1952

The preparation of the superoxides of the alkaline earth metals

Donald Joseph Baumann
Iowa State College

Recommended Citation

Baumann, Donald Joseph, "The preparation of the superoxides of the alkaline earth metals " (1952). *Retrospective Theses and Dissertations*. 13203.
https://lib.dr.iastate.edu/rtd/13203

THE PREPARATION OF THE SUPEROXIDES OF THE ALKALINE EARTH METALS

by

Donald Joseph Baumann

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1952

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

I. INTRODUCTION

The superoxides are a group of oxygen compounds which have come into some prominence in recent years and have been the subject of considerable investigation. They are not a new class of compounds. Potassium superoxide, formerly called potassium tetroxide, was first described almost a century ago.

The alkali and the alkaline earth metals are the only elements which have been reported to form superoxides. Of the alkali metals, the superoxides of potassium, rubidium, and cesium have long been known although only recently so named. The methods of preparation, the physical and chemical properties, as well as many of the thermodynamic properties of these compounds have been reported. More recently, several methods of preparation and the principal physical properties of sodium superoxide have been established. The superoxide of the remaining alkali metal, lithium, has never been reported. The literature on the alkaline earth superoxides is very sparse. There have been reports of the formation of oxides of these metals which contained more oxygen than could be accounted for by either the formation of the normal oxide or of the well known peroxide. The interpretation of the composition of these compounds or mixtures has been of a conflicting nature.

This investigation was undertaken to determine if the alkaline earth metals formed superoxides by the action of hydrogen peroxide on different alkaline earth metal compounds, and the effect of the concentration of the hydrogen peroxide in the reactions.

II. REVIEW OF LITERATURE

A. Structure of the Superoxides

Potassium superoxide, originally called potassium tetroxide with the assigned formula K_2O_4, was first described by Harcourt (9) in 1861. At that time, he described fully the method of preparation as well as the physical and chemical properties of this yellow to orange oxide of potassium. In the years which followed, other of the alkali metals were reported to form similar oxides. The alkali metal oxides of the general formula M_2O_4 were assigned the name tetroxides as it was believed that they were ionic compounds containing the O_4^{-2} anion analogous to the S_4^{-2} anion in the tetrasulfides.

The postulation of the 3-electron bond by Pauling (27) later led him to suggest to Neuman (24) an investigation of the structure of the so-called potassium tetroxide. Pauling believed that the compound might contain the O_2^{-1} anion having a 3-electron bond. He also held that such a compound, containing the O_2^{-1} ion, would be colored and paramagnetic, while the compound, if containing the O_4^{-2} ion, would be colorless and diamagnetic if analogous to the tetrasulfides. The yellow to orange color of the so-called potassium tetroxide was well known. Neuman (24) determined the magnetic susceptibility of the compound and found it to be paramagnetic. The substance showed a magnetic moment of approximately 2.04 Bohr magnetrons at room temperature. The spin dipole moment of one unpaired electron is equal to 1.73 Bohr magnetrons according to Pauling (28). From this data, Pauling's belief of the existence of an unpaired electron in the anion of this oxide of potassium was supported. Neuman (24) suggested, at the recommendation of W. C. Bray and E. D. Eastman of the University of California, that the oxides containing this anion be called superoxides since the general formula for the previously named alkali metal tetroxides actually was MO_2 and contained the superoxide ion (O_2^{-1}). The superoxide ion was considered to occupy a position intermediate to that of the oxygen molecule and the peroxide ion.

There was still considerable controversy regarding the correct formula and name for these compounds. Klemm and Sodomann (19) investigated three preparations of an oxide of potassium prepared in the manner given by Harcourt (9). The magnetic susceptibilities of the preparations were measured at different temperatures. They reported that their data did not give sufficient evidence to support the assignment of KO_2 as the formula for the highest oxide of potassium. They indicated the name tetroxide should be retained. In

1936, Kasatochkin (14), and in 1937, Kasatochkin and Kotov (15), by x-ray investigation of potassium oxides, confirmed the existence of the superoxide ion (O_2^{-1}). Powder photographs of KO_2 established that it possessed a tetragonal face-centered lattice of the calcium carbide type. The superoxide ion occupied the carbide position in the oxide. The structure was analogous to the alkaline earth metal peroxides. The oxygen to oxygen distance in the superoxide ion was determined by these authors as 1.28 ± 0.07 Å, which, according to Pauling (28), was in good agreement with the value expected for an electron pair bond plus a 3-electron bond between two oxygen atoms.

In 1939, the tetragonal structure was confirmed for RbO_2 and CsO_2 by Helms and Klemm (10). These men suggested the use of the name dioxide for these compounds rather than superoxide. In the same year, Helms and Klemm (11) reported the result of an investigation on the so-called sesquioxides of rubidium and cesium by x-ray diffraction and magnetic susceptibility measurements. No potassium analog of these compounds could be prepared. The composition of the sesquioxides was found to be consistent with the formulae Rb_4O_6 and Cs_4O_6, but the physical measurements indicated that the sesquioxides were mixtures of the peroxide and the superoxide corresponding to a proportion of 1 O_2-2 to 2 O_2 . Both the superoxide and the peroxide had a face-centered tetragonal crystal lattice.

A review was given in 1940 by Kazarnovskii (16) on the use of physical measurements and physical calculations in the investigation of the structure of the oxides of the alkali metals.

In 1948, Schechter, Sisler, and Kleinberg (36) reported evidence of the formation of sodium superoxide. Two years later, Templeton and Dauben (45) reported the result of structure studies of sodium superoxide as well as the other alkali metal superoxides. These investigators used samples of varying composition of superoxide and peroxide of sodium prepared by Kleinberg and co-workers. They reported that the structures of KO_2, RbO_2, and CsO_2 were face-centered tetragonal lattices of metal ions interpenetrated by a similar face-centered lattice of superoxide ions which formed a distorted sodium chloride structure. The superoxide ion in the three cases was oriented with the oxygen-oxygen axis parallel with the tetragonal "c" crystallographic axis. Consequently, "c" was somewhat larger than "a" giving the tetragonal structure for the three superoxides KO_2, RbO_2, and CsO_2. However, powder diffraction patterns of the mixtures of sodium peroxide and sodium superoxide, showed a face-centered cubic phase, the relative intensity of which corresponded to the degree of yellow color of the samples. The more yellow the color of the sample, the greater was the intensity of the cubic phase and the higher the concentration of the superoxide. They stated that the symmetry of the cubic system required that the superoxide ion have a disordered orientation in sodium superoxide. This, they reported, was reasonable because for the larger potassium, rubidium, and cesium cations in the superoxide crystals, the dumb-bell shaped anion had more room; therefore, the coulombic cation attraction would be more dominant and would consequently orient in the direction of the nearest cations. In the cubic structure of sodium superoxide, the attraction of sodium ions would be uniform in all directions. They reported the unit cell dimensions for the alkali metal superoxides as shown in the following table.

Table 1

Cell Dimensions of Alkali Metal Superoxides[a]

Axis	NaO_2	KO_2	RbO_2	CsO_2
"a"	5.49 Å	5.71 Å	6.01 Å	6.29 Å
"b"	--	6.76 Å	7.04 Å	7.28 Å

[a] Table adapted from Templeton and Dauben, J. Am. Chem. Soc., 72, 2251 (1950).

These authors reported that the oxygen-oxygen distance in the superoxide ion was in the range of 1.33 ± 0.06 Å. They pointed out that if the superoxide ion was considered to have a single bond and a 3-electron bond in the Pauling sense, then the bond distance of the superoxide ion might be expected to be intermediate between that of the oxygen molecule with a single bond and two 3-electron bonds, and that of the peroxide ion with a normal single bond. These distances were given as 1.2076 Å and 1.47 ± 0.02 Å respectively, of which the mean was 1.34 Å. This, they pointed out, was in excellent agreement with their experimentally determined value of 1.33 ± 0.06 Å.

There have been no structure studies reported on alkaline earth metal superoxides.

B. Preparation of the Superoxides

Five general methods have been established as methods for the preparation of superoxides or methods which result in the formation of superoxides.

1. The action of air or oxygen on the metal, hydroxide, or peroxide

Harcourt (9) described in detail the preparation of KO_2 which he carried out by passing air over the freshly distilled metal at a temperature of 100° C. Holt and Sims (12) studied the action of oxygen on freshly distilled lithium, sodium, and potassium and reported that only the latter metal gave the superoxide. In both of the above reports, this oxide of potassium was referred to as the tetroxide. Neuman (24) used this method of preparation of KO_2 in his structure studies previously described. De Forcrand (5) reported that the yellow peroxide, Na_2O_2, was the highest oxide of sodium obtained when heating the metal in air or oxygen. Rengade (32, 33) reported the preparation of the oxides since named superoxides, of rubidium and cesium by heating the metals in oxygen. Fischer and Ploetzer (8) reported the preparation of the superoxides of potassium, rubidium, and cesium by the action of oxygen on the respective metal hydroxide using pressures up to 100 atmospheres and temperatures ranging from 375° C. to 570° C. Yields of superoxide ranged from 70% to 90% by this procedure.

Kleinberg (18) stated that apparently the most important factor with regard to the formation of superoxides by the burning of metals seemed to be the size of the cation. Lithium gave the monoxide as the highest oxide, sodium the peroxide, while potassium, rubidium, and cesium gave high yields of the superoxide by this method.

In a United States patent of 1947, a method of preparing potassium superoxide or of sodium peroxide was described by Miller (23). The heated metal vapor was passed through a heated chamber with excess air or oxygen. The product was described as being precipitated by means of a Cottrell precipitator.

None of the superoxides of the alkaline earth metals have been reported prepared by the action of air or oxygen on the metal or metal hydroxide. However, a German patent issued in 1943 to Stepanck (42), covered a method of preparing a higher oxide of calcium by heating calcium peroxide in an atmosphere of oxygen from 500° C. to 2000° C. under 2 to 100 atmospheres pressure for at least 100 hours. The reaction was described as being carried out in the presence of a complex salt, $(CaK)_2Pt_2(CN)_{10}$, as a catalyst. The product, which was not described in any detail and to which no definite formulation was made, was to be used as a rust inhibitor.

In 1949, Stephanou and co-workers (43) succeeded in preparing sodium superoxide by treating samples of sodium peroxide with oxygen at temperatures ranging up to 500° C. and at pressures up to 300 atmospheres. They reported that there was no appreciable absorption of oxygen by the peroxide at pressures below 32 atmospheres and at temperatures of less than 250° C. As pressure and temperature were increased, the final product became more yellow and finally bright orange as the ratio of superoxide to peroxide increased. A high yield of 92% sodium superoxide was attained at a pressure of 298 atmospheres and a temperature of 490° C. The time allowed for the reaction was 100 hours. In a seminar given at Iowa State College in 1951, devoted to a discussion of the superoxides of the alkali metals, Kleinberg indicated that the time factor could be reduced to 6 hours in these preparations without loss of percentage yield. This was accomplished by the simple expediency of not using the cover on the pyrex liner which contained the peroxide sample and which fit into the stainless steel bomb of the high pressure apparatus used in these preparations.

2. The action of oxygen on solutions of the metal in liquid ammonia

From a survey of the literature on the superoxides, it was apparent that the most common method which had been employed in the preparation of the alkali metal superoxides had been the oxidation of the respective metal dissolved in liquid ammonia. Joannis (13) and Rengade (31) were the first investigators to utilize this procedure. Kraus and Whyte (21) reported in detail the preparation of the oxides of sodium and potassium by oxidation of the metal in liquid ammonia by a controlled stream of oxygen.

Kraus and Parmenter (20) published an improved method for oxidation of potassium in liquid ammonia and stated that the following oxides were characterized at different stages during the oxidation process: K_2O; K_2O_2; K_2O_3; and K_2O_4 (actually KO_2). These authors were the first to describe the formation of the sesquioxide, K_2O_3, which they considered to be the chocolate-brown material formed in the liquid ammonia solution of the metal intermediate to the formation of the light cream colored K_2O_2 and the light yellow colored K_2O_4. Raikhshtein and Kazarnovskii (29, 30), at later dates, reported evidence from thermal data which indicated that the sesquioxide of potassium was not a chemical compound, but that it was simply a mixture of the peroxide and the superoxide. Helms and Klemm (10), as well as Klemm and Sodomann (19), used this same method of preparation in their structure studies of the so-called alkali tetroxides.

Joannis (13), as well as Kraus and Whyte (21), reported that considerable hydroxide and nitrite were formed when slow oxidation of the metals in liquid ammonia was carried out. Joannis (13) reported that when sodium metal was dissolved in liquid ammonia and oxidized slowly at -50° C. by a stream of oxygen, the ammonated monoxide, $Na_2O \cdot NH_3$, was formed; this compound was then converted to the sesquioxide upon further oxidation. Schechter, Thompson, and Kleinberg (37) believed that the interpretation of the data by Joannis was in error as the formation of the sesquioxide was postulated by this early investigator on the basis of his determined value of the percentage of sodium in the oxidation product. The percentage oxygen was determined only by difference. It was pointed out by Schechter and co-workers (37) that a mixture of three parts sodium hydroxide to one part sodium nitrite gave very nearly the same percentage of sodium as that calculated for the sodium content of the sesquioxide, Na_2O_3. Kleinberg (18) explained the formation of hydroxide and nitrite during the slow oxidation of the metal in liquid ammonia as possibly taking place in the following manner:

$$2\ Na + O_2 = Na_2O_2 \qquad (1)$$

$$Na_2O_2 + 2\ Na = 2\ Na_2O \qquad (2)$$

$$2\ Na_2O + 2NH_3 = 2\ NaOH + 2\ NaNH_2 \qquad (3)$$

$$2\ NaNH_2 + 3/2\ O_2 = NaOH + NaNO_2 + NH_3 \qquad (4)$$

It was Kleinberg's experience that even with rapid oxidation of sodium in liquid ammonia, the superoxide produced was badly contaminated with the hydroxide and nitrite when the temperature at which the oxidation took place was higher than -50° C.

