INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UNIVERSITY OF CINCINNATI

MAY 19 19 53

I hereby recommend that the thesis prepared under my supervision by FLOYD ROMESBERG

entitled PREPARATIONS, PROPERTIES, AND REACTIONS OF THE ALKALI METAL PEROXIDES, PEROXIDE PEROXYHYDRATES, AND SUPEROXIDES

be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

Approved by:

George L. Cunningham

Form 668—G.S. and T.C.—1M—4-51

PREPARATIONS, PROPERTIES, AND REACTIONS OF THE ALKALI METAL PEROXIDES, PEROXIDE PEROXYHYDRATES, AND SUPEROXIDES

A dissertation submitted to the

Graduate School of Arts and Sciences
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1953

by

Floyd E. Romesberg

B.S. The Pennsylvania State College 1949

M.S. Bucknell University 1950

ACKNOWLEDGEMENTS

Acknowledgement is due to the Army Ordnance Corps. for the funds which made this investigation possible.

The author is sincerely grateful for the valuable suggestions, cooperation and criticism offered by Dr. George L. Cunningham who initiated and directed this research.

TABLE OF CONTENTS

I. INTRODUCTION

Before World War II sodium peroxide and barium peroxide were the only peroxides of the alkali and alkaline earth metals to have extensive uses. Since the war potassium superoxide (KO_2) has found use as a source of oxygen in breathing apparatus for fire fighting and rescue work aboard ship (34).

The Germans attached extraordinary importance to concentrated hydrogen peroxide as a war time chemical for rockets, submarine engines, torpedoes, and starting auxiliaries for airplanes (25,40). Sodium peroxide or hydrogen peroxide, made faintly alkaline with ammonia, is used as a bleaching agent for delicate fibers such as silk and wool where the use of stronger bleaching agents results in deterioration of the fibers (29). Peroxide bleaching, however, is not done on a large scale because of the relatively high cost of the peroxides compared to chlorine.

More recently emphasis has been placed on the use of the alkali metal and alkaline earth metal superoxides for rocket fuels and tracer bullets.

In order to understand more clearly the necessity for more economical methods for the preparation of the alkali and alkaline earth metal peroxides and superoxides as well as hydrogen peroxide it is necessary to consider some of the properties and the methods available for the preparation of these compounds.

A. Sources of Hydrogen Peroxide.

The large scale production of hydrogen peroxide is dependent upon either the action of acids on metal peroxides or the hydrolysis of persulfates. The former method, which is based upon the formation of barium peroxide by the reaction of barium oxide with atmospheric oxygen and its treatment with sulfuric acid, is largely superseded by the latter (26). The latter method is based on the electrolysis of ammonium sulfate to ammonium persulfate in rather complicated electrolytic cells requiring platinum and stainless steel (1,40). The ammonium persulfate is converted to potassium persulfate which is separated from the electrolyte and hydrolyzed with steam to produce 30% to 35% hydrogen peroxide. During the war the Germans developed special large-scale vacuum apparatus to concentrate the hydrogen peroxide made in this fashion to 82% to 85% (1,25).

It is quite clear that hydrogen peroxide produced by the above methods would be quite costly. The first method consumes costly barium oxide which must be converted to peroxide while the second method requires the use of costly and complex apparatus as well as considerable amounts of electricity.

B. Review of Methods for the Preparation of Peroxides and Superoxides of the alkali and Alkaline Earth Metals.

It should be kept in mind that the methods used for these

preparations require the use of the pure metals (BaO_2 is an exception) or hydrogen peroxide.

1. Reaction of the metals and metal oxides with oxygen. It is well known that the alkali metals yield on combustion mainly Li_2O, Na_2O_2, KO_2, RbO_2, and CsO_2. The alkaline earth metals give CaO, SrO, and BaO_2 (27). With strontium some peroxide results, but the yield is low even when the pressure was increased as high as 98 atmospheres at 400° C. (11,16).

Barium peroxide is made commercially by the simple procedure of passing air over barium oxide at elevated temperature (34). Sodium peroxide is also made by this method, however, the starting material is metallic sodium and again rather high temperatures are required (21,23,24,40). Since the oxidation is generally carried out in iron rotary furnaces the product is contaminated with iron salts and is of about a 95% purity. A higher quality product can be obtained by carrying out the oxidation in nickel furnaces (21).

Potassium peroxide is not made conveniently by oxidation of the metal with oxygen or air because it is easily converted to the superoxide in the presence of excess oxygen (15,24). This method, therefore, serves for the preparation of potassium superoxide.

Although sodium peroxide is quite stable to excess oxygen, it may be converted to very pure sodium superoxide by treatment with excess oxygen at high temperature and pressure.

Yields as high as 92% have been obtained (19).

A mixture of sodium peroxide and potassium superoxide can be made by the vapor-phase oxidation of the metallic product of the high temperature reaction between metallic sodium and potassium chloride (17).

2. Direct reaction of metals dissolved in liquid ammonia with oxygen. - Controlled oxidation of potassium metal dissolved in liquid ammonia may be made to yield successively the compounds K_2O_2, K_2O_3, and KO_2 (20,27). A compound corresponding to the formula K_2O_3 can also be prepared by the thermal decomposition of KO_2 (5,20). Actually it was shown that K_2O_3 does not exist but may be regarded as $2KO_2 \cdot K_2O_2$ (14).

When sodium is oxidized in liquid ammonia there is a tendency for sodium amide and nitrite to form especially on prolonged oxidation (35,36). Rapid oxidation produced a mixture of peroxide and superoxide in such a ratio to correspond to the hypothetical compound $NaO_{1.67}$.

Reaction of the alkaline earth metals with oxygen in liquid ammonia appears to be fairly easy (27). Strontium peroxide has been prepared in this way but the yield for calcium was low.

3. Reactions using hydrogen peroxide. - Hydrogen peroxide may interact in two ways. With bases hydrated peroxides may form while with many salts it may enter the crystal

lattice as hydrogen peroxide of crystallization. The latter forms most easily at higher concentration of hydrogen peroxide and lower water concentration. These compounds are designated peroxyhydrates. Some well known peroxyhydrates are $(NH_4)_2SO_4 \cdot H_2O_2$, $K_2CO_3 \cdot 2H_2O_2$, and $Na_2HPO_4 \cdot H_2O_2$. The crystalline compound with urea $CON_2H_4 \cdot H_2O_2$ stabilized by a trace of citric acid has been sold commercially. The crystalline compound $(NH_4)_2SO_4 \cdot H_2O_2$, obtained from 30% hydrogen peroxide and ammonium sulfate, gives concentrated hydrogen peroxide when distilled in vacuum (29).

Lithium peroxide is best prepared by drying in a vacuum desiccator in the cold the precipitate $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ formed by the reaction of 30% hydrogen peroxide on lithium hydroxide in water and ethyl alcohol (7,8).

A crystalline precipitate of $Na_2O_2 \cdot 8H_2O$ may be made from a solution of sodium hydroxide, hydrogen peroxide, and ethyl alcohol (10).

The most convenient method for preparing calcium peroxide is by the action of hydrogen peroxide on a calcium hydroxide slurry. Calcium peroxide crystallizes with two or eight molecules of water and may be dried under vacuum to give a calcium peroxide product of about 60% purity (21,12, 32). Strontium peroxide may be precipitated in an analogous manner with eight, ten, or twelve molecules of water (7,16, 29). Strontium peroxide of high purity may be made from

dehydration of $SrO_2 \cdot 8H_2O$ under vacuum at 0° to 5° C. (16,32).

When a barium hydroxide solution is treated with hydrogen peroxide $BaO_2 \cdot 8H_2O$ may form (32). On the other hand $BaO_2 \cdot H_2O_2$ is prepared in a similar manner using more concentrated hydrogen peroxide (5,39). In the latter case barium peroxide diperoxyhydrate ($BaO_2 \cdot 2H_2O_2$) may also form (28). It is best prepared, however, by the reaction of a soluble barium salt with 30% hydrogen peroxide and ammonia (32).

The diperoxyhydrates of calcium and strontium peroxide have been prepared by treatment of the metal peroxide octahydrate with 30% hydrogen peroxide in the cold (32,39).

Other peroxyhydrates that have been reported are $NaOOH \cdot 0.5H_2O_2$, $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$, $K_2O_2 \cdot 2H_2O_2$ and $K_2O_2 \cdot 4H_2O_2$ (4,38). The diperoxyhydrate of sodium peroxide was prepared on mixing 30% hydrogen peroxide with NaOEt and absolute alcohol, by the action of an ether solution of hydrogen peroxide with sodium, by the reaction of hydrogen peroxide and sodium peroxide in ether solution, and by treating sodium hydroperoxide (NaOOH) with cold ethyl alcohol (4).

The only information available with regard to the stability and properties of the peroxyhydrates of the peroxides is that given by Traube and Schulze (39) on the formation of the superoxides CaO_4 (8.7% in CaO_2) and BaO_4 (8%) from $CaO_2 \cdot 2H_2O_2$ and $BaO_2 \cdot H_2O_2$ formed by the action of 30% hydrogen peroxide on the corresponding hydroxides. It was reported that the

superoxide formation was catalyzed by ultra-violet light.

However, after the completion of this work a paper was published on the mechanism of the decomposition of hydrogen peroxide in potassium peroxide diperoxyhydrate (18). The $K_2O_2 \cdot 2H_2O_2$ was prepared by room-temperature evaporation over concentrated sulfuric acid of solutions containing two moles of hydrogen peroxide and one mole of potassium hydroxide. The material could be kept without undue decomposition at the temperature of solid carbon dioxide.

The above authors made a study of the spontaneous decomposition of the $K_2O_2 \cdot 2H_2O_2$ at 0° C. and reported that the molar ratio of oxygen evolved to superoxide formed remained approximately constant and equal to one up to about 50% conversion. Beyond that point the amount of KO_2 that formed fell off rapidly. When the water that formed was removed by evacuation the conversion was raised to 91%. They showed that the main reaction was:

$$K_2O_2 \cdot 2H_2O_2 \longrightarrow 2KO_2 + H_2O$$

and the secondary reaction was the decomposition of the superoxide by the water according to:

$$2KO_2 + 3H_2O \longrightarrow 2(KOH \cdot H_2O) + 3/2O_2.$$

The main reaction was taken to occur through the passage of an electron from the peroxide ion to the H_2O_2 with rupture to the O-O bond with the formation of the OH radical according to:

$$K_2O_2 \cdot 2H_2O_2 \longrightarrow KO_2 + KOH + H_2O_2 + OH$$

The OH radical then reacted with the H_2O_2 to give HO_2. Greater than 50% conversion was postulated to occur by the reaction of the HO_2 with KOH:

$$KOH + HO_2 \rightleftharpoons KO_2 + H_2O$$

Removal of water under low vacuum was postulated to shift the latter reaction to the right and, therefore, increase the amount of KO_2 formed.

4. Reactions utilizing anthrahydroquinone, hydrazobenzene and similar compounds. - During the war the Germans operated a small plant to prepare hydrogen peroxide by the oxidation with air or gaseous oxygen of anthrahydroquinone or its derivatives in benzene mixed with water. The products formed were anthraquinone and hydrogen peroxide which was removed in the water layer (1). The process was made cyclic by catalytic reduction of the anthraquinone to anthrahydroquinone with hydrogen gas.

By a somewhat similar reaction Manchot and Hersog (22) described the preparation of sodium hydroperoxide (NaOOH) by the reaction between oxygen and a methyl alcohol solution of hydrazobenzene and sodium methylate.

Pfleiderer (30) reacted gaseous oxygen with hydrazobenzene or similar so-called leuco-compounds in the presence of sodium alcoholate in alcohol-water solutions to give precipitates of $Na_2O_2 \cdot 8H_2O$ or NaOOH depending on the amount of water

present.

Pfleiderer (31) also described a process for the preparation of NaOOH by the reaction of oxygen with hydrazobenzene in a solution of ethyl alcohol and benzene containing NaOEt. This process was made cyclic by carrying out the reduction of the azobenzene with sodium amalgam and alcohol.

In the above processes sodium peroxide is not recovered as such but as the sodium hydroperoxide or as the sodium hydroperoxide monohydrate ($NaOOH \cdot H_2O$). This is due, no doubt, to the fact that sodium peroxide reacts with alcohol to give sodium alcoholate and the hydroperoxide (3).

This difficulty was overcome by Cunningham (3) by affecting the oxidation of hydrazobenzene with oxygen or oxygen containing gases such as air in the presence of sodium methylate in benzene and methyl alcohol with the concentration of the alcohol reduced to such an extent as to depress the formation of the hydroperoxide.

The preparation of NaOOH also was described in this work and the process was made cyclic by reduction of the azobenzene with sodium amalgam and methyl alcohol. The disadvantage of producing sodium peroxide by this method was that the reduction step was slow when the alcohol concentration was reduced and the sodium peroxide product was not sufficiently stable.

Other intermediates that are known to react with oxygen

to produce peroxides in the above manner in addition to hydrazobenzene and anthrahydroquinone include the hydrazotoluenes, particularly p-hydrazotoluene, p-amino hydrazobenzene, p-ethyl hydrazotoluene, p-ethyl hydrazobenzene, the hydrazotriazoles, phenylhydrazone, di-hydrophenanthrenechinone, and the amino substituted aromatic hydrazo compounds such as the amino substituted hydrazobenzenes, toluenes, xylenes and naphthalenes, and the corresponding azo compounds (3).

C. Purpose of Study.

The purpose of this investigation was to study the cyclic process involving: (1) The reduction with alkali and alkaline earth metal amalgams and alcohols containing less than five carbon atoms per molecule of auto-oxidizable compounds such as azobenzene in benzene or similar solvents and the alcohol to form the leuco compound such as hydrazobenzene and the metal alcoholate in particular sodium methylate. (2) Oxidation of the leuco compound with gaseous oxygen or purified air in the presence of the alcoholates including the alcoholates of calcium, lithium, sodium, and potassium. In particular to carry out the oxidation with the alcoholates present in reduced amounts with respect to the leuco compound.

The second objective of this work was to study the stability, properties and reactions of the various metal peroxide compounds produced in the oxidation procedure.

The third objective of this work was to determine if superoxides of the alkali and alkaline earth metals could be prepared by some modification of the above process.

II. EXPERIMENTAL

A. Materials.

The materials chosen to carry out this work consisted mainly of benzene, methyl alcohol, absolute ethyl alcohol, azobenzene, anhydrous calcium chloride, sodium hydroxide, and mercury.

A commercial grade of thiophene-free benzene and synthetic methyl alcohol was used in all cases. This means that any process developed would not rely on specially purified solvents.

The azobenzene (Eastman Kodak) used was a practical-grade product of 95% purity and was available at a much lower cost than the purified material. After passing the azobenzene through the cyclic process one time it became very pure.

The mercury used was washed several times through dilute nitric acid and then distilled under vacuum in a conventional manner. For experimental purposes a reagent grade of sodium hydroxide was used.

The materials necessary for analysis of peroxides and superoxides consisted primarily of glacial acetic acid, diethylphthalate (Eastman Kodak), potassium iodide, starch and phenolphthalein indicators, ammonium molybdate, and standard solutions of hydrochloric acid, sodium hydroxide, and sodium thiosulfate.

B. Apparatus and Procedure.

The apparatus necessary to carry out the first phase of this investigation consisted mainly of an electrolytic cell, a reduction vessel, and an oxidation vessel.

The electrolytic cell was constructed such that it is very similar to one type of industrial mercury cathode cell in that it represents a section of a commercial cell operating on sodium chloride brine. The cell, constructed in this way, produced sodium amalgam continuously and of uniform strength by the electrolysis of a sodium hydroxide solution between a mercury cathode and a nickel anode.

A diagram of the cell and the reduction assembly is shown in Figure 1. A view of the same is shown in Figure 2. The cell was constructed as follows: Five pieces of mild steel were screwed together to make a rectangular box. Two thin sheets of polystyrene, supported by the two steel sides, served to electrically insulate the steel sides from the anode and caustic solution, and served to prevent undue corrosion of the steel by the alkaline solution. Two hard rubber (Ebonite) sheets were fitted into grooves on the metal bottom in such a manner to allow mercury to flow over the steel bottom while the caustic solution was retained in the central compartment perfectly insulated from the steel. Mercury entered the cell at one end, passed under the first rubber partition, over the cell bottom and out the other end of the cell during which time it served as the cathode.

FIGURE 1

ELECTROLYTIC CELL AND REDUCTION ASSEMBLY

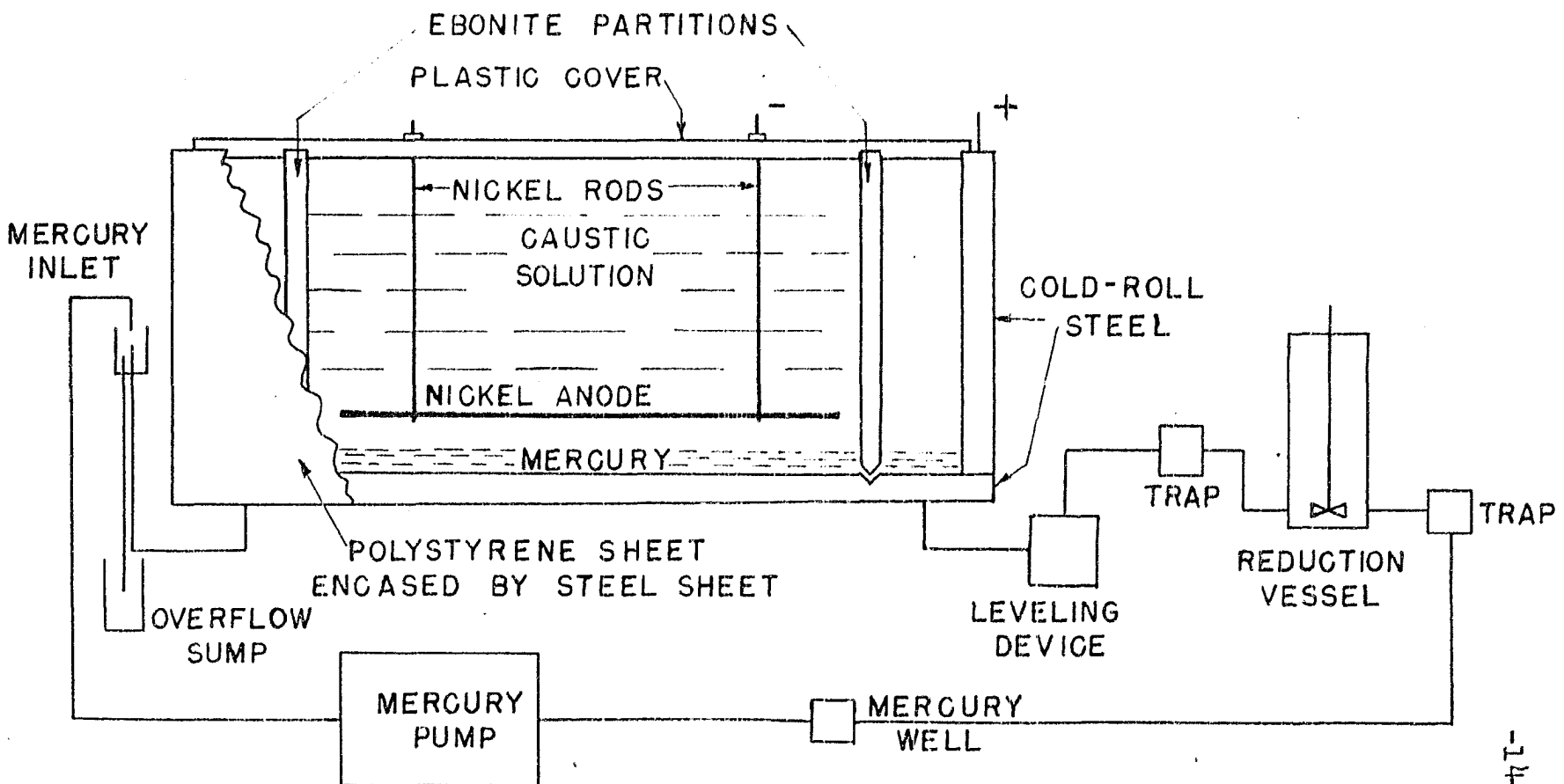
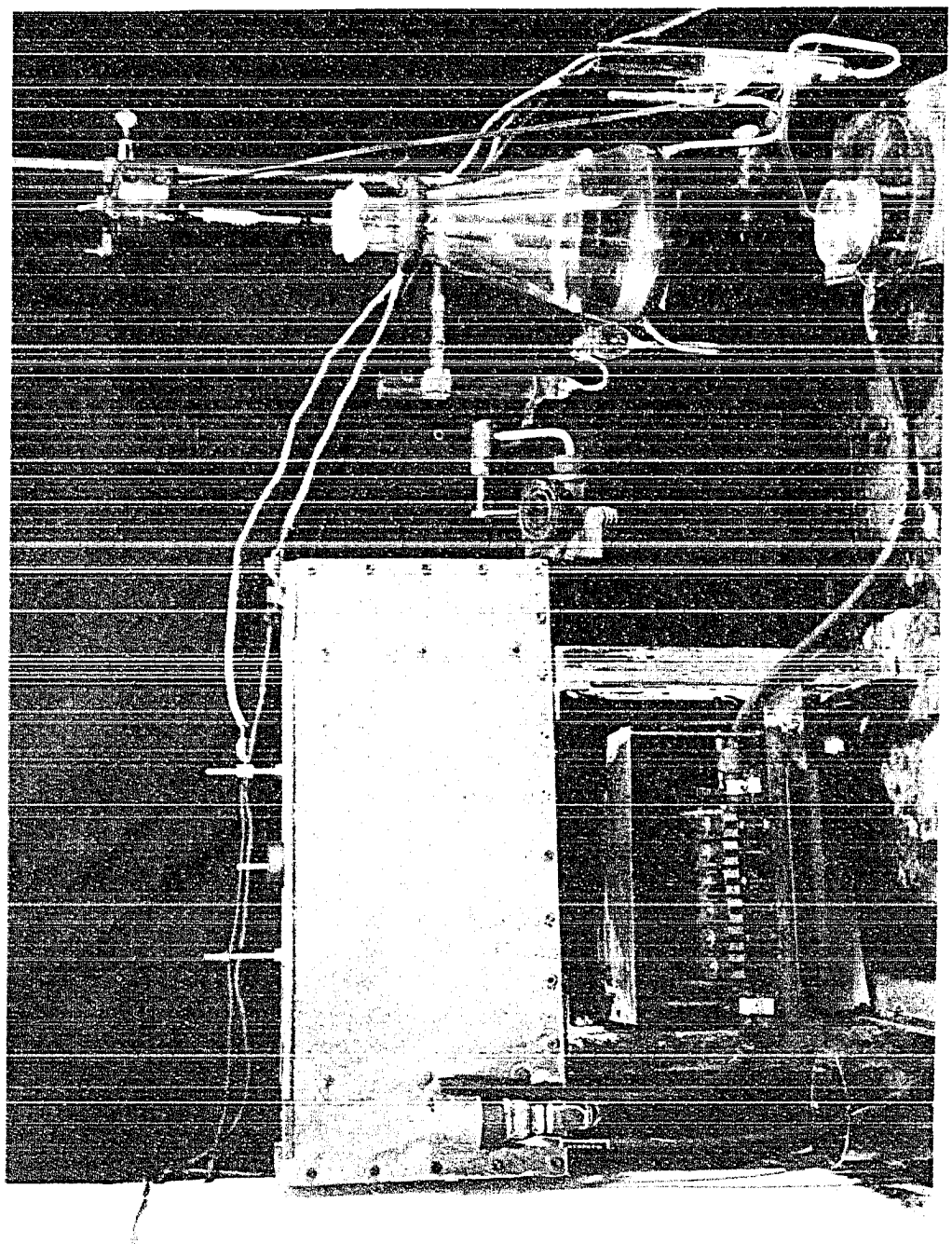


FIGURE 2

VIEW OF CELL AND REDUCTION ASSEMBLY



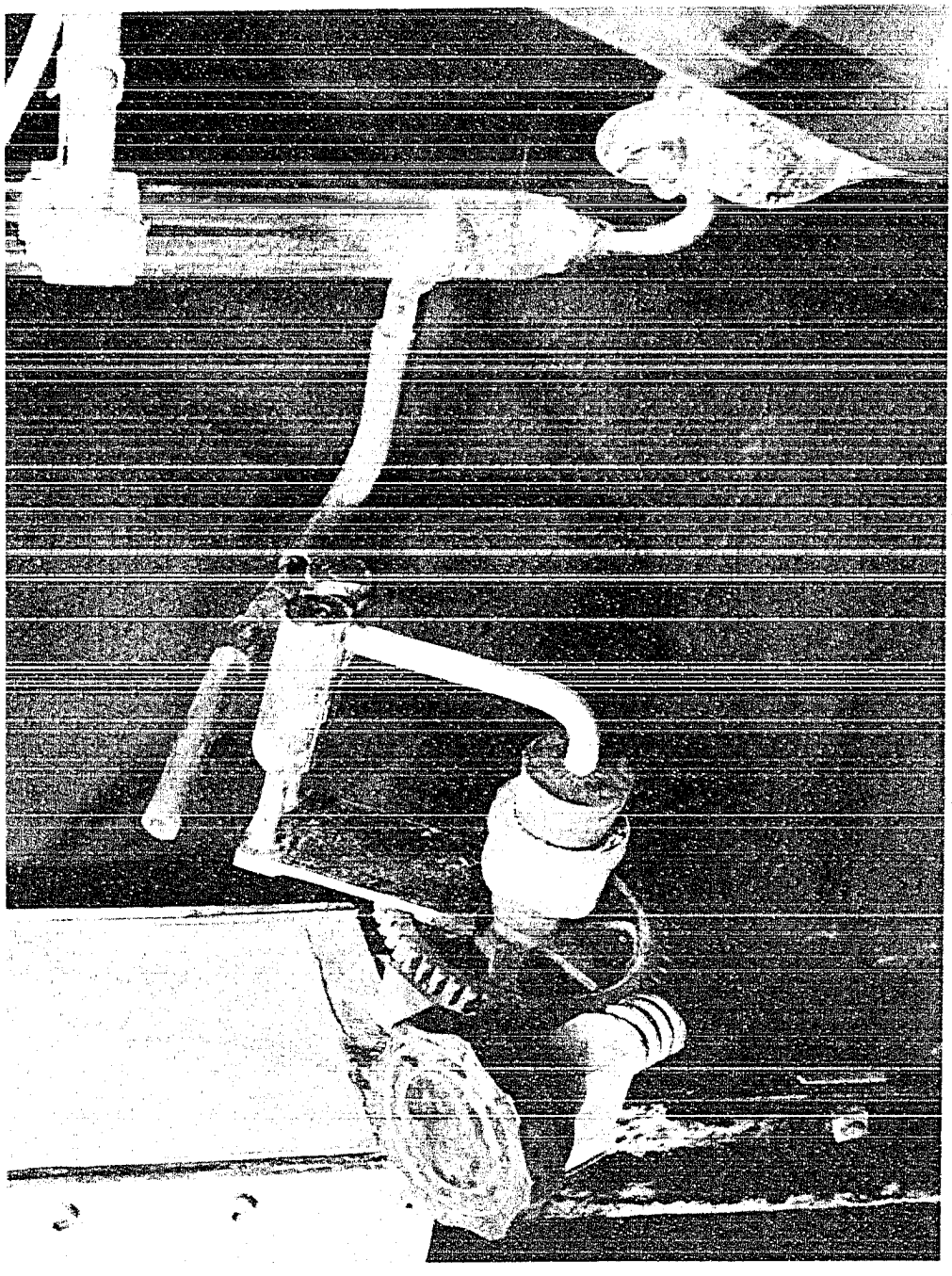
Neoprene gaskets were used to seal the rubber partitions and the steel bottom and ends with the styrene sheets over which the steel sides were screwed.

