperatures in the presence of the oxide without being attacked. In this case, only peroxide of less than 60% purity was obtained. Temperatures up to 500° with pressures as high as 240 atmospheres were used.

Barium peroxide (of 96% purity, Buffalo Electro-Chemical Co.) was also tested as a starting material. In this case, alundum crucibles were not attacked and were used in all the experiments. No evidence for the formation of a higher oxide was obtained. Temperatures up to 600° and pressures up to 265 atmospheres were used.

In a number of runs in which barium oxide or barium peroxide was used as the starting material, the final product was light gray in color. This color, which was due to reaction between the iron of the bomb and the oxide, was eliminated when a porous alundum crucible liner was substituted for the glass liner which contained small openings to permit passage of oxygen.

A similar though less extensive study was made

with strontium peroxide (of 95% purity, University of Arkansas Research Foundation) as the starting material. Alundum crucibles again proved satisfactory. Temperatures up to 500° and pressures up to 165 atmospheres were used. No evidence for the formation of a higher oxide was obtained.

Trial runs were also made with lithium peroxide prepared by the "wet" method as the starting material. The highest temperature used was 800° at a pressure of 135 atmospheres. No higher oxide was formed.

Mixed-oxide Studies

Materials. The starting compounds used in the study of the reaction between alkali metal superoxides and alkaline earth metal salts were the purest that could be obtained. Anhydrous barium nitrate and strontium nitrate were Baker's Analyzed grade, while the calcium iodide was from the same company and of the same grade except that it contained an unknown quantity of water of crystallization. The potassium superoxide analyzed to be of 99% purity and was supplied by the Naval Research Laboratory, Washington, D. C. The sodium superoxide was of 96% purity and was prepared from sodium peroxide by treatment with oxygen at high pressure and temperature (1).

Experimental procedure. The system used in the preparation of mixed oxides (Fig. 2) consisted of a reaction cell C-D of about 200 cc. capacity, surrounded by a Dry Ice bath E and connected to a source of gaseous ammonia or dry oxygen and to the safety manometer F. The reaction cell C-D was composed of the cell-head C connected to the cell-body D by means of a ground-glass joint. Fitted into the bottom of the cell-body D were a sintered-glass filter disk and a stopcock to permit filtration of any solid products formed. A sampling capsule B for the introduction of solid