Schechter and co-workers (36, 37) were able, however, to prepare sodium superoxide with reproducible results by oxidation of the metal in liquid ammonia only when they took special precautions to avoid amide formation. This was accomplished by the slow addition of a solution of the metal in liquid ammonia to another portion of ammonia through which oxygen was rapidly passed. They reported a constant composition product regardless of the temperature used (within the liquid ammonia range) by this procedure. They stated that there would be amide formation and subsequent nitrite formed even at -77° C. if the blue color of the metal persisted for even a short time in the ammonia solution through which the oxygen was being passed. Unless precautions were taken to avoid amide formation, neither the gain in weight of the metal nor the volume of oxygen liberated upon decomposition of the product would constitute a reliable criterion for assigning a definite formula to the product. By this modified method, Schechter and co-workers (36, 37) were able to prepare with reproducible results, a yellow oxide of sodium which had an empirical formula, $NaO_{1.67}$. This substance, they showed, constituted a mixture of one part sodium peroxide to four parts sodium superoxide.

In a similar manner, Thompson and Kleinberg (46) more recently attempted the oxidation of lithium and the alkaline earth metals, calcium, strontium, and barium. They reported the results of the attempted oxidation by both the older method of passing oxygen directly through the solution of the metal in liquid ammonia, and the modified method of passing oxygen through liquid ammonia into which was slowly passed a solution of the metal in liquid ammonia. All the alkaline earth metals yielded mixtures of monoxide and peroxide. No higher oxide was found in the products. The solution of lithium in liquid ammonia, however, became lemon yellow in color during the oxidation when carried out at -78° C. Although no lithium superoxide could be isolated from this solution, absorption spectra of this oxidized solution indicated that lithium formed a soluble superoxide in liquid ammonia at the indicated temperature.

3. The action of ozonized air or oxygen on the dry hydroxide or on the metal in liquid ammonia

Investigations have been reported on the treatment of alkali and alkaline earth metals or of their compounds with ozonized air or oxygen. Baeyer and Villiger (2) observed that the action of ozonized air on dry caustic potash caused the dry hydroxide to become tinted with a cinnamon-orange color. Upon addition of water to this substance, the color disappeared and oxygen was evolved. They considered the orange substance to be potassium ozonate, a salt of the hypothetical ozonic acid, H_2O_4. In 1935, Weiss (51) indicated that potassium ozonate was identical to potassium superoxide. Bach (1) arrived at the conclusion that the orange substance obtained by the treatment of the hydroxide by ozonized air was the acid salt of ozonic acid, KHO_4. Traube (47, 48) established that the product of the reaction of ozonized air with caustic potash represented a mixture of unreacted KOH with an orange colored substance which had the composition $KOH \cdot O_2$ or $(KOH)_2 \cdot O_2$. Manchot and Kampschulte (22) showed that the alkaline earth metal hydroxides also gave a yellow to orange colored product when treated with ozonized air. They reported that $Ba(OH)_2$ decomposed ozone rapidly at room temperature giving a strongly yellow colored product. $Ca(OH)_2$ reacted slightly with the ozone while $Mg(OH)_2$ did not react at all. They also reported that the presence of water prevented reaction of the hydroxide with ozone.

In 1920, Strecker and Thienemann (44) reported the result of an investigation on the action of ozonized air on solutions of the alkali and the alkaline earth metals in liquid ammonia. In the case of the alkali metals dissolved in liquid ammonia, they reported that a white gelatinous mass, which they considered to be the hydroxide, was first formed upon passing ozonized air through the solution; upon further addition of ozone, this white precipitate dissolved, and a deep orange colored liquid and an orange colored precipitate formed. The ease of formation and stability of this orange colored product increased in the order of increasing atomic weight of the alkali metals. They reported that calcium and barium metals dissolved in liquid ammonia gave a sepia brown precipitate when ozonized air was passed through the solutions. This sepia brown colored precipitate decomposed rapidly upon evaporation of the ammonia. The unstable products were postulated by these investigators as being the ozonides of the alkaline earth metals.

In 1949, Kazarnovskii and co-workers (17) reported the result of an investigation which was initiated in an attempt to isolate the orange colored compound formed by the action of ozone on the alkali metals in liquid ammonia. They wished to isolate these products if possible, and to establish, definitely, their true composition and structure. The procedure used in this work was modified from that of previous investigators. Working under as anhydrous conditions as possible, they passed 6% to 8% ozonized oxygen over finely powdered potassium hydroxide. The resultant colored product was then extracted with liquid ammonia, and after separation from insoluble material, the ammonia was allowed to evaporate. Reddish-brown needles crystallized from the ammonia extract as the ammonia evaporated. The composition of this reddish-brown product varied slightly with each of eight preparations that were carried out. Analysis of this product showed that it was not primarily a superoxide but a higher oxide to which these authors assigned the name "ozonide" and which they believed represented a new class of oxides with the general formula $M^n(O_3)_n$. A typical analysis of one of their preparations was as follows: KO_3 -- 93.3%; KO_2 -- 1.3%; KOH -- 4.0%; the remaining 1.4% was believed to be principally $KOH \cdot H_2O$. Magnetic data gave a magnetic moment of 1.67 Bohr magnetrons for the substance KO_3 which indicated a resonance hybrid structure for the ozonide ion involving a 3-electron bond similar to that of the superoxide ion.

In 1951, Whaley and Kleinberg (52) described the repetition of the work of Kazarnovskii and confirmation of his results in the preparation of potassium ozonide, KO_3. These investigators found also, that CsOH which had been finely powdered and treated with a stream of ozonized oxygen, gave upon extraction with liquid ammonia and subsequent evaporation of the solvent, a red solid -- the composition of which could most reasonably be assigned as CsO_3 from the analytical data. They reported also that the corresponding sodium compound was apparently not soluble in liquid ammonia, but analysis of the crude product formed by treatment of the dry hydroxide with ozonized oxygen indicated the presence of a similar oxide. These colored, paramagnetic compounds, decomposed violently with water with the evolution of oxygen and liberation of energy in the form of light. The aqueous solutions of these oxides did not give a positive peroxide test with glacial acetic acid as do the superoxides. Whaley and Kleinberg (52) used the term ozonate for these oxides in keeping with the older concept that they were salts of ozonic acid but agreed with Kazarnovskii that this was a misnomer and that they would be more properly called ozonides.

4. The action of hydrogen peroxide or peroxide solutions on metallic hydroxides or other salts

The use of hydrogen peroxide in the preparation of peroxides of the alkaline earth metals dates back to Thenard in 1817. Conroy (4) repeated Thenard's experiments in the preparation of strontium peroxide octahydrate by combining an aqueous solution of sodium peroxide of his own preparation with a soluble strontium salt. Schone (38, 39) and De Forcrand (6) reported the preparation of various hydrates of the alkaline earth peroxides by the action of hydrogen peroxide on the hydroxides of the metals. The two investigators differed, however, in their interpretation of the formulae of the hydrates formed under similar conditions. Riesenfeldt and Nottebohm (34, 35) carried out an investigation of the action of hydrogen peroxide on solutions of hydroxides or other salts of the alkaline earth metals. They investigated chiefly, the effect of temperature on the nature of the product formed in these reactions rather than the effect of concentration of the peroxide. It was found that the octahydrate of each of the alkaline earth metal peroxides was formed when dilute solutions of hydrogen peroxide reacted with solutions of alkaline earth metal hydroxides or other soluble salts at room temperature. By modifying the procedure slightly, that is, by the addition of ammonium hydroxide to a chilled solution of a barium salt to which hydrogen peroxide was added, the diperoxyhydrate of barium peroxide, $BaO_2 \cdot 2H_2O_2$, was obtained. Above 30° C., under otherwise the same conditions, the monoperoxyhydrate, $BaO_2 \cdot H_2O_2$, was reported formed. They reported that both of these latter preparations were essentially white crystals with a trace of yellow in the products.

Traube and Schulze (49) were the first investigators to report, definitely, the formation of a higher oxide of the alkaline earth metals with this reagent. They reported that 30% hydrogen peroxide with calcium peroxide octahydrate at 100° C. gave a yellow colored product which reacted with acids to form a peroxide solution and about 2.7% gaseous oxygen. This they considered to be evidence of the existence of an addition compound, $CaO_2 \cdot O_2$, in the yellow preparation. A similar barium compound or mixture was reported formed by the same reaction. They referred to this small per cent of the higher oxide as a tetroxide of calcium and barium but seemed to believe that it was an addition compound of peroxide with molecular oxygen. In 1944, Ehrlich (7) reported the preparation of calcium tetroxide, CaO_4, by the action of hydrogen peroxide on calcium peroxide octahydrate. The maximum content of tetroxide in the mixture of tetroxide and peroxide was calculated to be 5%. The mixture was shown to be paramagnetic however, which indicated the presence of the superoxide ion.

Carlton (3) reported the preparation of a so-called new oxide of barium by adding excess hydrogen peroxide to an aqueous solution of barium hydroxide at 15° C. A granular precipitate was reported to be formed which became buff colored upon standing; after being dried in vacuo over P_2O_5 for several days, a cream colored amorphous powder was reported formed which analyzed as BaO_3.

A modification of the method of preparation of superoxides described in this section, one which would be most reasonable for investigation, was reported by Seyb and Kleinberg (41) in 1951. They attempted to prepare alkaline earth metal superoxides by treatment of the nitrates of these metals with alkali metal superoxides. The reactions were carried out in liquid ammonia. In the reaction of barium nitrate with potassium superoxide, a chocolate-brown colored solid was formed in the liquid ammonia solvent when a formula weight ratio of 1:4 of the nitrate to superoxide was used. The product was reported to be a stable mixed superoxide-peroxide salt having a composition $K_2Ba(O_2)_2O_2$. The reaction was formulated as being:

$$Ba(NO_3)_2 + 4\ KO_2 = K_2Ba(O_2)_2O_2 + 2KNO_3 + O_2 \qquad (5)$$

No other combination of nitrates of the alkaline earth metals with superoxides of the alkali metals in liquid ammonia gave evidence of formation of an alkaline earth metal superoxide or even a mixed oxide.

5. The rearrangement of peroxide hydrates

Kleinberg (18) stated that the peroxide hydrates of the alkali metals rearrange when standing in vacuo for several days. The monohydrate rearranged for example, according to the reaction:

$$3(K_2O_2 \cdot H_2O) = 2\ KO_2 + 4\ KOH + H_2O \qquad (6)$$

Rearrangement of the dihydrate proceeded in a similar manner:

$$3(K_2O_2 \cdot 2H_2O) = 2KO_2 + 4\ (KOH\ H_2O) \qquad (7)$$

No experimental evidence was given by the author in support of this observation. The degree of completeness of these reactions was not indicated.

C. Reactions and Analysis of the Superoxides

The literature on the chemical properties and reactions of superoxides is sparse, although many of the physical and thermodynamic properties of the alkali metal superoxides have been determined.

Harcourt (9) stated that the potassium tetroxide, shown later to be identical to potassium superoxide, reacted rapidly in dilute alkalies, water, and dilute acids at room temperature liberating oxygen gas and giving a peroxide solution. The equation in texts such as Partington (26), Parkes and Mellor (25), and other standard inorganic reference works for the reaction of superoxides in aqueous solution is given as:

$$2KO_2 + 2\,H_2O = O_2 + H_2O_2 + 2\,KOH \qquad (8)$$

Weiss (51) reported that the alkali metal superoxides were quite stable in concentrated alkalies at low temperatures.

Kraus and Parmenter (20) were reportedly able to make a two step analysis of mixtures of potassium superoxide and peroxide on the basis that the superoxide liberated oxygen with water at 0° C. while the peroxide did not. At room temperature water or acids decomposed both superoxide and peroxide.

(a) Water at 0° C.:

$$2\,KO_2 + 2H_2O = O_2 + H_2O_2 + 2\,KOH \qquad (9)$$

$$K_2O_2 + 2\,H_2O = H_2O_2 + 2\,KOH \qquad (10)$$

(b) Water or acids at room temperature:

$$2\,KO_2 + 2\,H_2O = 3/2\,O_2 + H_2O + 2\,KOH \qquad (11)$$

$$K_2O_2 + H_2O = 1/2\,O_2 + 2\,KOH \qquad (12)$$

Kleinberg (18) found that determination of superoxide in mixtures of superoxide and peroxide by the method of Kraus and Parmenter (20) always gave high results for the superoxide content, possibly due to local heating and decomposition of the peroxide. In 1951, Seyb and Kleinberg (40) published a method for the quantitative determination of superoxide in mixtures of superoxide and peroxide. This analysis was accomplished by treatment of such mixtures with glacial acetic acid and diethyl phthalate as diluent at 0° C. Two-thirds of the total available oxygen from the superoxide was liberated by this reagent under these conditions while the peroxide present was not decomposed as shown by equations 13 and 14. The volume of oxygen liberated was measured by a gas buret.