Two nickel rods, supported on a plastic lid, were screwed into a sheet of nickel which dipped into the caustic solution and served as the anode. The rods were threaded to allow adjustment of the distance between the anode and mercury cathode. The nickel sheet was about one-quarter inch thick and was about 44 square inches in area. Holes were drilled in the sheet to allow the oxygen to escape. The plastic lid consisted of two sheets of polystyrene bolted over a sheet of neoprene to make a tight seal to prevent the entrance of air which in contact with the caustic solution would cause carbonate formation. Two small covers were made in a similar fashion to cover the end compartments.

The mercury level inside the cell and the mercury flow were regulated by a leveling device shown in Figure 3. On the back of a knob mounted on a stationary support, there was located a worm gear which when turned rotated a wheel to which was attached a Pyrex glass tubing bent at a right angle and inserted in a rubber stopper placed in the exit line. In this manner the tubing could be rotated accurately to start and stop the flow of mercury and to regulate the rate of mercury flow. The tubing had an air vent at its highest point to prevent siphoning action. This allowed the mercury level inside the cell to be maintained.

FIGURE 3

VIEW OF LEVELING DEVICE



The mercury was allowed to flow out of the cell by means of the leveling device and through a small trap containing methyl alcohol to remove traces of water and dirt. From this trap the mercury passed through the reduction vessel. See Figure 4 and Figure 5. This vessel consisted of a 500 cc. or a one-liter Erlenmeyer flask with glass tubing sealed at two edges of the bottom to form an inlet and exit for the mercury. Both pieces of tubing were bent in the form of a U to allow the mercury to support the solution inside and at the same time to allow a thin layer of mercury to pass over the bottom of the flask. The outlet tube had an air vent at the highest point to prevent siphoning action. The mercury passed from this outlet tube through a second methyl alcohol trap and into a mercury well leading to a pump. A special mercury pump was built to lift the mercury back into the cell.

The mercury pump operated in the following manner: A series of cam-operated "fingers" pressed in sequence against a flexible tubing and imparted positive unidirectional movement to the mercury. The cycle of the fingers was timed so that the tubing was always closed at some point to eliminate the need of valves. This type of pump has the obvious advantage of eliminating contact of the mercury with any metals or oils.

The source of power, necessary for the electrolysis, was

FIGURE 4

REDUCTION VESSEL

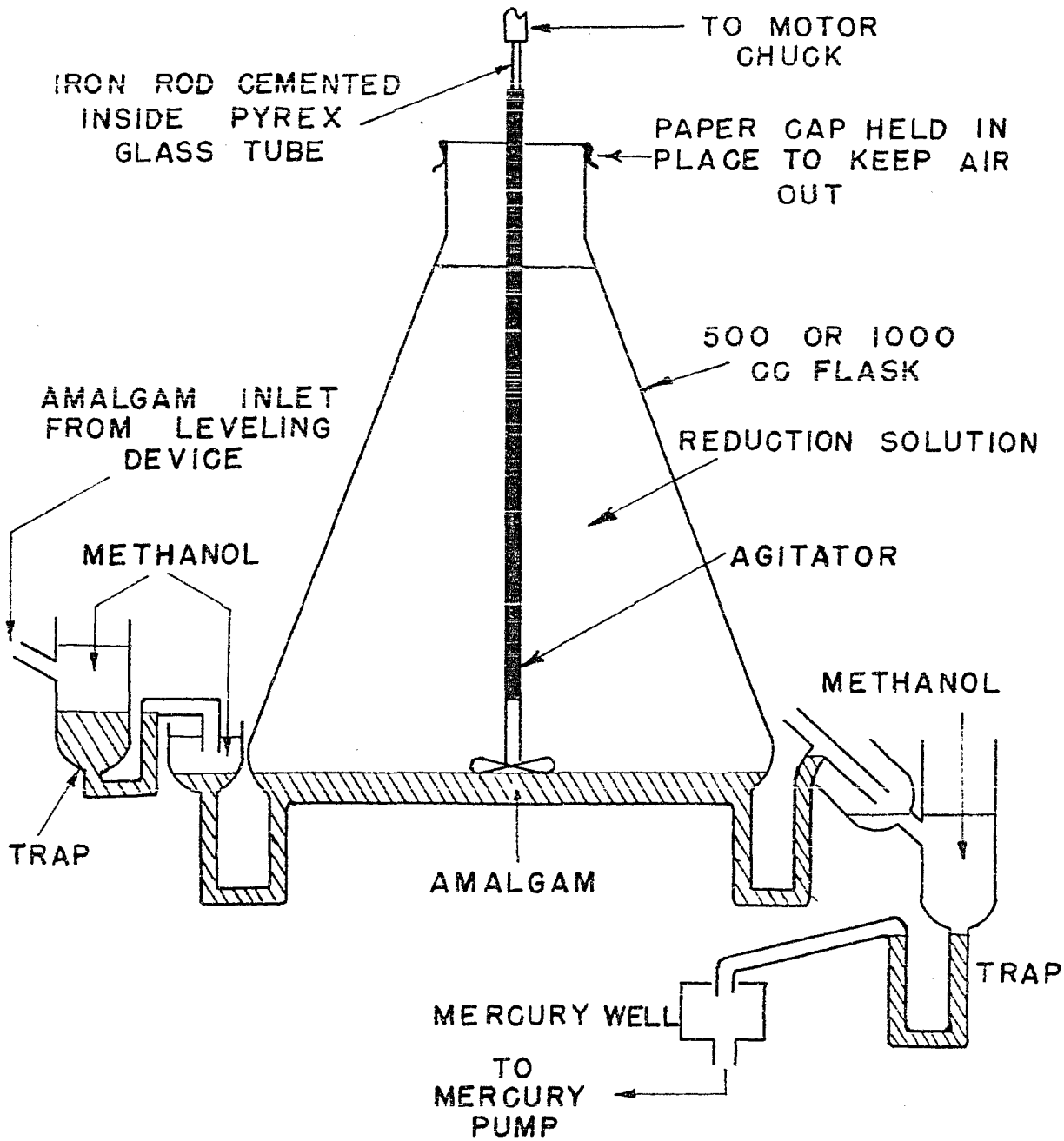
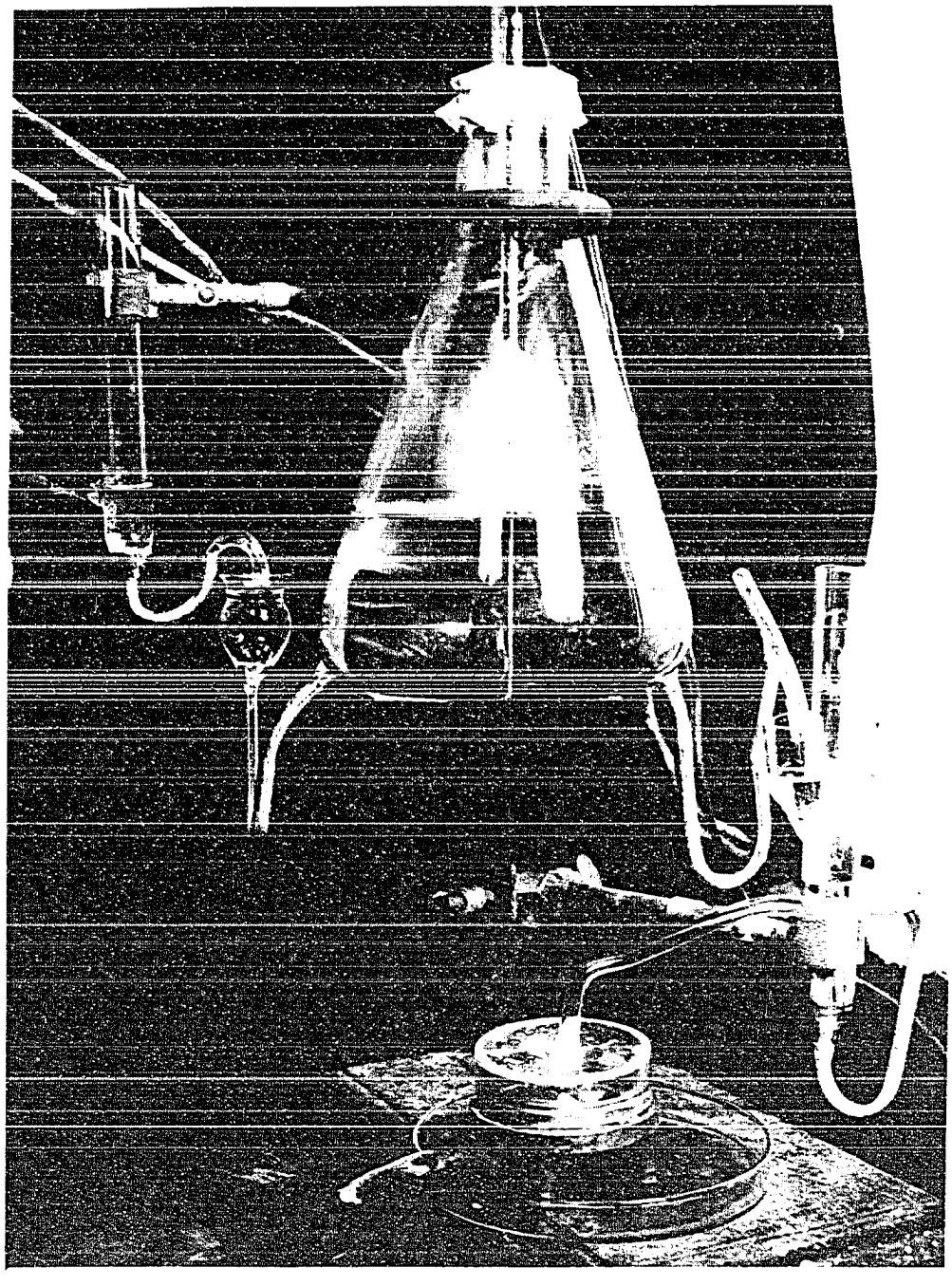


FIGURE 5

VIEW OF REDUCTION VESSEL



125 volts A.C. which was passed through a transformer and selenium bridge rectifier to produce a voltage of from 0 to 5 volts D.C. The nickel anode was adjusted in an 18% caustic solution to give a current of from 0 to 50 amperes. In operation the caustic concentration was maintained between 13% and 18%. The circuit for the power supply is shown in Figure 6.

In operating the apparatus the mercury was allowed to flow from the cell and at first to by-pass the first trap and the reduction vessel. The height of the exit tube from the leveling device was adjusted to give a steady flow of mercury. A definite current was passed through the cell until the sodium content in the amalgam reached the desired value. At this time the amalgam was passed through the reduction vessel and the reduction of the azobenzene was carried out until the bright cherry-red color of the azobenzene was converted to the straw-yellow color of the hydrazobenzene solution.

The reduced solution was removed from the reduction vessel by means of suction applied on a large flask to which a tube was attached and dipped into the solution to be removed.

After the reduced solution was prepared for oxidation it was placed in an oxidation apparatus, a diagram of which is shown in Figure 7. A view of the oxidizer is shown in Figure 8. This oxidizer consisted, for example, of a

FIGURE 6

D.C. POWER SUPPLY

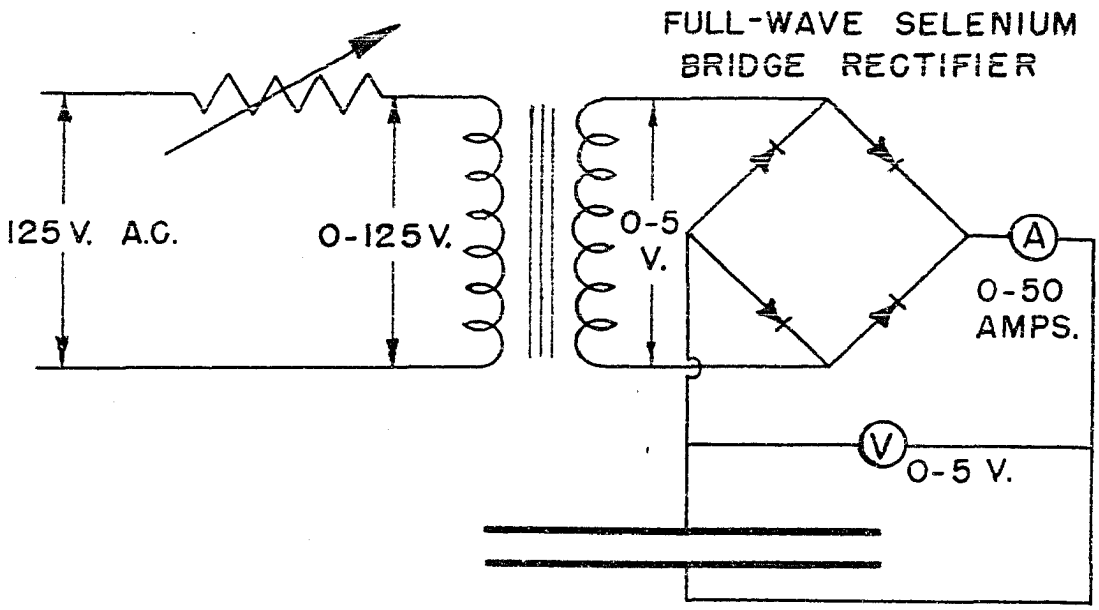


FIGURE 7

OXIDATION VESSEL

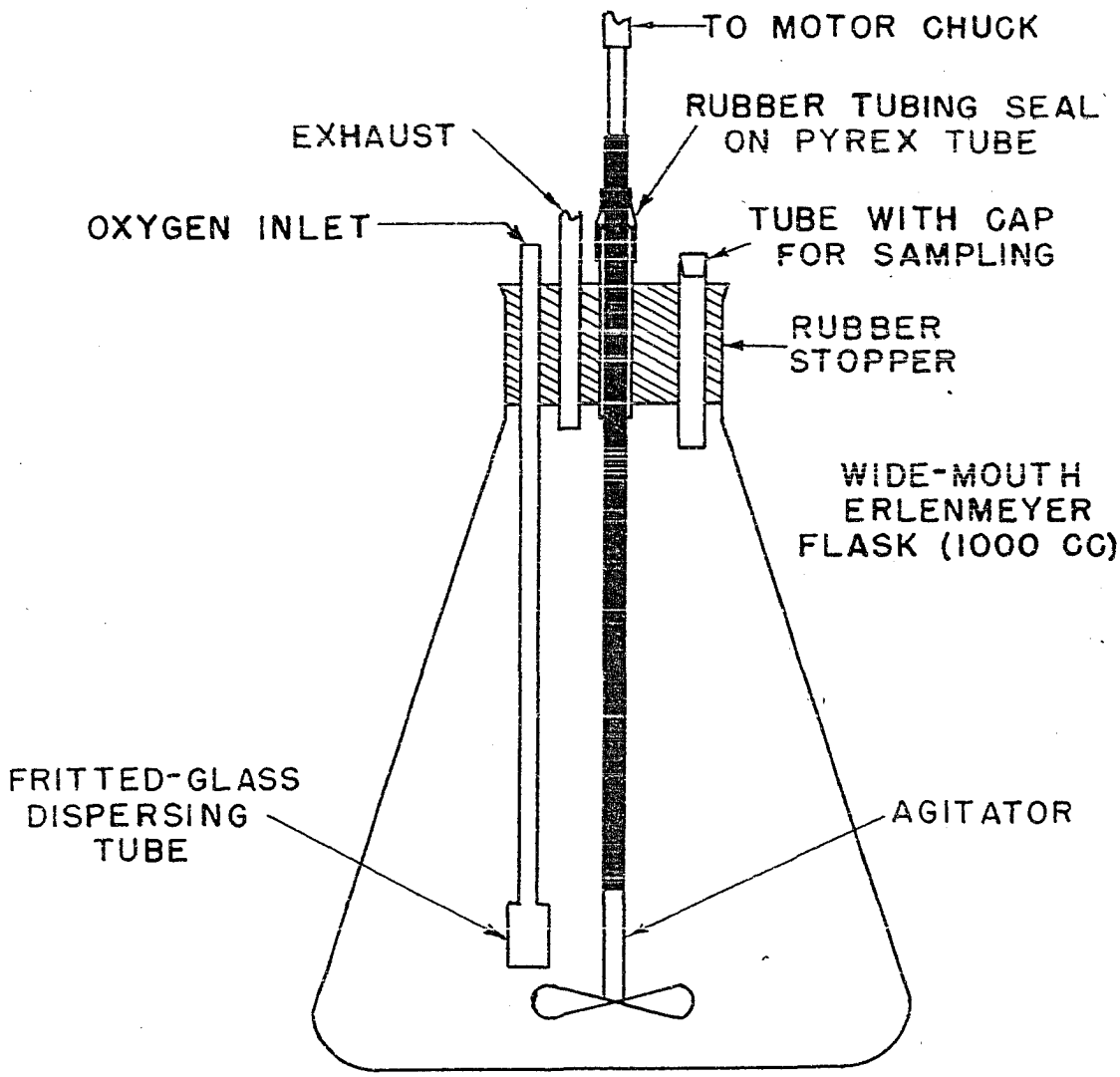
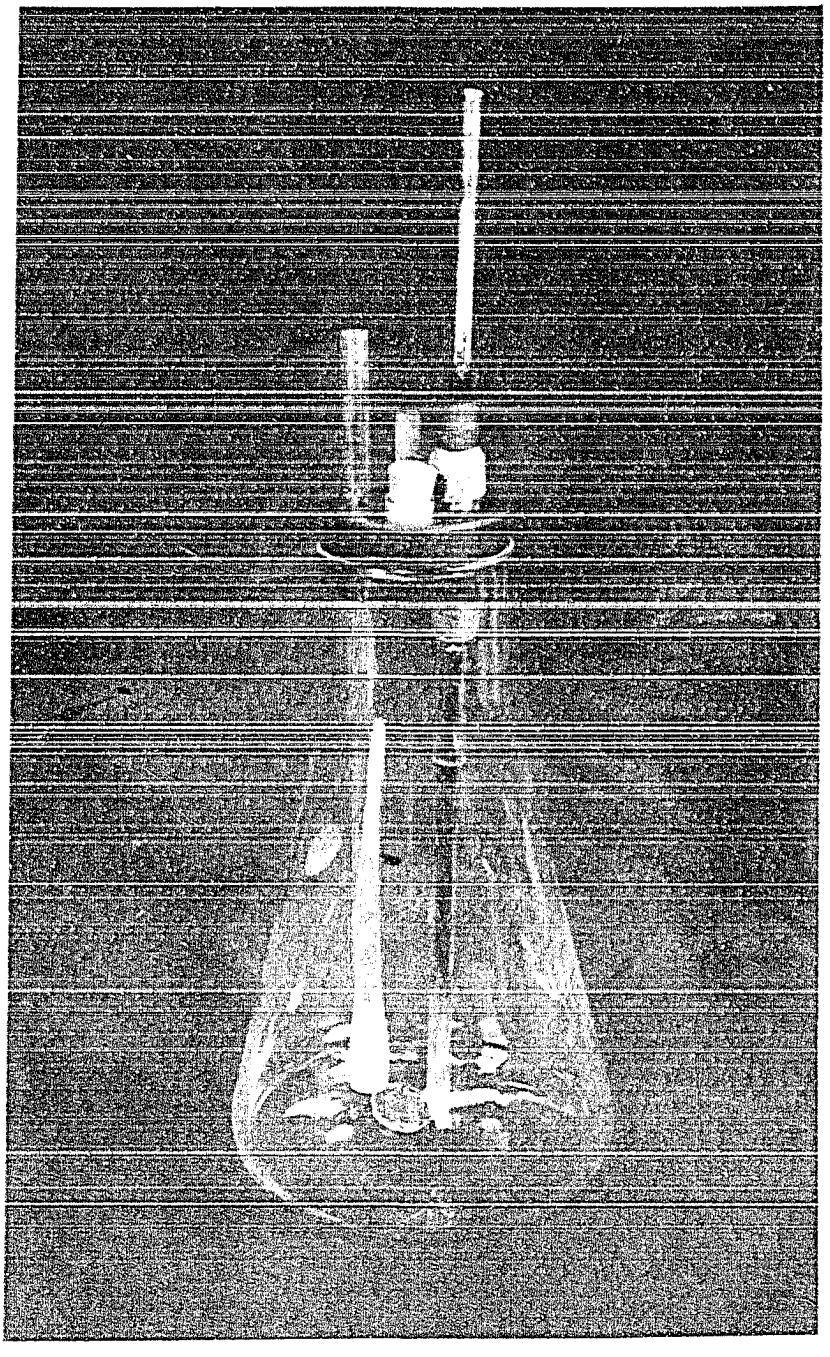


FIGURE 8

VIEW OF OXIDIZER



1000 cc. wide-mouth Erlenmeyer flask fitted with a rubber stopper through which passed a fritted-glass oxygen dispersing tube, a tube and cap through which samples were removed, an exhaust tube, and a stirring rod passing through a glass tube with a rubber-tube seal. During oxidation the vessel was immersed in a steel beaker and the apparatus placed behind a safety screen.

The procedures used to prepare the various solutions for oxidation are discussed in detail with reference to the specific preparations.

After completion of the oxidation and removal of the precipitates by filtration, the azobenzene was recovered for re-use by extracting the alkali and alcohol with water and then evaporating the benzene with a current of air.

When oxidation of the hydrazobenzene was incomplete further air oxidation was made in the benzene and alcohol in the presence of sodium hydroxide before recovering the azobenzene. When 95% practical grade azobenzene was used, the reduced solution was strongly discolored. Upon oxidation the dark-colored material was slightly more difficult to wash from the precipitates than the azobenzene; however, the above extraction operation removed essentially all of this material from the benzene solution and in this manner the azobenzene was purified.

The second phase of this investigation involved the conversion of sodium peroxide diperoxyhydrate ($Na_2O_2 \cdot 2H_2O_2$) to

sodium superoxide (NaO_2) and the corresponding conversion of the potassium compounds. These reactions produced water which needed to be removed from the reaction site to prevent its decomposition of the superoxide formed. This work involved the use of vacuum pumps, vacuum desiccators containing barium oxide, and some miscellaneous apparatus designed to remove the water by making use of a vacuum or a stream of oxygen or ammonia gas.

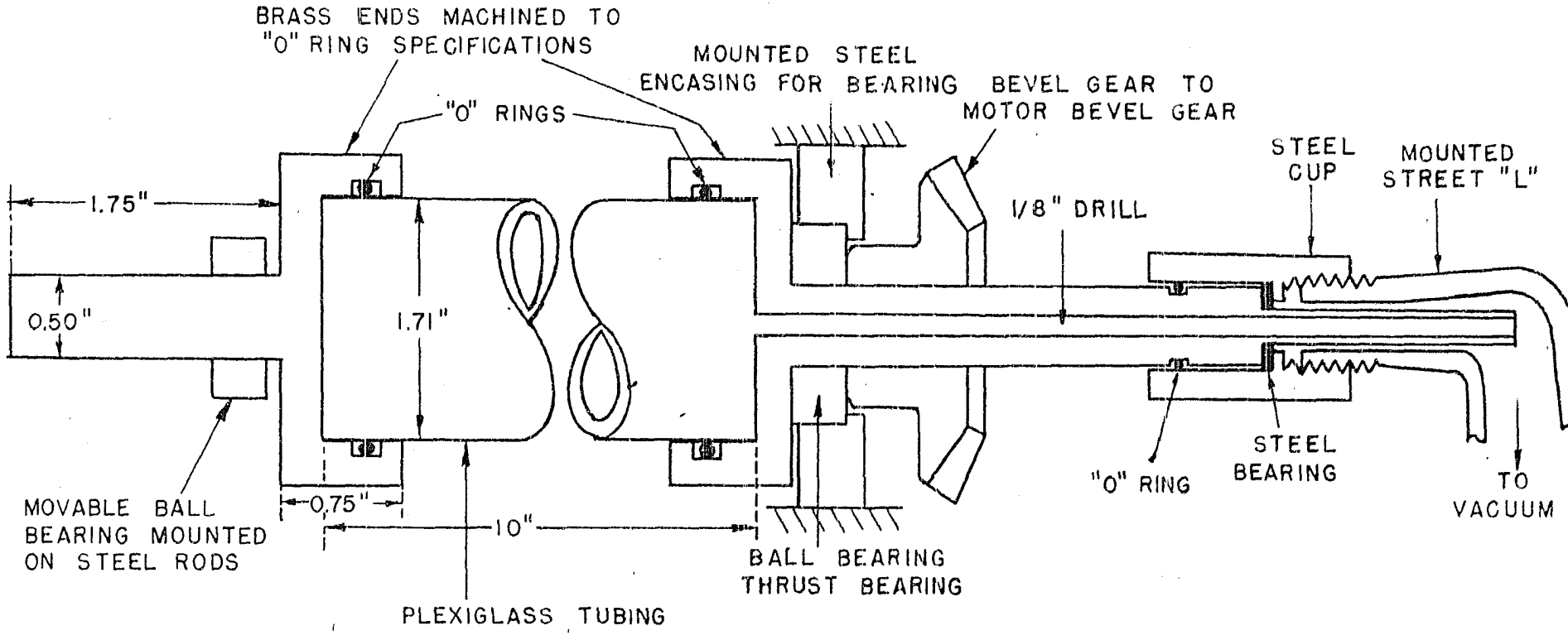
This latter work also made use of ultra-violet light which was obtained from a mercury-arc lamp (250 volts), a General Electric R-S sunlamp, or a 8 volt Germicidal lamp.