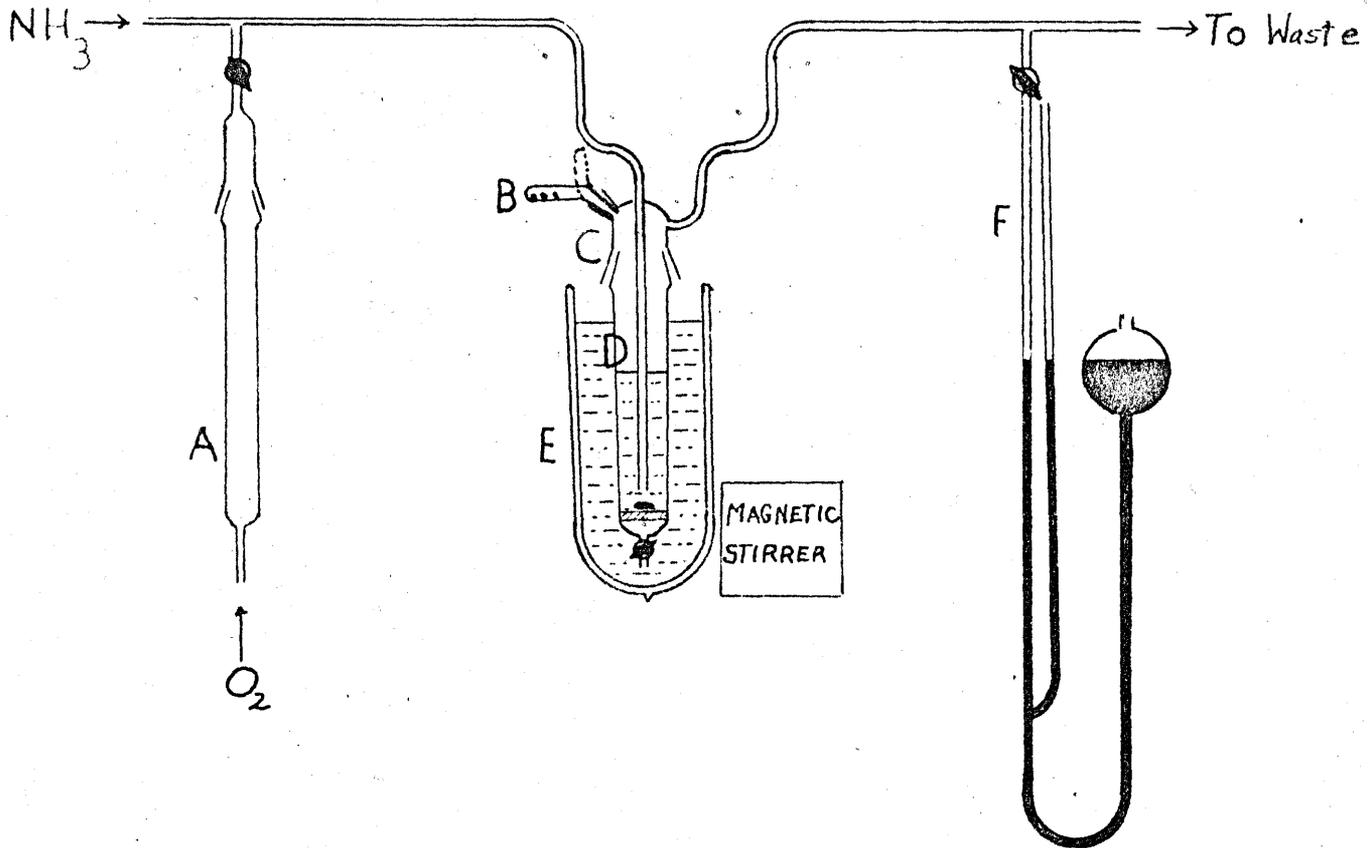


Fig. 2

reactants could be joined to the cell-head C by means of a ground-glass joint. During the process of drying the apparatus, the opening into which capsule B could be fitted was closed with a ground-glass plug.

The system was dried by sweeping with anhydrous ammonia (refrigeration grade, du pont) and then approximately 150 cc. of liquid ammonia was condensed into the cell-body D by means of the Dry Ice-cellosolve bath E. A weighed sample of the desired alkaline earth metal salt (approximately 1.0-1.5 g.) was transferred in a dry box to capsule B which was then rapidly fitted into the cell-head. The sample was slowly introduced into the body of the cell by turning capsule B from a horizontal to a vertical position. When the alkaline earth metal salt had dissolved in liquid ammonia, a weighed quantity of alkali metal superoxide was also introduced into the cell-body, the Dry Ice bath removed, and the liquid ammonia solution stirred for an hour by means of the magnetic stirrer. The product was filtered by suction from an aspirator pump and washed with two portions (approximately 75 cc. each) of liquid ammonia. The system was then swept out with oxygen which was dried by passage through anhydrous magnesium perchlorate in A. When all the ammonia had been removed, the cell-body was separated from the cell-head, rapidly stoppered, and

placed in the dry box where the product was transferred to ground-glass stoppered weighing bottles. The product was then analyzed.

Results and Discussion. Although these experiments were initiated with the hope of obtaining alkaline earth metal superoxides, it soon became evident that no ordinary metathetical reaction was taking place. For example, the mixing of anhydrous barium nitrate and potassium superoxide in the formula weight ratio of approximately 1:2, with the barium nitrate being in slight excess (5-10%), resulted in the evolution of oxygen and the slow formation of a chocolate brown material which contained both superoxide and peroxide oxygen as well as potassium and barium, but practically no nitrate.

Considerable difficulty was encountered at first in obtaining a product which upon analysis gave consistent values for the various components. It was soon discovered that the mode of removal of ammonia played an important role in determining the oxygen content of the product; evaporation of the last traces of ammonia by the use of a hot plate invariably resulted in low values for combined oxygen. Tests subsequently showed that the chocolate brown material lost its color and also practically all of its superoxide oxygen when heated at 110° for a short time. When the last traces of

ammonia were permitted to evaporate at room temperature, the oxygen content of the product was essentially constant from run to run. It was also learned that excessive washing of the brown precipitate with liquid ammonia, to remove nitrate, lowered the oxygen content to some extent. Eventually a correlation also appeared between the length of the reaction time and the ratio of barium to potassium in the final product.

All these observations pointed to the necessity for a standardized procedure which would permit the formation of a definite reproducible product. The reaction time was set at one hour to permit sufficient time for the slow reaction to take place. Each sample was washed only twice with liquid ammonia since additional washings lowered the oxygen content; and finally, the sample was left overnight in the cell at room temperature with oxygen sweeping out the system while the last traces of the ammonia evaporated.