(a) $2\ KO_2 + 2\ HC_2H_3O_2 = 2\ KC_2H_3O_2 + H_2O_2 + O_2$ (13)

(b) $K_2O_2 + 2\ HC_2H_3O_2 = 2\ KC_2H_3O_2 + H_2O_2$ (14)

The total oxygen liberated from both the superoxide and peroxide was determined by either of two methods. The superoxide determination may be followed by decomposition of the peroxide remaining in the sample by the addition of a solution 1 M. with respect to HCl and 3 M. with respect to $FeCl_3$, or this same catalytic solution may be used to decompose both the superoxide and peroxide of a new sample. Both methods were reported to give the same reliable results for total oxygen. The authors reported that no oxygen was found to be liberated from sodium peroxide at 0° C. by the reagent of glacial acetic acid and diethyl phthalate, while water at 0° C. always liberated varying amounts of oxygen from the peroxide.

Stephanou and co-workers (43), in their early work on the preparation of sodium superoxide, found that the magnetic moment measurements gave a reliable criterion for the superoxide content in their preparations. They found that the gram susceptibility of the product obtained by high pressure oxidation of sodium peroxide increased linearly with the quantity of oxygen absorbed. By plotting gram susceptibility versus weight per cent sodium superoxide, on the basis of the oxygen evolved, values for superoxide content were obtained which agreed within ± 3% of those obtained by purely chemical analysis.

III. EXPERIMENTAL

A. The Action of Hydrogen Peroxide on Barium Salts

1. Objective

The experimental work described in this section was carried out in the early stages of this entire investigation. The work was confined, primarily, to the investigation of the action of hydrogen peroxide of various concentrations on barium salts and the analyses of these preparations. The preparations were treated in various ways in an attempt to determine which methods of treatment resulted in high values for total available oxygen liberated upon decomposition. There were no superoxide oxygen determinations made on any of the preparations described here. At the time this part of the work was carried out, there had not appeared in the literature any method for determination of superoxide oxygen.

2. Procedure

a. Analysis of barium peroxide. As a first step in the study of barium preparations and the analyses of these preparations, it was necessary to establish a satisfactory method. The material selected for this purpose was an analyzed lot of Bakers' BaO_2 (C.P., Lot 1831). The material was labeled 89.22% BaO_2 and was indicated to be free of carbonate and sulfate.

The per cent BaO_2 of this material was determined by both the permanganate and iodometric methods given by Wagner (50) for analysis of peroxides. The permanganate method was recommended as being the more reliable by this investigator. In the permanganate titration, 250 ml. of a solution containing 25 ml. of concentrated HCl, 10 ml. of 85% H_3PO_4, and 1 ml. of 10% $MnCl_2 \cdot 6H_2O$ solution per liter, were added to the weighed sample of peroxide. The titration with standard potassium permanganate proceeded immediately upon addition of the acid solution and continued rapidly, with stirring of the solution, until the end point was reached. In the iodometric method, 15 ml. of 10% KI solution, 10 ml. of 85% H_3PO_4 solution, and 100 ml. of water were added to the iodine flask containing the weighed sample of peroxide. The titration flask was stoppered and allowed to stand for forty minutes at which time the free iodine was titrated with standard sodium thiosulfate solution with the starch indicator added as the end point was neared. Any additional iodine liberated was titrated after another thirty minute time period.

b. Preparation and analysis of barium peroxide octahydrate. Several preparations of barium peroxide octahydrate were prepared by the general method described by Riesenfeldt and Nottebohm (34, 35). The octahydrate, a stable hydrate of the alkaline earth metal peroxide at ordinary temperatures, was prepared to check the best method of analysis of peroxides. The per cent total available oxygen was determined by titration with standard permanganate solution. The per cent BaO was determined by titration with standard HCl solution using a mixture of methyl red and brom-cresol green indicator to give an end point of blue to red in the acid-base titration. The per cent water was calculated by difference in all cases. The accuracy of the titrimetric method of analysis for per cent BaO was checked on two of the preparations of the octahydrate by the gravimetric determination of $BaSO_4$.

The barium peroxide octahydrate was prepared by slowly pouring, with stirring, 50 ml. of 3% H_2O_2 into 500 ml. of saturated barium hydroxide solution at room temperature. The fine crystals of the octahydrate were filtered by means of a suction filter; then they were washed on the filter with water, a small amount of anhydrous alcohol, and finally, a small amount of anhydrous ether. The preparations were dried for a short time between filter paper and then analyzed.

When it was seen that the ratio of BaO to O was slightly larger than 1.00 to 1.00 as shown in preparations A to E of Table 3 (p. 34), the method of preparation of the octahydrate was modified by slowly passing the saturated solution of barium hydroxide directly into a 0.3% H_2O_2 solution. Precautions were taken to prevent the barium hydroxide solution from coming in contact with carbon dioxide of the air. This modified method of preparation served to circumvent the formation of a film of barium carbonate on the surface of the hydroxide solution during the precipitation of the octahydrate. Such a film was observed to be formed by the original method of preparation. Preparation F and G of Table 3 were prepared by the modified method.

c. *Preparation and analysis of other barium peroxides.* Further investigations were carried out on the action of various concentrations of hydrogen peroxide on barium salts. Conditions were modified in various ways in the preparation and treatment of these products in order to study the effect on the composition. A description of the treatment and conditions under which each of the preparations were carried out is as follows:

Preparation H. Saturated barium hydroxide solution was passed directly into 3% H_2O_2 (not diluted).

Preparation I. Was prepared the same as preparation H with the precipitate, however, not washed with water. Anhydrous alcohol and anhydrous ether were used to wash the precipitate on the filter.

Preparation J. Saturated barium hydroxide solution was passed directly into 30% H_2O_2 (not diluted). The light yellow precipitate formed was washed with anhydrous alcohol and anhydrous ether.

Preparation K. Was prepared the same way as preparation J. Analysis of the material was carried out after the preparation had remained in a desiccator over Anhydrone for two hours.

Preparation L. A portion of preparation G was treated with excess 30% H_2O_2 for sixteen hours at room temperature. The material was then filtered and washed with anhydrous alcohol and anhydrous ether.

Preparation M. Was prepared in the same manner as preparations F and G except the precipitate was not washed with water.

Preparation M_1. A portion of preparation M was treated with excess 30% H_2O_2 at room temperature for twenty-four hours. The material then was filtered and washed with anhydrous alcohol and anhydrous ether.

Preparation N. Was prepared in the same manner as preparation M.

Preparation N_1. A portion of preparation N was treated with excess 30% H_2O_2 at 0° C. for twenty-four hours.

Preparation O. Was prepared in the same manner as preparations M and N with the single difference of chilling the peroxide solution to 0° C. before and during the slow addition of saturated barium hydroxide solution.

Preparation O_1. A portion of preparation O was treated with excess 30% H_2O_2 at 0° C. for twenty-four hours.

Preparation P. Was prepared in the same manner as preparation O. The precipitate was treated immediately with excess 30% H_2O_2. The temperature of the reaction flask and contents was maintained at 55° C. for twenty-four hours.

Preparation Q. Was prepared in the same manner as preparation O. A portion of the preparation was treated with excess 30% H_2O_2 at 0° C. for twenty-four hours.

Preparation Q_1. A portion of preparation Q was kept in a 100° - 110° C. oven for twenty-four hours.

Preparation Q_2. A portion of preparation Q was kept in a closed contained in a refrigerator at 0° C. for twenty-four hours.

Preparation R. Was prepared in the same manner as preparation O.

Preparation R_1. A portion of preparation R was placed in a 100° - 110° C. oven for twenty-four hours.

3. Calculations and results

The titration data obtained in the analyses of Bakers' analyzed sample of barium peroxide are summarized in Table 2 (p. 33). Runs 1 to 9 inclusive were carried out by the permanganate method. Runs 10 and 11 were carried out by the iodometric method. The expression used to calculate the per cent barium peroxide of the samples was as follows:

$$\% \ BaO_2 = \frac{\text{ml. x N. of titr. soln. x m.e. wt. of } BaO_2 \text{ x } 100}{\text{wt. of sample}} \qquad (15)$$

Both the permanganate and iodometric methods of titration of the analyzed sample of barium peroxide gave satisfactory results for per cent BaO_2. The fact that the value obtained for the per cent peroxide was slightly lower than that given on the label was of no particular concern as the material was several years old. The permanganate method was the one adopted for use in further analyses of preparations for peroxide and total available oxygen because it was much less time consuming and in general, more satisfactory than the iodometric method.

Table 2

Analysis of Barium Peroxide

Run	Wt. of sample	Ml. of titrating solution	N. of titrating solution	% BaO_2
1	0.5581 g.	55.28	0.1054	88.40
2	0.5886 g.	58.39	0.1054	88.58
3	0.3988 g.	39.60	0.1054	88.63
4	0.3785 g.	37.50	0.1054	88.42
5	0.4713 g.	46.72	0.1054	88.50
6	0.2950 g.	29.18	0.1054	88.30
7	0.5085 g.	50.40	0.1056	88.60
8	0.3700 g.	36.65	0.1056	88.57
9	0.4637 g.	45.85	0.1056	88.39
			Mean:	88.49
10	0.1841 g.	19.33	0.09943	88.43
11	0.2147 g.	22.62	0.09943	88.73
			Mean:	88.58

Table 3 summarizes the data obtained from the analyses of the barium peroxide octahydrate preparations. The calculations shown were made in the following manner:

$$\% \text{ BaO} = \frac{\text{ml. HCl x N. HCl x m.e. wt. BaO x 100}}{\text{wt. of sample}} \qquad (16)$$

$$\% \text{ total } O_2 = \frac{\text{ml. x N. } KMnO_4 \text{ x m.e. wt. O x 100}}{\text{wt. of sample}} \qquad (17)$$

$$\% \ H_2O = 100 - \% \text{ BaO} + \% \text{ total } O_2 \qquad (18)$$

The ratio of the constituents were calculated in the usual manner from the per cent composition.

Table 3

Analysis of Barium Peroxide Octahydrate

Prep.	% BaO	% total O_2	% H_2O	Ratio:		
				BaO	O	H_2O
A	54.56	5.28	40.16	1.07	1.00	6.75
B	53.09	5.10	41.87	1.08	1.00	7.29
--[a]	52.97	5.10	41.93	1.08	1.00	7.30
C	50.89	5.04	44.07	1.05	1.00	7.76
--[a]	50.91	5.04	44.05	1.05	1.00	7.76
D	50.42	4.91	44.67	1.07	1.00	8.08
E	51.33	4.90	43.77	1.09	1.00	7.93
F	50.74	5.12	45.14	1.03	1.00	7.84
G	51.11	5.19	43.70	1.03	1.00	7.48
--[b]	51.86	4.98	43.16	1.08	1.00	7.71
--[c]	88.69	8.29	3.02	1.11	1.00	0.32

[a] Analysis of preparation listed immediately above by determining % BaO on the gravimetric basis.

[b] Reanalysis of Prep. G after eleven days storage in a closed bottle at room temperature.

[c] Reanalysis of Prep. G after eleven days storage of preparation in a closed bottle and an additional eighteen hours in a 100°-110° C. oven.

The ratio of the constituents BaO, O, and H_2O, as calculated from the percentage values determined for the preparations given in Table 3, showed that the composition agreed very closely with that calculated for barium peroxide octahydrate. By using the modified method of procedure in the preparation of the octahydrate, as illustrated by preparations F and G, closer values to that of the theoretical ratio were obtained. The gravimetric and titration methods, used to determine the per cent BaO in the preparations, agreed very closely. The latter method was used to calculate per cent BaO in the remainder of the analyses as it was the simpler and quicker method. Reanalysis of preparation G, after a period of time at room temperature, indicated that the octahydrate was stable at room temperature. Reanalysis of the same preparation, after a period of time in a 100°-110° C. oven, showed that the peroxide was stable at the temperature indicated, and the dehydration of a sample of the octahydrate in a 100°-110° C. oven could serve as a good method of obtaining anhydrous barium peroxide.

The results of the action of various concentrations of hydrogen peroxide on barium salts and the varied treatment of the resulting preparations are summarized in Table 4 (p. 36). The same analytical steps and calculations were carried out on preparations H to R_1 as were described for the analysis of the barium peroxide octahydrate.

The preparations of barium peroxide octahydrate, as given by M and N in Table 4, gave slightly closer values for the ratio of BaO, O, and H_2O to the theoretical values for the octahydrate than preparations F and G in Table 3 (p. 34). This was interpreted as indicating that the water used in the washing of the latter preparations was instrumental in giving a slightly lower value for total oxygen. Even closer values to the theoretical were obtained when the

Table 4

Analysis of Barium Peroxide Preparations

Prep.	% BaO	% total O_2	% H_2O	Ratio:		
				BaO	O	H_2O
H	74.78	15.01	10.21	1.04	2.00	1.20
I	74.60	14.77	10.63	1.05	2.00	1.28
--[a]	81.09	7.99	10.92	1.06	1.00	1.21
J	70.87	15.78	13.35	0.94	2.00	1.50
K	76.94	13.58	9.48	1.18	2.00	1.24
--[b]	87.79	9.31	2.90	0.94	1.00	0.27
L	67.00	17.24	15.76	1.22	3.00	2.44
M	50.13	5.16	44.71	1.01	1.00	7.69
M_1	63.98	17.62	18.40	1.14	3.00	2.78
N	49.72	5.10	45.18	1.02	1.00	7.84
N_1	60.46	18.46	21.08	1.02	3.00	3.04
--[c]	63.87	18.09	18.04	1.10	3.00	2.66
O	49.32	5.13	45.56	1.00	1.00	7.89
O_1	62.39	19.19	18.42	1.02	3.00	2.56
P	73.85	13.54	12.61	1.14	2.00	1.65
Q	61.76	18.58	19.66	1.04	3.00	2.82
--[d]	70.97	15.46	13.56	0.96	2.00	1.56
--[e]	80.32	12.47	7.21	1.34	2.00	1.03
Q_1	88.26	8.36	3.37	1.10	1.00	0.36
Q_2	66.07	15.55	18.38	0.87	2.00	2.10
R	49.17	4.92	45.91	1.04	1.00	8.29
R_1	89.46	8.81	1.73	1.06	1.00	0.17

---

[a] A portion of Prep. I analyzed after storage of the material in a closed bottle at room temperature for forty-eight hours.