One apparatus that was constructed to carry out preliminary investigations on the conversion of $Na_2O_2 \cdot 2H_2O_2$ to NaO_2 is shown in Figure 9. This apparatus was designed so that a sample of powder could be mixed inside a tube, through which the transmission of ultra-violet light was high, and so that the tube could be rotated to give the mixing while a vacuum was maintained inside the tube.

Two brass fittings were machined according to "O" ring specifications so that the tube when pressed inside the fittings gave a vacuum seal. The tube was caused to rotate at about 16 r.p.m. by a motor geared to the one brass fitting by means of beveled gears. A moving vacuum seal was made at one end of the brass fitting by means of an "O" ring so that the brass fitting rotated inside a steel cup attached to a vacuum line. The brass end passed deep into the vacuum line

FIGURE 9

ROTATING VACUUM EXPOSURE TUBE



to prevent the small amount of powder that passed into the line from coming into contact with the moving parts. This powder was removed in glass-wool traps and a dry-ice trap containing frozen water to prevent its entering the vacuum pump.

Both brass fittings were mounted in ball bearings to give alignment and ease of turning. The brass fitting connected to the line was stationary while the second fitting was held in place by a movable bearing so that it could be moved to the left to remove the tube.

In operation both brass fittings and the tube rotated.

C. Preliminary Work on the Preparation of Calcium Peroxide.

The object of this work was to replace the sodium methylate in the oxidizing solution with calcium methylate by reacting the sodium methylate with calcium chloride, and to carry out the oxidation of hydrazobenzene in the presence of the calcium methylate to prepare anhydrous calcium peroxide.

A reduction solution consisting of 80 grams of purified azobenzene dissolved in 600 cc. of benzene and 400 cc. of methanol was used in this and subsequent work and is designated standard reduction solution. The reduction operation was carried out in the reduction vessel as previously described to convert the azobenzene solution to a hydrazobenzene and sodium methylate solution in the benzene and

methanol. With an initial amalgam concentration of about 0.2% sodium, 1000 cc. of the standard reduction solution required about one hour for complete reduction to the straw-colored hydrazobenzene solution.

1. Reaction of calcium chloride with sodium methylate in benzene and methanol containing hydrazobenzene. - After completion of the reduction operation the solution was removed from the reduction vessel and the concentration of the sodium methylate was determined by titrating with standard hydrochloric acid using phenolphthalein as an indicator. About 80 cc. of 0.1 N acid were required for 10 cc. of the solution. For each 10 cc. of the reduced solution the amount of 96% calcium chloride added was determined by multiplying the volume of the acid used by 0.00573.

At first the anhydrous calcium chloride was dissolved in methanol (about 10 grams to 100 cc. of solution) and this solution added slowly with stirring to the sodium methylate solution. A precipitate of sodium chloride and gelatinous calcium methylate resulted.

The solubility of the calcium methylate was found to be about 0.02 grams $Ca(OCH_3)_2$ per 100 grams of methanol and essentially zero in benzene. The concentration of the calcium methylate was determined by adding a large excess of hydrochloric acid and back titrating with standard base.

More conveniently the calcium chloride was added directly in the solid form to the reduced solution. When the ben-

zene concentration in the solvent was greater than 60% by volume the calcium chloride did not readily go into solution and, therefore, did not react readily with the sodium methylate. For the standard solution used precipitation took place within about 15 minutes.

2. Oxidation with gaseous oxygen of hydrazobenzene in the presence of insoluble calcium methylate in benzene and methyl alcohol. - After completing the reduction step and precipitation of calcium methylate and sodium chloride, the resulting slurry then was placed in the oxidizer and oxygen was passed through the gas-dispersing tube into the rapidly stirred mixture.

The object of this oxidation step was to produce anhydrous calcium peroxide in the presence of sodium chloride by the reaction of the hydrogen peroxide, produced in the oxidation step, with the calcium methylate.

After oxidizing for various lengths of time, two 25 cc. samples of the slurry were removed by means of a pipette and filtered. The precipitate was washed with methanol and benzene and the filtrate returned to the oxidizer. The slurry was rapidly stirred to insure uniform sampling. The calcium peroxide content of the precipitate was determined by liberating iodine with dilute acetic acid and 10% potassium iodide solution using ammonium molybdate as a catalyst. The total alkali present in the precipitate was determined by adding excess standard hydrochloric acid and back titrat-

ing with standard base. The ratio of the equivalents of peroxide to the total equivalents of alkali was calculated at various times. The ratio (designated Z) was invariably found to be of the order of 0.58 after from two to three hours of oxidation. This showed that 58% of the calcium methylate was converted to calcium peroxide. Based on the original sodium methylate formed on reduction, therefore, the yield was 58%.

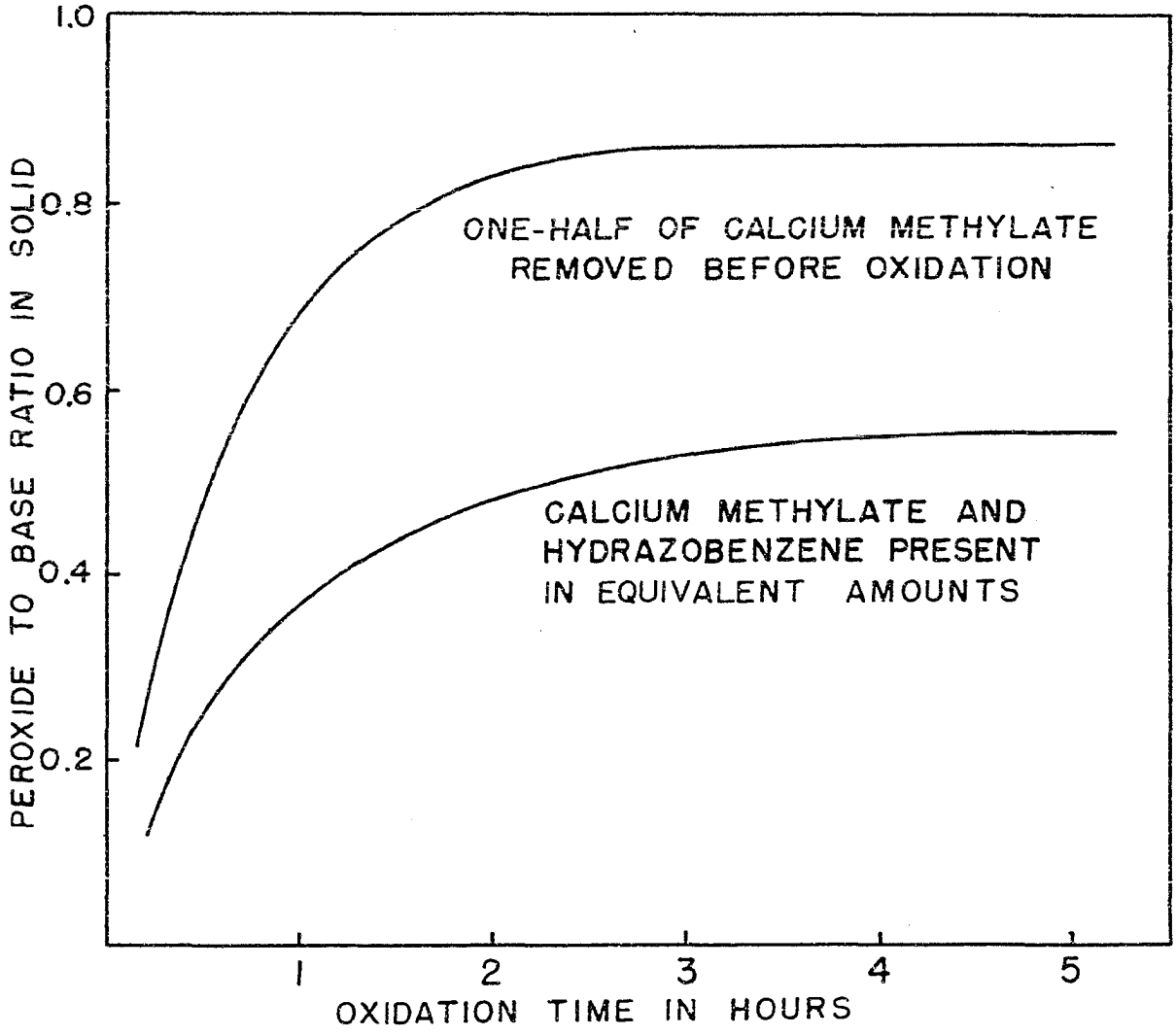
To decrease the calcium methylate content of the product, the above-mentioned reduction and precipitation of calcium methylate and sodium chloride were repeated. Then one-half of the slurry was filtered, washed with methyl alcohol and benzene, and added to the unfiltered portion of the slurry. The ratio of peroxide to total base in the precipitate was determined as described above at various time intervals. These results are shown in Figure 10. In the latter case the peroxide to base ratio was increased to only about 0.86. This showed that 86% of the calcium methylate was converted to calcium peroxide; however, the overall yield was only 43%.

To increase the alkalinity of the solution insufficient calcium chloride was added to the reduced solution before the oxidation. In one experiment about 10% of the sodium methylate was left in the solution. The results were not much better than those obtained when all of the sodium methylate was precipitated.

FIGURE 10

RATE OF FORMATION OF CALCIUM PEROXIDE

OXIDATION OF HYDRAZOBENZENE IN BENZENE AND METHANOL IN THE PRESENCE OF INSOLUBLE CALCIUM METHYLATE AT 25 °C



Although calcium ethylate was shown to be much more soluble than calcium methylate, substitution of ethyl alcohol in the reduction solution gave nearly identical results as obtained above with methanol.

3. Miscellaneous experiments on the preparation of calcium peroxide. - Pure calcium ethylate was prepared by adding calcium metal to absolute ethyl alcohol and refluxing to initiate the reaction. Then the solution was refluxed for about two hours. Cooling was necessary to prevent too rapid boiling of the alcohol in some cases. The boiling solution was filtered and the filtrate allowed to cool to precipitate $Ca(OEt)_2 \cdot 2EtOH$.

The very pure calcium ethylate precipitate was added to a solution of benzene and methyl alcohol containing hydrogen peroxide and azobenzene. Nearly all of the peroxide disappeared from the solution while a negligible amount was found in the precipitate. The hydrogen peroxide solution was prepared by oxidizing a hydrazobenzene solution containing a small amount of sodium methylate, the remainder of the methylate being removed by adding calcium chloride followed by filtration of the calcium methylate and sodium chloride.

The calcium ethylate precipitate, with a solubility at room temperature of about 2.0 grams per 100 cc. of ethyl alcohol, also was added to a solution of hydrogen peroxide in absolute ethyl alcohol. The ethyl alcohol solution of hydrogen peroxide was prepared by the interaction of hydrogen

chloride, formed from hydrochloric acid and sulfuric acid, with $Na_2O_2 \cdot 2H_2O_2$, the preparation of which is described in a later section. The calcium ethylate precipitate, which was very difficult to filter, contained 17.4% CaO_2.

In the above mentioned work it was noted that calcium ethylate like sodium ethylate rapidly oxidized to form a dark-yellow resinous material. A suitable anti-oxidant for calcium ethylate and other alcoholates was found to be ethylene diamine dihydrochloride. After several months tubes of calcium ethylate containing not over 0.1% by weight of this material were as clear as they were when first prepared. Without a stabilizer, calcium ethylate or its solutions darkened in about one day.

An investigation was made to prepare a more soluble calcium alcoholate by the reaction of calcium chloride with the sodium alcoholates. Calcium ethylate was the most soluble alcoholate prepared of the alcohols ranging from methyl alcohol to hexanol. However, when calcium methylate was heated on a steam bath in a solution of methyl alcohol and glycerol, a considerable amount of calcium went into solution. When this solution was added to a hydrazobenzene solution followed by oxidation no precipitation resulted.

An attempt was made to prepare calcium peroxide by oxidizing hydrazobenzene in benzene and methyl alcohol with calcium oxide and with calcium hydroxide held in suspension with vigorous stirring. There resulted a negligible amount

of peroxide in the solid phase as well as in the solution.

A further attempt was made to prepare calcium peroxide by the interaction of sodium hydroperoxide (NaOOH) with calcium ethylate in ethyl alcohol. Considerable decomposition resulted and the precipitate had a peroxide to base ratio of only 0.65.

During the preparation of sodium hydroperoxide by the reaction of oxygen with hydrazobenzene in the presence of essentially an equivalent amount of sodium methylate in benzene and methyl alcohol, it was noted that a considerable amount of heat was evolved. To increase the stability of the precipitate and lessen danger of any possible violent decomposition or interaction with the solvents, ice was placed in the steel beaker in which the oxidation vessel was immersed in order to cool the solution. Operating in this manner a precipitate was formed that contained a peroxide to base ratio of about three. This value corresponded to the compound sodium peroxide diperoxyhydrate ($Na_2O_2 \cdot 2H_2O_2$). This result led to the study of the preparation of the peroxyhydrates of the alkali metal peroxides. The work is covered in detail in the following section.

D. Methods of Removing Sodium Methylate from the Reduced Solution.

When one mole of azobenzene was reduced with sodium amalgam and methyl alcohol, two moles of sodium methylate were produced according to reaction (1).

$$Ph_2N_2 + 2\ CH_3OH + 2\ NaHg_x \longrightarrow Ph_2N_2H_2 + 2\ CH_3ONa + 2x\ Hg \quad (1)$$

Therefore, in a cyclic process to produce peroxide compounds, like $Na_2O_2 \cdot 2H_2O_2$, containing a ratio of peroxide equivalents to base equivalents higher than one it was necessary to remove part of the sodium methylate produced during the reduction step. The following methods of removing all or any desired fraction of the sodium methylate are essential in preparing the reduced solutions for oxidation for the various preparations such as the preparation of $Na_2O_2 \cdot 2H_2O_2$.

1. Anhydrous calcium chloride method. - In the work directed toward the preparation of calcium peroxide it was found that the solubility of calcium methylate was very low in the benzene-methyl alcohol solvent. Since sodium chloride is also practically insoluble, solid calcium chloride or a methyl alcohol solution of the anhydrous calcium chloride was added to the hydrazobenzene solution followed by filtration to remove all or any desired fraction of the sodium methylate.

Since the calcium methylate precipitated in the above procedure was in the form of very fine crystals, the filtra-

tion step was found to be quite difficult. In addition the filter cake of sodium chloride and calcium methylate adsorbed hydrazobenzene quite strongly. After the filter cake was washed several times with methyl alcohol and benzene, the sodium chloride was extracted with liquid ammonia to give a product of almost pure calcium methylate.

2. Water extraction of the sodium methylate and methyl alcohol. - A very simple method that was used to remove all of the sodium methylate was by the addition of large amounts of distilled water. In this manner the methyl alcohol and sodium methylate were removed in the water phase. The benzene layer, containing all of the hydrazobenzene, was washed with water and dried with calcium chloride.

This method was of use where it was desirable to remove all of the alkali. For example, to study the oxidation in the presence of potassium methylate, the solution was prepared for oxidation by extracting with water and then adding a methyl alcohol solution of potassium methylate prepared by the reaction of potassium metal with methyl alcohol.

Any desired fraction of the sodium methylate was removed by extracting the desired fraction of the solution and then adding the resulting benzene layer to the remainder of the reduced solution.

3. Phase separation method. Recovery of sodium methylate. - When sodium amalgam and methyl alcohol were used to reduce azobenzene in the alcohol and benzene two liquid layers formed after the alkali content reached a certain value depending on the temperature of the solution. The separation was more pronounced at lower temperatures. During the reduction the heat evolved raised the temperature of the solution to the boiling point so that after the reduction the solution was at or near boiling. When the standard solution was used just sufficient sodium methylate formed to cause two phases to separate while hot.

One liquid layer contained the greater portion of the hydrazobenzene dissolved mainly in benzene while the other layer contained almost all of the sodium methylate dissolved in a solution of about equal volumes of methanol and benzene. The results taken from two preparations of $Na_2O_2 \cdot 2H_2O_2$ are tabulated in Table I to show the distribution of the sodium methylate in the standard solution after reduction. The sodium methylate content was determined by titrating a 10 cc. sample of each phase. In Run No. 55 the benzene and alcohol concentrations were determined by water extraction of an aliquot volume. The volume remaining after extraction was assumed benzene, while the decrease in volume was assumed methanol.

TABLE I

Distribution of $NaOCH_3$ in the Two Liquid Phases in Reduced Solution

Run No.	More Dense Phase			Less Dense Phase		
	Benzene cc.	Methanol cc.	$NaOCH_3$ meq.	Benzene cc.	Methanol cc.	$NaOCH_3$ meq.
54	660 total		102	1090 total		1460
55	940	192	172	970	840	1935

For Run No. 54, the less dense phase consisted of 62% of the total volume and contained 93.5% of the total alkali. The corresponding distributions for Run No. 55 were 60% and 92%.

The procedure used to remove sodium methylate to prepare the reduced solutions for oxidation was to separate the two phases that formed after reduction. In this manner the benzene layer contained about 8% of the alkali. To increase the alkali content in the benzene layer to any desired value the next step was to return the correct amount of the alcohol layer to the benzene layer. The hydrazobenzene left in the alcohol layer was then largely removed by extracting several times with benzene.

4. Fractionation of methyl alcohol from the reduced solution containing toluene to precipitate $NaOCH_3$. - After the reduction step, the standard reduced solution was placed in a distillation apparatus and the fractionation was carried out in a column 30 inches in length packed with glass helices.

In this case an azeotrope of benzene and methanol boiled over at a concentration close to the solvent charge. Cooling the solution after continued distillation resulted in precipitation of hydrazobenzene and sodium methylate.

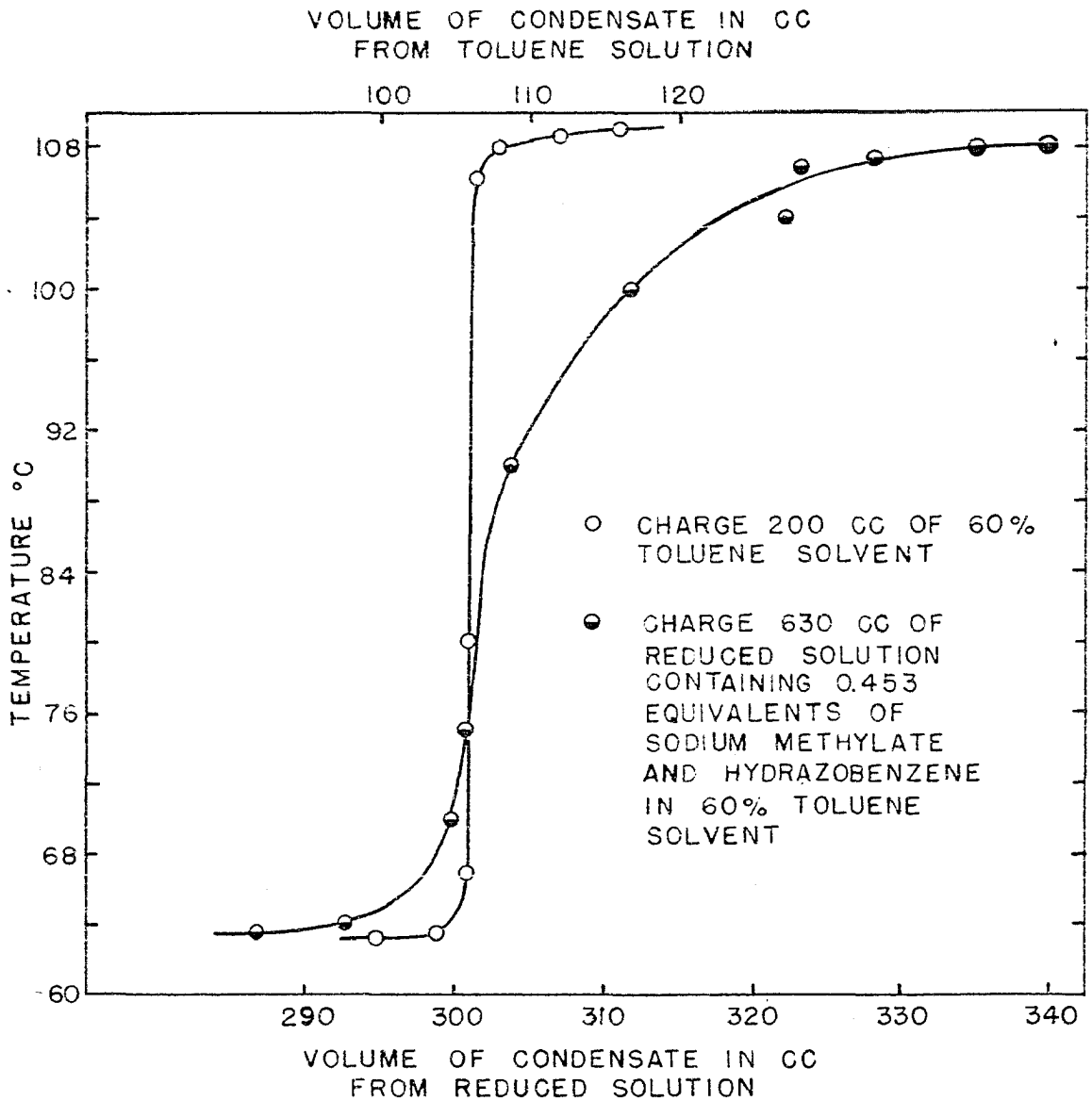
By substituting toluene for benzene in the reduction solution, fractionation was carried out with the removal of mainly methyl alcohol and finally pure toluene. The distillation curve is given in Figure 11 along with the curve for a charge of toluene and methanol. After all of the alcohol was removed, the partially cooled mixture of a solution of hydrazobenzene in toluene and sodium methylate was filtered and the precipitate washed with toluene. The filtrate consisted of hydrazobenzene in toluene while the precipitate contained 98.8% $NaOCH_3$ as shown by titrating a sample with hydrochloric acid. The sodium methylate was slightly discolored due to a trace of azobenzene.

E. Preparation of Sodium Peroxide Diperoxyhydrate ($Na_2O_2 \cdot 2H_2O_2$)

It was discovered that when a portion of the sodium methylate was removed from the reduced solution, sodium peroxide diperoxyhydrate formed. Sodium methylate was removed by one of the methods previously described. The methods used made use of calcium chloride to precipitate calcium methylate and sodium chloride, water extraction of the alcohol and methylate from any desired fraction of the solution, or separation of two liquid phases after reduction with the one phase

FIGURE II

FRACTIONATION OF METHANOL FROM TOLUENE AND FROM REDUCED SOLUTION CONTAINING TOLUENE



containing about 92% of the sodium methylate. Generally, $Na_2O_2 \cdot 2H_2O_2$ was prepared by removing one-half (1/2) or two-thirds (2/3) of the sodium methylate before the oxidation steps. However, $Na_2O_2 \cdot 2H_2O_2$ did form at 0° C. with no methylate removed before oxidation.

In one preparation using the phase separation method (Run No. 55) about one-half of the sodium methylate was removed. The top layer contained 1.935 equivalents of $NaOCH_3$ in a solution of about 970 cc. of benzene and 840 cc. of methanol. The bottom layer contained 0.172 equivalents in about 940 cc. of benzene and 192 cc. of methanol. To the bottom layer 525 cc. of the top layer and 300 cc. of methanol were added to give a solution of about 60% benzene. Three grams of calcium chloride were added to remove any water present as calcium hydroxide. The solution was filtered to remove the calcium methylate after the solution was allowed to stand over night. Some hydrazobenzene was left in the remainder of the top layer.

The filtered solution was oxidized for three and one-half hours at 0° C. The solution then was filtered and the precipitate dried for forty-five minutes under a vacuum of about two mm. of mercury pressure. After drying a small sample, added to ice water, required 2.07 meq. of acid and 6.18 meq. of thiosulfate. Therefore, the peroxide to base ratio was 2.98. Thirty-two grams were collected.

1. Oxidation of hydrazobenzene in benzene and methyl alcohol in the presence of varying amounts of sodium methylate at 0° C. and 25° C. - The object of this work was to study under what conditions NaOOH and $Na_2O_2 \cdot 2H_2O_2$ were the stable solid phases present in the oxidation solution and to determine the rate of formation of these compounds. The standard reduction solution of 80 grams of azobenzene in 600 cc. of benzene and 400 cc. of methyl alcohol was used in all the experiments.

The first step in this experimental work was to carry out the reduction as previously described. The amount of methylate produced was then determined by titrating a sample added to water with standard acid.