The standardized procedure gave a chocolate brown powder of reproducible composition. The peroxide and superoxide contents were measured quantitatively by the methods described in Part I of this thesis. The total base content was determined by titration with standard hydrochloric acid to a phenolphthalein endpoint. Barium was determined by the standard sulfate

method, and potassium also was weighed as the sulfate.

It became evident from various analyses that the presence of barium invariably accounted for very nearly one-half of the total number of equivalents of base. This indicated that the variable quantities of potassium found were due to the presence of variable quantities of potassium nitrate as impurity. This was shown experimentally to be the case. Therefore, after the first few experiments, the potassium content in the product was determined by difference from the observed values of barium and total base in the product. The ion ratios obtained on four products prepared by the use of the standardized procedure described above are shown in Table I.

The manner in which the superoxide and peroxide values listed in Table I were obtained is shown by the following calculations for the first sample.

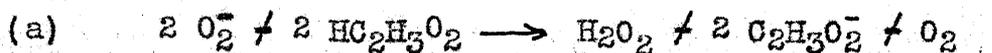
Complete analysis of the sample gave 66.5 cc. (STP) O_2 / g. liberated in the superoxide step, 134 cc. O_2 / g. liberated on total decomposition, 12.00 milliequivalents / g. of total base on titration, and 3.05 millimoles / g. of barium from gravimetric sulfate determination.

An examination of the equation for the superoxide decomposition step shows that half a mole of oxygen is released for each mole of superoxide decomposed.

Table I

Analysis of Products Formed by Reaction Between $\text{Ba}(\text{NO}_3)_2$ and KO_2 in Liquid Ammonia
 (Approximate Formula Weight Ratio of $\text{Ba}(\text{NO}_3)_2$ and KO_2 : 1 : 2)

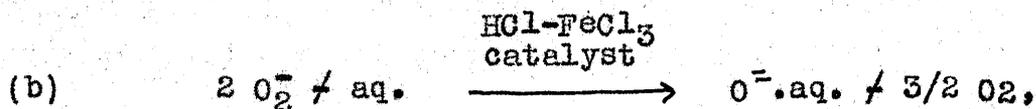
cc. (STP) superoxide $\text{O}_2 / \text{g.}$	cc. (STP) total decomp. $\text{O}_2 / \text{g.}$	Total base, m. e. / g.	Barium, m. e./g.	Ion Ratios				% product accounted for	5 2
				Ba	K	O_2^-	O_2^+		
66.5	134	12.00	6.10	1	1.93	1.95	1.00	94	
67.0	135	12.76	6.26	1	2.08	1.92	0.985	97	
69.3	139	11.90	6.08	1	1.92	2.03	1.02	95	
98.0	135	11.96	5.84	1	2.09	2.08	1.02	93	



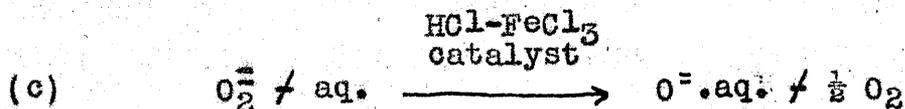
Thus, the number of moles of superoxide per gram of material is found by dividing 66.5 cc. by 11,200 cc.

$$\frac{66.5}{11,200} = 5.94 \times 10^{-3} \text{ mole } \text{O}_2^- / \text{g.}$$

On total decomposition the superoxide releases oxygen according to the equation:



whereas the peroxide is decomposed in the following manner:



Equations (a) and (b) show that two-thirds of the superoxide oxygen is released in the first step of the analysis. Thus, three-halves of the oxygen released in the first step will be liberated upon total decomposition of superoxide. The remaining oxygen released on total decomposition comes from peroxide originally present. Therefore, the peroxide content is obtained by the following calculation.

$134 - (3/2 \times 66.5) = 34.2 \text{ cc. } \text{O}_2 / \text{g.}$ from peroxide
Equation (c) shows that half a mole of oxygen is released for each mole of peroxide originally present, hence

$$\frac{34.2}{11,200} = 3.05 \times 10^{-3} \text{ mole } O_2^- / g.$$

The potassium present as oxide is calculated by difference between total base and barium content,

$$12.00 - (2 \times 3.05) = 5.90 \text{ m. e. K / g.}$$

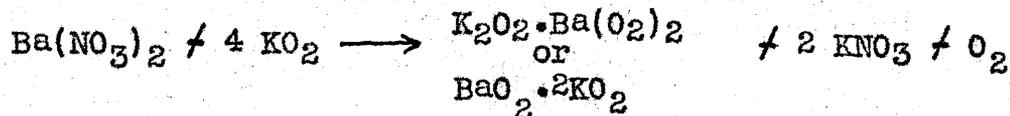
A tabulation of the quantities of each ion present in millimoles per gram of sample is shown below:

