

A STUDY OF THE REACTION BETWEEN SODIUM PEROXIDE  
AND OXYGEN: THE PREPARATION AND PROPERTIES  
OF SODIUM SUPEROXIDE

by

Stephen E. Stephanou

B.S., Massachusetts Institute of Technology, 1942  
M.S., University of Kansas, 1947

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Advisory Committee:

Jacob Kleinberg  
Chairman

William J. Argeruizen Jr

Ray L Brewster

L. N. Leonardella

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## INTRODUCTION

The preparation and use of the higher oxides of the alkali and alkaline earth metals have received considerable attention in the last decade. The use of higher oxides as a source of oxygen has stimulated research in the preparation and properties of these compounds.

The purpose of this investigation was three-fold: (1) to explore the possibility of preparing superoxides of the alkali and alkaline earth metals in a stainless steel bomb by reaction of oxygen with the metals or lower oxides at high temperature and pressure, (2) to study the properties of superoxides prepared by this method, and (3) to develop analytical methods for the determination of superoxides in mixtures of oxides.

In a previous report (1) from this laboratory evidence was presented for the existence of sodium superoxide. In the first experiments using the bomb attempts were made to burn sodium metal and study its reaction with oxygen. As the work progressed, however, it became apparent, for reasons which will be discussed later in this report, that the use of sodium

peroxide as starting material provided a better method of obtaining sodium superoxide. A few preliminary experiments have also been performed with oxides of lithium, calcium, magnesium and barium, but no evidence for superoxide formation has been obtained. Although the original program has only been partially fulfilled, the success of the work with sodium makes it desirable that similar studies be carried out with oxides of the alkaline earth metals.

In the section which follows the results of investigations which have been performed on the reaction of oxygen with alkali metals and their oxides are summarized. Since the complete program sponsored by the Navy includes the preparation of higher oxides of the alkaline earth metals, similar researches involving these compounds have also been reviewed.

## HISTORICAL REVIEW

The reaction of sodium peroxide with oxygen to give sodium superoxide has not been previously reported in the literature. Although other alkali metal superoxides can be obtained by combustion of the metal in an excess of oxygen (2, 3, 4, 6), the highest oxide of sodium that can be obtained by this method is the peroxide.

### The Combustion of Alkali Metals

The reaction of oxygen with alkali metals has been the subject of considerable research during the last hundred years. Prior to 1860 Gay Lussac and Thenard (2) studied the reactions of sodium and potassium metals with oxygen, and, in 1861, Harcourt (3) found that the highest product obtained by the combustion of potassium is  $K_2O_4$ ,\* but he could isolate no intermediate oxides. The work of Holt and Sims (4) in 1894 was outstanding in this field. They found that potassium and sodium metals may be

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\* X-ray diffraction studies and magnetic data have shown this compound to be  $KO_2$ .

distilled in dry air without oxidation occurring, and that potassium superoxide can be made by heating potassium in air or oxygen. By using limited quantities of oxygen they were able to obtain products with chemical compositions corresponding to  $K_2O_2$  and  $K_2O_3$ .  $K_2O_2$  when exposed to the air slowly deliquesced while  $K_2O_3$  was violently oxidized to  $K_2O_4$  with the evolution of sufficient heat to cause fusion of the oxide. Similar experiments with sodium yielded no oxide higher than sodium peroxide. The metal heated below its melting point in a sheet-iron boat in a stream of moderately dry oxygen was soon coated over with an oxide film of a composition corresponding to no definite oxide. When heated above its melting point, the metal caught fire and burned vigorously. In a limited supply of oxygen and at temperatures below  $180^\circ C$  the greyish white  $Na_2O$  was formed; using an excess of oxygen and higher temperatures the yellow-white sodium peroxide formed. Oxygen at atmospheric pressure was passed over sodium peroxide at  $300-350^\circ$  for 16 hours, but no evidence of oxygen absorption was found. Using nitrous oxide as the oxidizing agent, Holt and Sims obtained both  $K_2O_2$  and  $K_2O_3$  from potassium and only  $Na_2O$  from sodium.



The use of higher oxides of nitrogen gave a mixture of nitrites and nitrates. They also found that lithium metal, when heated to  $250^{\circ}$  C. in a stream of oxygen, burned to almost pure  $\text{Li}_2\text{O}$  with the formation of only traces of peroxide.

In 1907 Rengade (5) prepared the oxides  $\text{Cs}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  by introducing into a tube containing the pure alkali metal, slightly less than the required quantity of oxygen, and, after the oxygen had been absorbed, distilling off the excess metal. He found that rubidium absorbed oxygen at slightly lower temperatures than did either potassium or sodium. In a paper published a year later (6), he reported that the rate of oxidation of the alkali metals is largely dependent upon the presence of moisture and that cesium and rubidium are attacked by dry oxygen but potassium and sodium undergo no change at room temperature. By the oxidation of the metals in liquid ammonia solution Rengade obtained the oxides  $\text{Cs}_2\text{O}_2$ ,  $\text{Cs}_2\text{O}_3$ ,  $\text{Cs}_2\text{O}_4$ ,  $\text{Rb}_2\text{O}_2$  and  $\text{Rb}_2\text{O}_4$ . He submitted samples of his products to de Forcrand whose thermochemical studies on the heats of formation of the alkali and alkaline earth metal oxides (7, 8) are still used as standard references in this field.

Using the heats of formation of other alkali metal oxides as a guide, de Forcrand found the value of 130.0 K. cal. for the heat of the hypothetical reaction



His thermochemical data showed that the heat of formation of the monoxides decreases with increasing atomic weight of the alkali metal while the heat of complete "superoxidation" ( $\text{M}_2\text{O} \rightarrow \text{M}_2\text{O}_4$ ), as he called it, increases in the order named. He also estimated that the reaction  $\text{Na}_2\text{O}_2 + \text{O}_2 \rightarrow \text{Na}_2\text{O}_4$  evolves about 10.3 K. cal. at room temperature. On the basis of his data he predicted that  $\text{Na}_2\text{O}_3$  and  $\text{Na}_2\text{O}_4$  would be very unstable and would have temperatures of dissociation in the vicinity of  $200^\circ \text{C}$ . He further stated that these compounds could not be prepared by direct oxidation under conditions which would produce superoxides of the other alkali metals.

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

Closely related to the absorption of oxygen by metals and their oxides is the study of dissociation pressures of the higher oxides. The main bulk of the research in this field has been performed on normal

oxides and peroxides which do not have dissociation pressures exceeding two atmospheres at temperatures up to 1000° C. For such systems an all-glass apparatus and a glass mercury manometer may be employed. De Forerand (7), one of the earliest workers to make dissociation pressure measurements on alkali metal oxides, found that at 480° C. a pressure of oxygen of 155 mm. was sufficient to completely prevent the dissociation of  $K_2O_4$  ( $KO_2$ ), and that consequently  $KO_2$  can be prepared at 480° C. in a current of atmospheric air where the partial pressure of the oxygen is about 160 mm. Hildebrand (9), in his study of the thermal decomposition of  $BaO_2$  into  $BaO$  and  $O_2$ , showed the presence of two solid solutions, one of  $BaO$  dissolved in excess  $BaO_2$  and the other of  $BaO_2$  in excess  $BaO$ . He found that the dissociation was reversible, and that the role of  $H_2O$  in the process was extremely important. Hildebrand suggested that the presence of water caused the equilibrium reaction



to take place. Kraus and Whyte (10) investigated the dissociation of  $KO_2$  by weighing the material into glass tubes, evacuating and then heating the tubes to the melting point of the oxide. The oxygen evolved on

heating was removed by a Töpler pump and its volume determined. Kraus' experiments showed that the dissociation,  $2K_2O_2 \rightarrow K_2O + 3/2 O_2$ , was reversible and that the evolution of oxygen is greatly influenced by moisture. Kraus attempted to determine the dissociation pressure of  $KO_2$  at various temperatures, but found that, although the process is reversible, the pressures appear to depend upon the oxygen content of the solid phase. At  $300^\circ C$ . he obtained the equilibrium pressure of 0.2 mm. for the reaction  $K_2O_4 = K_2O_3 + 1/2 O_2$ . However, the data of Blumenthal (11) for potassium superoxide is in poor agreement with this value:

p (mm)	30	111	323	441	550
t ( $^\circ C$ )	198	279	461	540	589

Kasarnovskii and Raikhshtein (12) found for the same dissociation the following values:

p (mm)	0.35	1.45	1.65
t ( $^\circ C$ )	300	360	370

Kraus' value of 0.2 mm at  $300^\circ C$ . checks that of Kasarnovskii and Raikhshtein fairly closely, but the data of Blumenthal appear to be out of line.