The second step was to remove the desired fraction of the sodium methylate. For this experimentation the calcium chloride method was used. After filtering and washing the precipitate of sodium chloride and calcium methylate, the alkali content of the solution was again determined. The fraction, f, of the original methylate left after the calcium chloride treatment was calculated.

The third step was to carry out the oxidation after which the azobenzene was recovered by extracting any alkali and the alcohol with water and then evaporating the benzene.

The oxidation step was studied at 25° C. and 0° C. with no alkali removed (f = 1), with one-half (1/2) removed (f = 1/2), and with two-thirds (2/3) removed (f = 1/3). The

rate of peroxide precipitated and the solid phase present were determined by removing with a pipette with a large opening a 10 cc. sample of the well-agitated mixture at various time intervals. The mixture was filtered and the precipitate washed with the benzene-alcohol solvent to remove excess methylate and azobenzene.

The precipitate was added to ice water and the equivalents of base determined by titrating with standard acid. Thereafter, the equivalents of peroxide were determined by the thiosulfate method. The peroxide to base ratio, Z, was indicative of the solid phase present.

To determine the fraction of the methylate removed during the oxidation, the filtrate from the 10 cc. sample was titrated for base content. The yield (Y) was calculated from equation (2).

$$Y = f \cdot Z \cdot x \ (100)\% \qquad (2)$$

where

Y = the yield based on the original methylate formed during reduction

f = the fraction of the original methylate left after the calcium chloride treatment

x = the fraction of the methylate left after the calcium chloride treatment removed during oxidation

Z = the peroxide to base ratio of the precipitate

The results of a series of runs are plotted in Figure 12. These results show that NaOOH, with a value of Z equal to 2, was the stable phase present throughout the oxidation at 25° C. when no alkali was removed. During the oxidation about 45% of the methylate was removed as NaOOH. Sodium hydroperoxide was also the stable phase present in the oxidation solution during the initial oxidation time at 0° C. with no methylate removed prior to the oxidation. However, this was gradually converted to $Na_2O_2 \cdot 2H_2O_2$ and finally at 0° C. with no alkali removed prior to the oxidation, about 30% of the methylate was removed as $Na_2O_2 \cdot 2H_2O_2$.

When one-half (1/2) of the methylate was removed prior to the oxidation at 0° C. and 25° C., $Na_2O_2 \cdot 2H_2O_2$ was the stable solid phase. In this case about 60% of the remaining methylate was removed as $Na_2O_2 \cdot 2H_2O_2$. When two-thirds (2/3) of the methylate was removed, $Na_2O_2 \cdot 2H_2O_2$ again was the stable phase and about 90% of the methylate remaining after the calcium chloride treatment was removed during oxidation as $Na_2O_2 \cdot 2H_2O_2$. In the latter case the yield, Y, was equal to x, the fraction of the methylate removed during oxidation.

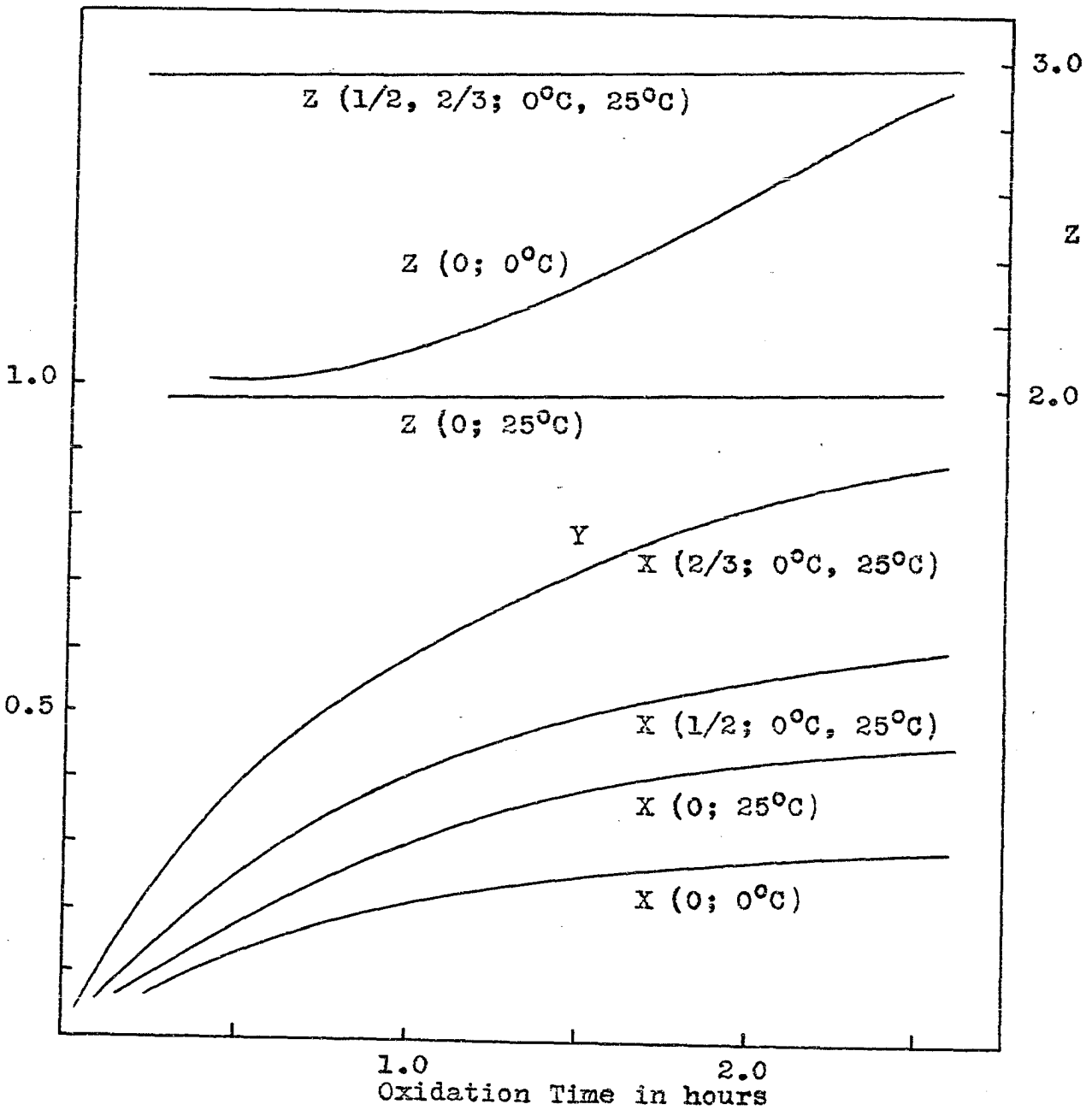
The Z values plotted in Figure 12 show a wide range of conditions under which the diperoxyhydrate was more stable than the hydroperoxide.

At least two oxidations were made for each condition. In many cases a larger number of oxidations were made to obtain comparisons. Emphasis was not placed on the rate of

FIGURE 12

FORMATION OF SODIUM PEROXIDE DIPEROXYHYDRATE AND SODIUM HYDROPEROXIDE AT 0°C AND 25°C

Oxidation Solution Obtained from the Reduction of 80 Grams of Azobenzene in 600 cc of Benzene and 400 cc of Methanol



Z - peroxide to base ratio in precipitate

Y - yield based on alkali

X - fraction of alkali removed during oxidation

Z (0; 25°C) - results for no alkali removed before oxidation for oxidation at 25°C

peroxide formation except to determine about how long the oxidation step required. The rate was found to depend on the amount of agitation and especially on the flow of oxygen which was not accurately controlled. At 0° C. with no methylate removed, the rate in some cases appeared somewhat lower.

Sodium peroxide diperoxyhydrate prepared in the above manner was dried from one-half to eight hours in a vacuum desiccator at low pressure and was recovered in a state of of rather high purity.

The peroxide to base ratio generally was about 2.96 and the purity was about 97.8% based on the peroxide content determined by the thiosulfate method. This assumed all of the peroxide present as $Na_2O_2 \cdot 2H_2O_2$.

Sodium hydroperoxide of a purity of 97% to 98% was also recovered.

At one occasion when a solution was oxidized at 0° C. with no methylate removed and when a small sample was removed at the early stages of oxidation, the precipitate was found to contain a peroxide to base ratio of about 5. This corresponded to the compound $Na_2O_2 \cdot 4H_2O_2$.

F. Some Properties and Reactions of Sodium Peroxide Diperoxyhydrate.

The solution from which $Na_2O_2 \cdot 2H_2O_2$ was precipitated in the above process consisted essentially of 60% by volume benzene and 40% methyl alcohol. During the oxidation and thereafter when the precipitate was filtered only very small amount of peroxide remained in the liquid phase. This showed that the solubility of $Na_2O_2 \cdot 2H_2O_2$ in the above system was very small. In addition the diperoxyhydrate remained stable in the oxidation solution after standing at 25° C. 30 hours before filtration.

Sodium peroxide diperoxyhydrate was crystalline and very easy to filter and wash free from sodium methylate and azobenzene. Sodium hydroperoxide was more difficult to filter. Methyl alcohol could be used for washing without causing noticeable decomposition. However, generally the precipitate was washed with a benzene-methyl alcohol solvent corresponding to the solvent in which the precipitate was formed.

Although $Na_2O_2 \cdot 2H_2O_2$ was very easily filtered the size of the crystals was quite small. The fact that the crystal size was not always the same was indicated by different rates of filtration and the ease of pouring the dried powder. Larger crystals were grown when oxygen was passed into the solution slowly. In one case the standard solution was prepared for oxidation then mixed with a small amount of

oxygen and allowed to stand over night. A small amount of precipitate formed. In this case the crystals were quite large, being needle-like and of the order 0.2 of a centimeter in length.

The precipitate of $Na_2O_2 \cdot 2H_2O_2$ was very easy to handle in that it did not rapidly decompose, it did not rapidly pick up water from the atmosphere, and it could be poured on the dry skin without causing burning. The latter fact was very significant because of the fact that $Na_2O_2 \cdot 2H_2O_2$ is equivalent to 70% hydrogen peroxide on a weight basis.

When samples of $Na_2O_2 \cdot 2H_2O_2$ were stored at about 6° C. without any stabilizer, a varying amount of decomposition took place for different samples. The amount of decomposition was calculated as the percent decrease in the peroxide to base ratio and amounted to 0% to 3% during a period of about four weeks. The milliequivalents of peroxide and base and the peroxide to base ratio are given in Table II for the samples of $Na_2O_2 \cdot 2H_2O_2$ and NaOOH used for stability tests. In Table II the Run No. refers to the $Na_2O_2 \cdot 2H_2O_2$ preparation. In these preparations calcium chloride was used to remove methylate for all the runs except 54, 19, 32, and 40.

Runs No. 18, No. 19, and No. 55 were made at 6° C. for the specified periods of time and then stored at 25° C. The percent decomposition was calculated relative to the original peroxide to base ratio.

Table II

Stability Data on $Na_2O_2 \cdot 2H_2O_2$ and NaOOH

Run No.	Shelf Time (wks.)	Temp. Stored °C.	Meq. Peroxide per Gram	Meq. Base per Gram	Z	% Decomp.
			$Na_2O_2 \cdot 2H_2O_2$			
18	0	-	39.0	13.2	2.96	--
	4	6	38.0	13.2	2.88	2.7
	2	25	10.0	17.1	0.58	80.0
20	0	-	40.2	13.6	2.96	--
	21	6	36.2	13.2	2.74	7.4*
21	0	-	38.8	13.5	2.98	--
	6	6	36.1	13.5	2.68	10.0
	25	6	28.8	14.2	2.03	32.0*
22	0	-	40.1	13.5	2.97	--
	18	6	35.6	13.7	2.60	12.5
23	0	-	--	--	2.96	--
	50	6	18.4	15.2	1.21	59.1
54	0	-	--	--	2.72	--
	21	6	23.0	14.3	1.68	38.3
55	0	-	--	--	2.98	--
	4	6	--	--	2.975	0.17
	12	6	--	--	2.96	0.67
	13**	6	--	--	2.90	2.68
	2	25	--	--	2.66	10.7
			NaOOH or $Na_2O_2 \cdot 2H_2O_2$			
19	0	-	35.2	17.6	2.00	--
	3	6	33.0	17.6	1.94	3.0
	2	25	12.8	16.6	0.77	61.5
32	0	-	33.1	17.3	1.91	--
	8	6	31.9	17.6	1.82	5.0
40	0	-	34.4	16.2	2.12	--
	34	6	23.9	16.6	1.45	31.6

* Considerable oxygen evolved on solution in ice water.
** Bulk sample.

In order to increase the stability of $Na_2O_2 \cdot 2H_2O_2$ five percent (5%) by weight of calcium oxide was added to one sample and 5% calcium sulfate added to a second to remove any water formed (Run No. 55, Table II). Several small samples of each to be used for titrations were separated and stored at 6° C. with the bulk samples. After 13 weeks the samples were stored in a desiccator at 25° C. with the caps turned on loosely to allow any gas to escape. The results on these samples are tabulated in Table III.

A sample of $Na_2O_2 \cdot 2H_2O_2$ when heated on a melting point apparatus did not undergo any apparent change at 122° C. The crystals turned slightly yellow at 130° C. and became white again at 190° C. Further investigation showed that a small amount of sodium superoxides had formed. Heating samples under vacuum gave a more intensely colored product. This led to the further study of the preparation of sodium superoxide from $Na_2O_2 \cdot 2H_2O_2$.

Hydrogen peroxide dissolved in organic solvents such as amyl alcohol was obtained by passing hydrogen chloride gas into the solution at 0° C. in which the $Na_2O_2 \cdot 2H_2O_2$ was dispersed by stirring. The resulting sodium chloride was filtered off and a solution of 5.85 grams of H_2O_2 in 100 cc. of alcohol was obtained.

Hydrogen peroxide water solutions saturated with sodium sulfate were obtained by the addition of sulfuric acid to the solid $Na_2O_2 \cdot 2H_2O_2$ dispersed in cooled carbon tetrachloride.

Table III

Stability of $Na_2O_2 \cdot 2H_2O_2$ Containing CaO and $CaSO_4$

Sample	Shelf Time (wks.)	Temp. Stored °C.	Z*	% Decrease
Control	0	6	2.98	--
	4	6	2.975	0.17
	12	6	2.96	0.67
Bulk Sample	13	6	2.90	2.68
	2	25	2.58	13.1
Bulk Sample	2	25	2.66	10.7
5% $CaSO_4$	0	6	2.98	--
	4	6	2.96	0.67
	12	6	2.90	2.68
Bulk Sample	13	6	2.94	1.34
			2.94 Check	
	2	25	2.45	17.8
Bulk Sample	2	25	2.66	10.7
5% CaO	0	6	2.78	--
	4	6	2.83	--
	12	6	2.92	--
Bulk Sample	13	6	2.57	9.2
	2	25	2.60	6.5
Bulk Sample	2	25	2.31	16.9**

* Peroxide to base ratio.
** Essentially no CaO in sample analyzed.

The resulting precipitate was filtered and the two liquid phases separated. Table IV shows the hydrogen peroxide solutions obtained from varying concentrations of sulfuric acid.

Table IV

H_2O_2 Solutions Obtained from $Na_2O_2 \cdot 2H_2O_2$ and H_2SO_4

H_2SO_4 cc.	H_2O cc.	N*	cc. $Na_2O_2 \cdot 2H_2O_2$ Used	gms.	C**	Precipitate
5.45	89	--	37	5.7	11.29	$Na_2SO_4 \cdot 10H_2O$
10	75	4.18	12.95	4.2	21.0	$Na_2SO_4 \cdot 10H_2O$
16	84	6.55	15.5	7.8	29.4	$Na_2SO_4 \cdot 9H_2O \cdot H_2O_2$
--	--	conc.	0.8	2.1	--	$Na_2SO_4 \cdot 3H_2O_2 \cdot xH_2O$

* Normality of sulfuric acid
** Concentration of H_2O_2 solution in grams of H_2O_2 per 100 cc. of solution.

The precipitate of $Na_2SO_4 \cdot 3H_2O_2 \cdot xH_2O$ was 73.6% $Na_2SO_4 \cdot 3H_2O_2$ and contained some carbon tetrachloride. This sample was placed in a distillation flask and evacuated at about 2 mm. mercury pressure to attempt to distill off the H_2O_2. After one-half hour the precipitate contained 54% $Na_2SO_4 \cdot 3H_2O_2$ based on the peroxide present. The hydrogen peroxide removed was largely decomposed.

Sodium peroxide diperoxyhydrate was converted to urea monoperoxide by the reaction with urea of the hydrogen

peroxide solutions produced above. The resulting slurry upon evaporation gave a product of 69% urea monoperoxide mixed with sodium sulfate. The product was quite stable when stored at room temperature.

G. Preparation of Potassium Peroxide Diperoxyhydrate.

The object of this work was to replace the sodium methylate in the reduced solution with potassium methylate so that potassium peroxide diperoxyhydrate ($K_2O_2 \cdot 2H_2O_2$) would precipitate during the oxidation step.

The standard reduction solution consisting of 80 grams of azobenzene dissolved in 600 cc. of benzene and 400 cc. of methyl alcohol was used. The reduction step was carried out as previously described. All of the sodium methylate was removed by the use of calcium chloride or water extraction.

When calcium chloride was used to remove all of the sodium methylate, a large amount of precipitate formed and, therefore, a considerable amount of hydrazobenzene was adsorbed on the gelatinous calcium methylate. The filtration and washing steps were quite difficult.

The water-extraction method was most easily used. This was accomplished by adding water to the reduced solution and then separating the benzene phase which was washed with water and then dried with calcium chloride.

A potassium methylate solution was prepared by reacting potassium metal with methyl alcohol. This reaction was

carried out carefully to eliminate fire and to cut down the amount of metal oxides added. A solution of about 50 cc. of benzene and 50 cc. of methyl alcohol was placed in a 3-neck, round-bottom flask equipped with a condenser and an agitator. The flask was placed in a cold water bath. The potassium was cleaned and cut under benzene and transferred rapidly into the stirred solution. More methyl alcohol was added when the potassium methylate began to crystallize or when the metal reacted only slowly. The final solution contained 3.59 meq. $KOCH_3$ per cc. of solution.

This potassium methylate solution was added to the hydrazobenzene solution so that the potassium methylate was present in an amount equivalent to one-third of the original sodium methylate.

When the hydrazobenzene was oxidized in the presence of the potassium methylate, a precipitate of the rather unstable $K_2O_2 \cdot 2H_2O_2$ was formed. When the potassium methylate was added in an amount equivalent to one-half (1/2) of the original sodium methylate, $K_2O_2 \cdot 2H_2O_2$ formed again. All oxidations were made at 0° C. because of the instability of the $K_2O_2 \cdot 2H_2O_2$. Several times products were obtained that had a peroxide to base ratio of 3.5. This value would correspond to the compound $K_2O_2 \cdot 2.5H_2O_2$. It was concluded that this material consisted of a mixture of $K_2O_2 \cdot 2H_2O_2$ and $K_2O_2 \cdot 4H_2O_2$.

Potassium peroxide diperoxyhydrate was crystalline and very easy to filter and wash. The particles appeared larger than the crystals of $Na_2O_2 \cdot 2H_2O_2$ and filtration was somewhat easier than filtration of the solution from the $Na_2O_2 \cdot 2H_2O_2$.

The rate of oxidation of the hydrazobenzene in the presence of potassium methylate was not made. However, the strong orange color of the azobenzene solution appeared to form more rapidly than when sodium methylate was in the oxidation solution.

However, more peroxide remained in the oxidation solution during the preparation of $K_2O_2 \cdot 2H_2O_2$ than during the preparation of $Na_2O_2 \cdot 2H_2O_2$. This showed that the solubility of $K_2O_2 \cdot 2H_2O_2$ was greater than the solubility of $Na_2O_2 \cdot 2H_2O_2$, or it showed that $K_2O_2 \cdot 2H_2O_2$ may have been slower to precipitate.

An attempt to determine the solubility of $K_2O_2 \cdot 2H_2O_2$ in methyl alcohol and a solution of 40% by volume methyl alcohol in benzene at 0° C. was made by adding a freshly prepared sample to 10 cc. of the cooled solvents and shaking the tubes with cooling in an ice bath. In both cases considerable bubbling resulted. This showed that decomposition was resulting in both cases. After about one-half hour the solutions were filtered and the amount of alkali and peroxide determined in 5 cc. of the solutions. One hundred cc. of the 40% alcohol solution contained 6 milliequivalents (meq.) of base and 0.935 meq. peroxide while 100 cc. of the alcohol

solution contained 48.9 meq. base and 30.6 peroxide.

These titrations gave a peroxide to base ratio of the dissolved material of 0.15 in the 40% alcohol solution and 0.64 in the alcohol. Based on the peroxide present the solubility found was 0.028 and 0.90 grams $K_2O_2 \cdot 2H_2O_2$ per 100 cc. of the 40% alcohol solution and the pure alcohol respectively. The amount of thiosulfate solution required to titrate a sample of the filtrate obtained after oxidation was the same as that required to titrate the 40% alcohol solution above.

H. Preparation of Lithium Peroxide and Lithium Peroxide Monoperoxyhydrate.

The standard solution of azobenzene was converted to a solution of hydrazobenzene and sodium methylate in the methyl alcohol-benzene solvent by reduction with sodium amalgam and the alcohol. To this reduced solution an amount of anhydrous lithium chloride dissolved in methyl alcohol was added to convert all of the sodium methylate to lithium methylate and precipitate sodium chloride according to reaction (3).

$$LiCl + NaOCH_3 \longrightarrow LiOCH_3 + NaCl \qquad (3)$$

The resulting solution was filtered and the precipitate washed with the methyl alcohol-benzene solvent. The filtrate was added to the oxidizer and the oxidation carried out at

0° C. The precipitate had a peroxide to base ratio slightly greater than one. When these samples were stored at room temperature considerable decomposition took place with the formation of some lithium hydroxide. The final peroxide to base ratio was slightly below one.

A lithium peroxide product with a peroxide to base ratio of 1.57 was obtained when exactly one-half of the methylate was removed by the water extraction method. After oxidation for three hours at 0° C. the material was removed by filtration and washed with a cooled 90% benzene solution. The product contained 28.0 meq. of base and 43.8 meq. of peroxide per gram. If this product were pure $Li_2O_2 \cdot H_2O_2$ and Li_2O_2 plus an inert impurity it would have contained 47.1 meq. of peroxide per gram. Therefore, the purity was 93.0%. After drying eighteen days at 25° C. and about two mm. mercury pressure it contained 35.7 meq. base and 41.5 meq. peroxide. If this product, with a peroxide to base ratio of 1.16, were pure $Li_2O_2 \cdot H_2O_2$ and Li_2O_2 plus an inert material it would have had 45.2 meq. peroxide per gram and, therefore, the purity of the product was 91.7%. After a total of 27 days the ratio was 1.065, the peroxide content was 40.1 meq. per gram and the purity 90.6%.

The above material was very white when prepared. After evacuation for eighteen days it became slightly orange-yellow in appearance; however, essentially no oxygen was evolved on solution in ice water and a 0.2 gram sample evolved only

0.3 cc. when analyzed for superoxide.

Lithium peroxide monoperoxyhydrate was prepared by the oxidation of hydrazobenzene in the presence of lithium methylate present in an amount equivalent to two-thirds (2/3) of the original sodium methylate produced in the standard reduced solution. The first portion of the sodium methylate was removed by means of calcium chloride, while the remainder was converted to lithium methylate with lithium chloride. This solution was oxidized at 0° C., but when the final precipitate was washed at 25° C. with a solvent mixture of equal volumes of benzene and methanol, the product decomposed to give a brownish-yellow material containing 35.9 meq. of base and 32.5 meq. of peroxide per gram. A superoxide analysis showed 5.8% LiO_2.

The rate of peroxide precipitated was determined for an experiment when 69% of the $NaOCH_3$ was removed with calcium chloride and the remainder was converted to $LiOCH_3$ with LiCl. The results are tabulated in Table V.

The results show that 98% of the $LiOCH_3$ was converted to LiOOH ($Li_2O_2 \cdot H_2O_2$). $Li_2O_2 \cdot 2H_2O_2$ did not appear to form. Since $Li_2O_2 \cdot 2H_2O_2$ did not form, the yield of solid peroxide could not exceed about 0.592 for at this yield 100% of the $LiOCH_3$ would have been precipitated in the above preparation.

After washing the $Li_2O_2 \cdot H_2O_2$ precipitate with a benzene solution containing 10% methanol, the product decomposed

Table V

Preparation of Lithium Peroxide Monoperoxyhydrate
($f^* = 0.29$)

Oxidation Time min.	X**	Z***	Yield Y
16	0.406	1.82	0.214
60	0.95	1.29	0.493
120	0.989	1.90	0.545
180	0.980	2.04	0.58

* $LiOCH_3$ present in an amount equivalent to 29% of original $NaOCH_3$.
** Fraction of $LiOCH_3$ precipitated.
*** Peroxide to base ratio in precipitate.

rapidly to LiOH. The oxidation and filtration were done at 0° C.

To prepare Li_2O_2 a solvent of equal volumes of ethyl alcohol and benzene was used for the solvent for the azobenzene. After the reduction the sodium ethylate was replaced by lithium ethylate by the addition of anhydrous lithium chloride dissolved in methyl alcohol. The sodium chloride was removed by filtration and washed with the benzene and ethyl alcohol solvent. All of the lithium ethylate remained in the solution when 80 grams of azobenzene was used per 1000 cc. of solvent.

The solubility of lithium ethylate in ethyl alcohol was about 12.6 grams LiOEt per 100 cc. and in a 40% ethyl alcohol solution of benzene about 5.8 grams per 100 cc. of solution. The solubility of lithium methylate was about 13.0 grams $LiOCH_3$ per 100 cc. of methyl alcohol and 4.5 grams per 100 cc. of the 40% methyl alcohol in benzene solvent.