[b] A portion of Prep. K analyzed after being held in a desiccator over Anhydrone at room temperature for twenty hours.

[c] A portion of Prep. N_1 analyzed after an additional one and one-half hours drying between filter paper at room temperature.

[d] A portion of Prep. Q analyzed after storage of the material in a closed bottle at room temperature for four hours.

[e] A portion of Prep. Q analyzed after storage of the material in a closed bottle at room temperature for four hours and an additional eighteen hours in a desiccator over Anhydrone at room temperature.

precipitation of the octahydrate was carried out after having first chilled the dilute hydrogen peroxide solution to 0° C. This was illustrated by preparation O.

All preparations, which were formed by passing a saturated solution of barium hydroxide into hydrogen peroxide of 3% concentration or higher, gave upon analysis a calculated ratio greater than 1.00 to 1.00 of oxygen to barium oxide. These preparations included H, I, J, and K. Three per cent H_2O_2 was used for the preparation of H and I and 30% H_2O_2 was used for J and K. These preparations varied in color from buff to light yellow. Analysis of the product several hours after preparation, as shown for K, indicated a slight loss of total oxygen when the preparation was kept in a desiccator over Anhydrone. There was an even greater loss of total oxygen from this preparation when the analysis was carried out after an additional eighteen hours storage over Anhydrone. The same loss of total oxygen occurred when the preparations were allowed to stand at room temperature in a closed bottle for a period of time as indicated by the analysis of preparation I after a period of forty-eight hours.

The treatment of barium peroxide octahydrate preparations with 30% H_2O_2 at various temperatures are illustrated by the preparations L, M_1, N_1, O_1, P, and Q. These preparations were all light yellow in color. The preparations which were treated with excess 30% H_2O_2 at 0° C. for twenty-four hours, namely, N_1, O_1, and Q, gave approximately the same high value for total oxygen content. Preparations L and M_1, which were prepared at room temperature, gave a lower value for total oxygen; and preparation P, which was prepared at 50° C., resulted in a product which was still lower in total oxygen. The stability of these products were illustrated by the analysis of the preparations after various modes of storage. Twenty-four hours at 0° C. resulted in a loss of total oxygen as illustrated by preparation Q_2. Analysis of preparation Q, after various periods of time in a closed bottle and in a desiccator over Anhydrone, showed a slightly greater loss of total oxygen.

The dehydration of the octahydrate in a 100°-110° C. oven could serve as a method of preparing a relatively pure form of the peroxide as shown by preparation R and R_1. This was shown previously from the data given in Table 3 (p. 34).

B. The Action of Hydrogen Peroxide on Alkaline Earth Metal Salts with Analysis of Preparations for Superoxide Oxygen Content

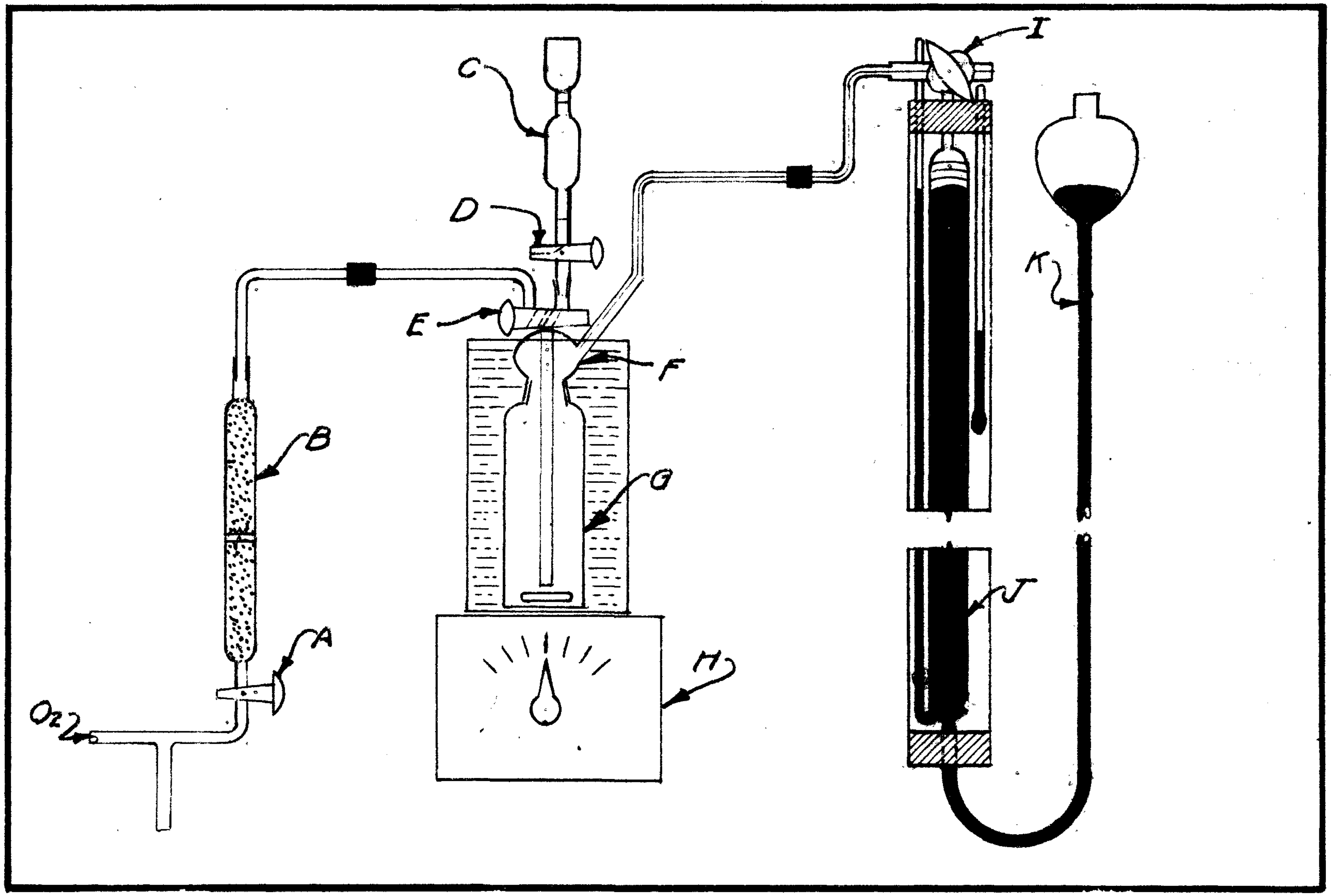
1. Objective

It was observed, during the investigation of the action of different concentrations of hydrogen peroxide on barium hydroxide as described in the earlier section of this paper, Table 4 (p. 36), that many of the products obtained were buff to light yellow in color. This indicated the possibility that the products contained a variable concentration of the superoxide of the metal. A publication by Seyb and Kleinberg (40) in January, 1951, of a quantitative determination of superoxide oxygen in mixtures of peroxide and superoxide of the alkali metals, led to a more extensive investigation of the composition of the products obtained by the action of hydrogen peroxide on alkaline earth metal compounds with special emphasis placed on the analysis of these preparations for superoxide oxygen. A systematic investigation of the effect of the concentration of the hydrogen peroxide used in the treatment of alkaline earth metals salts was undertaken.

2. Procedure

a. Description of apparatus. An apparatus similar to that described by Seyb and Kleinberg (40) was constructed for the purpose of determining both superoxide oxygen and total available oxygen present in the preparations which were investigated. A sketch of the apparatus used is shown by Figure 1 (p. 40). It consisted of a reaction cell, F - G, of about 100 ml. capacity which was connected to a water jacketed gas buret, J, by means of capillary tubing. The

Figure 1. Apparatus for Gasometric Analyses.


C
I
D
K
E
F
B
G
J
A
H
O_2

reaction cell was composed of a cell head, F, joined to the cell body, G, by a ground glass joint. The solutions used in the analyses to decompose the samples were added through the dropping funnel, C, which was connected to the cell head, F, by means of the three-way stopcock, E. This funnel was calibrated to deliver an identical quantity of reagent in each determination. The three-way stopcock, D, with the hole at the end of the plug, was incorporated on the funnel to facilitate rapid adjustment of the level of the reagent to the upper calibration mark.

Several pairs of reaction cells with ground glass caps were constructed. All samples analyzed were weighed in one of these cells equipped with a cap, and a second cell and cap were used as a counterpoise. Oxygen gas, used to sweep out the system, was dried by passage through anhydrous magnesium perchlorate in B. The reaction cell was thermostated at 0° C. for the superoxide oxygen determination by means of an ice-water bath. The buret reading was adjusted initially in each run by means of the leveling bulb, K, to the same reading of 0.5 ml. after equilibrium was established. In each determination, effective stirring of the contents of the reaction cell was accomplished by means of the magnetic stirrer, H.

b. Analysis of potassium superoxide. A sample of analyzed potassium superoxide was obtained from the Naval

Research Laboratories, Washington, D. C. Several analyses were carried out on this material in order to gain proficiency in the use of the apparatus, to check the precision of the method of analysis, and to determine if the analysis duplicated that given for the material by the Naval Research Laboratories.

In the determination of the superoxide oxygen of the analyzed sample of KO_2, as well as in subsequent superoxide determinations of preparations of calcium, strontium, and barium, a sample of the material was weighed in a reaction cell equipped with a ground glass cap. An identical reaction cell and cap were used as a counterpoise. Exactly ten milliliters of chilled diethyl phthalate were added rapidly to the reaction cell containing the sample before the cell was attached to the cell head. Dried oxygen gas was then allowed to sweep slowly through the system while the reaction cell was surrounded by the ice-water mixture. After equilibrium had been established, the level in the gas buret was adjusted at a reading of 0.5 ml. at existing atmospheric pressure. The oxygen gas was turned off at A and E. The three-way stopcock, I, on the gas buret was then turned and an exact quantity (appr. 18 ml.) of a mixture of glacial acetic acid and diethyl phthalate (8 vols. to 2 vols. respectively) was slowly added from funnel, C, by adjusting the stopcock, E. The contents of the reaction cell were stirred continuously for about fifteen minutes by means of the magnetic stirrer during the addition of the reagent. The leveling bulb, K, of the gas buret was lowered manually as the reagent was added in such a manner as to maintain the oxygen gas above the mercury at slightly less than atmospheric pressure. After all of the reagent was added and gas evolution from the sample was complete, the leveling bulb was adjusted until the level of the mercury in the bulb, gas buret, and side arm remained at the same point for five minutes. A blank was run after each analysis on the reagent using the reaction cell that was used as the counterpoise in weighing the sample. The same quantity of reagent, time of the analysis, and method of adjusting the reading the buret were duplicated as closely as possible in running the blank as in the analysis carried out with the sample.

The total available oxygen of the analyzed sample of KO_2 and subsequent preparations of alkaline earth metal preparations were determined in a similar manner. The determination of total available oxygen was made in all cases on a separate portion of the material. The weighings were performed in the same manner as described, and the cell body with sample was transferred rapidly to the cell head. The reaction cell was not thermostated at 0° C. for the total available oxygen determinations. The decomposition was carried out at room temperature. The sample was decomposed by the addition of an exact amount of a solution 1 M. with respect to HCl and 3 M. with respect to $FeCl_3$. The contents of the cell were stirred as before, and the leveling bulb was handled in the same manner. It was found that the first several drops of this catalytic solution decomposed the sample almost completely. A blank was determined in exactly the same manner for the reagent as previously described for the superoxide oxygen determination.

At first, an attempt was made to take into account the vapor pressure of the reagents used in the decomposition of the samples when converting the volume of oxygen liberated at laboratory conditions to volume of dry oxygen at standard conditions. It was found that it was difficult to determine exactly what this vapor pressure correction would be for the two reagents -- the values varying also with the temperature -- nor could information on the vapor pressure of these solutions be found in the literature. During a discussion with Dr. Kleinberg, it was learned that he had not taken into account the vapor pressure of the solutions used in any of his analyses but had simply run a blank with each determination. The analyzed sample of KO_2, it was learned, had been analyzed in the same manner. This then, was the procedure followed in this and subsequent analyses for both superoxide and total oxygen. The data obtained in the analyses of the analyzed sample of KO_2 are summarized in Table 5 (p. 55).

c. Preparation and analysis of some barium peroxides. After it was established that the gasometric method of analysis for both total available oxygen and for superoxide oxygen was precise and accurate for potassium superoxide, the investigation was continued with the analyses of different barium preparations. The first alkaline earth metal preparation investigated for superoxide oxygen content was a sample of barium peroxide which had been prepared and analyzed ten months earlier. The material had been prepared as the octahydrate and had been placed over P_2O_5 in an evacuated desiccator for forty-eight hours. At that time, the analysis indicated the preparation to be a very pure sample of barium peroxide. Ten months after the preparation of the peroxide, a portion of the peroxide, which had remained in the desiccator, was analyzed in the same manner as had been carried out earlier. Another portion of the same material was analyzed for both total oxygen and superoxide oxygen by the gasometric method. The result of these analyses are given in Table 6 (p. 56).