Blumenthal also studied the dissociation of  $K_2O_3$  (11),  $K_2O_2$  (11),  $Li_2O_2$  (11),  $Na_2O_2$  (13), and  $CaO_2$  (14). Using Merck's  $Na_2O_2$  (probably about 93-96 %

pure) he obtained the dissociation pressure values:

p (mm)	9	26	69	154	259	385	546	671
t (°C)	468	557	591	609	621	633	642	646

He found that dissociation takes place above the melting point of sodium peroxide which he determined to be 460° C. From his data, using the Nernst equation, he calculated the heat of dissociation of Na<sub>2</sub>O<sub>2</sub> to be 37.7 K. cal. as compared with de Forcrand's calorimetric value of 38.2 K. cal. Attempts to prepare Na<sub>2</sub>O<sub>3</sub> by the oxidation of Na<sub>2</sub>O<sub>2</sub> at temperatures above 290° C. and atmospheric pressure failed.

The following dissociation pressures were obtained by Blumenthal for CaO<sub>2</sub> (14) for the reaction

$$2\text{CaO}_2 \rightarrow 2\text{CaO} + \text{O}_2:$$

p (mm)	163	348	562	731	750
t (°C)	68	81	93	97	102

The value of the heat of dissociation, 12.6 K. cal., calculated from these data by means of the Nernst equation is in good agreement with de Forcrand's thermochemical value of 10.8 K. cal. Blumenthal claims that the dissociation is reversible but the attainment of equilibrium is very slow and that the speed of dissociation is much greater than the speed of association.

For  $\text{Li}_2\text{O}_2$  Blumenthal (11) obtained the values:

p (mm)	5	12	47	66	122	189	271	497	790
t (°C)	43	54	87	93	116	127	148	181	198

Employing the Nernst equation the heat of dissociation is  $\Delta$  13.6 K. cal. as compared with the calorimetric value of  $\Delta$  15.9 K. cal.

The work of Kasarnovskii and Raikhshtein (12) shows that during the thermal decomposition of  $\text{KO}_2$  to  $\text{K}_2\text{O}_2$  there is no intermediate compound  $\text{K}_2\text{O}_3$  formed. They claim that  $\text{K}_2\text{O}_3$  described by many authors is not an individual compound but a mixture of superoxide and peroxide.

#### High Pressure Studies

The reaction of metals and their oxides with oxygen at high temperature and pressure seems to be a line of investigation which has not received much attention from previous workers.

Bergius (15) made peroxides of the alkaline earth metals by heating the corresponding monoxides in a current of air or oxygen. The monoxide was heated with  $\text{NaOH}$  or  $\text{KOH}$  until molten and then air or oxygen passed through the fused mass. After cooling the melt was treated with alcohol in order to dissolve

out the alkali, the peroxide remaining undissolved. Calcium peroxide was prepared by heating a mixture of CaO and alkali (NaOH / KOH) at 350° C. for several days in a steel bomb containing oxygen at about 12½ atmospheres pressure. Bergius then measured the pressure above the solution and found the following values:

p (atmospheres)	93	101	107	12½
t (°C)	200	250	300	350

This method for the determination of the dissociation pressure of calcium peroxide is not accurate due to the vapor pressure of the alkali. The heat of the reaction  $\text{CaO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CaO}_2$  was calculated to be 3.3 K. cal. which is in poor agreement with the value 10.8 K. cal. found by de Forcrand (8).

In 1912 Fischer and Floetze (16) constructed a furnace in which a temperature of 1000° C. could be attained under a pressure of 100 atmospheres. They were able to obtain a 15% yield of SrO<sub>2</sub> by the oxidation of the monoxide at 400° C. and 98 atmospheres pressure. Attempts to make CaO<sub>2</sub> from CaO in a similar manner failed. The hydroxides of potassium, rubidium, and cesium formed peroxides when heated in oxygen at pressures up to 100 atm., the amounts increasing from potassium to cesium. Under the same conditions the

hydroxides of lithium and sodium did not form peroxides.

The most outstanding and complete research on the reaction between alkaline earth oxides and oxygen at high pressure was carried out by Holtermann (17, 18) in 1939 and 1940. The monoxides of calcium, strontium and barium were subjected to oxygen pressures up to 300 atmospheres and temperatures as high as 600° C. The samples were contained in porcelain, aluminum or nickel crucibles in an autoclave of 100 cc. capacity. The inert character of CaO toward oxygen, already reported by Fischer and Ploetze (16), was verified by Holtermann. SrO<sub>2</sub> of 99.2 to 99.5% purity was prepared by the action of dry oxygen on SrO (free from Sr(OH)<sub>2</sub> and SrCO<sub>3</sub>) at 350-400° C. and 200-250 atmospheres pressure. Pure SrO<sub>2</sub> was also prepared by the dehydration of SrO<sub>2</sub>·8H<sub>2</sub>O under 150-200 atmospheres pressure at 50-100° C. or in vacuo at 0-5° C. The dissociation of SrO<sub>2</sub> was studied up to pressures of 250 atmospheres and the value of 22.0 K. cal. calculated for the heat of the reaction,  $\text{SrO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SrO}_2$ . Holtermann also studied the system BaO<sub>2</sub> - BaO - O<sub>2</sub> up to pressures of 220 atmospheres and temperatures of 520° C. No product higher than 86% BaO<sub>2</sub> was obtained.



## EXPERIMENTAL METHODS AND RESULTS

Experimental Procedure for High Pressure Studies

The <sup>b</sup> apparatus employed (Fig. 1) consisted of a stainless steel bomb A of about 150 ml. capacity, equipped with such an arrangement of needle valves that the system could be completely evacuated or filled with oxygen under pressure. The bomb tubing and accessories were obtained from the American Instrument Company, Inc., of Silver Spring, Maryland. The equipment was supplied as a hydrogenation apparatus, but was adapted for use with oxygen by the removal of all oil and grease with carbon tetrachloride and acetone and replacement of the valve packing with a special oil-free packing obtained from the Puritan Compressed Gas Corporation, Kansas City, Kansas. The seat of each needle valve was lubricated with a trace of mutton fat. A series of different gages varying in range between 0-5000 lb. per sq. in. could be fitted into the right valve of Fig. 1. The heating jacket B of the bomb was insulated with magnesia. An iron-constantan thermocouple H inserted in the wall of the bomb and connected to a Brown Electronik Recorder and Regulator C permits temperature control.

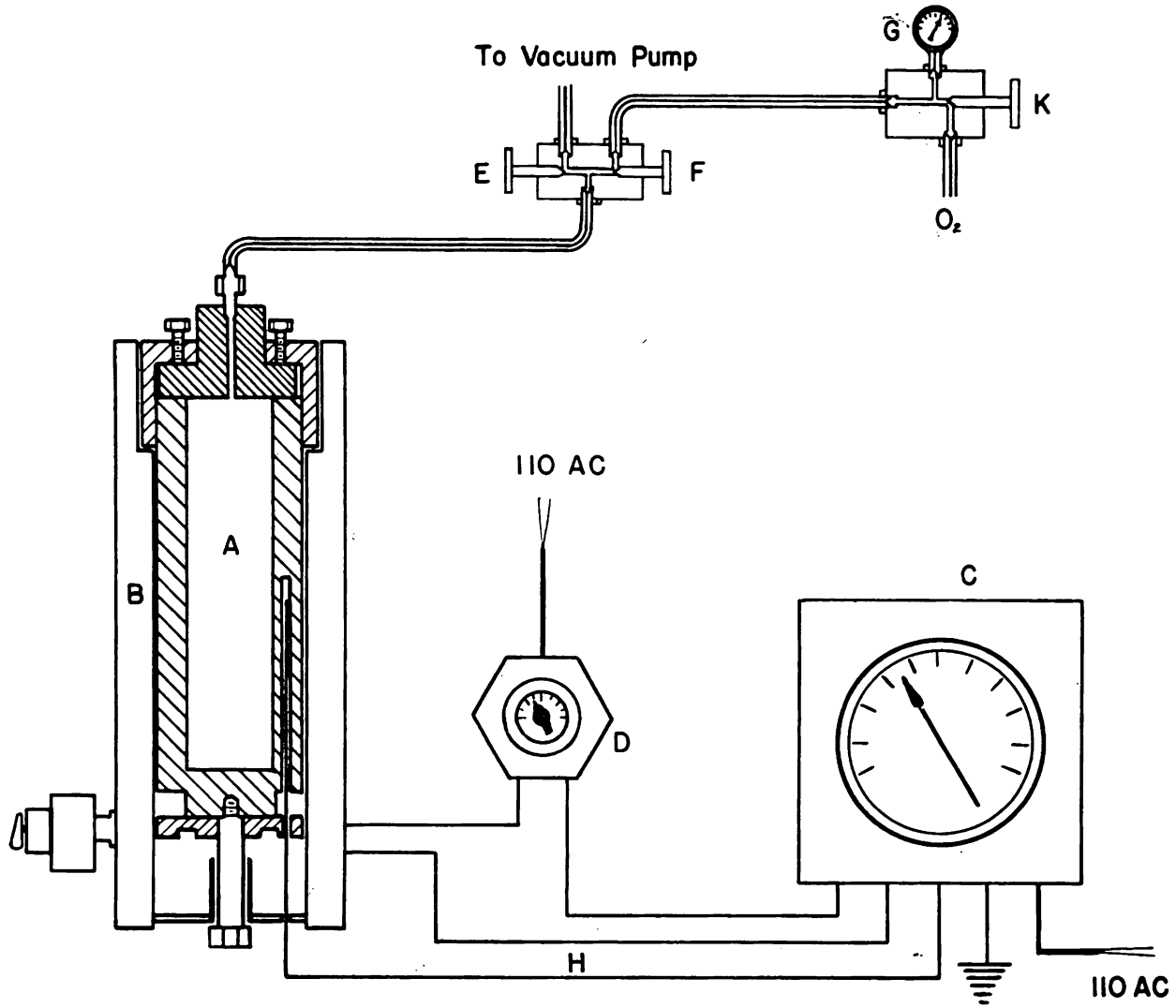


Fig. 1

The voltage across the heating elements of the bomb jacket B was adjusted by means of the Powerstat D.