When the hydrazobenzene was oxidized in the above ethyl alcohol-benzene solution containing lithium ethylate, 97% of the LiOEt was precipitated as Li_2O_2 . Lithium peroxide also precipitated when the lithium ethylate was present in an amount equivalent to one-half (1/2) of the original sodium ethylate. The two samples had a peroxide to base ratio of 0.98 and 0.96 respectively. The samples contained 91% and 90% by weight Li_2O_2 and only a trace of chloride.

On storing the above samples sixty-five days at 25° C., there resulted a loss of available oxygen of 3.0% and 2.0% respectively. No trace of oxygen was evolved on solution in ice water. Both samples were very finely divided and quite low in density. Samples of the powder appeared to remain unreacted after twenty-four hours exposure to atmospheric conditions.

I. Preparation of Sodium Superoxide and Potassium Superoxide from the Diperoxyhydrates of Sodium Peroxide and Potassium Peroxide.

The second phase of this work involved the conversion of $Na_2O_2 \cdot 2H_2O_2$ to NaO_2 and $K_2O_2 \cdot 2H_2O_2$ to KO_2. The reaction resulted in the formation of both superoxide and water. Several procedures were used to carry out the conversion under conditions favorable for the escape of the water to prevent its decomposition of the superoxide. The $K_2O_2 \cdot 2H_2O_2$ and $Na_2O_2 \cdot 2H_2O_2$ samples were prepared as previously described.

After filtrating and washing $K_2O_2 \cdot 2H_2O_2$ with a solvent containing 40% by volume methyl alcohol in benzene cooled to 0° C., the white crystalline material was added to a vacuum desiccator to dry. Rapid decomposition resulted, and after about fifteen minutes a layer of yellow material was removed and analyzed for superoxide by measuring the amount of oxygen evolved by treating the sample with a solution of acetic acid and diethylphthalate (method of Seyb and Kleinberg). The amount of superoxide in this first sample was found to be about 46%.

At a later date more stable $K_2O_2 \cdot 2H_2O_2$ was obtained by washing the precipitate with a 10% methyl alcohol solution in benzene cooled to 0° C. Some of these samples showed a much slower rate of decomposition under vacuum. Two different experiments produced products with 62% and 61.5% KO_2

when the $K_2O_2 \cdot 2H_2O_2$ was decomposed at 25° C. in two and one-half hours and one week respectively. A second rather stable preparation of $K_2O_2 \cdot 2H_2O_2$ was decomposed at 0° C. and 25° C. under about one to three mm. mercury pressure. After two weeks the sample decomposed at 0° C. showed a 61.2% KO_2 content while the sample at 25° C. had a 69.6% KO_2 content.

Since Traube and Schulze (39) reported that ultra-violet light had catalyzed the formation of BaO_4 and CaO_4 from the peroxyhydrates of barium and calcium peroxide, this method was applied to the preparation of NaO_2 and KO_2. Two methods were used utilizing ultra-violet light, the one using a vacuum to remove water and the other a stream of gas to sweep away the water formed.

The first method utilizing ultra-violet light to prepare NaO_2 and KO_2 made use of a current of oxygen or ammonia gas to remove the water vapor as it formed. In this method the diperoxyhydrates were washed after preparation and left on the 600 cc. fritted-glass funnel. The gas was then drawn through the funnel to remove as much as possible of the water as it was formed.

A quartz glass plate was cemented onto a neoprene sheet with a circular hole cut just smaller than the funnel so that the neoprene could be stretched over the funnel to make a tight seal. An opening was made in the neoprene at the edge of the quartz plate to pass in the gas.

In one experiment using this procedure, ammonia gas was passed into the funnel and drawn through a $K_2O_2 \cdot 2H_2O_2$ sample by means of a water aspirator. A sunlamp was placed about ten inches above the quartz window. The material began to decompose immediately and in about fifteen minutes the product was analyzed for superoxide. The sample contained 69% KO_2.

Oxygen gas was used with a larger sample of $K_2O_2 \cdot 2H_2O_2$. Three separate analyses of this product gave 59%, 47%, and 53% KO_2. It was believed that the variation in the values obtained was due largely to the non-homogenity of the product.

The data obtained on the preparation of KO_2 is summarized in Table VI. A vacuum of about three mm. of mercury was used.

Table VI

Conversion of $K_2O_2 \cdot 2H_2O_2$ to KO_2

Run No.	Z* Original	Method Used	Time of Reaction	Meq. Base per Gram	Z	% KO_2
S3	3.4	Vacuum, 25° C.	30 min.	--	--	46.5
S4	2.24	F	30 min.	--	0.45	69
S6	3	B	30 min.	--	--	53
S27A	3	Vacuum, 0° C.	2 wks.	12.9	0.65	61.2
S27B	3	Vacuum, 25° C.	2 wks.	12.8	1.0	69.6
S29	3	" "	1 wk.	12.8	0.88	61.5
S30	3	" "	2.5 hrs.	13.56	0.60	62.2

* Peroxide to base ratio.
F - Sunlamp, NH_3 gas drawn through sample in funnel.
B - Sunlamp, O gas drawn through sample in funnel.

Sample No. S29 was allowed about seven hours on the funnel while a stream of ammonia gas was pulled through the sample. The sample remained quite stable while some yellow product formed. Since the sample did not readily decompose it was placed in a vacuum desiccator.

The accuracy of the results tabulated in Table VI was not extremely good. The superoxide content was estimated to be accurate to about five percent. The values obtained were, no doubt, slightly high due to liberation of peroxide oxygen. In making the superoxide analyses, the reaction flask was kept exactly at a temperature of the order of 12° C. for Runs S27A through S30.

When relatively pure $Na_2O_2 \cdot 2H_2O_2$ was placed in a vacuum desiccator to remove benzene and alcohol essentially no superoxide formed at 25° C. in from four to eight hours of drying.

Rapid heating of $Na_2O_2 \cdot 2H_2O_2$ resulted in complete decomposition to sodium hydroxide. Slow heating gave traces of NaO_2. Heating under vacuum gave a gradual color change from white to pale yellow. Further heating resulted in more rapid decomposition with considerable evolution of oxygen. Two samples containing 8.6% and 12.6% superoxide were obtained in this manner.

Since $Na_2O_2 \cdot 2H_2O_2$ was quite reluctant in its conversion to NaO_2, ultra-violet light was used initially to carry out the conversion. Since $Na_2O_2 \cdot 2H_2O_2$ was quite stable, however,

it was much easier to handle than the $K_2O_2 \cdot 2H_2O_2$.

In order to get good conversion it was assumed necessary to get good exposure of as much as possible of the $Na_2O_2 \cdot 2H_2O_2$ particles with the light. To accomplish this, an apparatus was constructed in which the powder sample was mixed inside a rotating Plexiglass tube through which the transmission of ultra-violet light was high. The apparatus, as previously described, was constructed so that a vacuum was maintained in the tube while it rotated and mixed the sample due to the tumbling action.

A mercury-arc lamp was used as a source of ultra-violet light. Since this lamp generated a considerable amount of heat, a fan was placed over the tube to prevent excess heating.

About five grams of $Na_2O_2 \cdot 2H_2O_2$ were placed in the tube and a vacuum of about three mm. was maintained while the tube was rotated under the light. After a short period of time the sample turned pale yellow. In one run after fifteen minutes a product was removed and analyzed for superoxide, peroxide, and base. The peroxide to base ratio was 1.08 and the superoxide content was 16.1%. A second sample contained 13.4% NaO_2 and had a peroxide to base ratio of 1.93 after four hours.

Since $K_2O_2 \cdot 2H_2O_2$ could not be prepared dry and allowed to warm without decomposition, an investigation of the decomposition of $K_2O_2 \cdot 2H_2O_2$ in the above apparatus was not made.

Conversion of $Na_2O_2 \cdot 2H_2O_2$ to NaO_2 by passing oxygen gas through the precipitate on a fritted-glass funnel to sweep out the water formed was not very successful unless the sample was stirred. In one experiment a thin layer of the dark-yellow NaO_2 formed on the surface while the sample remained very white underneath. At the same time the heat generated by the sunlamp raised the temperature of the $Na_2O_2 \cdot 2H_2O_2$ after which the material decomposed very rapidly.

In order to give better contact with the ultra-violet light on the $Na_2O_2 \cdot 2H_2O_2$ particles and at the same time prevent too much heating of the particles, several streams of oxygen were directed into the funnel from a glass tubing with small tips drawn out at various positions so that the jets of oxygen could be directed over the entire surface of the funnel and the pyrex window. By rotating the tubing the dry $Na_2O_2 \cdot 2H_2O_2$ particles were stirred and mixed with the whirling gas. In one hour a product was obtained that analyzed 27.2% NaO_2 while the peroxide to base ratio was 2.15. This product was largely NaO_2 and undecomposed $Na_2O_2 \cdot 2H_2O_2$.

In a similar manner $Na_2O_2 \cdot 2H_2O_2$ was added to a glass beaker mounted on a platform rigged on a motor shaft. The $Na_2O_2 \cdot 2H_2O_2$ sample was placed in the rotating beaker in which several jets of oxygen were blown to agitate the powder and remove the water as it formed. This allowed the ultra-violet light to come into better contact with the fine particles. However, two samples converted in this fashion con-

tained 18% and 25% superoxide after about two hours reaction time. The top of the beaker was open to the atmosphere.

Samples of $Na_2O_2 \cdot 2H_2O_2$ gave rather low yields of NaO_2 (7%) with very little decomposition of the remaining $Na_2O_2 \cdot 2H_2O_2$ when evacuated in a 500 cc. quartz flask which was shaken in front of a sunlamp. See Runs S10 and S12 in Table VII. Run S11 gave 18.7% NaO_2; however, the sample was largely decomposed to sodium hydroxide. The latter sample was run for three hours during which time the flask was allowed to become quite warm.

A third procedure, utilizing ultra-violet light, was used to remove the water in the preparation of NaO_2 and KO_2. In this method the samples were added to liquid ammonia at its boiling point at atmospheric pressure. The $Na_2O_2 \cdot 2H_2O_2$ sample was placed in a beaker and a sunlamp placed about one foot above the well-stirred solution. After two hours the product was removed by filtering the ammonia through a glass-cloth filter. On drying the material violently decomposed. Two small samples, reserved while still wet, were analyzed. The superoxide content was 7.9% while the peroxide to base ratio was 2.14.

A $K_2O_2 \cdot 2H_2O_2$ sample turned yellow when stirred in a quartz flask in liquid ammonia. A sunlamp was placed at the bottom of the flask. After filtration this sample also decomposed.

The results for the various preparations of NaO_2 utilizing ultra-violet light are tabulated in Table VII.

Table VII

Conversion of $Na_2O_2 \cdot 2H_2O_2$ to NaO_2 with Ultra-violet Light

Run No.	Z* Original	Method Used	Reaction Time hrs.	Meq. Base per Gram	Z	% NaO_2
S5	--	A	2	--	--	25.0
S8	2.99	B	1	--	--	17.7
S9	2.99	C	2	14.5	2.14	7.9
S10	--	D	1.5	13.7	2.73	6.2
S11	--	D	3	13.0?	0.60	18.7
S12	--	D	1	13.5	2.87	6.0
S13	Sample S12	B	1	14.0	2.15	27.2
S14	2.86	B	1.5	--	1.93	18.5
S17	2.86	D	4	21.5	0.30	40.3
S18A	2.35	E	0.25	19.4	1.08	16.1
S18B	2.22	E	4.5	16.1	1.93	13.4
			11.5	16.9	1.59	11.6
			16.5	17.5	1.39	12.6

* Peroxide to base ratio.
A - Sunlamp, O_2 gas passed over sample in beaker.
B - Sunlamp, O_2 gas through sample in funnel.
C - Sunlamp, sample in liquid NH_3 at -33° C.
D - Sunlamp, vacuum, sample in quartz flask.
E - Mercury-arc lamp, in rotating plexiglass tube with vacuum of about 3 mm.

For the NaO_2 samples the peroxide to base ratio, Z, was much lower for some samples than others with essentially the same superoxide content. In some cases unreacted $Na_2O_2 \cdot 2H_2O_2$ remained while other samples contained a considerable amount of sodium hydroxide. Unless the analysis for Run S13 was high, the sample consisted essentially of 27% NaO_2 with the remainder $Na_2O_2 \cdot 2H_2O_2$.

Sodium peroxide diperoxyhydrate was converted slowly to NaO_2 under vacuum. Samples were stored in small glass bottles in vacuum desiccators containing barium oxide. At various time intervals the samples were removed for analysis of the superoxide content and peroxide to base ratio. Before removing samples for analysis the desiccators were filled with oxygen gas passed through a magnesium perchlorate drying tube. This was to cut down the addition of water and carbon dioxide to the samples.

The results obtained for the various preparations of NaO_2, utilizing a vacuum of about three mm. of mercury to remove the water, are tabulated in Table VIII.

Table VIII

Decomposition of $Na_2O_2 \cdot 2H_2O_2$ to NaO_2 Under Vacuum

(P = 3 mm., T = 25° C.)

Run No.	% Original	Time days	Meq. Base per Gram	%	% NaO_2
S15	2.25	2	--	1.42	22.5*
		4	17.7	1.15	36.6*
		7	17.9	1.00	44.2*
		28	18.8	0.61	61.2*
		115	18.9	0.45	67.2
		142	18.4	0.47	58.2
S16	2.72	3	15.5	2.14	10.7*
		24	17.6	1.56	28.1*
		37	17.5	1.35	44.6*
		45	16.8	1.25	49.4*
		55	17.5	0.94	67.0*
		112	18.3	0.57	72.0
		129	18.0	0.56	66.5
S19	2.98	40	15.4	2.30	6.8
		72	17.3	1.69	16.9
		90	18.5	1.10	31.2
		100	18.9	1.12	29.4
S20	at 40° C. 2.98	39	23.6	0.18	9.3
S21	2.95	33	18.1	1.58	10.0
		56	20.6	0.82	24.3
		65	22.9	0.56	28.9
S22 (in dark)	2.95	33	18.1	1.58	10.0
		65	21.3	0.61	28.0
S23**	2.95	17	13.8	2.64	6.5
S24	2.91	33	19.4	1.13	20.3
		64	22.8	0.22	27.7
S26	2.70	15	15.3	1.88	14.5
		33	17.6	1.15	22.0
		43	19.5	0.70	29.0

Table VIII (Continued)

Decomposition of $Na_2O_2 \cdot 2H_2O_2$ to NaO_2 Under Vacuum

(P = 3 mm., T = 25° C.)

Run No.	% Original	Time days	Meq. Base per Gram	%	% NaO_2
S31	2.75	5	16.9	2.01	8.7
		7	17.7	1.57	18.4
		10	18.6	1.25	29.6
		17	--	0.81	53.3
S32	2.90	5	16.8	2.02	2.5
		7	17.4	1.82	7.9
		10	17.8	1.58	17.4
		17	18.5	1.05	41.8

* Analysis of NaO_2 made with reaction flask at room temperature; all other analyses made with flask at 12° C.

** Sample four days in glass tube with 8 volt Germicidal lamp located inside tube. Temperature held at 12° C. by water jacket, 3 mm. Hg pressure maintained.

The solutions used for the preparation of the $Na_2O_2 \cdot 2H_2O_2$ samples that were used for the NaO_2 preparation tabulated in Table VIII were prepared as follows:

Run S15 - Oxidation of the layer rich in methylate, Run No. 54, no $CaCl_2$ used.

Run S16 - Standard phase-separation method, Run No. 54, no $CaCl_2$ used.

Runs S19, S20 - Standard phase-separation method, Run No. 55, small amount of $CaCl_2$ used to remove H_2O.

Runs S21, S22, S23, S24 - Calcium chloride method.

Run S26 - Essentially no methylate removed, $CaCl_2$ used to remove water.

Run S31 - Na $NaOCH_3$ removed, no $CaCl_2$ added.

Run S32 - Water extraction method, Run No. 59B, no $CaCl_2$ used.

J. Methods of Analysis of Peroxide Compounds and Superoxides.

The alkali content of samples containing calcium peroxide and calcium methylate was made by adding a weighed sample to a small amount of water and then adding an excess of 0.1 N hydrochloric acid. After all of the solid went into solution, the excess acid was back titrated with 0.1 N sodium hydroxide solution using phenolphthalein as an indicator.

The peroxide content of the above samples was determined by a modification of "Kingzetts Iodide Method" (13). About 0.4 grams of the calcium peroxide products and 10 cc. of glacial acetic acid were added to a beaker containing water with ice. Immediately about 40 cc. of a 10% potassium iodide solution was added. Then a few drops of a saturated solution of ammonium molybdate was added to hasten the liberation of iodine according to the reaction:

$$H_2O_2 + 2\ KI + 2\ HC_2H_2O_2 \longrightarrow I_2 + 2\ KC_2H_2O_2 + 2\ H_2O$$

Within three minutes the iodine was titrated with a 0.1 N thiosulfate solution.

The peroxide and base content of peroxide compounds of the alkali metals, namely Li_2O_2, $Li_2O_2 \cdot H_2O_2$, NaOOH, $Na_2O_2 \cdot 2H_2O_2$, and $K_2O_2 \cdot 2H_2O_2$, were made by slowly dissolving a weighed sample of about 0.2 grams in a mixture of ice and water followed by titration of the base with 0.1 N hydrochloric acid and then determination of the peroxide by the thiosulfate method.

One cc. of 0.1 N sodium thiosulfate solution corresponded to the following amounts of the following compounds:

0.001701 gram H_2O_2

0.002294 gram Li_2O_2

0.001997 gram LiOOH or $Li_2O_2 \cdot H_2O_2$

0.002801 gram NaOOH or $Na_2O_2 \cdot H_2O_2$

0.002451 gram $Na_2O_2 \cdot 2H_2O_2$ or $NaOOH \cdot 1/2H_2O_2$

0.002970 gram $K_2O_2 \cdot 2H_2O_2$ or $KOOH \cdot 1/2H_2O_2$

The alkali and peroxide content of potassium superoxide and sodium superoxide products were made by slowly dissolving the weighed samples in water containing ice and proceeding as above.

The solution of the peroxide in ice water with the liberating of the superoxide oxygen without undue decomposition of the peroxide was discussed by Kraus and Whyte (20) and can be represented by:

$$2\ KO_2 + \text{water} \longrightarrow K_2O_2 \cdot aq + O_2$$

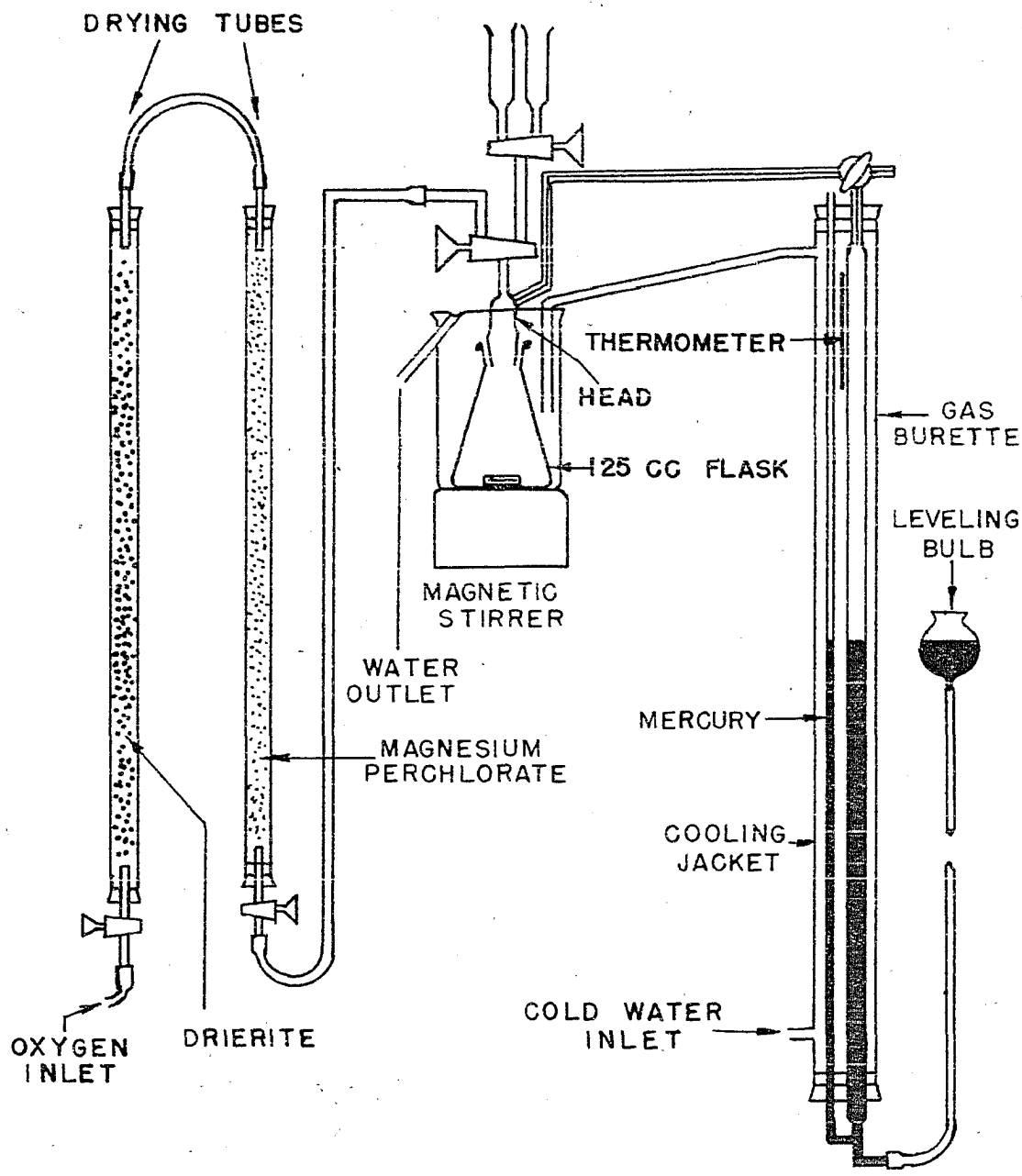
It was pointed out that this method was not extremely accurate due to some decomposition of the peroxide.

The superoxide content was determined by a procedure developed by Seyb and Kleinberg (37). A diagram of the apparatus similar to the one described by the above authors is shown in Figure 13.

In this procedure samples of about 0.2 grams were transferred to a small vial in a dry box containing anhydrous

FIGURE 13

APPARATUS FOR SUPEROXIDE ANALYSIS



magnesium perchlorate. Extra precaution was taken for potassium superoxide because these samples picked up water vapor very rapidly from the air. The vial was weighed and the contents rapidly transferred to a 125 cc. ground-glass Erlenmeyer flask previously flushed out with oxygen which was dried by passing over anhydrous magnesium perchlorate. The flask was immediately transferred to the cell head which contained a coating of stopcock grease to give a tight seal to the flask. The flask was held tightly in place by means of a rubber band.

A stream of oxygen was passed through the drying tubes, into the flask to flush out any air, and out of the system through a three-way stopcock located on the top of the gas burette. At this time the cold water bath and the magnetic stirrer were raised so that gas inside the reactor flask came to constant temperature. During this time the vial was reweighed to determine the weight of the sample and a second sample was analyzed for peroxide and base content.

After about 10 minutes to allow the temperature to become constant, about 4 cc. of diethylphthalate (DEP) were added to the flask. Then exactly 10 cc. of a mixture of 80% glacial acetic acid and 20% DEP were added slowly during which time the solution was stirred. The remainder of exactly 5 cc. of DEP was added then to remove any acetic acid from the glass tubing to prevent any of the acetic acid from being added initially to the next sample to be analyzed.

The burette reading was made after all of the yellow material had disappeared from the sample. The superoxide content was calculated from

$$\% = f(R/w)(273P/760T)$$

where

f = 0.491 for NaO_2 and 0.635 for KO_2

T = temperature of the cooling water

P = barometric pressure

R = burette reading minus 15

Since the temperature of the tap water was of the order of 10° C., the majority of the analyses were made with tap water for the temperature control.

III. RESULTS AND CONCLUSIONS

A. Oxidation of Hydrazobenzene in the Presence of Calcium Methylate and Calcium Ethylate and the Reaction of Hydrogen Peroxide with the Alcoholates in Non-aqueous Solutions

The sodium amalgam and methyl alcohol reduction of azobenzene in the alcohol and an inert solvent such as benzene was discussed by several investigators (3,30,31). This reduction reaction produced, for example, hydrazobenzene and sodium methylate according to reaction (4).

$$Ph_2N_2 + 2\ CH_3OH + 2\ NaHg_x \longrightarrow Ph_2N_2H_2 + 2\ CH_3ONa + 2x\ Hg \quad (4)$$

In this investigation calcium chloride dissolved in methanol or in the solid form was added to the reduced solution. A precipitate of sodium chloride and calcium methylate resulted as shown by reaction (5).

$$CaCl_2 + 2\ CH_3ONa \longrightarrow Ca(OCH_3)_2 + 2\ NaCl \quad (5)$$

The solubility of sodium chloride was known to be essentially zero in benzene and quite low in methyl alcohol at room temperature. For this reason it was known that the sodium ions could be removed as sodium chloride almost quantitatively from the standard solution consisting of about 60% benzene. However, it was found that calcium methylate was only very slightly soluble in methyl alcohol, the solu-

bility being of the order of 0.02 grams of calcium methylate per 100 grams of alcohol; the solubility in benzene was essentially zero.

These results showed that the exchange reaction (5) gave complete precipitation of the sodium methylate as calcium methylate with essentially an equivalent amount of sodium chloride.

When oxygen gas was passed through the slurry of gelatinous calcium methylate and sodium chloride in the hydrazobenzene solution, hydrogen peroxide formed and reacted with the calcium methylate as predicted by reactions (6) and (7).

$$Ph_2N_2H_2 + O_2 \longrightarrow Ph_2N_2 + HOOH \qquad (6)$$

$$Ca(OCH_3)_2 + HOOH \longrightarrow CaO_2 + 2\ CH_3OH \qquad (7)$$

Some calcium hydroperoxide methylate ($CaOOHOCH_3$) may have formed.