It was noted that this material, as well as several other preparations of barium peroxide which had remained in an evacuated desiccator for ten months to a year, all reacted violently with glacial acetic acid at room temperature. The acid was oxidized by the materials with evolution of considerable heat and light, and the reaction was of explosive violence. A small portion of KO_2 was found to react in the same manner with this acid reagent while commercial BaO_2 (89%) did not react visibly. The preparations of barium peroxide, which had been kept in the desiccator, were all slightly buff colored, while the commercial BaO_2 was white.

An analysis was then made of newly prepared barium peroxide octahydrate and of portions of the material which were dehydrated over anhydrous P_2O_5. This was done to determine if the superoxide was present in the newly prepared octahydrate and if the superoxide content of the preparation of barium peroxide, which had been kept over P_2O_5 for nearly a year, could be duplicated if the octahydrate was dehydrated over P_2O_5 for a period of only a few days. The barium peroxide octahydrate was prepared by the same method which was found in the earlier part of the investigation to give the purest form of the octahydrate. A saturated solution of $Ba(OH)_2$ was added slowly, with stirring, to a chilled (ice bath) solution of H_2O_2, made 0.3% by adding 50 ml. of 3% H_2O_2 to water to make 500 ml. of solution. The crystals were filtered by suction, washed with a small amount of anhydrous ether, and dried for a short time between filter paper. Then they were analyzed or treated further as indicated.

Table 7 (p. 59) summarizes the data obtained by the analyses of various barium peroxide preparations. These preparations were carried out and treated under varying conditions in order to determine which conditions were favorable for superoxide formation. Total analysis of each preparation was not usually made. A description of each preparation follows:

Preparation 1a. Barium peroxide octahydrate was prepared by the method indicated on page 28.

Preparation 1b. A portion of preparation 1a was placed in an evacuated desiccator over P_2O_5 and analyzed after seventy hours.

Preparation 2a. Was prepared in the same manner as preparation 1a.

Preparation 2b. A portion of preparation 2a was treated with excess 30% H_2O_2 at 0° C. for four days.

Preparation 2c. A portion of preparation 2b was placed in an evacuated desiccator over P_2O_5 and analyzed after six days.

Preparation 2d. A portion of preparation 2b was placed in an evacuated desiccator over P_2O_5 and analyzed after seven days.

Preparation 3a. Barium peroxide octahydrate was prepared by the usual method. The entire preparation was treated with excess 30% H_2O_2 at room temperature and analyzed after four days.

Preparation 4a. Was prepared in the same manner as preparation 1a and preparation 2a.

Preparation 4b. A portion of preparation 4a was treated with excess 30% H_2O_2 in a 100°-110° C. oven for twelve hours. Dry residue was analyzed.

Preparation 4c. A portion of preparation 4a was treated with excess 30% H_2O_2 at room temperature and analyzed after four and one-half days.

Preparation 4c$_1$. A portion of preparation 4c was placed in an evacuated desiccator over P_2O_5 and analyzed after seven days.

Preparation 4d. A portion of preparation 4a was placed in an evacuated desiccator over P_2O_5 and analyzed after three days.

Preparation 5a. Barium peroxide octahydrate was prepared by the usual method. The entire preparation was treated with excess 50% H_2O_2 at room temperature and analyzed after sixty hours.

Preparation 5b. A portion of preparation 5a was left in excess 50% H_2O_2 for an additional seventy hours before analysis.

d. Comparison of gasometric and titrimetric methods for determination of total oxygen. A comparison was made of the two methods used to determine the total available oxygen content of the preparations -- the gasometric method as used when the analyses were carried out with the apparatus and the titration method as used in the early part of the investigation with standard permanganate solution.

It was observed that the calculation of the per cent total available oxygen, on the basis of the volume oxygen liberated from the barium preparations by the gasometric method, always gave a larger value than when the same calculation was made on the same preparations on the basis of titration data using standard permanganate solution.

A comparison of the two methods was carried out by a determination of per cent total oxygen, on the basis of titration with standard permanganate, of the analyzed sample of KO_2 obtained from the Naval Research Laboratories. The results of these analyses, as well as the calculation of the per cent total oxygen obtained for the same material on the basis of the gasometric method of analysis, are given in Table 8 (p. 62).

e. Preparation and analysis of alkaline earth metal peroxides. A systematic investigation was carried out on the superoxide content of the products obtained by the action of various concentrations of hydrogen peroxide on different calcium, strontium, and barium salts.

Various concentrations of hydrogen peroxide, ranging from 0.3% to 90%, were in each case thermostated at 0° C. by an ice water bath, and a saturated solution of calcium, strontium, or barium hydroxide was added slowly, with stirring, to the chilled hydrogen peroxide solution. Fifty ml. of hydrogen peroxide solution were used in each case. The saturated solution of the hydroxide of the respective alkaline earth metal was added, in each case, until no further precipitate was seen to be formed or until it appeared that precipitation was complete. The preparations were then filtered by means of a suction filter. The white to yellow preparations were washed on the filter with small chilled portions of anhydrous alcohol followed by anhydrous ether. Each preparation was dried for a few minutes between filter paper, after which time the preparation was divided into two portions. One portion was analyzed immediately for per cent metal oxide by titration with standard acid and for per cent superoxide and per cent total oxygen by the gasometric method. A second portion of each of these preparations was placed in a desiccator over P_2O_5 and left in the evacuated desiccator for ninety hours, at which time the same series of analytical steps were carried out with this portion. Tables 10 to 15 (pp. 64 to 69) inclusive, summarize the data obtained in this series of preparations.

Another series of investigations were carried out by treating the alkaline earth metal peroxide octahydrate with various concentrations of hydrogen peroxide ranging from 0.3% to 90%. In each case, approximately 2 grams of the octahydrate was placed in a flask to which was added 50 ml. of a particular concentration of hydrogen peroxide. The flask, whose contents were protected from reacting with carbon dioxide of the air by means of the absorbent "Ascarite", was allowed to stand at room temperature for twenty-five hours. At the end of this period of time, the material was filtered, washed quickly on the filter with anhydrous alcohol and ether, and analyzed in the identical manner as described in the preceeding paragraph.

The octahydrate of the alkaline earth metals used in this series was prepared by the method found in an earlier stage of the investigation to give the purest form of the octahydrate. This method was that described for preparation O for which the analysis is given in Table 4 (p. 36). The data obtained in this series of investigations are summarized in Tables 16, 18 and 20 (p. 71, 73 and 75).

Still another series of investigations were carried out on the action of various concentrations of hydrogen peroxide on alkaline earth metal salts. The anhydrous peroxide of each of the alkaline earth metals, obtained by dehydration of the respective alkaline earth peroxide octahydrate over P_2O_5 in an evacuated desiccator for two weeks, was treated with various concentrations of hydrogen peroxide at room temperature for a period of twenty hours. The same precautions to avoid reaction of the solution with carbon dioxide were taken. The same method of filtering and washing the material was followed. The method of analysis and calculations made were the same. These data are summarized in Tables 17, 19 and 21 (p. 71, 73 and 75).

3. Calculations and results

The analysis of the sample of KO_2 obtained from the Naval Laboratories was given as 96% KO_2. The labeled material was indicated as having liberated 227 ml. of oxygen per gram at standard conditions when total oxygen was determined.

The theoretical volume of oxygen liberated from 100% KO_2 is 236 ml. per gram when the gasometric method of decomposing the sample for total oxygen is carried out. The theoretical volume of oxygen liberated from the same material, when only superoxide oxygen is decomposed, is 157 ml. per gram. The following equations and calculations, modified from the report of Seyb and Kleinberg (40) to apply to KO_2, show the chemical reactions and calculations involved in the analysis of potassium superoxide. When total catalytic decomposition of a sample of a mixture of potassium superoxide and peroxide was carried out, equations 19 and 20 were given as representing the chemical changes involved. The calculation for the superoxide content was given by expression 21. When the peroxide was not the impurity in the superoxide preparation, then expression 22 represented the calculation for the superoxide content.

$$2\ KO_2 + 2\ H^+ = 2\ K^+ + H_2O + 3/2\ O_2 \qquad (19)$$

$$K_2O_2 + 2\ H^+ = 2\ K^+ + H_2O + 1/2\ O_2 \qquad (20)$$

$$\%\ KO_2 = \frac{\text{ml. of } O_2/\text{g. of sample} - 102 \times 100}{236 - 102} \qquad (21)$$

$$\%\ KO_2 = \frac{\text{ml. of } O_2/\text{g. of sample} \times 100}{236} \qquad (22)$$

When only superoxide oxygen was liberated with glacial acetic acid-diethyl phthalate mixture, two-thirds of the total oxygen from the superoxide and none of the peroxide oxygen was liberated. Equations 23 and 24 were given as illustrations of these reactions, and expression 25 was given as the calculation of the superoxide content.

$$2\ KO_2 + 2\ HC_2H_3O_2 = 2\ KC_2H_3O_2 + H_2O_2 + O_2 \qquad (23)$$

$$K_2O_2 + 2\ HC_2H_3O_2 = 2\ KC_2H_3O_2 + H_2O_2 \qquad (24)$$

$$\%\ KO_2 = \frac{\text{ml. of } O_2/\text{g. of sample} \times 100}{2/3 \times 236} \qquad (25)$$

Table 5 summarizes the data obtained upon gasometric analysis of the analyzed sample of KO_2 obtained from the Naval Laboratories. Runs 1 to 3 were carried out by liberating total oxygen of the samples, while runs 4 to 6 were carried out by liberating only superoxide oxygen. The calculations made for % KO_2 were those given by expressions 22 and 25.

Table 5

% KO_2 on Basis of Gasometric Analysis

Run	Wt. of sample	Vol. of O_2 S.T.P.	ml./g.	% KO_2
1	0.1282 g.	28.85	225	95.4
2	.1860	41.8	225	95.3
3	.2894	65.7	227	96.2
			Mean:	95.6
4	.3379	50.4	149	95.0
5	.3723	55.6	149.5	95.2
6	0.4788	72.8	152	96.9
			Mean:	95.7

The data and calculations of Table 5 showed that the precision of the two gasometric methods for determining per cent superoxide content of the analyzed sample of KO_2 was very good. The results of the analyses agreed closely with that given for the material by the Naval Laboratories.

Table 6 compares the data obtained when a sample of anhydrous barium peroxide, which had been prepared ten months earlier, was analyzed by the gasometric method with that of the results of the two separate analyses of the material by the titrimetric method.

The data of Table 6 indicated that the anhydrous barium peroxide changed only slightly in composition during the ten months storage over P_2O_5. There was, however, a slight

Table 6

Analysis of Anhydrous Barium Peroxide

Time of analysis	% BaO	% total O_2 (titri-metric)	% H_2O	% total O_2 (gaso-metric)	% Superoxide O_2 (gasometric)
48 hours over P_2O_5	90.39	9.13	0.48	--	--
10 months over P_2O_5	90.42	9.18	0.47	9.40	0.48

increase in total oxygen content during this period. The higher value obtained for per cent total oxygen by the gasometric method was not understood at this time but was fully explained later as the result of further investigation. The value of almost 0.5% superoxide oxygen, which represented slightly more than three ml. of superoxide oxygen liberated per gram of sample, indicated that the barium peroxide preparation actually contained a small amount of superoxide.

The results of further investigation of the superoxide content of barium peroxide preparations are given in Table 7 (p. 59). The equations and calculations involved in determining the superoxide content in the preparations were calculated as those given below if the alkaline earth metal compounds could be assumed to react in a similar manner as the alkali metal compounds. When total catalytic decomposition of the samples were carried out, equations 26 and 27 would represent the reactions involved in the decomposition of the superoxide and peroxide.

$$Ba(O_2)_2 + 2\ H^+ = Ba^{++} + H_2O + 3/2\ O_2 \qquad (26)$$

$$BaO_2 + 2H^+ = Ba^{++} + H_2O + 1/2\ O_2 \qquad (27)$$

When the preparations were treated with glacial acetic acid-diethyl phthalate mixture at 0° C., only two-thirds of the total oxygen from the superoxide would be liberated and none of the oxygen from the peroxide would be liberated. Equations 28 and 29 would represent these reactions.

$$Ba(O_2)_2 + 2\ HC_2H_3O_2 = Ba(C_2H_3O_2)_2 + O_2 + H_2O_2 \qquad (28)$$

$$BaO_2 + 2HC_2H_3O_2 = Ba(C_2H_3O_2)_2 + H_2O_2 \qquad (29)$$

The per cent $Ba(O_2)_2$ could have been calculated on either the basis of the total oxygen evolved or on the basis of the superoxide oxygen evolved. The calculation was made on the latter basis and is given by the following expression.

$$\%\ Ba(O_2)_2 = \frac{\text{ml. superoxide } O_2/\text{g. of sample} \times 100}{2/3 \times 167} \qquad (30)$$

The calculations for per cent BaO and per cent total oxygen, based on titration data, were given by expressions 16 and 17. The per cent total oxygen and the per cent superoxide oxygen, based on the gasometric data, are given by expressions 31 and 32 respectively.

$$\% \text{ total } O_2 = \frac{\text{ml. of } O_2/\text{g. of sample} \times 32 \times 100}{22{,}400} \qquad (31)$$

$$\% \text{ superoxide } O_2 = \frac{\text{ml. of superoxide } O_2/\text{g. of sample} \times 32 \times 100}{22{,}400} \qquad (32)$$

A consideration of the data shown in Table 7 showed that the preparations of barium peroxide octahydrate, as illustrated by preparation 1a and 4a, gave a consistent but a low concentration of superoxide oxygen in the preparation. After several days over P_2O_5, these preparations analyzed higher for per cent superoxide oxygen as shown for preparations 1b and 4d. This should not necessarily be interpreted that there was additional superoxide formed during standing of the material over P_2O_5.