A sample of the metal or oxide being studied was weighed out in a suitable container and the latter placed in a glass-stoppered Pyrex liner which fitted snugly into the bomb. The system was evacuated to 1-3 mm. for several hours; valve E was then closed and oxygen from a cylinder added slowly through valve F until the desired initial pressure was attained. Valve K was then closed and the bomb heated to the desired temperature. The absorption of oxygen at a particular temperature could be followed by reading the pressure gage G at frequent intervals. When a constant pressure reading was obtained, the bomb was cooled to room temperature and the oxygen bled slowly from the system through valve K, until the pressure was equal to that of the atmosphere. The bomb was then opened and the Pyrex liner containing the sample removed and placed in the dry-box where the product was transferred to an analysis cell. Because of the highly hygroscopic nature of both the starting materials and products, all transferring of samples from one vessel to another was carried out in a dry-box containing phosphorus pentoxide.

### The Combustion of Sodium Metal

Preliminary experiments in which sodium metal was burned in a glass apparatus at oxygen pressures up to 2 atmospheres showed that all the sodium did not react until the temperature was above its melting point. This observation is in agreement with those reported in the literature for the burning of sodium in air or oxygen at atmospheric pressure. Investigation of incompletely oxidized samples indicated that an oxide coating formed which prevented further oxidation. The nickel crucible employed in these initial experiments at comparatively low oxygen pressures was not attacked by the hot metal.

In the first experiment using the stainless steel bomb, about 0.9 g. of sodium, contained in a nickel crucible, was placed in the Pyrex liner. The liner was inserted in the bomb, the system evacuated and oxygen permitted to enter until the pressure was about 15 atmospheres absolute. The temperature of the bomb was gradually raised by 50° increments, starting at 100° C., but burning of the sodium did not take place until 300° C. Considerable oxygen appeared to have been absorbed in the process but subsequent examination of the solid residue in the

bomb showed that the nickel crucible had disintegrated completely due to oxidation. A similar experiment using 0.5 g. of sodium and a magnesium oxide ( $MgO$ ) crucible in the bomb at an initial oxygen pressure of 6.6 atmospheres and temperatures up to  $490^{\circ} C.$  gave a product analyzing 95% sodium peroxide according to potassium permanganate titration. The magnesium oxide was also attached but did not completely disintegrate as did the nickel crucible. The use of an alundum ( $Al_2O_3$ ) crucible showed that this material was also unsuitable for use in burning sodium in oxygen at high pressure. Of the various materials employed for containing the hot sodium, magnesium oxide appeared to be the most resistant to disintegration, although it, too, was attacked.

In the final experiment of this series the metal, contained in a magnesium oxide crucible, was burned in oxygen at a pressure of about 180 atmospheres and a temperature of  $300^{\circ} C.$  A bright yellow product was obtained which, on the basis of increase in weight alone, was apparently a mixture of about 38%  $Na_2O$  and 62%  $Na_2O_2$ , assuming only these two oxides to be present. However, the bottom of the magnesium oxide crucible was attacked to some extent and some of the oxygen may have been absorbed in this process.

The oxidized sodium fused solidly to the magnesium oxide crucible and analysis was almost impossible. A single quantitative test on a portion of the oxide condensed (or splattered) on the upper sides of the crucible yielded an analysis indicating that the sample was about 70% of the way to sodium superoxide,  $\text{NaO}_2$ . The analysis was accomplished by the liberation of the total available oxygen using an aqueous suspension of manganese dioxide as catalyst and titration of the residual solution with standard acid. The experimental results and calculations for this run are summarized below:

TABLE I

Experimental Data for the Burning of Sodium Metal in  
Oxygen at 300° C. and 180 atm. pressure.

A.

Weight sodium metal	1.638 g.
Moles sodium metal	0.0713
Moles O <sub>2</sub> absorbed (from increase in weight)	0.0491
Moles O <sub>2</sub> required for conversion, Na to NaO <sub>2</sub>	0.0357
Moles O <sub>2</sub> absorbed over Na <sub>2</sub> O <sub>2</sub>	0.0134
Moles O <sub>2</sub> required for conversion, Na <sub>2</sub> O <sub>2</sub> to NaO <sub>2</sub>	0.0357
Wt. % NaO <sub>2</sub> if MgO reaction ignored,	

$$\frac{0.0134}{0.0357} \times 100 = 38\%$$

B.

cc. O <sub>2</sub> at 23° C. evolved by sample	28.2
cc. O <sub>2</sub> evolved by sample, calculated to S.T.P.	24.6
Blank for catalyst solution	10.3
Corrected volume of O <sub>2</sub> at S.T.P.	14.3
cc. stand. HCl (.099-N) used	12.2
gram sodium calculated	0.0278
cc. O <sub>2</sub> per gram of sodium for sample	514
cc. O <sub>2</sub> per gram of sodium for pure NaO <sub>2</sub>	730
% of complete oxidation, Na to NaO <sub>2</sub>	70

From the above experiments it is evident that the main problem in the burning of sodium in oxygen at high pressures is that of finding a suitable material for the crucible. In view of the success of the sodium peroxide studies, to be described later, in preparing sodium superoxide, this line of investigation was discontinued. However, the last experiment did show that sodium superoxide could be prepared by combustion of sodium metal at high pressures of oxygen.

#### The Reaction of Sodium Peroxide with Oxygen

Although previous investigators (16, 17, 18) have studied the reaction between alkaline earth metal oxides and oxygen at elevated temperatures and pressures in attempts to prepare higher oxides, no similar experiments have been performed with sodium peroxide. Holt and Sims (4) passed oxygen at atmospheric pressure over sodium peroxide at 300-350° C. for 16 hours but obtained no evidence of oxygen absorption. In a previous report (1) from this laboratory, dealing with the rapid oxidation of sodium in liquid ammonia, evidence for the existence of sodium superoxide was described. In this phase of the investigation sodium peroxide was subjected to treatment with oxygen at



high pressures and temperatures in order to explore the possibility of preparing higher oxides by this method. Such treatment results in the formation of high yields of sodium superoxide.

A weighed sample of the sodium peroxide was placed inside a Pyrex container in the bomb and the system evacuated to 1-3 mm. for several hours; valve E was then closed and oxygen from a cylinder added slowly through valve F until the desired initial pressure was attained. Valve K was closed and the bomb heated to the desired temperature. The absorption of oxygen at a particular temperature could be followed by reading the pressure gage G at frequent intervals. When a constant pressure reading was obtained the bomb was cooled to room temperature, the product removed and analyzed. The analysis was accomplished by decomposition of the sample with a catalyst solution which was 2M with respect to hydrochloric acid and 1M in ferric chloride, using the gas volumetric method. From the corrected volume of oxygen evolved per gram of product, assuming only peroxide and superoxide to be present, the weight per cent of sodium superoxide could be calculated using the equation,

$$\left[ \frac{\text{cc. oxygen evolved / gram product} - 144}{162} \right] \times 100 = \% \text{ NaO}_2,$$

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

The starting material (du Pont Calorific Grade) analyzed as 99% sodium peroxide, calculated on the basis of the total oxygen evolved upon decomposition with the hydrochloric acid-ferric chloride solution mentioned above. The presence of carbonate was tested for by passage of the gas evolved through concentrated potassium hydroxide solution and noting any decrease in volume. The sodium peroxide used in these experiments proved to be carbonate free. To avoid decomposition due to exposure to atmospheric moisture both starting materials and products were handled in a dry-box containing phosphorus pentoxide.