When all of the calcium methylate produced by reaction (5) was left in the slurry, about 58% of the $Ca(OCH_3)_2$ was converted to CaO_2. This showed that either or both of the reactions (6) and (7) were incomplete. The yield of calcium peroxide was about 86% after three hours of oxidation when one-half of the calcium methylate was removed before the oxidation. In this case the oxidation yield was only about 46%. The products obtained in both cases were very stable. Nearly identical results were obtained when ethyl alcohol

was substituted for methanol in the azobenzene solution.

Poor results for the above reactions were due, no doubt, to two factors. First, since calcium methylate was quite insoluble in the solvent mixture used, the resulting solution was only very weakly alkaline. It appeared that hydrazobenzene splits off its hydrogen atoms with oxygen to form hydrogen peroxide at a reasonably rapid rate only in fairly alkaline solution under the conditions used. This assumption was reasonably verified by the fact that oxidation in the presence of calcium methylate never reproduced the strong cherry-red color characteristic of the original azobenzene solution.

However, when 10% of the sodium methylate was left in the solution to increase the alkalinity, essentially the same results were obtained. This indicated a negative catalytic effect caused by the calcium methylate.

The second factor causing low yields of calcium peroxide was believed to be the catalytic decomposition on the surface of the calcium methylate. Actually excess hydrogen peroxide was never found in the solution and its decomposition by solid calcium alcoholates was shown to be quite strong. When solid calcium ethylate was added to a hydrogen peroxide solution of ethyl alcohol and a hydrogen peroxide solution in benzene and methyl alcohol containing azobenzene, nearly complete decomposition resulted while very little peroxide was found in the solid phase.

When working with calcium ethylate, which was precipitated from a hot ethyl alcohol solution as $Ca(OEt)_2 \cdot 2EtOH$, it was noted that the precipitate became dark due to oxidation. The formation of the yellow-resinous material was arrested by the addition of about 0.1% ethylene diamine dihydrochloride to the precipitate or solution of about 2% $Ca(OEt)_2$ in ethyl alcohol at room temperature.

B. Methods of Removing Sodium Methylate from the Reduced Solution.

Four methods were used to remove all or any desired fraction of the sodium methylate in the methanol and benzene solution containing hydrazobenzene. All of the $NaOCH_3$ was removed when the oxidation step was studied in the presence of $KOCH_3$, $LiOCH_3$, and LiOEt. Various fractions of the $NaOCH_3$ were removed to study the preparation of $Na_2O_2 \cdot 2H_2O_2$.

While the addition of calcium chloride to the reduced solution of hydrazobenzene and sodium methylate did not afford a method of producing a high-grade calcium peroxide product, it did provide a convenient means of removing any desired fraction of the sodium methylate. The solubility of $Ca(OCH_3)_2$ in methanol was about 0.02 grams per 100 grams of the methanol and essentially zero in benzene. However, the precipitate of sodium chloride and calcium methylate, probably as $Ca(OCH_3)_2 \cdot 2CH_3OH$, was found to be gelatinous and very difficult to filter. Slow addition of a calcium

chloride solution in methanol to the rapidly stirred sodium methylate solution gave a precipitate that filtered much more readily. However, in both cases considerable hydrazobenzene was adsorbed on the precipitate and was quite difficult to remove by washing. For this reason considerable hydrazobenzene was lost before the oxidation step and, therefore, the yield of peroxide products was cut down somewhat.

One advantage of the calcium chloride method was that any water that may have been in the hydrazobenzene solution was removed by reaction with calcium methylate as shown by reaction (8).

$$Ca(OCH_3)_2 + 2\ H_2O \longrightarrow Ca(OH)_2 + 2\ CH_3OH \qquad (8)$$

A second advantage offered by this method resulted in the purification of the 95% azobenzene before oxidation. The dark colored impurities were removed during the filtration step. When this step was eliminated and impure azobenzene was used, adsorption of the resinous material resulted on the peroxide precipitates.

However, as the filtration step was carried out with much difficulty, since hydrazobenzene was lost due to adsorption and since calcium methylate has no general use in the chemical industry at present, other methods were worked out to recover the sodium methylate which at present is an article of commerce.

A convenient method of removing sodium methylate from the hydrazobenzene solution was to separate two liquid phases that formed after completion of the reduction step. The one phase contained the greater portion of the hydrazobenzene in mainly benzene while the second phase contained about 93% of the sodium methylate in a solution of about equal volumes of benzene and methanol.

By making use of this method of removing sodium methylate to produce peroxide compounds such as $Na_2O_2 \cdot 2H_2O_2$ in a cyclic process the reduction of the azobenzene with sodium amalgam and methyl alcohol would be made as previously described. Two-thirds (2/3) of the sodium methylate would be removed in the phase rich in methylate. Thereafter, the hydrazobenzene would be removed from the remainder of this phase by extracting with benzene. The benzene solution would be added to the oxidation solution before oxidation to precipitate $Na_2O_2 \cdot 2H_2O_2$. Two-thirds of the sodium methylate produced on reduction would be recovered by evaporating the alcohol from the solution after the benzene extraction. The obvious advantage of this procedure would be the recovery of the valuable sodium methylate.

The phase diagram for sodium methylate, methanol, and benzene was worked out by Robinson (33). In this work the concentration of sodium methylate in a solution of benzene and methanol was determined; however, the tie lines showing the two liquid phases in equilibrium were not given. For

this reason it was very difficult to make use of the phase diagram.

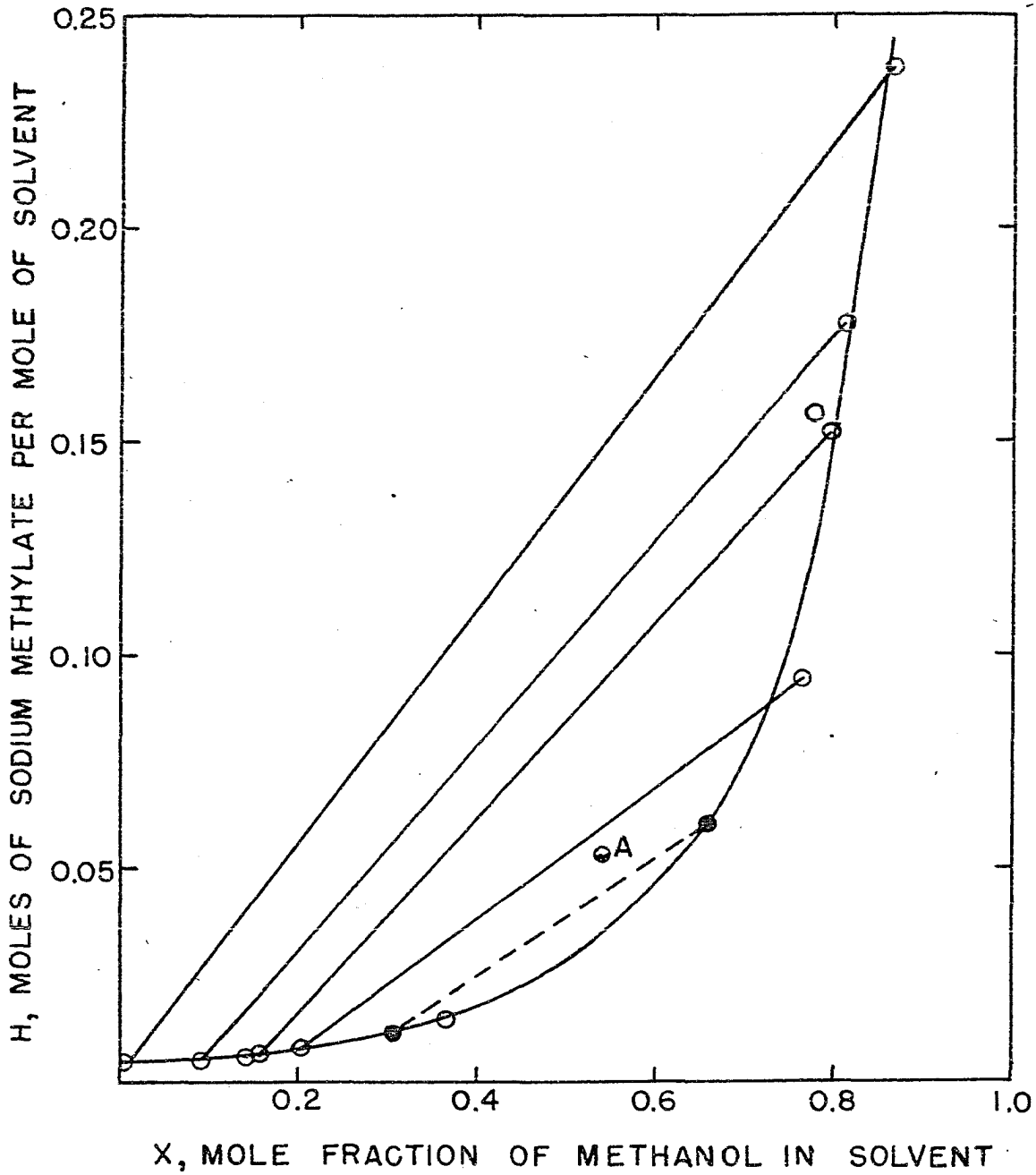
The above phase system was redetermined at room temperature by Doptoglon (9) and the tie lines showing the two liquid phases in equilibrium were determined. This phase system is presented in Figure 14.

In this diagram the mole fraction of methanol in the alcohol-benzene solvent is plotted on the abscissa. The ordinate, H, represents the moles of methylate per mole of total solvent. From Figure 14 it can be observed that with a sufficient amount of sodium methylate present two phases will separate, the concentrations of which can be read directly from the tie lines.

In the reduced solution hydrazobenzene represents a fourth component. To determine about what point on the phase diagram was reached when the standard solution was used, the hydrazobenzene was assumed to be equivalent to benzene. With complete reduction 80 grams of azobenzene required 0.88 moles of methyl alcohol and gave 0.88 moles of sodium methylate and 0.44 moles of hydrazobenzene assumed equivalent to 0.88 moles of benzene. The 600 cc. of benzene and 400 cc. of methyl alcohol were equivalent to 6.71 and 9.74 moles respectively. The mole fraction of alcohol in the final solution was, therefore, 0.54 and the moles of methylate per mole of solvent was 0.0535. This point is

FIGURE 14

PHASE SYSTEM BENZENE, METHANOL AND SODIUM METHYLATE



located at "A" on the phase diagram. It represents the maximum concentration of methylate that can be obtained on reduction of the standard solution.

The tie line located below point "A" was found by analysis of the two phases obtained after reduction of 3000 cc. of the standard solution. The sodium methylate content was determined by titration and the benzene and alcohol content by extracting the alcohol and methylate with a large amount of water. The hydrazobenzene remained in the benzene after extraction and the volume of the benzene solution was measured as pure benzene. The top layer contained 10.9 moles of benzene, 20.8 moles of alcohol, and 1.935 moles of methylate. The bottom layer contained 10.6 benzene, 4.78 alcohol, and 0.172 methylate. These results gave a mole fraction of alcohol of 0.66 with 0.061 moles of methylate per mole of solvent in the top layer. The respective values in the lower layer were 0.31 and 0.011. These results are represented on the diagram as the broken line.

The fact that this tie line lies below point "A" was due mainly to the presence of hydrazobenzene in the azobenzene in the original solution. Hydrazobenzene was present after oxidation in many cases due to incomplete oxidation. After oxidation the azobenzene was recovered by extracting the alcohol and alkali with water and then evaporating the benzene. In any actual cyclic process this recovery step would not be necessary.

From Figure 14 the effect of removing benzene and methanol from the system can be determined. Upon fractionation of the reduced solution containing hydrazobenzene and sodium methylate in a solvent of 40% methanol in benzene, an azeotrope boiled over at a concentration close to the solvent charge. The effect of this evaporation was to increase the ordinate, H, essentially on a vertical line. This resulted in a benzene phase lower in methylate and a methanol phase higher in methylate.

From Figure 14 the effect of adding sodium methylate to the reduced solution was found to increase the methylate content in the alcohol layer and decrease the concentration in the benzene layer while at the same time to increase the benzene and hydrazobenzene concentration in the benzene layer and decrease the benzene and hydrazobenzene concentration in the alcohol layer. The effect of adding methylate was also to increase the difference in density of the two phases, and, therefore, give better separation. Actually when the standard solution was used the benzene layer was slightly more dense than the alcohol layer; whereas, when the methylate was increased sufficiently in the alcohol phase, the benzene layer became less dense.

When toluene was substituted for benzene in the reduction solution and this solution fractionated after the reduction operation a condensate of all of the methanol was collected with about 13% of the toluene charge. The concen-

tration of the condensate, the major portion of which boiled at 63.3° C., was about 84% methanol. The solution remaining in the still pot consisted of hydrazobenzene in toluene. All of the sodium methylate was precipitated as $NaOCH_3$.

The advantage of this method was that the solid sodium methylate was recovered and that the product contained no alcohol of crystallization. Industrially the sodium methylate is recovered from a rather dilute solution of the alcohol by distillation of the alcohol. The fact that the precipitate $CH_3ONa \cdot 2CH_3OH$ forms in the evaporator necessitates special distillation equipment to remove the alcohol.

The fact that the methyl alcohol was more difficult to remove from the toluene and sodium methylate precipitate than from the toluene alone was shown by the distillation curves obtained. When the methanol was fractionated from toluene, the temperature remained constant and then rose sharply to the boiling point of toluene. When the methanol was fractionated from toluene and the methylate, during removal of the last portion of the alcohol there was a gradual increase in temperature. During this period the alcohol of crystallization was removed.

A very simple method used to remove any desired fraction of the sodium methylate from the reduced solution was by extracting the desired fraction of the solution with water. This left a hydrazobenzene solution in benzene which could be dried with calcium chloride. This method worked well for

laboratory work, but would not be desirable for the industrial preparation of $Na_2O_2 \cdot 2H_2O_2$, for example, because of the loss of the valuable sodium methylate and methyl alcohol into the water phase.

C. Preparation, Properties and Uses of Sodium Peroxide Diperoxyhydrate.

Sodium peroxide diperoxyhydrate ($Na_2O_2 \cdot 2H_2O_2$)or $NaOOH \cdot 1/2H_2O_2$ was prepared by D'Ans and Friederich (4): (a) from H_2O_2 and Na_2O_2 in Et_2O solution, (b) from NaOOH and H_2O_2 to Et_2O solution, (c) from NaOEt and H_2O_2, (d) by treating NaOOH with cold EtOH, and (e) by treating sodium with H_2O_2 in Et_2O solution.

The preparation of sodium hydroperoxide has been described by Manchot and Herzog (22) by the reaction of oxygen and a methanol solution of hydrazobenzene and sodium methylate. The preparation was described also in cyclic process whereby azobenzene was reduced by sodium amalgam and methyl or ethyl alcohol in benzene and the alcohol to produce the hydrazobenzene as well as essentially an equivalent amount of sodium methylate (3,31).

The reactions were repeated to produce the sodium hydroperoxide for use as an intermediate in the preparation of calcium peroxide. When the solution was cooled during the oxidation it was noted that a precipitate resulted with a ratio of peroxide equivalents to base equivalents higher

than that corresponding to sodium hydroperoxide. A value of this ratio, Z, close to 3.0 was obtained many times. The formula for the compound of sodium peroxide and hydrogen peroxide with a peroxide to base ratio of 3.0 was represented as $Na_2O_2 \cdot 2H_2O_2$ (sodium peroxide diperoxyhydrate). The compound may also be designated as $HOOH \cdot 2NaOOH$ or $NaOOH \cdot 1/2H_2O_2$.

The preparation of NaOOH by the above method may be described by reactions (9), (10), and (11).

$$Ph_2N_2 + 2\ CH_3OH + 2\ NaHg_x \longrightarrow Ph_2N_2H_2 + 2\ CH_3ONa + 2x\ Hg \quad (9)$$

$$Ph_2N_2H_2 + O_2 \longrightarrow Ph_2N_2 + HOOH \quad (10)$$

$$CH_3ONa + HOOH \longrightarrow CH_3OH + NaOOH \quad (11)$$

The preparation of $Na_2O_2 \cdot 2H_2O_2$ may be described by reactions (12), (13), and (14).

$$3\ Ph_2N_2 + 6\ CH_3OH + 6\ NaHg_x \rightarrow 3\ Ph_2N_2H_2 + 6\ CH_3ONa + 6xHg \quad (12)$$

$$3\ Ph_2N_2H_2 + 3\ O_2 \longrightarrow 3\ Ph_2N_2 + 3\ HOOH \quad (13)$$

$$2\ CH_3ONa + 3\ HOOH \longrightarrow 2\ CH_3OH + Na_2O_2 \cdot 2H_2O_2 \quad (14)$$

The reactions (12) and (13) are identical with (9) and (10).

The above equations show that when NaOOH (Z = 2.0) was precipitated at 100% oxidation yields, only one-half of the alkali was removed; whereas when $Na_2O_2 \cdot 2H_2O_2$ (Z = 3.0) was precipitated only one-third of the alkali was removed.

These reactions showed clearly why sodium methylate must be removed in a cyclic process producing, for example, $Na_2O_2 \cdot 2H_2O_2$.

A series of oxidations were made in order to determine about what rate the various solid peroxides precipitated and under what conditions $Na_2O_2 \cdot 2H_2O_2$ was the stable solid phase present in the oxidation solution. Various fractions of the sodium methylate were removed by the precipitation of calcium methylate and sodium chloride with calcium chloride. The oxidation step was carried out at 0° C. and 25° C. with no alkali removed, with one-half removed, and with two-thirds removed.

These reactions were made in an anhydrous medium of methyl alcohol and benzene. Any water, present in the original methanol and benzene or any water added during the reduction and handling of the solution, was removed by the calcium methylate as shown by reaction (8).

The results showed that NaOOH was the stable phase present when all the sodium methylate produced in the reduction step according to reaction (9) was left in the solution during the oxidation at temperatures of about 25° C. Sodium hydroperoxide was also the stable phase present in the oxidation solution during the initial oxidation time at 0° C. when no methylate was removed prior to the oxidation. However, this was gradually converted to $Na_2O_2 \cdot 2H_2O_2$. At a 90% yield only 30% of the methylate was removed from the

solution. It was concluded that the precipitate present during the oxidation at 0° C. consisted of mixed crystals of NaOOH and $Na_2O_2 \cdot 2H_2O_2$ and was not a solid solution.

When one-half (1/2) of the methylate was removed prior to the oxidation at 0° C. and about 25° C., $Na_2O_2 \cdot 2H_2O_2$ was the stable solid phase. In this case 60% of the remaining methylate was removed as $Na_2O_2 \cdot 2H_2O_2$.

When two-thirds (2/3) of the methylate was removed, $Na_2O_2 \cdot 2H_2O_2$ again was the stable phase and about 90% of the methylate remaining after the calcium chloride treatment was removed during oxidation as $Na_2O_2 \cdot 2H_2O_2$.

The above results showed a wide range of conditions under which $Na_2O_2 \cdot 2H_2O_2$ was more stable than NaOOH in the oxidation solution. Results obtained at a later date showed that it was quite difficult to prepare NaOOH by oxidation of the solution containing all of the sodium methylate. NaOOH was easily prepared when ethyl alcohol was substituted for the methyl alcohol in the reduction solution.

The above results showed that the sodium methylate concentration and the temperature were important factors in determining what solid phases were stable. Low temperature favored the formation of peroxyhydrates of increased peroxide to base ratio while high sodium methylate concentration favored the formation of peroxyhydrates of lower peroxide to base ratio.

The effect of the alcohol concentration was shown in this and previous work. Cunningham (3) showed that by decreasing the methanol concentration anhydrous sodium peroxide precipitated rather than NaOOH. D'Ans and Friederich, on the other hand, showed that $Na_2O_2 \cdot 2H_2O_2$ formed when NaOOH was treated with cold ethyl alcohol. The latter reaction was observed in this investigation when sodium hydroperoxide was prepared and washed with a methanol and benzene solvent. The NaOOH was partially converted to $Na_2O_2 \cdot 2H_2O_2$ for Runs No. 40 and No. 54. In both cases the precipitate had a peroxide to base ratio close to 2.0. After washing with methanol and benzene the peroxide to base ratios were 1.12 and 1.25 respectively.

The rate of precipitation of peroxide and the overall yield was essentially the same in all cases. The yield was based on the sodium methylate formed during the reduction operation. However, the reduced solution contained a small excess of methylate due to local discharge of the amalgam according to reaction (15).

$$2\ NaHg_x + 2\ CH_3OH \longrightarrow 2\ CH_3ONa + 2x\ Hg + H_2 \qquad (15)$$

For this reason there were less equivalents of hydrazobenzene than sodium methylate, and, therefore, at 100% oxidation of the hydrazobenzene all of the methylate could not have been removed. In addition a considerable amount of hydrazobenzene was lost in the calcium methylate precipitate

during filtration. On the other hand, the azobenzene used for the reduction always contained some hydrazobenzene due to incomplete oxidation during the previous preparation.

The results showed that the rate of oxidation of the hydrazobenzene was independent of the precipitate formed and the amount of methylate in solution. However, it should be noted that at least 10% of the methylate left after the calcium chloride treatment was always left in the solution after oxidation. When three-fourths (3/4) of the methylate was removed, $Na_2O_2 \cdot 2H_2O_2$ was precipitated and a very small amount of methylate remained with a considerable amount of hydrogen peroxide. In this case the yield of solid peroxide was reduced. In other cases the rate of oxidation appeared slightly less when no alkali was removed. For example at 0° C., this may have been due, in part, to the sharp separation of the two liquid layers.

In the above work the object was not to accurately determine the rate of oxidation. Important factors affecting the rate of oxidation that were not carefully controlled were the rate at which oxygen was bubbled into the solution and the rate of agitation. Under the conditions used, in general, it took from two to three hours to give a 90% yield based on the sodium methylate.

Three-fourths of the sodium methylate was removed in one case in an attempt to prepare $Na_2O_2 \cdot 4H_2O_2$. In this case $Na_2O_2 \cdot 2H_2O_2$ formed when oxidation was carried out at 0° C.

In one oxidation carried out at 0° C. with no methylate removed at the early stages of the oxidation a precipitate was obtained that had a peroxide to base ratio of about five. This corresponded to $Na_2O_2 \cdot 4H_2O_2$.

The $Na_2O_2 \cdot 2H_2O_2$ precipitate was obtained in a state of rather high purity. The peroxide to base ratio of the product was generally of the order of 2.96 when calcium chloride was used to remove the methylate. The equivalents of peroxide per gram were of the order of 0.040. Assuming all of the peroxide present as $Na_2O_2 \cdot 2H_2O_2$, the product would be about 97.5% $Na_2O_2 \cdot 2H_2O_2$. However, with a peroxide to base ratio of 2.96, the precipitate may be assumed to be 96 moles of $Na_2O_2 \cdot 2H_2O_2$ to four moles of $Na_2O_2 \cdot H_2O_2$. It can readily be shown that this mixture would have about 0.04085 equivalents of peroxide per gram. Under this assumption the above mixture would have a purity of 98.0%, and about 2% was still unaccounted for. This may have been solvent, azobenzene, or water.

When $Na_2O_2 \cdot 2H_2O_2$ and NaOOH samples were stored at 6° C. a varying amount of decomposition, ranging from about 0% to 3% in four weeks, took place. Some samples showed marked decomposition after varying periods of time after four weeks. However, this is to be expected since the samples were stored in closed bottles such that the water liberated when a small amount decomposed could not escape

and, therefore, remained on the sample and caused further decomposition.

To increase the stability of $Na_2O_2 \cdot 2H_2O_2$, 5% of CaO and 5% of $CaSO_4$ were added to remove water to prevent its further decomposition of the product. The results were difficult to interpret due to the fact that the control sample was quite stable. The sample containing CaO did not give consistent results. This may have been due to segregation of the CaO. The largest decomposition resulted with CaO in the bulk sample. This sample contained lumps while the other samples poured freely. CaO may have decomposed the $Na_2O_2 \cdot 2H_2O_2$ due to its alkaline reaction with the very weak acetic H_2O_2.

The results also showed that the larger samples of about ten grams gave about the same stability data as very small samples of about 0.2 grams. This is important in considering the shipment of large lots of the material.

Several factors were believed to cause some samples of $Na_2O_2 \cdot 2H_2O_2$ to show less decomposition than others. This may have been due to impurities in the crystals or to the crystal structure. Similar results were obtained in the decomposition of $Na_2O_2 \cdot 2H_2O_2$ to give sodium superoxide (NaO_2) in that some samples were considerably more stable than others.

It was shown that when $Na_2O_2 \cdot 2H_2O_2$ was precipitated from a solution (Run No. 55, Table II) which was dried with calcium methylate over night the precipitate obtained was

pure (Z = 2.98) and remained very stable compared to samples prepared by oxidizing a solution in which the sodium methylate was removed by the phase separation method (Run 54). The latter precipitate had a peroxide to base ratio of 2.72 and showed about 14 times more decomposition when stored at 6° C. for 21 weeks than the former showed when stored for 13 weeks at 6° C.

The former preparation showed excellent stability at room temperature compared to the preparations previously made. This sample was stored 13 weeks at 6° C., then two weeks at 25° C. The total decomposition was only 10.7%. A previous sample showed 80% decomposition after storage at 6° C. for four weeks, then at 25° C. for two weeks.

From the above results, it was concluded that when precipitation was made from solutions from which water was completely removed, the $Na_2O_2 \cdot 2H_2O_2$ (and NaOOH) precipitated in a more stable form. When small amounts of water were present this may have entered the crystal lattice and decreased the stability of the crystals. This does not appear to be the case when precipitates form such as $Na_2O_2 \cdot 8H_2O$ and $NaOOH \cdot H_2O$. Small amounts of these compounds may form when water is present in the oxidation solution. Small amounts of $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ also may have formed.