When the octahydrate was treated with 30% H_2O_2 at various temperatures, a higher superoxide content was obtained in the product. Preparation 2b formed by treating the octahydrate with excess H_2O_2 for several days at 0° C. gave a slightly higher superoxide content and a much higher total oxygen content. The superoxide oxygen content remained approximately the same for the material after as long as a week over P_2O_5 in an evacuated desiccator. The action of 30% H_2O_2 on the octahydrate at room temperature for a period of four days gave a high value for both total oxygen and superoxide oxygen in the product as shown by preparations 3a and 4c. On the other hand, treatment of the

Table 7

Analysis of Various Barium Peroxide Preparations

Prep	% BaO	% total O_2 (titrimetric)	% total O_2 (gasometric)	% superoxide O_2	% $Ba(O_2)_2$
1a	49.14	5.09	5.27	0.19	1.20
1b	90.40	8.80[a]	9.48	0.24	1.50
2a	---[b]	5.25[c]	5.51[d]	---	---
2b	64.44[e]	19.59[f]	20.28	0.49	3.09
2c	---	---	---	0.47	2.93
2d	---	---	---	0.45	2.84
3a	65.65[g]	18.31[h]	20.40	1.04	6.55
4a	---	---	---	0.19	1.20
4b	---	---	---	0.38	2.40
4c	---	---	---	1.77	11.1
$4c_1$	---	---	---	0.26	1.66
4d	---	---	---	0.43	2.68
5a	---	---	---	1.72[i]	10.81[j]
5b	57.77	---	8.10	0.50	3.13

[a] Average of two determinations: 8.84; 8.77

[b] Blank space indicates that the determination was not made

[c] Average of two determinations: 5.25; 5.25

[d] Average of three determinations: 5.58; 5.44; 5.50

[e] Average of two determinations: 64.46; 64.42

[f] Average of two determinations: 19.59; 19.59

[g] Average of two determinations: 65.30; 66.00

[h] Average oftwo determinations: 18.50; 18.13

[i] Average of two determinations: 1.72; 1.72

[j] Average of two determinations: 10.84; 10.78

octahydrate with 30% H_2O_2 at 100° C. resulted in a product slightly lower in superoxide content than that obtained at 0° C.

The action of 50% H_2O_2 on the octahydrate at room temperature for sixty hours gave approximately the same high result for superoxide oxygen in the product as the action of 30% H_2O_2 on the octahydrate. However, additional time of treatment with the hydrogen peroxide resulted in a product with lower superoxide oxygen content.

Good precision was shown in all of the analyses as shown by the footnotes to Table 7 (p. 59). However, it was observed that in every case where per cent total oxygen was determined by both the gasometric and titrimetric method, the former gave a higher value than the latter method. The differential between the two values for total oxygen was greater the higher the superoxide content of the preparations.

A consideration of the reactions involved in the titration of an acidified solution of peroxides shows that all of the available oxygen would be detected in the titration with permanganate solution. However, in the case of superoxides, only one-third of the total oxygen liberated would be detected in the titration as one mole of oxygen gas is liberated for each mole of hydrogen peroxide formed.

$$K_2O_2 + 2\ H^+ = 2\ K^+ + H_2O_2 \qquad (33)$$

$$2\ KO_2 + 2\ H^+ = 2\ K^+ + O_2 + H_2O_2 \qquad (34)$$

$$5\ H_2O_2 + 2\ KMNO_4 + 6\ H^+ = 2\ K^+ + 2\ MN^{++} + 8\ H_2O + 5\ O_2 \qquad (35)$$

The results obtained by a comparison of the per cent total oxygen determined by the titrimetric and gasometric methods of analysis of the analyzed sample of KO_2 are given in Table 8. The calculation of per cent total oxygen from the titrimetric method is given by expression 17. The calculation of per cent total oxygen from the gasometric method is given by expression 31. The data used for the calculation of per cent total oxygen on the basis of the gasometric analysis were the same as given in Table 5 (p. 55) upon which the calculation of per cent potassium superoxide was determined.

The analysis of the analyzed sample of KO_2 by the permanganate method gave slightly less than one-third the value for per cent total oxygen than that obtained on the basis of the gasometric method. It was concluded that the titrimetric method of determining total oxygen by titration of the samples with standard permanganate could not be used to determine the composition of mixtures of barium peroxide with barium superoxide.

Table 8

% Total Oxygen of KO_2 by Titrimetric and Gasometric Methods of Analysis

Run	Wt. of sample	Ml. of $KMnO_4$ solution	Vol. of O_2 S.T.P.	% total O_2
1	0.2440 g.	31.45	----	10.49
2	.3156	39.80	----	10.26
				Mean: 10.38
	.1282	----	28.85	32.15
	.1860	----	41.8	32.10
	0.2894	----	65.7	32.43
				Mean: 32.23

The fact that only one-third of the superoxide oxygen was detected by the titrimetric method explained the consistently lower results obtained for total oxygen on this basis than those obtained by the gasometric method. This was shown in the analyses of various barium peroxide preparations as given in Table 7 (p. 59).

Table 9 shows the calculated values for per cent total oxygen that would be obtained for mixtures of barium peroxide and barium superoxide when using both methods of analysis.

Subsequent analyses of per cent total oxygen on all preparations were made by the gasometric method.

Table 9

Per Cent Composition of Mixtures of BaO_2 and $Ba(O_2)_2$

% BaO_2	% $Ba(O_2)_2$	% BaO	% total O_2 ($KMnO_4$)	% total O_2 (gasometric)	% superoxide O_2
100	0	90.55	9.45	9.45	0.00
99	1	90.41	9.43	9.59	0.16
98	2	90.26	9.42	9.74	0.32
97	3	90.13	9.40	9.88	0.48
96	4	89.98	9.39	10.02	0.64
95	5	89.83	9.38	10.17	0.79
90	10	89.12	9.30	10.89	1.59
50	50	83.36	8.69	16.64	7.95
0	100	76.16	7.95	23.84	15.89

The data obtained in the systematic investigation of the superoxide content of the products obtained by the action of various concentrations of hydrogen peroxide on different calcium, strontium, and barium salts are summarized in Tables 10 to 21 (pp. 64 to 75).

The calculations that were made were similar but dependent upon which alkaline earth metal was involved. The per cent total oxygen and the per cent superoxide oxygen were in all cases calculated by expressions 31 and 32 respectively. The per cent metal oxide was calculated by expression 16 using the milliequivalent weight of the respective metal oxide involved. Per cent water was determined in each case by difference as given by expression 18. The per cent metal superoxide, based on the superoxide oxygen liberated, was calculated in the case of barium preparations by expression 30. In the case of the calcium and strontium preparations, the per cent metal superoxide was calculated by similar expressions.

$$\% \ Ca(O_2)_2 = \frac{\text{ml. superoxide } O_2/\text{g. of sample} \times 100}{2/3 \times 323} \qquad (36)$$

$$\% \ Sr(O_2)_2 = \frac{\text{ml. superoxide } O_2/\text{g. of sample} \times 100}{2/3 \times 221.6} \qquad (37)$$

Table 10

Hydrogen Peroxide with Calcium Hydroxide

% H_2O_2	% CaO	ml./g. superoxide O_2	% superoxide O_2	% $Ca(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
0.3	25.98	0.26	0.04	0.12	52.8	7.55	66.47
3.0	25.98	0.14	0.02	0.06	52.2	7.46	66.56
30.	26.13	0.77	0.11	0.36	54.2	7.75	66.12
50.	25.65	0.64	0.09	0.30	48.4	6.91	67.44
90.	26.02	3.1	0.44	1.4	54.2	7.74	66.24

	Ratio 1:			Ratio 2:		
	CaO	O	H_2O	CaO	O	H_2O
0.3	1.00	1.02	7.97	0.98	1.00	7.82
3.0	1.00	1.01	7.98	0.99	1.00	7.92
30.	1.00	1.04	7.88	0.96	1.00	7.58
50.	1.00	0.94	8.18	1.06	1.00	8.67
90.	1.00	1.04	7.93	0.96	1.00	7.60

Table 11

Calcium Peroxide Preparations (Table 10) After Ninety Hours Over P_2O_5

% H_2O_2	% CaO	ml./g. superoxide O_2	% superoxide O_2	% $Ca(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
0.3	74.44	4.4	0.63	2.0	148.6	21.23	4.33
3.0	75.49	5.9	0.85	2.8	137.1	19.59	4.92
30.	75.20	6.2	0.89	2.9	152.5	21.80	3.00
50.	73.90	3.7	0.52	1.7	141.5	20.21	5.89
90.	75.16	7.6	0.94	3.1	152.0	21.71	3.13

	Tatio 1:			Ratio 2:		
	CaO	O	H_2O	CaO	O	H_2O
0.3	1.00	1.00	0.18	1.00	1.00	0.18
3.0	1.00	0.91	0.20	1.10	1.00	0.22
30.	1.00	1.02	0.12	0.99	1.00	0.13
50.	1.00	0.96	0.25	1.04	1.00	0.26
90.	1.00	1.01	0.13	0.99	1.00	0.13

Table 12

Hydrogen Peroxide with Strontium Hydroxide

% H_2O_2	% SrO	ml./g. superoxide O_2	% superoxide O_2	% $Sr(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
0.3	39.26	0.70	0.10	0.47	36.57	5.23	55.51
3.0	39.16	0.89	0.13	0.60	25.66	3.67	57.17
30.	51.21	0.60	0.09	0.40	140.6	20.08	28.71
50.	42.55	0.57	0.08	0.38	72.01	10.29	47.16
90.	55.02	0.34	0.05	0.23	91.60	13.08	31.90

	Ratio 1:			Ratio 2:		
	SrO	O	H_2O	Sr	O	H_2O
0.3	1.00	0.86	8.13	1.16	1.00	9.43
3.0	1.00	0.61	8.40	1.65	1.00	13.8
30.	1.00	2.54	3.22	0.39	1.00	1.27
50.	1.00	1.57	6.38	0.64	1.00	4.07
90.	1.00	1.54	3.34	0.65	1.00	2.16

Table 13

Strontium Peroxide Preparations (Table 12) After Ninety Hours Over P_2O_5

% H_2O_2	% SrO	ml./g. superoxide O_2	% superoxide O_2	% $Sr(O_2)_2$	ml./g. total O_2	R total O_2	% H_2O
0.3	85.11	2.5	0.35	1.66	87.66	12.52	2.37
3.0	84.42	4.8	0.69	3.28	82.91	11.84	3.74
30.	85.68	7.2	1.04	4.90	70.07	10.01	4.31
50.	82.20	10.1	1.44	6.85	92.21	13.17	4.63
90.	85.40	7.1	1.01	4.80	75.90	10.84	3.76

	Ration 1:			Ratio 2:		
	SrO	O	H_2O	SrO	O	H_2O
0.3	1.00	0.95	0.16	1.05	1.00	0.17
3.0	1.00	0.91	0.25	1.10	1.00	0.28
30.	1.00	0.76	0.29	1.32	1.00	0.38
50.	1.00	1.04	0.32	0.96	1.00	0.31
90.	1.00	0.82	0.25	1.22	1.00	0.31

Table 14

Hydrogen Peroxide with Barium Hydroxide

% H_2O_2	% BaO	ml./g. super-oxide O_2	% super-oxide O_2	% $Ba(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
0.3	49.30	1.33	0.19	1.19	31.73	4.53	46.17
3.0	56.07	2.50	0.36	2.29	54.39	7.77	36.16
30.	64.38	0.74	0.11	0.67	135.1	19.30	16.32
50.	64.75	1.55	0.22	1.39	53.2	7.60	27.65
90.	64.43	0.59	0.08	0.53	71.22	10.17	25.40

	Ratio 1:			Ratio 2:		
	BaO	O	H_2O	BaO	O	H_2O
0.3	1.00	0.88	7.97	1.13	1.00	9.05
3.0	1.00	1.33	5.49	0.75	1.00	4.13
30.	1.00	2.87	2.16	0.35	1.00	0.75
50.	1.00	1.12	3.64	0.89	1.00	3.23
90.	1.00	1.51	3.36	0.66	1.00	2.22