Preliminary experiments using initial oxygen pressures at room temperature ranging from 2 to 32 atmospheres showed no measurable absorption of oxygen up to temperatures of approximately 250° C. Above this temperature the sodium peroxide had a tendency to react with the walls of the Pyrex container and

become decomposed. As the starting pressure was increased this reaction became negligible and studies at higher temperatures and pressures were made without any appreciable decomposition taking place. It was found that, as the pressure and the temperature were increased, the final product became more yellow, and, upon analysis, evolved more oxygen than did pure sodium peroxide. In order to make a systematic study of the conditions of temperature and pressure necessary for maximum reaction of oxygen with sodium peroxide a series of runs was made with an initial pressure of about 2000 lb. per sq. in. The selection of this pressure was dictated by the limitations of the apparatus. The results of this study are summarized in Table II. The time allowed for reaction was 100 hours. A study of the effect of time on the extent of reaction showed that at a temperature of 400° C. the quantity of oxygen absorbed after 100 hours was negligible. The results of this study are shown in Table III. Complete reaction would occur in a shorter length of time for temperatures above 400° C.

TABLE II

The Absorption of Oxygen by Sodium Peroxide

Na <sub>2</sub> O <sub>2</sub> g.	Temp. (°C) for 100 hours	Initial press. (atm.) at ele- vated temp.	cc. O <sub>2</sub> (S.T.P.) evolved per g. of product	Calculated % NaO <sub>2</sub> <sup>a</sup>
9.9	32	137	140	0
11.2	150	187	147	3
11.2	200	205	161	11
10.1	250	222	181	24
11.1	300	238	215	45
12.4	350	257	274	81
10.3	400	280	286	88
9.8	450	281 <sup>b</sup>	292	92
11.2	490 <sup>c</sup>	298	291	92

a Corrected for the 1% impurity present in the starting material.

b A small leak developed in the system in this run.

c The Pyrex liner was attacked by the oxide mixture causing the formation of a white residue at the interface of the glass and the oxide.

TABLE III

The Effect of Time on the Extent of Reaction Between  
Sodium Peroxide and Oxygen at 400° C. <sup>a</sup>

$\text{Na}_2\text{O}_2$ g.	Time (hrs.) at 400° C.	cc. $\text{O}_2$ (S.T.P.) evolved per g. of product	Calculated % $\text{NaO}_2$ <sup>b</sup>
15.0	1	198	36
12.0	5	242	60
10.5	50	281	85
10.4	100	286	88
11.0	259	291	89

<sup>a</sup> The initial oxygen pressure for each run was 2000 lb. per sq. in.

<sup>b</sup> Corrected for the 1% impurity present in the starting material.

### The Properties of Sodium Superoxide

With increasing oxygen absorption by the sodium peroxide in the bomb, at increasingly higher temperatures and pressures, the color of the final product changes from a faint yellow to a bright yellow and finally, at temperatures above  $350^{\circ}$ , becomes bright orange. If the reaction temperature is higher than  $300^{\circ}$  C., the final product has the appearance of a fused homogeneous mass which may readily be pulverized in a mortar. The powder thus obtained is uniformly yellow and highly hygroscopic. Upon exposure to atmospheric moisture it evolves oxygen and gradually loses its yellow color. Continued exposure to the atmosphere leaves a white residue which is a mixture of sodium peroxide and hydroxide. The yellow material reacts vigorously with water with the formation of oxygen and sodium peroxide in solution. The material appears to be stable indefinitely when stored in a desiccator over phosphorus pentoxide.

The addition to the yellow material of a 20 per cent (by volume) solution of glacial acetic acid in carbon tetrachloride causes the oxygen absorbed by the peroxide in the bomb to be released

almost quantitatively. (Data showing this are given in the section entitled "Analytical Methods" in this report.) The anhydrous carbon tetrachloride was used as an inert diluent for the acetic acid. Treatment of the residue with an excess of potassium iodide solution and titration of the iodine liberated with standard thiosulfate solution showed the presence of about 95 per cent of the original peroxide used. The reaction with water described above and the behavior towards glacial acetic acid is exactly that to be expected of a superoxide. Kraus and Parmenter (19) have shown that potassium superoxide decomposes in water in accordance with the equation



Acidification of a superoxide would be expected to give the unstable acid  $\text{HO}_2$  which would decompose to hydrogen peroxide and oxygen.

The chemical composition, physical appearance and reactions of the yellow material formed by reaction between sodium peroxide and oxygen leave no doubt that it contains large percentages of sodium superoxide,  $\text{NaO}_2$ . Moreover, magnetic studies (discussed below) show that the material is highly paramagnetic, the moment calculated for pure sodium

superoxide being in excellent agreement with literature values for potassium superoxide.

### Magnetic Studies

As shown in the preceding sections, the reaction between sodium peroxide and oxygen at elevated pressures and temperatures yields products containing as much as 92% sodium superoxide. Since superoxides exhibit a marked paramagnetism (20, 21, 22) owing to the presence of an unpaired electron in the ion  $\left[ \text{:}\ddot{\text{O}} \text{---}\ddot{\text{O}} \cdot \right]^{-1}$ , it was decided to study the magnetic properties of the new compound in order (1) to determine its effective magnetic moment, and (2) to investigate the possibility of employing magnetic measurements for the quantitative estimation of sodium superoxide in the presence of diamagnetic impurities.

The susceptibilities were measured with a Gouy magnetic balance equipped with an electromagnet of the type described by Shaw (23). The apparatus was calibrated with deaerated distilled water and air, for which the volume susceptibilities at room temperature were taken as  $-0.720 \times 10^{-6}$  and  $+0.029 \times 10^{-6}$ , respectively.\* All magnetic

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\* The details of the calibration and a sample calculation are given in Appendix I.



susceptibilities in this report are given in c.g.s. units. All measurements were made at room temperature using a maximum field strength of 6800 gauss. The cylindrical sample tubes employed had cross-sectional areas of 0.495 or 0.187 sq. cm., and, when filled to a fixed mark 8 cm. from the bottom, contained about  $5 \frac{1}{2}$ <sup>or 2</sup> g. of sample. The samples were prepared by subjecting sodium peroxide to high oxygen pressures at different temperatures according to the method already described. The fused product obtained from the reaction in the bomb was ground in an agate mortar in a dry-box and the powder transferred to the sample tube. After an average of several magnetic readings was obtained, the total oxygen evolved (cc. at S.T.P.) per gram of material in the tube was determined by the gas volumetric method as previously described. The gram susceptibilities, calculated from the Gouy change in weight and the known field strength, were corrected to 20° C., assuming the validity of Curie's Law,  $\chi_M = \frac{C}{T}$ , where  $\chi_M$  is the molar susceptibility, C is the Curie constant and T the absolute temperature.\* The values thus obtained were plotted against the

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\* The equations and method of calculation used in obtaining the gram susceptibility of a sample are described in detail in Appendix II.

per cent sodium superoxide as calculated from the total oxygen evolved upon decomposition with hydrochloric acid-ferric chloride catalyst solution. It is estimated that the magnetic measurements are accurate to  $\pm 3\%$  and the chemical analyses (from the total oxygen evolved) to  $\pm 1\%$ . Part of the error in the susceptibility measurements is due to non-uniform packing of the powder in the sample tube.

The magnetic data obtained are summarized in Tables IV and V. The data of Table IV were plotted to obtain the calibration curve shown in Figure II. It is evident from the values of the gram susceptibilities shown in the tables that the reaction between oxygen and sodium peroxide at high temperatures and pressures yields a highly paramagnetic product. Furthermore, the gram susceptibility of this product increases linearly with the quantity of oxygen absorbed (indicated in Fig. II by an increasing calculated weight % of sodium superoxide). Extrapolation of the straight line in Fig. II to a quantity of oxygen absorbed corresponding to 100% conversion to sodium superoxide gives for the gram susceptibility of this substance a value of  $\pm 33.0 \times 10^{-6}$ . The "effective magnetic moment,"  $\mu$ , for pure sodium superoxide was calculated from the well-known relation,

$\mu = 2.83 \sqrt{\chi_M T}$ , where T is the absolute temperature and  $\chi_M$  the molar susceptibility. The value obtained, 2.07 molar Bohr magnetons, is in excellent agreement with the moments of other superoxides (20, 21, 22) reported in the literature.

The fact that the plot of gram susceptibility vs. weight of sodium superoxide is linear indicates that Wiedemann's mixture law (24) is being followed. In this case, the law assumes the familiar form,  $\chi = \chi_1 p_1 + \chi_2 p_2$ , where  $\chi$  is the susceptibility of the mixture,  $\chi_1$  and  $\chi_2$  the susceptibilities of sodium peroxide\* and sodium superoxide respectively, and  $p_1$  and  $p_2$  the respective weight fractions of the two compounds. The linearity is of significance in two respects: (1) it indicates that when sodium peroxide reacts with oxygen at high temperatures and pressures, the formation of an oxide intermediate between the peroxide and superoxide is quite unlikely; and (2) since the contribution of diamagnetic substances is small compared to that of the superoxide, it permits the use of magnetic measurements for the rapid determination of sodium superoxide in the presence of diamagnetic impurities.