The results showed that $Na_2O_2 \cdot 2H_2O_2$ prepared by utilizing calcium chloride was very stable and very difficult to

convert to superoxide and that $Na_2O_2 \cdot 2H_2O_2$ prepared by utilizing the phase separation method or water extraction and not utilizing calcium chloride was much less stable and very much more easily converted to superoxide as shown by evacuating the samples. It was concluded, therefore, that there was a definite relation between the rate of superoxide formation under vacuum and the decomposition of the samples stored at 6° C. It was verified definitely that sodium superoxide did form at 6° C. because of the fact that several samples evolved oxygen when dissolved in ice water and liberated oxygen when analyzed for superoxide.

It was concluded that the mechanism by which at least part of the $Na_2O_2 \cdot 2H_2O_2$ that decomposed at 6°, and also at room temperature was by the solid-solid oxidation reduction reaction shown by reaction (16).

$$Na_2O_2 \cdot 2H_2O_2 \longrightarrow 2\ NaO_2 + 2\ H_2O \qquad (16)$$

However, since the reaction produces water and the samples were stored in closed containers, decomposition of the superoxide took place according to reaction (17).

$$2\ NaO_2 + H_2O \longrightarrow Na_2O_2 + H_2O + O_2 \qquad (17)$$

The above results showed that when $Na_2O_2 \cdot 2H_2O_2$ was prepared by removing the sodium methylate by the phase separation method, calcium chloride or some other dehydrating agent should be used to remove water.

The above methods represent a convenient means of producing $Na_2O_2 \cdot 2H_2O_2$, a stable peroxide compound. Starting with sodium chloride brine, the overall reaction whereby $Na_2O_2 \cdot 2H_2O_2$ would be produced is given by reaction (18).

$$6\ NaCl + 3\ O_2 + 4\ CH_3OH \rightarrow 3\ Cl_2 + 4\ NaOCH_3 + Na_2O_2 \cdot 2H_2O_2 \quad (18)$$

All intermediate reactions may be carried out at normal pressure and near room temperature. The raw materials are sodium chloride, methyl alcohol, and purified air or oxygen.

Since $Na_2O_2 \cdot 2H_2O_2$ can be produced from the sodium chloride at high yields and low cost by the above-mentioned process, and since the product was of high purity and quite stable when held at temperatures of the order of 6° C. without any stabilizer, it is well worth while to consider its potential uses as a source of hydrogen peroxide.

Pure $Na_2O_2 \cdot 2H_2O_2$ is equivalent to 70% hydrogen peroxide by weight. Its potential use as a source of high grade alkaline hydrogen peroxide for bleaching purposes was quite obvious.

Since the $Na_2O_2 \cdot 2H_2O_2$ may be used as a bleaching agent for wood pulp, etc., the above process represents a source of three peroxide equivalents to one alkali. In the present method used to convert sodium chloride to chlorine and caustic by means of electrolysis, the chlorine and caustic are produced in equivalent amounts.

Any methods that have been used to produce hydrogen peroxide from sodium peroxide could be used to produce hydrogen peroxide solutions from $Na_2O_2 \cdot 2H_2O_2$. However, much less base need be removed.

D. Potassium Peroxide Diperoxyhydrate.

Potassium peroxide diperoxyhydrate ($K_2O_2 \cdot 2H_2O_2$) was prepared by the oxidation at 0° C. of hydrazobenzene in benzene and methyl alcohol with gaseous oxygen in the presence of potassium methylate. After reduction all of the sodium methylate was removed by procedures previously described. Potassium methylate was prepared by the reaction of potassium metal with methyl alcohol and this solution added to the hydrazobenzene solution.

Although this procedure was a convenient method to prepare the oxidation solution containing potassium methylate, on a large scale the solution would best be prepared by the use of potassium amalgam in the same manner that the sodium methylate solutions were prepared. In the procedure potassium methylate would need to be removed. On the other hand, potassium methylate could be used to reduce one-third of the required amount of hydrazobenzene solution, while the remainder would be prepared by sodium amalgam reduction followed by complete removal of the sodium methylate. This would eliminate the use of large amounts of potassium

chloride for the preparation of the required amount of amalgam and would give sodium methylate as the by-product.

The $K_2O_2 \cdot 2H_2O_2$ was crystalline and somewhat easier to filter than $Na_2O_2 \cdot 2H_2O_2$. This growth of larger crystals of $K_2O_2 \cdot 2H_2O_2$ than $Na_2O_2 \cdot 2H_2O_2$ agreed with the fact that more peroxide was left in the oxidation solution during oxidation in the presence of $KOCH_3$ than $NaOCH_3$. Obviously the larger solubility of the $K_2O_2 \cdot 2H_2O_2$ gave conditions more favorable for the growth of larger crystals.

Accurate analyses of $K_2O_2 \cdot 2H_2O_2$ were not made because of the instability of the material. However, the peroxide to base ratio was accurately determined by dissolving the freshly prepared sample, still wet with cold benzene, in ice water. The values obtained were generally close to three. However, several times a value of about 3.5 was obtained. It was concluded that this product was a mixture of $K_2O_2 \cdot 2H_2O_2$ and $K_2O_2 \cdot 4H_2O_2$.

Since low temperature favored the formation of $Na_2O_2 \cdot 2H_2O_2$, the oxidations for the preparation of $K_2O_2 \cdot 2H_2O_2$ were made at 0° C. In addition, the low temperature was necessary in order to prevent decomposition of the crystalline $K_2O_2 \cdot 2H_2O_2$.

When $K_2O_2 \cdot 2H_2O_2$ was added to methanol and a solution of 40% methanol in benzene at 0° C., some decomposition resulted with the evolution of oxygen. Some yellow KO_2 resulted in

the benzene solution. Titrations after one hour gave a peroxide to base ratio of dissolved material of 0.15 in the 40% alcohol solvent and 0.04 in the alcohol. Based on the peroxide present the solubility was 0.028 and 0.90 grams of $K_2O_2 \cdot 2H_2O_2$ per 100 cc. of the 40% alcohol solution and the pure alcohol respectively.

Although about eight times as much alkali went into the alcohol as in the 40% alcohol solvent, the relative amount of decomposition of dissolved material was larger for the 40% alcohol solvent. Nevertheless, the total amount of peroxide decomposed in the alcohol solution was about seven times larger than that decomposed in the 40% alcohol solvent.

The instability of $K_2O_2 \cdot 2H_2O_2$ was shown also by its rapid decomposition on allowing the powder to become warm after filtration and washing. This decomposition resulted in the formation of a considerable amount of potassium superoxide. This reaction was used to prepare potassium superoxide in good yields.

The most stable precipitates of $K_2O_2 \cdot 2H_2O_2$ were made by oxidizing at 0° C. The precipitate was removed by filtration, washed with a benzene solvent containing 10% methanol at 0° C. and then finally washed with cold benzene to remove the methanol. The presence of methyl alcohol caused the product to decompose more quickly on drying. Washing with liquid ammonia would be advantageous to remove

water as well as the alcohol to increase the stability of the $K_2O_2 \cdot 2H_2O_2$.

E. Lithium Peroxide Monoperoxyhydrate and Lithium Peroxide.

Lithium chloride, like calcium chloride in that it was quite soluble in methanol and ethyl alcohol, was added to the reduced solution of sodium methylate and sodium ethylate in benzene and the respective alcohols to give a precipitate of insoluble sodium chloride. In this manner hydrazobenzene solutions of lithium methylate and lithium ethylate were prepared for oxidation.

When the hydrazobenzene was oxidized in benzene and methyl alcohol containing an equivalent amount of lithium methylate lithium peroxide formed, However, the peroxide to base ratio of this product was generally greater than one. This showed that some $Li_2O_2 \cdot H_2O_2$ was present which gave a product of rather poor stability at room temperature.

In contrast to the oxidation in the presence of an equivalent amount of sodium methylate or sodium ethylate where NaOOH formed, the results showed that there was a strong tendency for Li_2O_2 to precipitate and remain stable under the conditions used, and showed that to prepare $Li_2O_2 \cdot H_2O_2$ the lithium methylate must be present in the standard reduced solution in an amount less than the equivalents of sodium methylate produced in the reduction step.

It also indicated that, since the lithium peroxide was fairly stable in the solution of methyl alcohol and benzene, the normal peroxide Li_2O_2 could be produced in a stable form in a ethyl alcohol and benzene solvent.

To prepare lithium peroxide ethyl alcohol was substituted for methanol in the reduction solution. Upon oxidation of a solution containing an amount of lithium ethylate equivalent to the original sodium ethylate, Li_2O_2 with a peroxide to base ratio of 0.98 formed. When the LiOEt was present in an amount equivalent to one-half of the original NaOEt, Li_2O_2 again formed with a peroxide to base ratio of 0.96. In both cases about 97% of the LiOEt was removed as the Li_2O_2.

These lithium peroxide samples were very finely divided and very light in density. No trace of hydrogen peroxide was left in the oxidation solution. This result showed a very low solubility of Li_2O_2 in the solution used. Since the solubility was very low, the growth of small crystals was expected. It was noted that there was a gradation of increased solubility and increased crystal size for the peroxides formed with lithium through sodium to potassium.

The Li_2O_2 products had about a 91% purity. The excess material was not lost under vacuum. It was concluded that this material was largely impurities in the lithium chloride. After sixty-five days the samples lost 2% and 3% available oxygen when stored at room temperature in closed bottles.

This instability may have been due to the impurities or small amounts of alcohol present.

A mixture of Li_2O_2 and $Li_2O_2 \cdot H_2O_2$ was made by oxidizing hydrazobenzene in benzene and methanol with one-half of the $LiOCH_3$ present. The oxidation was made at 0° C. and the precipitate was washed with the 90% benzene solvent at 0° C. The precipitate had a peroxide to base ratio of 1.57 which corresponded empirically to $Li_2O_2 \cdot 0.57H_2O_2$. The product contained 93.0% $Li_2O_2 \cdot 0.57H_2O_2$. The material lost hydrogen peroxide when stored at two to three mm. pressure in the presence of barium oxide. After eighteen days the product contained 91.7% $Li_2O_2 \cdot 0.16H_2O_2$ and after twenty-seven days 90.6% $Li_2O_2 \cdot 0.065H_2O_2$. These calculations neglected the presence of any lithium hydroxide that may have formed due to decomposition of a small amount of Li_2O_2.

These results were compared to those obtained by deForcrand (7) who prepared $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ from the reaction of hydrogen peroxide with lithium hydroxide in aqueous ethyl alcohol. On drying over phosphorus pentoxide in the cold the precipitate gradually lost water and hydrogen peroxide. After eight days $Li_2O_2 \cdot 0.15H_2O$ was obtained.

The fact that H_2O_2 distilled from the Li_2O_2 compounds and left undecomposed Li_2O_2 showed that the molecular structure of the peroxide compound with a peroxide to base ratio of 2.0 was $Li_2O_2 \cdot H_2O_2$ rather than LiOOH. The material which

was very white when prepared became pale brownish-yellow. This may have been due to the oxidation of some adsorbed organic material or, more logically, to the formation of the superoxide LiO_2, the existence of which has not yet been proven.

When $LiOCH_3$ was present in the oxidation solution in an amount equivalent to about one-third of the original $NaOCH_3$, $Li_2O_2 \cdot H_2O_2$ formed when the solution was oxidized. However, when the precipitate was washed with a solvent containing equal volumes of benzene and methanol, the white material decomposed with the formation of a brownish-yellow product that liberated oxygen when dissolved in ice water. The peroxide to base ratio was 0.905 and assuming the peroxide present as Li_2O_2, the material contained only 75% Li_2O_2. This material gave a superoxide content of 5.8% LiO_2 when analyzed by the method of Seyb and Kleinberg.

The above results indicated very strongly that the superoxide LiO_2 does exist. In the above preparation it was produced by the oxidation of peroxide oxygen by the hydrogen peroxide.

Very pure $Li_2O_2 \cdot H_2O_2$ was produced when the $LiOCH_3$ was present in an amount equivalent to about 30% of the original $NaOCH_3$ and oxidation was carried out at 0° C. The product was washed with a 90% benzene solvent at 0° C. and small samples added to ice water for analysis. The peroxide to

base ratio was 2.0. After warming before evacuation to remove the benzene the material decomposed rapidly to mainly lithium hydroxide.

The rate of oxidation of hydrazobenzene in the presence of lithium ethylate and lithium methylate appeared to be slightly slower than the rate in the presence of sodium methylate, which in turn appeared slightly slower than the rate in the presence of potassium methylate. The difference in rates, however, was not great; the controlling factor appeared to be the rate at which the oxygen reacts with the hydrazobenzene, which did not depend to a large degree on the alkali metal methylate present nor on the manner in which the hydrogen peroxide was precipitated.

F. Formation of Potassium Superoxide from Potassium Peroxide Diperoxyhydrate.

The study of the preparation of NaO_2 from $Na_2O_2 \cdot 2H_2O_2$ and KO_2 from $K_2O_2 \cdot 2H_2O_2$ followed from the fact that $Na_2O_2 \cdot 2H_2O_2$ formed a trace of yellow material when heated on a melting-point apparatus, and in the same manner $K_2O_2 \cdot 2H_2O_2$ decomposed to give a yellow product on warming after being prepared at 0° C. The yellow material dissolved in ice water with the evolution of oxygen.

The reaction that took place was postulated to be the oxidation of the peroxide oxygen attached to the metal ions by the hydrogen peroxide as shown by reaction (19).

$$K_2O_2 \cdot 2H_2O_2 \longrightarrow 2\ KO_2 + 2\ H_2O \qquad (19)$$

From the fact that the superoxide was formed as the result of the reduction of the hydrogen peroxide, the above conversion resulted in the formation of superoxide and water. Therefore, from the outset it was obvious that in order to obtain reasonable yields, the water would need to be removed from the reaction site to prevent its decomposition of the superoxide. Several procedures were used to carry out this conversion. Vacuum, a stream of oxygen gas and ammonia gas, and liquid ammonia were used to remove water. Ultra-violet light was used to catalyze the conversion in preliminary work. At the outset there was some question that while a high vacuum rapidly removed the water, it also may have removed oxygen from the hydrogen peroxide, or otherwise removed hydrogen peroxide, or caused the superoxide to dissociate. For this reason the use of a gas stream appeared advantageous.

The results obtained on the preparation of KO_2 showed that it formed from $K_2O_2 \cdot 2H_2O_2$ very rapidly by merely allowing the precipitate to warm after it had formed at 0° C. in the anhydrous benzene and methanol solvent. When the samples were placed in a desiccator and evacuated to about three mm. a large amount of water was removed and the superoxide content was increased to about 69% KO_2. A sample containing 69% KO_2 was obtained when a sample of about ten grams was

irradiated with a sunlamp while ammonia gas was drawn through the sample. When oxygen was used a product containing 53% KO_2 was obtained.

It was concluded that better results with ammonia gas compared to oxygen was because of the high dehydrating action of the ammonia gas.

The conversion with ultra-violet light in liquid ammonia at -33° C. appeared to be quite good. However, after filtration the material decomposed. This decomposition may have been avoided if the tightly packed sample were spread out. Decomposition also resulted when the conversion was made with $Na_2O_2 \cdot 2H_2O_2$.

The effect of ultra-violet light on the preparation of KO_2 was difficult to interpret. The results obtained without the use of the light appeared about the same. However, the decomposition began sooner and the decomposition time was slightly less when ultra-violet light was used. This may have been due largely to a heating effect.

When $K_2O_2 \cdot 2H_2O_2$ was added to a 40% methyl alcohol solution in benzene, decomposition with the formation of some yellow KO_2 resulted. Alcohols tended to decompose the diperoxyhydrates while, on the other hand, they tended to increase the ease of superoxide formation.

The above results showed that $K_2O_2 \cdot 2H_2O_2$ was readily converted to KO_2 at temperatures close to room temperature and considerably below room temperature. At -33° C., how-

ever, the rate of superoxide was not great. Since the conversion was rapid at room temperature, since liquid ammonia is a very strong dehydrating agent, and since superoxides are stable in liquid ammonia, the conversion of $K_2O_2 \cdot 2H_2O_2$ to KO_2 in liquid ammonia under pressure at temperatures close to room temperature is predicted to be an excellent means of obtaining a higher grade KO_2 product than obtained thus far.

Conversion of $K_2O_2 \cdot 2H_2O_2$ to KO_2 under high vacuum should also result in the formation of higher yields. It should be noted that a pressure of about three mm. mercury was used.

The accuracy of the analyses made for the KO_2 samples and also the NaO_2 samples depended largely on two factors. It was estimated that the superoxide content was accurate to about 5%. Analyses depending on magnetic susceptibility are accurate to only about 10%.

The accuracy of the total peroxide content depended on reaction (20).

$$2\ KO_2 + H_2O \longrightarrow K_2O_2 \cdot aq + O_2 \qquad (20)$$

It was previously pointed out that some peroxide decomposition resulted due to local heating effects. For this reason the peroxide content obtained in the above manner was somewhat low, the extent of which was not estimated.

To show more clearly the composition of the KO_2 products obtained from evacuation of $K_2O_2 \cdot 2H_2O_2$, it was assumed that no potassium carbonate or other impurities were present, and the percent by weight of the KO_2 samples was calculated from the data given in Table VI on the basis that the samples were composed of KO_2, KOH, $K_2O_2 \cdot 2H_2O_2$ and H_2O. These results are given in Table IX.

Table IX

Approximate Composition of KO_2 Samples

Basis: One gram

Run No.	Base meq.	Peroxide meq.	KO_2 gm.	$K_2O_2 \cdot 2H_2O_2$ gm.	KOH gm.	H_2O gm.
S27A	12.9	8.4	0.612	0	0.238	0.150
S27B	12.8	13.0	0.696	0.095	0.108	0.101
S29	12.8	11.3	0.615	0.076	0.182	0.127
S30	13.6	8.1	0.622	0	0.265	0.115

On an average the results from Table VI indicated that the KO_2 products contain roughly 2.5 moles of KO_2 to one mole of KOH and two moles of water. The water content appeared quite high. This may have been due largely to low peroxide values obtained or to the presence of carbonate.

The fact that, on an average, essentially no peroxide was present other than that in the superoxide, again showed the high thermodynamic instability of $K_2O_2 \cdot 2H_2O_2$.

Undoubtedly, the water was present as water of crystallization on the KOH. The above KO_2 samples could possibly be concentrated by utilizing difference in properties of the KO_2 and KOH, for example densities.

After the completion of this work a paper was published on the decomposition of $K_2O_2 \cdot 2H_2O_2$ at 0° C. under high vacuum (18). The authors reported a 91% conversion under high vacuum. The superoxide content was determined by magnetic susceptibility measurements and was reported accurate to within 10%. These results were better than the results reported in this work; however, a lower vacuum was used and possibly smaller samples were used such that the removal of the water was more easily accomplished.

G. Formation of Sodium Superoxide from Sodium Peroxide Diperoxyhydrate.

1. Effect of ultra-violet light and heat on the conversion of $Na_2O_2 \cdot 2H_2O_2$ to NaO_2. - Sodium superoxide formed much less readily from $Na_2O_2 \cdot 2H_2O_2$ than KO_2 formed from $K_2O_2 \cdot 2H_2O_2$. This is in agreement with the fact that potassium metal is readily converted to the superoxide while very high pressure and moderately high temperatures are required to oxidize sodium peroxide to the superoxide using pure oxygen.

When $K_2O_2 \cdot 2H_2O_2$ warmed after being prepared at 0° C. it rapidly converted to KO_2, while rather pure samples of

$Na_2O_2 \cdot 2H_2O_2$ and $Na_2O_2 \cdot H_2O_2$ (NaOOH) were stable when stored at 25° C. from two to eighteen hours under vacuum to remove solvent. When $Na_2O_2 \cdot 2H_2O_2$ was heated under vacuum some NaO_2 formed. This showed that the increased temperature produced sufficient activation for the oxidation reaction to proceed at a reasonable rate.

Since $Na_2O_2 \cdot 2H_2O_2$ was quite stable, the study of its conversion to NaO_2 was made first by means of ultra-violet light and vacuum or a stream of oxygen gas to remove the water formed.

The results obtained showed that a considerable amount of superoxide formed in relatively short periods of time ranging from one to hour hours. However, in many cases a considerable amount of decomposition resulted with the formation of sodium hydroxide or sodium monoxide. The effect of the ultra-violet light was difficult to interpret because considerable heating resulted. Gradual heating of $Na_2O_2 \cdot 2H_2O_2$ samples under vacuum produce a gradual color change from white to yellow. Further heating caused rapid decomposition such that the superoxide content reached only about 10%.

When samples were irradiated with a sunlamp, the surface rapidly turned yellow. It was concluded that this was due to the catalytic action of the ultra-violet light as well as the heating effect. The superoxide content of several preparations reached from 30% to 40% NaO_2. A

varied amount of decomposition to sodium hydroxide resulted as shown by the peroxide to base ratio recorded in Table VII. This varied amount of decomposition for the different samples, undoubtedly, depended on the temperature of the sample and several other factors including the efficiency at which the water was removed.

It should be noted that this initial work on the preparation of NaO_2 was done in rather crude apparatus. Refinement in the apparatus and procedure used would undoubtedly increase the yield of NaO_2 from methods utilizing ultra-violet light. In later work it was shown that considerable decomposition resulted at 40° C. The temperature of the $Na_2O_2 \cdot 2H_2O_2$ generally went above 40° C. during the preparations utilizing ultra-violet light and, therefore, the heating may have been responsible for a large fraction of the decomposition.

Although the amount of NaO_2 that formed in a given length of time was less when samples were placed in a quartz flask which was then evacuated and placed in front of the lamp at a sufficient distance to prevent excess heating, the amount of decomposition of the remaining $Na_2O_2 \cdot 2H_2O_2$ was also less. The amount of decomposition was also low in several cases where oxygen gas was passed through the sample during irradiation.

It would be a reasonable conclusion, therefore, that ultra-violet light did convert the $Na_2O_2 \cdot 2H_2O_2$ to NaO_2 and

water without much decomposition of the diperoxyhydrate as such; while heat alone caused considerable decomposition without superoxide formation as well as superoxide formation due to the supply of the required amount of thermal energy. The latter conclusion was reasonably verified by the fact that rapid heating of $Na_2O_2 \cdot 2H_2O_2$ resulted in the formation of sodium hydroxide without the formation of any trace of yellow superoxide. In either case the water formed in the presence of the superoxide and as a consequence of reaction (20) may have gone to decompose the superoxide if the water were not readily removed.

$$Na_2O_2 \cdot 2H_2O_2 \longrightarrow 2\ NaO_2 + 2\ H_2O \qquad (20)$$

Likewise, the water formed in the presence of superoxide as a result of the thermal decomposition of the $Na_2O_2 \cdot 2H_2O_2$ without superoxide formation as shown by reaction (21) may have gone to decompose any superoxide that may have formed by reaction (20).

In the latter reaction one-half of the water may have gone (21)

In the latter reaction one-half of the water may have gone to convert the sodium monoxide to sodium hydroxide. The detrimental effect of heating was, therefore, to decompose any superoxide that survives the water that must form along with the superoxide as shown by reaction (20).

Doptoglon (9) showed that light obtained from a R-S sunlamp produced BaO_4 from $BaO_2 \cdot 2H_2O_2$ while other light sources including the mercury-arc lamp failed to give BaO_4. The results obtained in this work are in agreement with this conclusion in that rather poor results were obtained with the mercury-arc lamp. However, in this case sufficient data was not available to draw a definite conclusion.

2. Removal of the water formed with the sodium superoxide by means of vacuum. - It was discovered that NaO_2 did form slowly from $Na_2O_2 \cdot 2H_2O_2$ without the application of heat or the use of ultra-violet light. In fact, it was concluded that the decomposition of the $Na_2O_2 \cdot 2H_2O_2$ samples stored at 6° C. was due, at least in part, to the superoxide formation and subsequent decomposition due to the water formed which obviously could not escape since the samples were stored in closed bottles.

In determining the peroxide content of the samples stored at 6° C., it was noted in many cases that some oxygen was evolved on dissolving the samples in ice water. These samples were always pale yellow in color. Oxygen was never evolved when freshly prepared samples were dissolved in ice water.

The above results were used to study the preparation of NaO_2 from the decomposition of $Na_2O_2 \cdot 2H_2O_2$ under vacuum. Barium oxide was used in the desiccators to lower the vapor

pressure of water. In this study it was discovered that of the polyperoxyhydrates of sodium peroxide, those samples with an initial peroxide to base ratio considerably below three were more readily converted to NaO_2 than the relatively pure samples. Likewise, the relatively pure samples gave better stability tests at 6° C.

For this reason the theoretical amount of superoxide possible from $Na_2O_2 \cdot H_2O_2$ (NaOOH) and $Na_2O_2 \cdot 2H_2O_2$ was calculated at various conversions.

If $Na_2O_2 \cdot 2H_2O_2$ reacted with complete conversion to NaO_2 according to reaction (22) and if there were complete loss of water, the final product would have been 100% NaO_2. If $Na_2O_2 \cdot H_2O_2$ decomposed according to reaction (23), the final product would have been 58.5% NaO_2 and would have a peroxide to base ratio (Z) of 1.0. On the other hand, if $Na_2O_2 \cdot H_2O_2$ decomposed according to reaction (24), the final product would have been 78% NaO_2 with a value for Z of 0.667.

$$Na_2O_2 \cdot 2H_2O_2 \longrightarrow 2\ NaO_2 + 2\ H_2O \qquad (22)$$

$$Na_2O_2 \cdot H_2O_2 \longrightarrow NaO_2 + 0.5Na_2O_2 + H_2O \qquad (23)$$

$$3\ Na_2O_2 \cdot H_2O_2 \longrightarrow 4\ NaO_2 + Na_2O + 3\ H_2O \qquad (24)$$

The theoretical reaction curves were calculated assuming complete loss of water according to the mechanisms shown by the above equation. The calculations are tabulated in Table X and the results are plotted in Figure 15.