Table 15

Barium Peroxide Preparations (Table 14) After Ninety Hours Over P_2O_5

% H_2O_2	% BaO	ml./g. super-oxide O_2	% super-oxide O_2	% $Ba(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
0.3	89.34	2.43	0.35	2.18	55.45	7.92	2.74
3.0	89.92	1.92	0.27	1.72	63.29	9.04	1.06
30.	89.73	4.09	0.58	3.67	50.03	7.15	3.12
50.	89.80	2.92	0.42	2.62	45.95	6.57	3.63
90.	89.73	1.43	0.20	1.28	62.81	8.97	1.30

	Ratio 1:			Ratio 2:		
	BaO	O	H_2O	BaO	O	H_2O
0.3	1.00	0.85	0.26	1.18	1.00	0.31
3.0	1.00	0.96	0.10	1.04	1.00	1.10
30.	1.00	0.76	0.30	1.31	1.00	0.39
50.	1.00	0.70	0.34	1.43	1.00	0.49
90.	1.00	0.96	0.12	1.04	1.00	0.13

Table 16

Hydrogen Peroxide With Calcium Peroxide Octahydrate

% H_2O	% CaO	ml./g. superoxide O_2	% superoxide O_2	% $Ca(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
---*	26.12	0.75	0.11	0.35	55.9	7.98	65.90
0.3	75.00	2.9	0.42	1.35	153.5	21.92	3.10
3.0	27.63	1.9	0.28	0.90	65.2	9.32	63.05
30.	71.24	0.3	0.05	0.15	154.3	22.04	6.72
50.	72.41	7.0	1.00	3.30	165.4	23.63	3.96
90.	43.53	28.2	4.04	13.12	238.7	34.10	22.37

	Ratio 1:			Ratio 2:		
	CaO	O	H_2O	CaO	O	H_2O
---*	1.00	1.07	7.85	0.93	1.00	7.33
0.3	1.00	1.02	0.13	0.98	1.00	0.13
3.0	1.00	1.18	7.10	0.85	1.00	6.01
30.	1.00	1.08	0.29	0.92	1.00	0.27
50.	1.00	1.14	0.17	0.87	1.00	0.15
90.	1.00	2.75	1.60	0.36	1.00	0.58

*Analysis of starting material

Table 17

Hydrogen Peroxide With Anhydrous Calcium Peroxide

% H_2O_2	% CaO	ml./g. superoxide O_2	% superoxide O_2	% $Ca(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
---*	74.33	5.0	0.72	2.3	146.1	20.87	4.80
0.3	74.46	5.7	0.81	2.6	136.0	19.42	6.12
3.0	73.19	7.4	1.05	3.4	162.6	23.23	3.58
30.	73.27	8.2	1.18	3.8	166.4	23.77	2.96
50.	44.36	6.9	1.0	3.2	187.3	26.76	28.88
90.	46.89	11.9	1.7	5.5	218.1	30.44	22.67

	Ratio 1:			Ratio 2:		
	CaO	O	H_2O	CaO	O	H_2O
---*	1.00	0.98	0.20	1.02	1.00	0.20
0.3	1.00	0.90	0.26	1.09	1.00	0.28
3.0	1.00	1.11	0.15	0.90	1.00	0.14
30.	1.00	1.14	0.13	0.88	1.00	0.11
50.	1.00	2.11	2.03	0.47	1.00	0.96
90.	1.00	2.28	1.51	0.44	1.00	0.66

*Analysis of starting material.

Table 18

Hydrogen Peroxide With Strontium Peroxide Octahydrate

% H_2O_2	% SrO	ml./g. super-oxide O_2	% super-oxide O_2	% $Sr(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
---*	39.36	1.70	0.24	1.15	44.63	6.37	54.27
0.3	39.61	1.85	0.27	1.26	46.41	6.63	53.76
3.0	39.47	2.50	0.35	1.67	45.67	6.52	54.01
30.	54.37	13.37	1.91	9.06	185.0	26.44	19.19
50.	53.00	19.84	2.83	13.43	191.0	27.28	19.72
90.	53.52	17.84	2.55	12.08	199.2	28.45	18.03

	Ratio 1:			Ratio 2:		
	SrO	O	H_2O	SrO	O	H_2O
---*	1.00	1.05	7.93	0.95	1.00	7.56
0.3	1.00	1.08	7.81	0.92	1.00	7.20
3.0	1.00	1.07	7.87	0.93	1.00	7.35
30.	1.00	3.15	2.03	0.32	1.00	0.65
50.	1.00	3.33	2.14	0.30	1.00	0.64
90.	1.00	3.44	1.94	0.29	1.00	0.56

*Analysis of starting material.

Table 19

Hydrogen Peroxide With Anhydrous Strontium Peroxide

% H_2O_2	% SrO	ml./g. super-oxide O_2	% super-oxide O_2	% $Sr(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
---*	85.63	2.7	0.38	1.8	87.2	12.45	1.92
0.3	40.57	0.9	0.13	0.6	24.9	3.56	58.87
3.0	40.41	0.7	0.10	0.5	21.25	3.04	56.55
30.	54.51	17.2	2.46	11.66	101.4	14.49	31.00
50.	54.34	18.8	2.68	12.70	129.0	18.43	27.23
90.	54.93	16.9	2.41	11.44	116.3	16.62	28.45

	Ratio 1:			Ratio 2:		
	SrO	O	H_2O	SrO	O	H_2O
---*	1.00	0.94	0.13	1.06	1.00	0.14
0.3	1.00	0.57	7.92	1.76	1.00	13.95
3.0	1.00	0.49	8.05	2.06	1.00	16.55
30.	1.00	1.76	3.27	0.58	1.00	1.90
50.	1.00	2.20	2.88	0.46	1.00	1.31
90.	1.00	1.96	2.98	0.51	1.00	1.50

*Analysis of starting material.

Table 20

Hydrogen Peroxide With Barium Peroxide Octahydrate

% H_2O_2	% BaO	ml./g. superoxide O_2	% superoxide O_2	% $Ba(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
---*	49.03	1.48	0.21	1.33	38.18	5.45	45.52
0.3	49.46	1.10	0.16	1.00	39.0	5.58	44.96
3.0	68.01	12.96	1.85	11.65	136.9	19.56	12.43
30.	66.16	14.42	2.06	12.95	141.9	20.27	13.57
50.	64.43	13.13	1.88	11.80	49.7	7.10	28.27
90.	62.35	10.30	1.47	9.26	34.5	4.93	32.72

	Ratio 1:			Ratio 2:		
	BaO	O	H_2O	BaO	O	H_2O
---*	1.00	1.07	7.90	0.94	1.00	7.42
0.3	1.00	1.08	7.76	0.92	1.00	7.16
3.0	1.00	2.76	1.56	0.36	1.00	0.56
30.	1.00	2.94	1.75	0.34	1.00	0.59
50.	1.00	1.05	3.72	0.95	1.00	3.54
90.	1.00	0.76	4.47	1.32	1.00	5.90

*Analysis of starting material.

Table 21

Hydrogen Peroxide With Anhydrous Barium Peroxide

% H_2O_2	% BaO	ml./g. superoxide O_2	% superoxide O_2	% $Ba(O_2)_2$	ml./g. total O_2	% total O_2	% H_2O
---*	89.77	2.80	0.40	2.52	61.44	8.78	1.45
0.3	53.04	3.06	0.44	2.75	15.03	2.15	44.81
3.0	52.84	3.85	0.55	3.46	41.01	5.86	41.30
30.	67.03	8.83	1.26	7.94	41.07	5.87	27.10
50.	65.19	13.92	1.99	12.52	105.7	15.10	19.71
90.	62.98	13.77	1.97	12.38	122.2	17.45	19.57

	Ratio 1:			Ratio 2:		
	BaO	O	H_2O	BaO	O	H_2O
---*	1.00	0.94	0.14	1.07	1.00	0.15
0.3	1.00	0.39	7.19	2.58	1.00	18.5
3.0	1.00	1.06	6.65	0.94	1.00	6.26
30.	1.00	0.84	3.44	1.19	1.00	4.10
50.	1.00	2.22	2.57	0.45	1.00	1.16
90.	1.00	2.66	2.65	0.38	1.00	1.00

*Analysis of starting material

From Tables 10 to 21, which summarize the data obtained by treating alkaline earth metal salts with various concentrations of hydrogen peroxide, several general observations were made. The treatment of corresponding calcium, strontium, and barium salts with the same concentration of hydrogen peroxide invariably resulted in a product considerably higher in superoxide content in the case of strontium and barium salts than with the calcium salt. With the strontium and barium salts, the latter gave approximately the same or slightly higher values than the former.

In general, the preparations carried out by treatment of the peroxide octahydrate and the anhydrous peroxide of the alkaline earth metals gave increasingly greater superoxide content in the resulting product with increase in concentration of the hydrogen peroxide used. The lowest superoxide content was obtained when 0.3% or 3% hydrogen peroxide was used. Contrary to expectations, the highest concentration of hydrogen peroxide used, namely, 90% H_2O_2, usually gave a slightly lower superoxide content in the product than that obtained with 30% and 50% hydrogen peroxide. In the case of the treatment of calcium salts, however, the 90% H_2O_2 always gave the highest yield of superoxide in the products. No appreciable amount of calcium superoxide was formed in any of the products when concentrations of hydrogen peroxide of less than this concentration were used.

Although the superoxide content of the preparations, which were kept over P_2O_5 for ninety hours from the time of their preparation, increased on a percentage basis, the ratio of oxygen to metal oxide decreased in almost every preparation.

Contrary to expectations, the treatment of the peroxide octahydrate of the alkaline earth metals with various concentrations of hydrogen peroxide usually gave a product slightly higher in superoxide oxygen content than when the anhydrous peroxide was treated in a similar manner.

IV. DISCUSSION OF RESULTS

In an attempt to secure a clearer picture of the exact composition of the products obtained by the treatment of alkaline earth metal salts with the higher concentrations of hydrogen peroxide, calculations were made based on the expressions given below. The expressions 38 to 46 were developed to calculate the composition of the barium preparations, which contained superoxide oxygen, on the basis that the products contained any of the following constituents and no others: $Ba(O_2)_2$; BaO_2; H_2O_2; H_2O. It was assumed that there would be little if any barium oxide, as such, or as the hydroxide or carbonate present when hydrogen peroxide of 30% concentration and higher was used in the treatment of the barium salts. Precautions had been taken in each preparation to avoid formation of carbonate.

The composition must be calculated from the three experimentally determined values of per cent barium oxide, per cent total oxygen, and per cent superoxide oxygen.

The ratio that was calculated was done in the usual manner by dividing the per cent of the constituents by the respective molecular weights to determine the ratio in terms of an integral number for one of them.

$$\% \text{ BaO} = \frac{\text{ml. HCl x N. HCl x m.e. wt. of BaO x 100}}{\text{wt. of sample}} \qquad (16)$$

$$\% \text{ total } O_2 = \frac{\text{ml. of } O_2\text{/g. of sample x 32 x 100}}{22,400} \qquad (31)$$

$$\% \text{ superoxide } O_2 = \qquad (32)$$

$$\frac{\text{ml. of superoxide } O_2\text{/g. of sample x 32 x 100}}{22,400}$$

$$\% \text{ Ba}(O_2)_2 = \frac{\text{ml. of superoxide } O_2\text{/g. of sample x 100}}{2/3 \text{ x } 167} \qquad (30)$$

$$\% \text{ } H_2O = 100 - (\% \text{ BaO} + \% \text{ total } O_2) \qquad (18)$$

$$\% \text{ peroxide } O_2 = \% \text{ total } O_2 - 3/2 \% \text{ superoxide } O_2 \qquad (38)$$

$$\% \text{ BaO from Ba}(O_2)_2 = \frac{\% \text{ Ba}(O_2)_2 \text{ x } 153.36}{201.36} \qquad (39)$$

$$\% \text{ BaO from BaO}_2 = \% \text{ total BaO} - \% \text{ BaO from Ba}(O_2)_2 \qquad (40)$$

$$\% \text{ BaO}_2 = \frac{\% \text{ BaO from BaO}_2 \text{ x } 169.36}{153.36} \qquad (41)$$

$$\% \text{ peroxide } O_2 \text{ from BaO}_2 = \frac{\% \text{ BaO}_2 \text{ x } 16}{169.36} \qquad (42)$$

$$\% \text{ peroxide } O_2 \text{ from } H_2O_2 =$$

$$\% \text{ peroxide } O_2 - \% \text{ peroxide } O_2 \text{ from BaO}_2 \qquad (43)$$

$$\% \text{ } H_2O_2 = \frac{\% \text{ peroxide } O_2 \text{ from } H_2O_2 \text{ x } 34.016}{16} \qquad (44)$$

$$\% \text{ } H_2O \text{ from } H_2O_2 = \frac{\% \text{ } H_2O_2 \text{ x } 18.016}{34.016} \qquad (45)$$

$$\% \text{ } H_2O \text{ (not as } H_2O_2) =$$

$$100 - (\% \text{ Ba}(O_2)_2 + \% \text{ BaO}_2 + \% \text{ } H_2O_2) \qquad (46)$$

Table 22 shows the complete composition of several barium preparations. The action of 30% and 50% H_2O_2 with a saturated solution of barium hydroxide did not yield a

Table 22

Complete Composition of Some Barium Preparations

Calculation of	30% H_2O_2 on $Ba(OH)_2$ Table 14 (p. 68)	50% H_2O_2 on $Ba(OH)_2$ Table 14 (p. 68)	30% H_2O_2 on $BaO_2 \cdot 8H_2O$ Table 20 (p. 74)	90% H_2O_2 on BaO_2 Table 21 (p. 75)
% BaO	64.38	64.75	66.16	62.98
% total O_2	19.30	7.60	20.27	17.45
% superoxide O_2	0.11	0.22	2.06	1.97
% $Ba(O_2)_2$	0.67	1.39	12.95	12.38
% H_2O (by diff.)	16.32	27.65	13.57	19.57
% peroxide O_2	19.14	7.27	17.18	14.50
% BaO from $Ba(O_2)_2$	0.51	1.06	9.86	9.43
% BaO from BaO_2	63.87	63.69	56.30	53.55
% BaO_2	70.53	70.34	62.17	59.14
% peroxide O_2 from BaO_2	6.66	6.65	5.87	5.59
% peroxide O_2 from H_2O_2	12.48	0.62	11.31	8.91
% H_2O_2	26.53	1.32	24.05	18.94
% H_2O from H_2O_2	14.05	0.70	12.74	10.03
% H_2O (not as H_2O_2)	2.26	26.95	0.83	9.54
Ratio: BaO_2	1.00	1.00	1.00	1.00
H_2O_2	1.87	0.09	1.93	1.60
H_2O	0.30	3.60	0.12	1.52
Composition: $Ba(O_2)_2$	0.67	1.39	12.95	12.38
BaO_2	70.53	70.34	62.17	59.14
H_2O_2	26.53	1.32	24.05	18.94
H_2O	2.26	26.95	0.83	9.54

product with an appreciable superoxide content. The difference in the per cent total oxygen was readily seen, however, to be due to the high per cent of H_2O_2 in the product formed by the action of 30% H_2O_2 on $Ba(OH)_2$. The ratio of BaO_2 to H_2O_2 for this preparation would strongly suggest that the di-peroxyhydrate of barium peroxide was the chief constituent of this preparation. The hydrogen peroxide content was negligible in the preparation formed by the action of 50% H_2O_2 on $Ba(OH)_2$. The calculated ratios would indicate that barium peroxide tetrahydrate was the principal constituent.