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\* The sodium peroxide used in these experiments was found to be diamagnetic, having a gram susceptibility of  $-0.23 \times 10^{-6}$ .

TABLE IV

Magnetic Susceptibilities of Na<sub>2</sub>O<sub>2</sub> - NaO<sub>2</sub> Mixtures  
Used in Plotting Calibration Curve (Fig. II)

<u>cc. O<sub>2</sub> evolved per g. product</u>	<u>% NaO<sub>2</sub> (chemical)<sup>a</sup></u>	<u>g. susceptibility x 10<sup>6</sup> at 20° C.</u>
142	0	- 0.23
161 <sup>b</sup>	11	3.75
199	37°	12.5
224 <sup>b</sup>	50	16.9
225	53°	17.4
249	66	21.4
254	69	22.5
261	73	23.2
282	86	27.7
286	88	29.5
288	90	29.2

Note: The first four magnetic results shown in this table were obtained using a sample cell of 0.495 sq. cm. cross-sectional area. The other magnetic values were obtained using a smaller cell of 0.187 sq. cm. cross-sectional area.

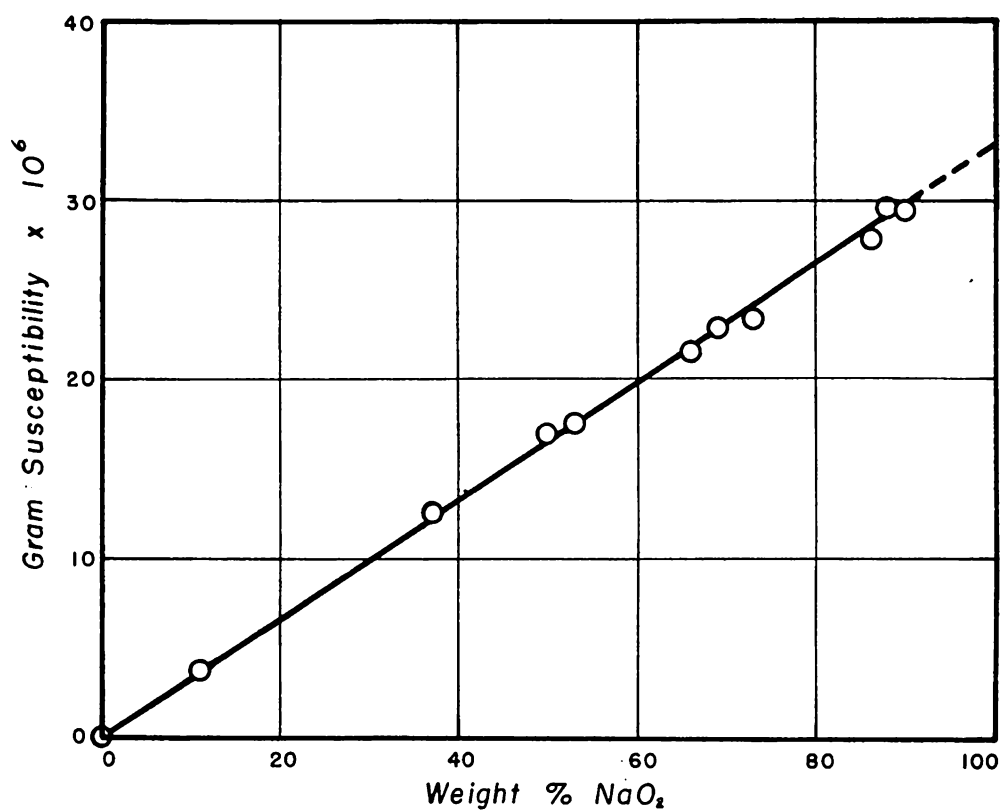


Fig. 1—Magnetic Susceptibilities of  $\text{Na}_2\text{O}_2$ - $\text{NaO}_2$  Mixtures

TABLE V

## A Comparison of Magnetic with Chemical Analyses

cc. O <sub>2</sub> evolved per g. product	$\epsilon$ , susc. $\times 10^6$ at 20°C.	% NaO <sub>2</sub> (magnetic) <sup>d</sup>	% NaO <sub>2</sub> (chemical) <sup>a</sup>	Difference in %	% Deviation
161 <sup>b</sup>	$\pm$ 3.75*	12	11	$\pm$ 1	9
161 <sup>b</sup>	$\pm$ 4.66	15	13 <sup>c</sup>	$\pm$ 2	15
202 <sup>b</sup>	$\pm$ 10.4	32	36	- 4	11
199	$\pm$ 12.5*	33	37 <sup>c</sup>	$\pm$ 4	3
224 <sup>b</sup>	$\pm$ 16.9*	52	50	$\pm$ 2	4
225	$\pm$ 17.4	53	53 <sup>c</sup>	0	0
237	$\pm$ 19.2	58	60 <sup>c</sup>	- 2	3
249	$\pm$ 21.4	65	66	- 1	2
254	$\pm$ 22.5	68	69	- 1	1
261	$\pm$ 23.2	71	73	- 2	3

\* These magnetic measurements were obtained using a sample cell of 0.495 sq. cm. cross-sectional area. The other magnetic values were obtained using a smaller cell of 0.157 sq. cm. cross-sectional area.

TABLE V (Continued)

cc. O <sub>2</sub> evolved per g. product	$\epsilon$ , msc. $\times 10^5$ at 20°C.	% NaO <sub>2</sub> (magnetic) <sup>d</sup>	% NaO <sub>2</sub> (chemical) <sup>a</sup>	Difference in %	% Deviation
282	27.7	84	86	-2	2
286	29.5	89	88	+1	1
288	28.8	87	90	-3	3
286	29.2	89	90	-1	1
292	29.1	88	92	-4	4

Notes on Tables IV and V

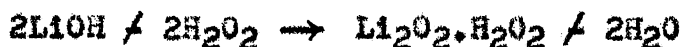
- a The weight per cent sodium superoxide was corrected for the 1% impurity present in the starting material according to the method described in Appendix IV.
- b These samples were synthetic mixtures made by grinding sodium peroxide with product from the bomb.
- c The weight per cent sodium superoxide was corrected for the 3% impurity present in the starting material according to the method described in Appendix IV.
- d The weight per cent sodium superoxide was calculated from the magnetic data by means of Wiedemann's mixture law (24). The method of calculation is discussed in detail in Appendix III.



The data of Table V show a comparison of the magnetic with the chemical analyses. The per cent sodium superoxide was calculated from the gram susceptibility of the sample by means of the Wiedemann law, using the value of  $33.0 \times 10^{-6}$  (obtained by extrapolation from the plot of Figure II) for the susceptibility of pure sodium superoxide.

#### Lithium Peroxide Studies

Lithium peroxide was prepared by the reaction of 30% hydrogen peroxide solution on lithium hydroxide monohydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ), according to the equation,



According to de Forcrand (25) the precipitate obtained has the formula,  $\text{LiO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ . The product was filtered from the mother liquor and dried over phosphorus pentoxide in a vacuum desiccator for two months before being used in the bomb. During the drying period samples were removed and analyzed for peroxide content. A final product containing 96% lithium peroxide was used for the bomb studies.

In the first experiment a sample (12.0 grams) of lithium peroxide was placed in a Pyrex liner in the bomb and treated with oxygen at various temperatures and pressures. The moles ( $n$ ) of oxygen

present at any time were calculated from the temperature and pressure of the bomb by means of a modification of the ideal gas law equation,

$$n = \frac{PV_B [1 + \alpha(T_B - T_B^0)]}{RT} + \frac{PV_G}{RT_G},$$

where  $P$  is the measured pressure (in absolute atmospheres);  $V_B^0$  the volume of the bomb at the calibration temperature  $T_B^0$  (21° C.);  $\alpha$  is a correction factor which includes the expansion of the bomb with temperature as well as the temperature gradient in the connection between the bomb and the left valve (see Figure 1);  $V_G$  is the volume of the gage;  $T_B$  is the temperature of the bomb;  $R$  is the gas constant expressed in cc-atm. per degree Kelvin. (More detailed information concerning this equation is given in Appendix V.) Gage readings taken at frequent intervals at each temperature and pressure shown in Table VI (Experiment 1) gave no evidence of oxygen absorption.

A second experiment was carried out with 4.9 grams of lithium peroxide starting at an initial oxygen pressure of 153 atm. at room temperature. The temperature was raised by 50° increments, starting at 100° C., but no oxygen absorption was observed up to temperatures of 250° C. and pressures of 254 atm.