<u>Ba</u>	<u>K</u>	<u>O₂⁻</u>	<u>O₂⁻</u>
3.05	5.90	5.94	3.06

When put in ion ratio form, the tabulation becomes

<u>Ba</u>	<u>K</u>	<u>O₂⁻</u>	<u>O₂⁻</u>
1	1.93	1.95	1.00

The data of Table I show that the product formed may be represented by either the formula $BaO_2 \cdot 2K_2O_2$ or $K_2O_2 \cdot Ba(O_2)_2$. Our data do not permit a choice (if indeed there is one) of one formula in preference to the other. All that can be said is that a stable crystal lattice is obtained containing barium, potassium, superoxide, and peroxide ions in the ratios indicated above. These data suggest that the reaction occurring in liquid ammonia solution is the following:



The equation shown above indicates that the initial ratios of the reacting substances could be 1 to 4 without having an excess of potassium present. Such initial ratios were tested in two runs which showed that the same product was formed. The data obtained are shown in Table II. The yield of mixed oxide in each case was practically quantitative.

The formation of a mixed peroxide-superoxide is not new, since the so-called "sesquioxides" of cesium and rubidium (Cs_4O_6 and Rb_4O_6), have been shown to possess both superoxide and peroxide ions, and are correctly formulated as $\text{M}_2\text{O}_2 \cdot 2\text{MO}_2$ (28,29). The similarity between these "sesquioxides" and the new barium-potassium mixed peroxide-superoxide is apparent and becomes of more interest when the respective ion sizes in the latter are compared. According to Pauling (27), the ionic radius of barium (1.3-1.4 Å) is close to that of potassium (1.33 Å), while the anions involved have similar dimensions with 1.31 Å for the peroxide ion and 1.28 Å for the superoxide ion.

When the chocolate brown mixed peroxide-superoxide, protected from carbon dioxide in the air by means of a potassium hydroxide tube, was heated in a drying oven at 110°, it rapidly lost its brown color and in 12 hours was entirely grayish white. At the same time it changed from a paramagnetic to a diamagnetic substance.

Table II

Analysis of Products Formed by Reaction Between $\text{Ba}(\text{NO}_3)_2$ and KO_2 in Liquid Ammonia
 (Approximate Formula Weight Ratio of $\text{Ba}(\text{NO}_3)_2$ and KO_2 : 1 : 4)

cc. (STP) Superoxide $\text{O}_2 / \text{g.}$	cc. (STP) total decomp. $\text{O}_2 / \text{g.}$	Total base, m. e. / g.	Barium, m. e./g.	Ion Ratios				% product accounted for
				Ba	K	O_2^-	$\text{O}_2^{=}$	
64.0	127	11.10	5.74	1	1.88	1.99	0.97	88
64.3	127	11.28	5.70	1	1.96	2.02	1.01	89

Analysis of the gray-white powder showed that it contained only traces of superoxide ion and not enough peroxide ion to be formulated as a single compound. Data from three runs gave ion ratios of barium to peroxide of 1 to 0.64, 1 to 0.60, and 1 to 0.54, respectively. The material was not further decomposed even when heated at 110° for two weeks. Qualitatively, it can be stated that both superoxide and peroxide ions decomposed at 110° .

When the mixed peroxide-superoxide was washed with liquid ammonia, analysis showed that both barium and peroxide ions were washed from the product. The following data give the results of analysis of two samples which were washed six times with 75 cc. portions of liquid ammonia.

Table III

Composition of Product Resulting from
Washing with Liquid Ammonia
(Values expressed in millimoles per g.)

<u>Ba</u>	<u>K</u>	<u>O₂^{••}</u>	<u>O₂⁻</u>
2.67	7.98	7.90	1.81
2.31	7.81	7.02	2.35

The ratio of potassium to barium is more than the 2 to 1 ratio established for the composition of the brown mixed oxide. It is also seen that the peroxide-superoxide ratio has dropped correspondingly. It is evident, therefore, that barium peroxide is washed from the compound with excessive washings.