The action of 30% H_2O_2 on the octahydrate of barium peroxide also showed a ratio of BaO_2 to H_2O_2 which would indicate that the composition of the product could be quite accurately described as constituting a mixture of 86.22% $BaO_2 \cdot 2H_2O_2$ and 12.95% $Ba(O_2)_2$. The action of 90% H_2O_2 on anhydrous barium peroxide octahydrate gave approximately the same superoxide content as the product just described but the significance of the ratio of BaO_2, H_2O_2, and H_2O was not readily seen.

The fact that the same calcium, strontium, and barium salt treated with the same concentration of hydrogen peroxide usually resulted in a product higher in superoxide content, in the case of the latter two metals, would indicate that either the ease of formation or the stability of the superoxides of the alkaline earth metals increases with increase in the ionic radii of the metal. This same conclusion was supported by the experimental data which showed that the concentration of hydrogen peroxide used in the treatment of the respective metal peroxide octahydrate was an important factor in determining the concentration of the superoxide in the product. Approximately the same maximum superoxide content was attained with each of the alkaline earth metals when 90%, 50%, and 30% H_2O_2 respectively, were used with the identical calcium, strontium, and barium salt.

The maximum superoxide content of approximately 13% obtained by the treatment of the alkaline earth metal salts with hydrogen peroxide of various concentrations was probably limited to such a value because of the method of preparation employed. The water from the hydrogen peroxide solution, no doubt, decomposed a considerable amount of any superoxide formed by this method of preparation. A method of preparation of the superoxides of the alkaline earth metals that might be deserving of further investigation would be the use of non-aqueous solvents. Liquid ammonia has been tried but found unsuccessful for this purpose.

V. CONCLUSIONS

1. A pure form of the alkaline earth metal peroxide was formed when a saturated solution of the hydroxide of the metal was slowly passed into a very dilute solution (0.3%) of hydrogen peroxide at 0° C.

2. The acid-base titration of alkaline earth metal peroxides, using a standard hydrochloric acid solution with a mixture of brom-cresol green and methyl red as the indicator, was found to be a precise and accurate method for the determination of per cent peroxide or per cent metal oxide.

3. A pure form of anhydrous barium peroxide was prepared by heating barium peroxide octahydrate in a 100°-110° C. oven for a period of eighteen to twenty-four hours.

4. The product, formed when a saturated solution of barium hydroxide was passed into a hydrogen peroxide solution of any concentration of 3% or higher at 0° C., was buff to light yellow in color and contained a variable amount of barium superoxide.

5. Preparations of barium peroxide octahydrate, kept over P_2O_5 for a period of several days, contained a small percentage of the superoxide of the metal.

6. A product containing a higher superoxide content was formed when barium peroxide octahydrate was treated with 30% H_2O_2 for several days at room temperature than when it was treated at either 0° C. or at 100° C.

7. The action of 50% H_2O_2 on barium peroxide octahydrate for several days at room temperature gave a product with approximately the same superoxide content as that formed by the action of 30% H_2O_2.

8. Prolonged treatment, for five days or more, of barium peroxide octahydrate with 50% H_2O_2 gave a product lower in superoxide content than when the treatment was carried out for two days.

9. Only one-third of the superoxide oxygen was detected in the analysis of metal superoxides or mixtures of metal superoxide and peroxide when titrating an acidified solution of the material with standard permanganate.

10. Treatment of corresponding salts of calcium, strontium, and barium with the same concentration of hydrogen peroxide usually gave a product containing a higher superoxide content of the metal in the case of strontium and barium than in the case of calcium.

11. Treatment of corresponding salts of strontium and barium with 30% and 50% H_2O_2 resulted in a product containing a higher superoxide content of the metal than when either 3% or 90% H_2O_2 was used.

12. No appreciable amount of calcium superoxide was formed by treatment of calcium salts with various concentrations of hydrogen peroxide other than with a concentration of 90% H_2O_2.

13. Treatment of strontium and barium peroxide octahydrate with various concentrations of hydrogen peroxide gave a product higher in superoxide content than corresponding treatment of the anhydrous metal peroxide.

14. The highest yield of superoxide, obtained by the treatment of barium salts with various concentrations of hydrogen peroxide, was an admixture of peroxide with 12.95% $Ba(O_2)_2$ obtained when barium peroxide octahydrate was treated with 30% H_2O_2.

15. The highest yield of superoxide, obtained by the treatment of strontium salts with various concentrations of hydrogen peroxide, was an admixture of peroxide with 13.43% $Sr(O_2)_2$ obtained when strontium peroxide octahydrate was treated with 50% H_2O_2.

16. The highest yield of superoxide, obtained in the treatment of calcium salts with various concentrations of hydrogen peroxide, was an admixture of peroxide with 13.12% $Ca(O_2)_2$ obtained when calcium peroxide octahydrate was treated with 90% H_2O_2.

VI. SUMMARY

1. In this investigation the effect of various concentrations of hydrogen peroxide on alkaline earth metal salts was studied and the analyses of the resulting preparations were carried out.

2. A method of preparing pure barium peroxide and barium peroxide octahydrate was established.

3. Any concentration of 3% H_2O_2 or higher gave a buff to yellow colored product with barium salts.

4. An apparatus was constructed to determine the superoxide content of the preparations carried out.

5. A comparison of the gasometric and titrimetric method of analysis for total oxygen content of preparations was made.

6. A complete analysis, including superoxide oxygen determination, was made on preparations carried out by treatment of alkaline earth metal salts with concentration of hydrogen peroxide ranging from 0.3% to 90%.

7. Strontium and barium salts invariably gave a product higher in superoxide content than calcium salts.

8. The treatment of the alkaline earth metal peroxide octahydrate with hydrogen peroxide gave a higher yield of

superoxide than the treatment of the corresponding anhydrous alkaline earth metal peroxide.

9. Approximately 13% metal superoxide was the highest yield obtained for each of the alkaline earth metals.

VII. LITERATURE CITED

1. Bach, *Ber.*, *35*, 342 (1902).
2. Baeyer and Villiger, *ibid.*, *35*, 3038 (1902).
3. Carlton, *J. Chem. Soc.*, *127*, 2180 (1925).
4. Conroy, *ibid.*, *26*, 808 (1873).
5. DeForcrand, *Compt. rend.*, *127*, 364 (1898).
6. DeForcrand, *ibid.*, *129*, 1246 (1899); *130*, 716 (1900).
7. Ehrlich, *Z. anorg. Chem.*, *252*, 370 (1944).
8. Fischer and Ploetzer, *ibid.*, *75*, 1 (1912).
9. Harcourt, *J. Chem. Soc.*, *14*, 267 (1861).
10. Helms and Klemm, *Z. anorg. Chem.*, *241*, 97 (1939).
11. Helms and Klemm, *ibid.*, *242*, 201 (1939).
12. Holt and Sims, *J. Chem. Soc.*, *65*, 432 (1894).
13. Joannis, *Compt. rend.*, *116*, 1370 (1893).
14. Kasatochkin, *J. Phys. Chem.*, (*U.S.S.R.*), *9*, 932 (1937).
15. Kasatochkin and Kotov, *J. Chem. Phys.*, *4*, 458 (1936).
16. Kazarnovskii, *J. Phys. Chem.* (*U.S.S.R.*), *14*, 320 (1940).
17. Kazarnovskii, Nikolskii and Abletsova, *Doklady Akad. Nauk S.S.S.R.*, *64*, 69 (1949).
18. Kleinberg, *Unfamiliar Oxidation States and Their Stabilization*, Univ. of Kansas Press, Lawrence, Kansas, 1950, p. 25.
19. Klemm and Sodomann, *Z. anorg. Chem.*, *225*, 273 (1935).
20. Kraus and Parmenter, *J. Am. Chem. Soc.*, *56*, 2384 (1934).

21. Kraus and Whyte, *ibid.*, *48*, 1781 (1926).

22. Manchot and Kampschulte, *Ber.*, *40*, 4984 (1907).

23. Miller, *U. S. pat.*, *2,414,116* Jan. 14, (1947). [*C. A.*, *41*, 2863 (1947)].

24. Neuman, *J. Chem. Phys.*, *2*, 31 (1934).

25. Parkes and Mellor, *Mellor's Modern Inorganic Chemistry*, Rev. Ed., Longman's, Green and Co., New York, 1939, p. 304.

26. Partington, *Textbook of Inorganic Chemistry*, 6th Ed., Macmillan and Co., London, 1950, p. 700.

27. Pauling, *J. Am. Chem. Soc.*, *53*, 3225 (1931).

28. Pauling, *The Nature of The Chemical Bond*, 2nd Ed., Cornell Univ. Press, Ithaca, New York, 1940, p. 93.

29. Raikhshtein and Kazarnovskii, *J. Phys. Chem.* (*U.S.S.R.*), *11*, 743 (1938).

30. Raikhshtein and Kazarnovskii, *ibid.*, *21*, 245 (1947).

31. Rengade, *Ann. chim. et phys.* (*8*), *2*, 348 (1907).

32. Rengade, *Compt. rend.*, *144*, 753 (1907).

33. Rengade, *ibid.*, *144*, 920 (1907).

34. Riesenfeldt and Nottebohm, *Z. anorg. Chem.*, *89*, 405 (1914).

35. Riesenfeldt and Nottebohm, *ibid.*, *90*, 371 (1915).

36. Schechter, Sisler and Kleinberg, *J. Am. Chem. Soc.*, *70*, 267 (1948).

37. Schechter, Thompson and Kleinberg, *ibid.*, *71*, 1816 (1944).

38. Schone, *Ber.*, *6*, 1172 (1873).

39. Schone, *ibid.*, *13*, 803 (1880).

40. Seyb and Kleinberg, *Anal. Chem.*, *23*, 115 (1951).

41. Seyb and Kleinberg, *J. Am. Chem. Soc.*, *73*, 2308 (1951).

42. Stepanck, *Ger. pat.*, *738,196* July 8, (1943). [*C. A.*, *38*, 4105 (1944)].

43. Stephanou, Schechter, Argersinger and Kleinberg, *J. Am. Chem. Soc.*, *71*, 1819 (1949).

44. Strecker and Thienemann, *Ber.*, *53*, 2096 (1920).

45. Templeton and Dauben, *J. Am. Chem. Soc.*, *72*, 2251 (1950).

46. Thompson and Kleinberg, *ibid.*, *73*, 1243 (1951).

47. Traube, *Ber.*, *45*, 2201 (1912).

48. Traube, *ibid.*, *40*, 1670 (1916).

49. Traube and Schulze, *ibid.*, *54B*, 1626 (1921).

50. Wagner, *Ind. Eng. Chem.*, *17*, 972 (1925).

51. Weiss, *Trans. Faraday Soc.*, *31*, 668 (1935).

52. Whaley and Kleinberg, *J. Am. Chem. Soc.*, *73*, 79 (1951).

VIII. ACKNOWLEDGMENTS

The writer wishes to express his sincere appreciation to Dr. J. A. Wilkinson for the suggestion of the problem and for his encouragement and kindly patience during the course of this investigation.

A word of thanks is also given to Dr. Jacob Kleinberg for his words of encouragement and interest in the problem.

The writer is also appreciative of the assistance given him by the Becco Sales Corporation, Buffalo, New York, for making available to him high concentrations of hydrogen peroxide which were not readily available on the market.

A word of appreciation is also given to R.R. Miller of the Naval Research Laboratory for supplying a sample of potassium superoxide which was worked with in the course of this investigation.