The temperatures and pressures at which observations were made in this study are also shown in Table VI (Experiment 2).

TABLE VI

Conditions of Temperature and Pressure at which Lithium Peroxide does not Absorb Oxygen

	<u>Temp., °C.</u>	<u>Pressure (atm.)</u>
Experiment 1	22	27
	100	33
	22	3.0
	100	3.6
	150	3.9
	200	4.3
	250	4.7
Experiment 2	29	154
	100	189
	150	214
	200	234
	250	255

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Studies with Oxides of the Alkaline Earth Metals

Barium Peroxide. Merck's anhydrous barium peroxide (minimum assay claimed, 85% barium peroxide) was analyzed by decomposition with hydrochloric acid-ferric chloride solution by the gas volumetric method and was found to contain only 57% barium peroxide on the basis of the total oxygen evolved. A sample (11.0 grams) of the material was treated with oxygen in the bomb at a temperature of 450° C. and a pressure of 314 atm. for 30 hours. The bomb was cooled to room temperature, the oxygen bled off, the product removed and analyzed again. The results of the analyses before and after treatment with oxygen were as follows:

	<u>cc. O<sub>2</sub> evolved (at S.T.P.) per gram material</u>
Before treatment with oxygen	38 (average of 3 results)
After treatment with oxygen	<u>28</u> (average of 2 results)
Loss	10 cc/gram

The product from the bomb was a fused homogeneous dark gray mass which could be readily pulverized in an agate mortar.

Calcium Peroxide. Calcium peroxide (furnished by the du Pont Company, Wilmington, Delaware, with a

minimum assay, 75% calcium peroxide) was analyzed by decomposition with hydrochloric acid-ferric chloride solution by the gas volumetric method and was found to contain only 19% calcium peroxide on the basis of the total oxygen evolved. A sample (11.8 grams) of the material was treated with oxygen in the bomb at a temperature of 450° C. and a pressure of 291-220 atm. for 48 hours. The pressure decreased from 291 to 220 atmospheres during the heating because of a leak in the apparatus. Since the final product appeared wet with moisture and had not changed in color at all, it was concluded that the starting material must have contained moisture and it was very unlikely that calcium superoxide could be formed under these conditions. Commercial peroxides (except barium and strontium peroxides) are usually prepared in the "wet" way, therefore the starting material in this experiment was probably the common octahydrate,  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ . Another sample of calcium peroxide (minimum assay claimed, 60% calcium peroxide), received from the Buffalo Electro-Chemical Company, Buffalo, New York, was also treated with oxygen in the bomb. The material used in this experiment was first dried for 6 hours at 55° C. in a vacuum oven and cooled in a desiccator over phosphorus pentoxide

overnight. It was then treated with oxygen at a temperature of  $400^{\circ}$  C. and a pressure of 320 atm. for 20 hours. Analyses of the final product yielded the value of 35 cc.  $O_2$  (at S.T.P.) evolved per gram of material, which corresponds to 23% calcium peroxide. The product did not appear to have undergone any physical change due to the oxygen treatment except that the slightly tan shade of the starting material had completely disappeared.

Calcium Oxide and Magnesium Oxide. In order to verify the work of Fischer and Floetze (16) and Holtermann (18) the monoxides of calcium and magnesium (Baker's C. P. material) were first ignited overnight at  $450^{\circ}$  C. and atmospheric pressure and then treated with oxygen at temperatures of  $450-480^{\circ}$  C. and pressures from 288-221 atm. for 40 hours. The pressure decreased from 288 to 221 atm. during the heating because of a leak in the apparatus. The products obtained were perfectly white as before with no apparent physical change from their original powdered state. Treatment of the residues with hydrochloric acid-ferric chloride solution gave no evolution of gas which indicated that neither superoxide nor peroxide was formed.

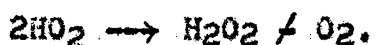
### Analytical Methods

The method of decomposition with acid catalyst solution used for the determination of superoxide in this investigation was particularly suitable because the starting material for the sodium peroxide-oxygen studies was 99% pure and contained no carbonate. Since sodium peroxide and superoxide were the only substances present capable of evolving a gas and since the per cent of impurity in the starting material (before treatment with oxygen) was known, it was comparatively simple to calculate the weight per cent of sodium superoxide present in the product from the bomb. However, in other cases, especially in the oxidation of metals directly or in liquid ammonia solution, superoxide and peroxide may be present along with such impurities as monoxide, hydroxide, amide, nitrite and carbonate. For such mixtures a direct method for the determination of peroxide and superoxide is needed. The so-called two-step method of analysis developed by Kraus (19) is supposed to fill this need, but it, too, appears to be unsatisfactory. In the two-step procedure, the mixture of oxides is added to ice-cold water, the oxygen evolved from the superoxide is measured, and

the resulting peroxide solution is catalytically decomposed to give a second volume of oxygen. From these data 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.

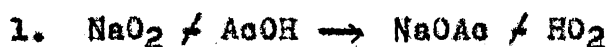
Although the theory of the method is sound, in practice it is impossible to add the mixed oxide sample to water without obtaining some decomposition of peroxide because of local heating.

In the present investigation an attempt was made to develop a method for the direct determination of peroxide and superoxide in a mixture of oxides. The method is based upon the fact that when acid is added to a superoxide the unstable acid  $\text{HO}_2$  is formed, which decomposes according to the equation



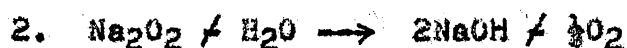
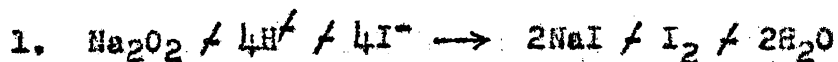
Measurement of the volume of oxygen liberated should give a direct value for superoxide oxygen. This is borne out by the data of Table VII which shows that peroxide, under similar treatment, decomposes only to the extent of 2%. The equations involved in the method are given below:

First step





## Second step



The details of the procedure are as follows:

1. About 5 cc. of dry carbon tetrachloride (dried over anhydrous sodium sulfate) are added to a mixed oxide sample of about 0.10 to 0.20 grams. This volume of carbon tetrachloride need not be exact but it must be added carefully to avoid splattering of the sample on the sides of the cell. The analysis cell used in these experiments consisted of a cylindrical, flat-bottomed, Pyrex glass tube (1 7/16 in. outside diameter) equipped with a 29/42 ground-glass joint. The overall length of the cell was about 6 in. and it was connected by capillary glass tubing to a gas buret. The apparatus was the same as that used in the total oxygen determination by the gas volumetric method.

2. The cell is then cooled in an ice bath (at 0° C.) and buret readings taken until equilibrium is attained in the closed system.

3. Exactly 10 cc. of acetic acid solution (20% by volume, in carbon tetrachloride) are added from a 10 cc. pipet to the reservoir above the cell and allowed to pass into the cell slowly with stirring. (A magnetic stirrer is required.) After all the acid

has been added the stirring is continued and buret readings taken every 5 minutes until a fairly constant reading (within 0.2 cc.) is obtained. Depending upon the quantity of superoxide present, this may take anywhere from 5 to 30 minutes. The yellow color due to superoxide should have disappeared completely when the final buret reading is taken.

4. Exactly 10 cc. of acidic potassium iodide solution\* are then added, with stirring, and the stirring continued until a constant buret reading is obtained as in step 3. The cell must be shaken vigorously several times by hand in this step in order to obtain complete reaction of the peroxide residue with the potassium iodide solution. There must be no solid present in the 2-phase mixture when the final buret reading is taken.

5. After washing down with distilled water or preferably carbon tetrachloride the iodine solution which may have been shaken on to the upper portions of the cell, the analysis cell is removed from the gas buret system and the iodine liberated by the peroxide titrated with standard sodium thiosulfate solution.

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\* Made just before use by mixing 5 cc. of 5% by volume acetic acid solution in carbon tetrachloride with 5 cc. of 20% KI solution (aqueous).

The per cent sodium superoxide is calculated from the difference in buret readings of steps 2 and 3. The volume thus obtained is corrected to S.T.P. and the blank for the acetic acid solution subtracted. The per cent sodium peroxide is calculated from the cc. of standard sodium thiosulfate used in step 5 and the oxygen evolved by the decomposition of some of the peroxide during its reaction with the potassium iodide. This second volume of oxygen is obtained from the difference in buret readings of steps 3 and 4, corrected to S.T.P. with the reagent blank subtracted. Results obtained by this method are shown in Table VII. For comparison, the per cent sodium superoxide calculated from the total oxygen evolved upon decomposition with acid catalyst solution is given in the last column of the table.