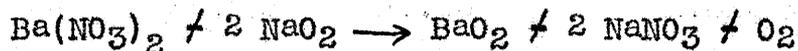
When barium nitrate and sodium superoxide (of 96% purity) react in the formula weight ratio of 1 to 2 in liquid ammonia, oxygen is evolved, the yellow color of the superoxide slowly disappears, and a heavy white product is formed. Analysis of the white product (Table IV) showed it to consist primarily of barium peroxide.

Table IV

Product of Reaction of $\text{Ba}(\text{NO}_3)_2$ and NaO_2

<u>Ba,</u> <u>millimoles</u> <u>/g.</u>	<u>Base (by titration),</u> <u>m. e. /g. sample</u>	<u>O_2</u> <u>millimoles</u> <u>/g.</u>	<u>%product</u> <u>accounted</u> <u>for</u>
5.44	10.83	5.33	91
5.64	11.25	5.74	95
5.44	10.90	5.00	90

The impurity in the product is apparently sodium nitrate. The reaction between barium nitrate and sodium superoxide in liquid ammonia is therefore formulated in the following manner:



The reaction of anhydrous strontium nitrate with potassium superoxide in the ratio 1 to 2 in liquid ammonia produces a substance which is light brown in color so long as it is wet with ammonia, but which becomes much lighter as the latter evaporates. The final product is a very light tan powder. Data from

analysis of the product gave the values shown below.

Table V

Product of Reaction of $\text{Sr}(\text{NO}_3)_2$ and KO_2

<u>Sr,</u> <u>millimoles</u> <u>/g.</u>	<u>Base (by titration),</u> <u>m. e. /g. sample</u>	<u>O_2^-</u> <u>millimoles</u> <u>/g.</u>	<u>% product</u> <u>accounted</u> <u>for</u>
7.70	15.35	7.46	91
7.73	15.50	7.60	92

An examination of the data indicates that the product is primarily strontium peroxide contaminated with potassium nitrate. The reaction, therefore, may be formulated as:



When strontium nitrate is treated with sodium superoxide in the ratio 1 to 2 in liquid ammonia, a reaction again occurs in which oxygen is given off, the yellow superoxide color fades, and a heavy white powder forms. After washing and drying, the product gives on analysis the following data.

Table VI

Product of Reaction of $\text{Sr}(\text{NO}_3)_2$ and NaO_2

<u>Sr,</u> <u>millimoles</u> <u>/g.</u>	<u>Base (titration),</u> <u>m. e. /g. sample</u>	<u>O_2^-</u> <u>millimoles</u> <u>/g.</u>	<u>% product</u> <u>accounted</u> <u>for</u>
8.13	16.3	7.28	95

Here the data indicate that strontium peroxide is the major product of reaction.

Because of time limitations, only qualitative observations have been made on the reaction with calcium. The difficulty in obtaining an anhydrous salt of calcium which is also soluble in liquid ammonia prevented an accurate study of the reaction. Calcium bromide was not sufficiently soluble in liquid ammonia, whereas calcium nitrate could not be made anhydrous. Calcium iodide possessing an indetermined water content gave a reaction with potassium superoxide in which oxygen was evolved and a white precipitate replaced the yellow superoxide. The white product when examined qualitatively contained both peroxide and calcium ions. No tendency for the formation of a brown product was exhibited.

Summary

Treatment of lithium peroxide and the monoxides and peroxides of the alkaline earth metals with oxygen at temperatures as high as 600° and 800° and pressures up to 265 atmospheres were used in an effort to obtain higher oxides. In no case was evidence for superoxide formation obtained.

The reaction between barium nitrate and potassium superoxide gave a chocolate brown product which on analysis was shown to contain barium, potassium, superoxide and peroxide ions in ratios corresponding to the empirical formula, $BaO_2 \cdot 2KO_2$ or $K_2O_2 \cdot Ba(O_2)_2$. Excessive washing of the chocolate brown mixed oxide with liquid ammonia removed barium and peroxide ions from the product. Heating at 110° in the absence of both carbon dioxide and moisture rapidly decomposed both peroxide and superoxide and yielded no definite compound. Barium nitrate and sodium superoxide reacted to give essentially barium peroxide.

Strontium nitrate and potassium superoxide reacted in liquid ammonia to give a light brown solution which decomposed when filtered and allowed to come to room temperature; the final product was a very light tan and gave an analysis corresponding to the formation of

strontium peroxide. Reaction of strontium nitrate with sodium superoxide gave strontium peroxide as the major product.

Qualitative experiments with calcium iodide containing some water of crystallization gave no evidence for the formation of a brown product.

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