It is evident from the results shown in Table VII that the per cent sodium superoxide obtained using the acetic acid method checks fairly closely with that obtained by total oxygen analysis. In every case, however, the calculated percentage of sodium peroxide is low. In view of the fact that the samples of sodium peroxide (97% pure by the total oxygen method and carbonate free) analyzed also gave low results by about the same amount, it appears that

TABLE VII

The Analysis of Mixed Oxide Samples Using the Acetic Acid-Carbon Tetrachloride Method

<u>Weight Sample, g.</u>	<u>cc. O<sub>2</sub> (at S.T.P.) evolved by AcOH</u>	<u>cc. O<sub>2</sub> (at S.T.P.) evolved by KI</u>	<u>cc. thio. soln. (.0973 N)</u>	<u>% Na<sub>2</sub>O<sub>2</sub></u>	<u>% NaO<sub>2</sub></u>	<u>% NaO<sub>2</sub> from Total oxygen evolved</u>
0.124	2.9	0.8	24.7	72	12	13
0.191	4.6	1.2	37.7	71	12	13
0.134	16.6	1.1	23.3	29	61	60
0.127	15.2	1.9	21.7	34	59	69
0.131	17.7	1.1	21.4	21	67	70
0.117	20.4	0.9	17.4	2	85	86
* 0.123	0.7	1.1	24.8	87	—	—
* 0.302	0.9	1.6	64.0	86	—	—

\* The material used in these analyses was sodium peroxide, carbonate free, analyzing 97% pure on the basis of the total oxygen evolved upon decomposition with acid catalyst solution.

all the peroxide cannot be quantitatively determined by this method. It is significant that the per cent sodium peroxide is low by an average of 10% in the case of samples of mixed oxides and also 10% low for 97% sodium peroxide samples. Furthermore, the quantity of oxygen liberated from the pure peroxide samples by the acetic acid corresponds to the decomposition of only 2% sodium peroxide, which would indicate that the superoxide determination could possibly give results which check the total oxygen method to within  $\pm 2\%$ . Apparently the chief loss of peroxide (about 8%) occurs in the second step of the method, namely, the addition of the potassium iodide and the titration of the liberated iodine with sodium thiosulfate solution. The second step, even with measurement of the oxygen evolved due to decomposition of a small portion of the peroxide during its reaction with the potassium iodide, does not quantitatively determine all the peroxide.

#### X-ray Diffraction Studies

In order to obtain information concerning the crystal structure of sodium superoxides, samples of sodium peroxide treated with oxygen at high temperature and pressure were sent (in very fine capillary tubes)

to Dr. Leo Brewer of the University of California for X-ray diffraction studies. Information obtained from these studies about the crystal lattices present and their similarity to those of other superoxides would be of considerable interest and importance in the study of the new compound, sodium superoxide. Samples containing 12, 70, 80 and 90 per cents sodium superoxide have been sent, each in duplicate. Preliminary experiments show the presence of two phases, one of which disappears upon exposure to the atmosphere. Also a crystal lattice similar to, but not identical with, that of potassium superoxide appears to be present. The results are not yet conclusive, however, and the work is still in progress at the University of California.

## SUGGESTIONS FOR FUTURE RESEARCH

The attempts to make lithium superoxide, the only alkali metal superoxide which has not yet been prepared, have so far been unsuccessful. More lithium peroxide should be prepared according to the method of de Forcrand (25) or any other method which will give the pure peroxide, and the dry carbonate-free material treated with oxygen at higher temperatures and pressures than those employed in this investigation.

In regard to the preparation of the superoxides of the alkaline earth metals, the experiments starting with peroxides and monoxides and treating with oxygen at high pressures should be continued at a series of different temperatures up to the limit of the apparatus. In view of the success of the work with sodium peroxide, it would seem desirable to start with the pure alkaline earth metal peroxides, if these can be obtained. If this procedure fails, it would be advisable to attempt burning the alkaline earth metals in oxygen at high temperature and pressure. The oxidation of the alkaline earth metals liberates less heat than does the combustion of the alkali metals. The container problem should therefore be less difficult

to solve. Stainless steel crucibles were not tried in the work with sodium and might be suitable for burning the metals.

Magnetic studies should be made on mixtures of potassium superoxide with diamagnetic material in order to provide a calibration curve which could be used for samples containing this superoxide.



## SUMMARY

1. The reaction between sodium metal and oxygen at elevated temperatures and pressures results in the formation of a bright yellow product which contains sodium superoxide.
2. The reaction between sodium peroxide and oxygen at elevated temperatures and pressures also gives sodium superoxide. Yields as high as 92% sodium superoxide have been obtained.
3. Some of the more important properties of sodium superoxide have been studied. Experiments have been performed which show that sodium superoxide resembles other known superoxides in its chemical, physical and magnetic properties.
4. Magnetic measurements on the products of reaction between sodium peroxide and oxygen show a linear relationship when gram susceptibility is plotted against weight per cent of sodium superoxide. Extrapolation to 100% sodium superoxides gives an effective magnetic moment of 2.07 Bohr magnetons for this compound. This value is in excellent agreement with those reported in the literature for other superoxides.

5. The determination of sodium superoxide in the presence of diamagnetic impurities may be effected with reasonable accuracy by means of the magnetic method.

6. Treatment of lithium peroxide with oxygen up to temperatures of  $250^{\circ}$  C. and pressures of 255 atmospheres does not yield any higher oxide.

7. No higher oxides are formed when calcium and magnesium oxides are treated with oxygen at temperatures of  $450-480^{\circ}$  C. and pressures of 221-288 atmospheres.

8. Treatment of impure calcium peroxide with oxygen at a temperature of  $400^{\circ}$  C. and a pressure of 320 atmospheres does not result in the formation of a higher oxide.

9. No higher oxide is formed when impure barium peroxide is treated with oxygen at a temperature of  $450^{\circ}$  C. and a pressure of 314 atmospheres.

## APPENDIX I

Calibration of the Gouy Magnetic Balance

The Gouy balance used in the magnetic measurements was calibrated with freshly boiled, distilled water, the volume susceptibility of which was taken as  $-0.720 \times 10^{-6}$  at room temperature. The empty cell was first weighed on the magnetic balance with and without current through the electromagnet. Similar weighings were made with the cell filled to a fixed mark with water. From these data and the volume susceptibility of air,  $+0.029 \times 10^{-6}$ , the field strength  $H$  of the magnetic field was calculated. A sample calculation for the cell with a cross-sectional area of 0.495 sq. cm. is given below:

Cell empty

current off	15.4594 g.	Temp. 23° C.
current on	15.4553	Current 4.03 amps.
(change in weight) $W_1$	-0.0041	

$$W_1 \text{ at } 4.50 \text{ amps.} = -0.0041 \times \frac{(4.50)^2}{(4.03)^2} = -0.0051 \text{ g.}$$

Cell with water

current off	19.4182	Temp. 23° C.
current on	19.4034	Current 4.61 amps.
$W_2$	-0.0148	

$$W_2 \text{ at } 4.50 \text{ amps.} = -0.0148 \times \frac{(4.50)^2}{(4.61)^2} = -0.0141$$

Calculation of Field Strength H

$$* H^2 = \frac{(2000)(W_2 - W_1)}{(\text{area})(1.019)(K_w - K_a)}$$

In the equation above the area in the denominator refers to the cross-sectional area of the cell; the factor 1.019 converts milligrams to dynes;  $(K_w - K_a)$  represents the difference between the volume susceptibility of air and water and is equal to  $-0.749 \times 10^{-6}$ .

$$H^2 = \frac{(2000)(-0.0141 - 0.0051)}{(0.495)(1.019)(-0.749 \times 10^{-6})}$$

$$= 47.7 \times 10^6$$

$$H = 6900 \text{ gauss}$$

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\* See reference (26) in bibliography.

## APPENDIX II

Calculation of Gram Susceptibility

The gram susceptibility of a sample can be calculated from the Gouy change in weight  $W_3$  for the sample and the calibration data. The Gouy change in weight is obtained by weighing the cell, filled to a fixed mark with powdered sample, with and without current passing through the electromagnet just as in the calibration. The data and calculations for a sample containing sodium superoxide are given below:

current on	21.0487 g.	Temp. 22° C.
current off	20.9135	Current 3.60 amps.
$W_3$	0.1352	

$$W_3 \text{ at } 4.50 \text{ amps.} = 0.1352 \times \frac{(4.50)^2}{(3.60)^2} = 0.2110 \text{ g.}$$

Weight cell + sample	20.1935 g.
Weight cell alone	15.4594
Weight sample	5.4541

$$X_g(\text{gram susc.}) \text{ at } 22^\circ \text{ C.} = \frac{(2000)(W_3 - W_1)}{H^2(\text{area})(1.019)(\text{apparent density})}$$

$$= \frac{(0.0832)(w_3 - w_1)(\text{vol. of cell})}{(\text{weight of sample})} \times 10^{-6}$$

$$= \frac{(0.0832)(0.2110 - 0.0051)(3.86)}{(5.45)} \times 10^{-6}$$

$$= 12.4 \times 10^{-6}$$

$$\chi_g \text{ at } 20^\circ \text{ C.} = 12.4 \times 10^{-6} \times \frac{295}{293} = 12.5 \times 10^{-6}$$

## APPENDIX III

Calculation of Per Cent Sodium Superoxide From  
Magnetic Susceptibility

The weight per cent of sodium superoxide can be calculated from the Wiedemann Mixture Law using the value of  $+33.0 \times 10^{-6}$  for the gram susceptibility of pure sodium superoxide and  $-0.23 \times 10^{-6}$  for that of pure sodium peroxide. In this case, the law assumes the familiar form,  $\chi = \chi_1 p_1 + \chi_2 p_2$  where  $\chi$  is the gram susceptibility of the mixture,  $\chi_1$  and  $\chi_2$  the gram susceptibilities of sodium peroxide and superoxide respectively, and  $p_1$  and  $p_2$  the respective weight fractions of the two compounds. A sample calculation using the gram susceptibility at  $20^\circ \text{C}$ . obtained in Appendix II, is shown below:

$$\chi = \chi_1 P_1 + \chi_2 P_2 \qquad P_1 = 1 - P_2$$

$$\chi = \chi_1 (1 - P_2) + \chi_2 P_2$$

$$\chi = \chi_1 + P_2 (\chi_2 - \chi_1)$$

$$P_2 = \frac{\chi - \chi_1}{\chi_2 - \chi_1}$$

$$= \frac{\chi + 0.23}{33.2} = \frac{12.5 + 0.2}{33.2}$$

$$\% \text{NaO}_2 = \frac{12.7}{33.2} \times 100 = 38\%$$

## APPENDIX IV

Calculation of Per Cent Sodium Superoxide From  
the Total Oxygen Evolved

In the preparation of sodium superoxide the peroxide is treated with oxygen at high temperature and pressure and the per cent sodium superoxide calculated from the total oxygen evolved by the sample upon decomposition with hydrochloric acid-ferric chloride solution. If no impurities are present in the starting peroxide the equation,

$$\left[ \frac{\text{cc. oxygen evolved/gram product} - 144}{162} \right] \times 100 = \% \text{NaO}_2$$

is satisfactory. The numerator of the bracketed term represents the cc. of oxygen evolved per gram beyond that required for pure sodium peroxide and the denominator the difference in cc. of oxygen evolved per gram between pure sodium superoxide and sodium peroxide. In most cases, however, the starting material is not 100% pure and per cent impurity must be corrected for in calculating the per cent sodium superoxide in the final product. Commercial sodium peroxide is sold in varying degrees of purity ranging up to 99%. The samples of sodium peroxide (du Pont Calorific Grade) used in these experiments analyzed



97-99% pure by the total oxygen method.\* The following empirical equation was employed for the calculation of the per cent sodium superoxide, taking into account the impurities present:

$$\frac{100(\text{cc. O}_2/\text{g. product}) - 144(100 - \% \text{ impurity})}{162} = \% \text{NaO}_2$$

The per cent impurity of fairly pure peroxide can be determined by total oxygen analysis. If carbonate is present, it can be determined by passage of the gas evolved through concentrated potassium hydroxide solution and noting any decrease in volume.

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\* No carbonate was found to be present in this material.

## APPENDIX V

Calibration of the Stainless Steel Bomb

In some of the experiments performed with the stainless steel bomb during this investigation the absorption of oxygen by a given weight of sample was followed quantitatively from temperature and pressure readings. In order to accomplish this it was necessary to calibrate the apparatus. The volume of the bomb and connections to the gage were found using the apparatus illustrated in Figure 3. The system was connected to the calibrating apparatus through stop-cock B, pressure was applied by raising the leveling bulb and the decrease in volume measured by means of a gas buret. From the increase in pressure as measured by the constant level manometer and the volume of gas added, as read from the buret, the volume of the system could be calculated. The mols (n) of oxygen present at any time were calculated from the temperature and pressure of the bomb by means of a modification of the ideal gas law equation,

$$n = \frac{PV_B [1 + \alpha (T_B - T_B^0)]}{RT} + \frac{PV_G}{RT_G}$$

where P is the measured pressure (in absolute atmospheres);

$\underline{V}_B^0$  the volume of the bomb at the calibration temperature  $\underline{T}_B^0$  ( $21^\circ \text{C.}$ );  $\underline{\alpha}$  is a correction factor which includes the expansion of the bomb with temperature as well as the temperature gradient in the connection between the bomb and the left valve (see Figure I);  $\underline{V}_G$  is the volume of the gas;  $\underline{T}_B$  is the temperature of the bomb;  $\underline{R}$  is the gas constant expressed in cc.-atm. per degree Kelvin. Values of  $\underline{\alpha}$  were obtained by taking a number of temperature and pressure readings, substituting in the above equation, and solving for  $\underline{\alpha}$ . The average value of  $\underline{\alpha}$  was calculated to be  $4.1 \times 10^{-4}$ .

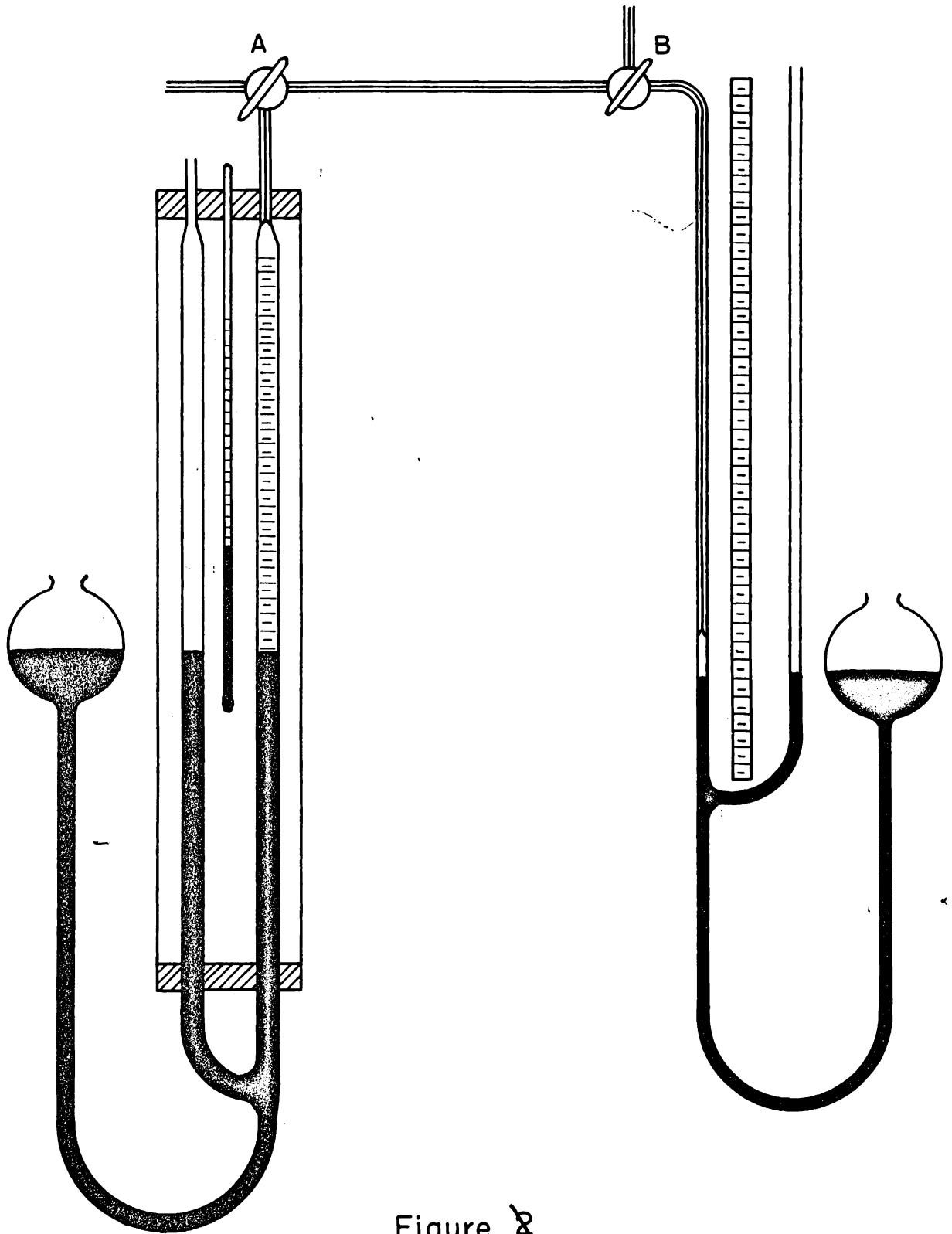


Figure 2  
3

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