Table X

Calculation of Ratio of Peroxide to Base vs. NaO_2

Starting Material	Fraction Reacted	Starting Material Left			Material Form			
		grams	Eq. Base	Eq. Peroxide	NaO_2 grams	NaO_2 Eq.	Na_2O_2 grams	Na_2O_2 Eq.
$Na_2O_2 \cdot 2H_2O_2$	0	142	2	6	0	0	0	0
146 grams Mech. (1)	0.25	109.4	1.5	4.5	27.5	0.5	0	0
	0.5	73	1	3	55	1	0	0
	0.75	36.4	0.5	1.5	82.5	1.5	0	0
	1	0	0	0	110	2	0	0
$Na_2O_2 \cdot H_2O_2$	0	112	2	4	0	0	0	0
112 grams Mch. (2)	0.25	84	1.5	3	13.75	0.25	9.75	0.2
	0.5	56.0	1.0	2	27.5	0.5	19.5	0.5
	0.75	28.0	0.5	1	41.25	0.75	29.25	0.7
	1	0	0	0	55	1	39	1
$3Na_2O_2 \cdot H_2O_2$	0	336	6	12	0	0	0	0
336 grams Mch. (3)	0.25	252	4.5	9	55	1	0	0
	0.5	168	3	6	110	2	0	0
	0.75	84	1.5	3	165	3	0	0
	1	0	0	0	220	4	0	0

* Calculations are theoretical and based on the assumed mechanisms:

(1) $Na_2O_2 \cdot 2H_2O_2 = 2NaO_2 + 2H_2O$ (2) $Na_2O_2 \cdot H_2O_2 = NaO$

(3) $3Na_2O_2 \cdot H_2O_2 = 4NaO_2 + Na_2O + 3H_2O$

Table X

on of Ratio of Peroxide to Base vs. NaO_2 Content*

Material Left		Material Formed							
Eq. ase	Eq. Peroxide	NaO_2 grams	Eq.	Na_2O_2 grams	Eq.	Na_2O grams	Eq.	Peroxide to Base Ratio	% NaO_2
2	6	0	0	0	0	0	0	3	0
1.5	4.5	27.5	0.5	0	0	0	0	2.5	20.05
1	3	55	1	0	0	0	0	2.0	39.8
0.5	1.5	82.5	1.5	0	0	0	0	1.5	64.0
0	0	110	2	0	0	0	0	1.0	100.0
2	4	0	0	0	0	0	0	2.0	0
1.5	3	13.75	0.25	9.75	0.25	0	0	1.75	12.8
1.0	2	27.5	0.5	19.5	0.5	0	0	1.50	26.7
0.5	1	41.25	0.75	29.25	0.75	0	0	1.25	41.8
0	0	55	1	39	1	0	0	1.0	58.5
6	12	0	0	0	0	0	0	0	0
4.5	9	55	1	0	0	15.5	0.5	1.67	17.1
3	6	110	2	0	0	31.0	1	1.33	35.6
1.5	3	165	3	0	0	46.5	1.5	1.0	55.9
0	0	220	4	0	0	62	2	0.67	78

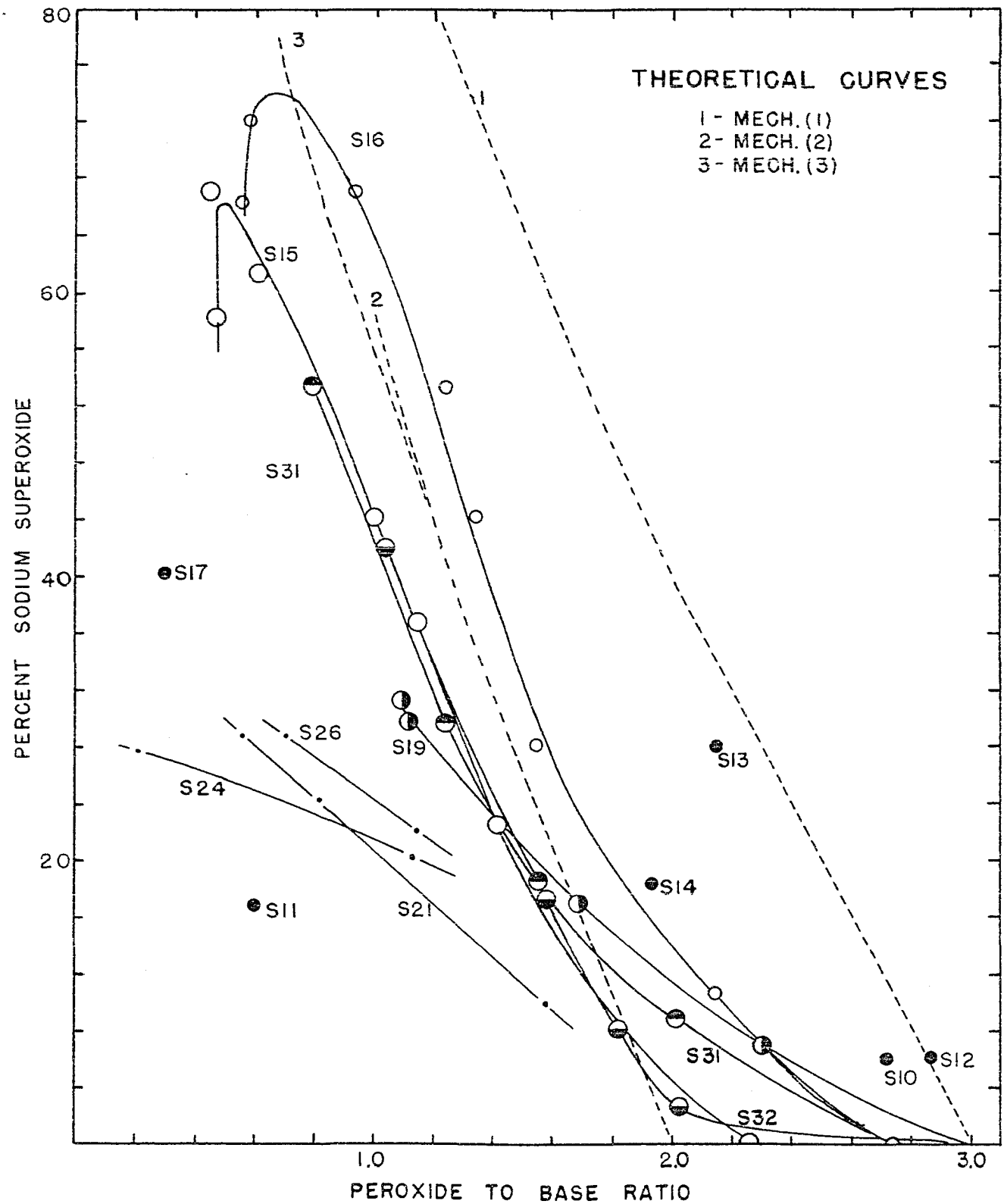
and based on the assumed mechanisms:

$_2 + 2H_2O$ (2) $Na_2O_2 \cdot H_2O_2 = NaO_2 + 0.5Na_2O_2 + H_2O$

$_2 + Na_2O + 3H_2O$

FIGURE 15

DECOMPOSITION OF SODIUM PEROXIDE PEROXYHYDRATES TO SODIUM SUPEROXIDE

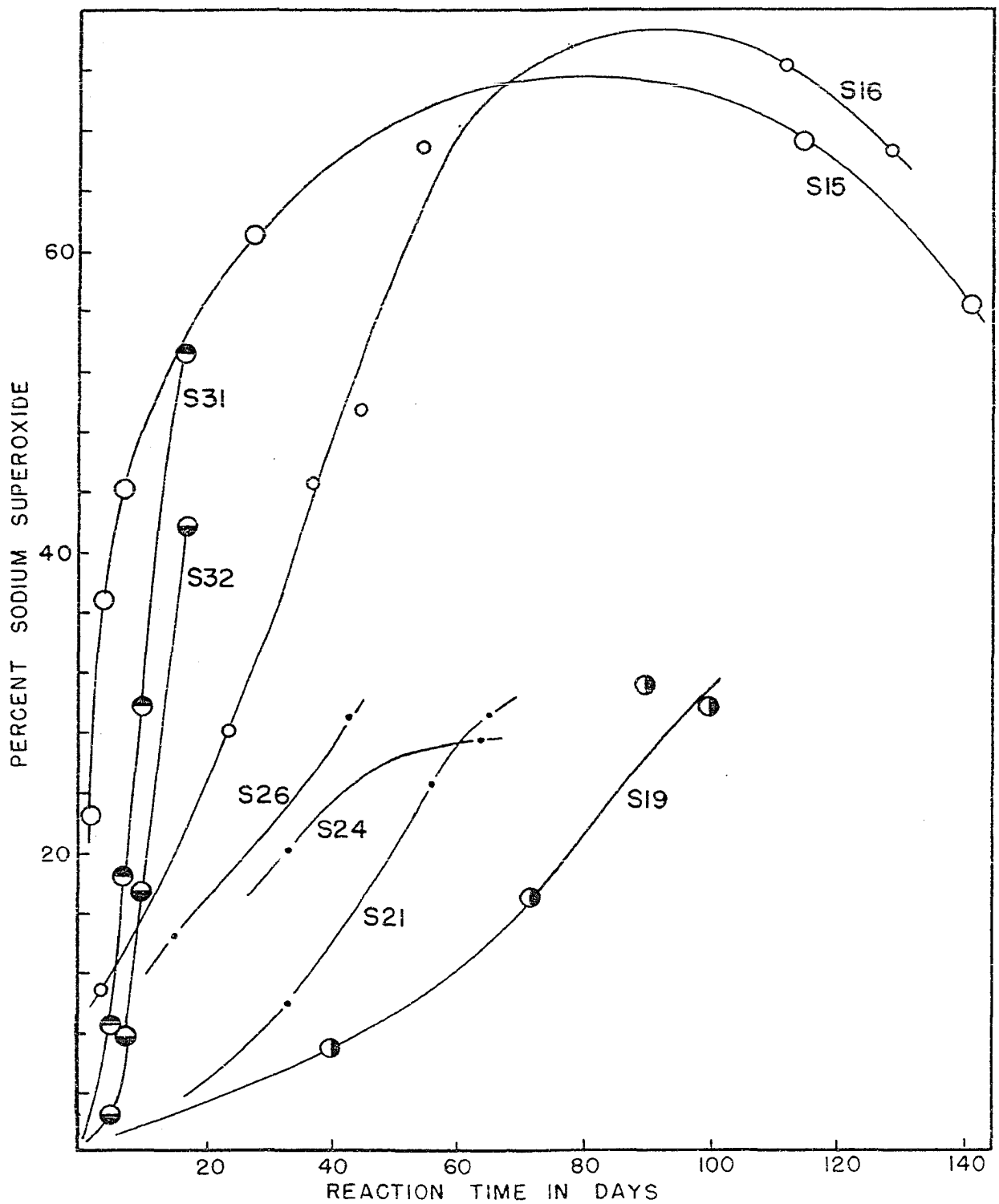


To show the relative amount of sodium hydroxide formed for the preparations recorded in Table VII, the exact points reached on the plot of superoxide content against peroxide to base ratio were plotted for Runs S10, S11, S12, S13, S14, and S17 utilizing ultra-violet light. The positions obtained for S10, S12, and S13 were very significant. The fact that the points lie very close to the theoretical curve for the conversion of $Na_2O_2 \cdot 2H_2O_2$ to NaO_2 showed that all of the $Na_2O_2 \cdot 2H_2O_2$ was converted to NaO_2 and water without any decomposition. However, these results should not be relied upon too heavily because the superoxide analyses were made at room temperature and, therefore, the value may be high due to decomposition of peroxide.

From Table VIII the peroxide to base ratio, Z, and the % NaO_2, obtained for the various preparations of NaO_2 by utilizing slow spontaneous decomposition and vacuum to remove the water, were plotted in Figure 15. The superoxide content at various time intervals was plotted in Figure 16. The data first obtained indicated that NaO_2 was produced at 25° C. without much decomposition for Runs S15 and S16. This was concluded from the fact that the actual curves ran quite parallel to the theoretical curves also shown in Figure 16, except at the beginning of the reaction where considerable decomposition was evident. Runs S15 and S16 also showed that the rate of superoxide formation was greater for the peroxyhydrate with the lower peroxide to base ratio.

FIGURE 16

RATE OF DECOMPOSITION OF SODIUM PEROXIDE PEROXYHYDRATES TO SODIUM SUPEROXIDE AT 25°C AND 3 MM PRESSURE



Again it should be noted that the values obtained for the peroxide to base ratio depended on reaction (25).

$$2\ NaO_2 + H_2O \longrightarrow 2\ Na_2O_2 \cdot aq + O_2 \qquad (25)$$

It was shown that considerable decomposition of the peroxide resulted if the superoxide samples were not added slowly with stirring to the ice water.

The NaO_2 content was determined by the method developed by Seyb and Kleinberg as previously described. For the first analyses made the reaction flask was not immersed in a cold water bath. For this reason when the acetic acid solution was not added very slowly with good stirring, a considerable amount of peroxide oxygen was liberated due to heating when the superoxide content was high. For this reason analyses showing NaO_2 contents of about 80% were discarded for runs S15 and S16. The final analyses were made with the reaction flask cooled to about 12° C.

Several samples were evacuated in order to repeat the good results obtained for runs S15 and S16. The data first obtained, however, were not as good and the deep yellow color of high purity NaO_2 was not produced. The results obtained for several preparations are plotted in Figure 15 and Figure 16. Runs S19 through S26 produced NaO_2 much more slowly and with considerably more decomposition that S15 and S16.

The results obtained for Runs S22 and S23 showed that the effect of the sunlight that passed through the desiccator was negligible. Two identical samples were stored in the same desiccator, one in an uncovered bottle while the second was in a bottle covered with dark paper. Identical results were obtained after 33 days under vacuum and very comparable results after 65 days. See Table VIII.

In Runs S19 and S20 two identical samples were stored under vacuum at 25° C. and 40° C. In the beginning superoxide formed more rapidly at 40° C., but the resulting product was mainly NaOH. The effect of too much heat in decomposing the $Na_2O_2 \cdot 2H_2O_2$ to give water which gives decomposition of the superoxide formed was shown as previously discussed.

Because the superoxide formation was considerably slower and much more decomposition resulted for the Runs S19 through S26 compared to S15 and S16 under identical conditions it was concluded that the rate and degree of superoxide formation was due to the method of preparation of the various peroxyhydrates of sodium peroxide. The essential difference in the manner in which the samples used for Runs S15 and S16 was that no calcium chloride was used to remove methylate or water in preparing the solutions for oxidation.

It was concluded that these results were related to the results previously discussed on the stability of $Na_2O_2 \cdot 2H_2O_2$. In one preparation (Run No. 55) the solution was prepared for

oxidation by the phase separation method as previously discussed. Then calcium chloride was added to remove any water and the solution allowed to stand over night before filtration and oxidation. The sample (Z = 2.98) gave very good stability data at 6° C. and a very slow rate of superoxide formation at the beginning of the reaction time as shown by Run S19.

The sample used for Run S15 was prepared by oxidizing the hydrazobenzene in the alcohol solution rich in sodium methylate. This was the one phase that separated after reduction. After oxidation the solution was filtered and the precipitate washed with a benzene-methanol solution. During the washing the precipitate appeared to undergo a change with a small amount of decomposition shown by bubbling. Since the peroxide to base ratio of the final product was 2.25, this showed that $Na_2O_2 \cdot 2H_2O_2$ or $NaOOH \cdot 0.5H_2O_2$ formed from the NaOOH and methanol according to reaction (26).

$$3\ NaOOH + CH_3OH \longrightarrow 2\ NaOOH \cdot 0.5H_2O_2 + CH_3ONa \qquad (26)$$

This same phenomenon was observed also when the rate of formation of NaOOH was determined. In addition, D'Ans and Friederich (4) reported that $NaOOH \cdot 0.5H_2O_2$ was prepared by reacting NaOOH with cold ethyl alcohol.

The sample used for Run S16 was prepared from the same reduced solution the sample used for Run S15 was made from.

The solution used for oxidation was composed of the phase poor in methylate plus a fraction of the phase rich in methylate as previously described.

The rate of superoxide formation for Runs S15 and S16 compared to Run S19 was extremely fast, especially in the early stages of conversion. In addition, the stability data previously obtained showed that the sample used for Run S16 gave about 14 times more decomposition in 21 weeks than the sample used for Run S19 gave in 13 weeks when stored at 6° C.

The relationship between superoxide formation under vacuum and decomposition at 6° C. was definitely shown.

Near the completion of this work sodium peroxide diperoxyhydrate was made from a solution prepared for oxidation by the water-extraction method in which no calcium chloride was used to carefully dry the benzene layer or to remove any of the sodium methylate or water before oxidation. After oxidation, filtration and washing with a 90% benzene solution and then with benzene, a precipitate was obtained with a Z value of 2.90 and a purity of 97.2% of the empirical compound $Na_2O_2 \cdot 1.9H_2O_2$. This precipitate was used for Run S32. The $Na_2O_2 \cdot 2H_2O_2$ sample used for Run S31 was prepared by oxidizing a solution at room temperature with no methylate removed. The Z value for this precipitate was 2.75. Generally NaOOH formed in this case but it was found that it did not remain stable in all cases, undoubtedly because of reaction (26). An attempt was made to prepare NaOOH

by oxidizing the standard solution after calcium chloride was used to remove a small amount of methylate; however, the precipitate contained a peroxide to base ratio of 2.70 and was used for Run S26. The methods used to prepare the various samples used for the preparation of NaO_2 were recorded in Table VIII.

The results obtained from Runs S31 and S32 showed that NaO_2 formed very much more rapidly from the peroxyhydrates prepared from solutions in which calcium chloride was not used to remove the sodium methylate and any water present. The results agreed with the original data obtained from Runs S15 and S16. The samples used for Runs S31 and S26 had nearly identical Z values and were both prepared from solutions containing essentially all of the sodium methylate. However, a much slower rate of NaO_2 formation was shown for Run S26 than Run S31, but a small amount of calcium chloride was used for the preparation of the sample used for Run S26. The reason that Run S26 did give a better rate of superoxide formation than other preparations utilizing calcium chloride may have been due to the formation of $Na_2O_2 \cdot H_2O_2$ from the NaOOH as shown by reaction (26). This reaction, however, was generally accompanied by a small amount of decomposition and, therefore, water formed and may have given rise to the formation of a less stable crystal lattice.

From Figure 15 it can be observed that, although Runs S31 and S32 gave a rapid superoxide formation with original

Z values of 2.75 and 2.90, considerable decomposition again took place at the beginning of the reaction and not until the Z value fell to a point close to the theoretical curves for the decomposition of NaOOH, did the superoxide content rise rapidly with decreasing Z value. In addition, the initial rate was higher for Run S31 with the original Z value of 2.75 compared to 2.90 for Run S32.

These results show that not all of the peroxide oxygen in $Na_2O_2 \cdot 2H_2O_2$ ($NaOOH \cdot 0.5H_2O_2$) went to form superoxide and and water according to the original theory. Since the curves in Figure 15 began to rise rapidly near the theoretical curves predicted for the decomposition of NaOOH, it appeared as though superoxide was forming only from the NaOOH. This indicated that the molecular structure of the peroxyhydrate with a Z value of 3.0 was $NaOOH \cdot 0.5H_2O_2$ as reported by D'Ans and Friederich.

The above results indicated very strongly that the decomposition of $Na_2O_2 \cdot 2H_2O_2$ or $NaOOH \cdot 0.5H_2O_2$ was accompanied or preceded by the loss of hydrogen peroxide about as shown by reaction (27).

$$2\ NaOOH \cdot 0.5H_2O_2 \longrightarrow 2\ NaOOH + H_2O + 0.5\ O_2 \qquad (27)$$

The resulting NaOOH then decomposed to form NaO_2 as previously discussed.

However, results were obtained, utilizing ultra-violet light to carry out the conversion, that showed that essen-

tially all of the $Na_2O_2 \cdot 2H_2O_2$ was converted to NaO_2 and water. These conversions were made over a short period of time and, therefore, removal of hydrogen peroxide according to reaction (27) may have been negligible. The use of ultra-violet light may have supplied sufficient energy to convert all of the $Na_2O_2 \cdot 2H_2O_2$ to the superoxide according to the original theory. This may indicate a different mechanism when ultra-violet light is used. The time required to convert some of the $Na_2O_2 \cdot 2H_2O_2$ samples to about 20% NaO_2 was of the order of hours while in some cases days or months were required when the samples were evacuated.

The above results were of interest in relation to superoxide formation from other peroxyhydrates. For example, $Li_2O_2 \cdot H_2O_2$ easily lost the hydrogen peroxide and was difficult to convert to LiO_2. $BaO_2 \cdot 2H_2O_2$ easily lost hydrogen peroxide and also was difficult to convert to BaO_4 (9,39). Since $NaOOH \cdot 0.5H_2O_2$ or $Na_2O_2 \cdot 2H_2O_2$ lost only a portion of the hydrogen peroxide and was easily converted to NaO_2, it may be possible that the hydroperoxide structure is much more readily converted to superoxide.

Since the rate of superoxide formation was slow until a considerable amount of hydrogen peroxide was lost, it appeared that reaction (27) may have been rate controlling at the beginning of the reaction for the $Na_2O_2 \cdot 2H_2O_2$ samples prepared from solutions in which calcium chloride was not used. When calcium chloride was used the rate was very slow

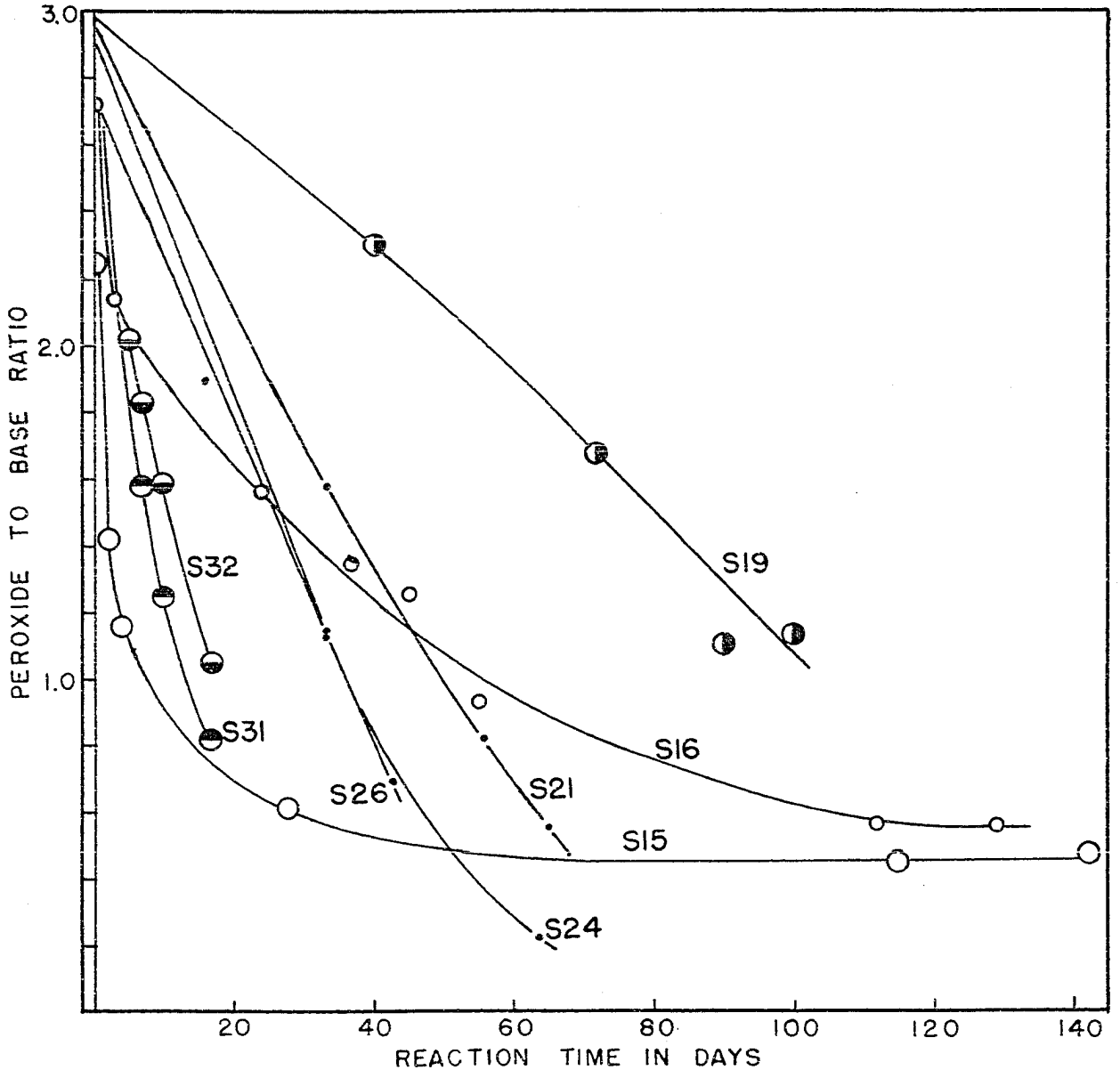
over a much longer time, and then increased somewhat during a period from thirty to sixty days. Considerably more decomposition resulted in the latter case. The rate of decrease of the peroxide to base ratio when calcium chloride was used was nearly constant as shown by Figure 17. The rate of decrease in the Z value was nearly constant but very rapid at the beginning of the decomposition when no calcium chloride was used.

From the above results it appeared that a much more stable crystal lattice formed when calcium chloride was used to remove methylate and any possible water. Peroxide loss was much slower as shown by stability data and decrease in Z value on evacuation. It was concluded that small amounts of water in the crystal lattice tended to make the stability much lower. This may have been due to strains set up in the crystals due to difference in size of the water molecules and the hydrogen peroxide molecules, as well as difference in molecular forces. Complete removal of water by means of the calcium chloride prevented the water from entering the crystal lattice. This gave better stability.

On the other hand, small amounts of calcium salts may have precipitated with the peroxyhydrates and served to increase the stability. The salts also may have acted as negative catalysts for the oxidation-reduction reaction responsible for the superoxide formation.

FIGURE 17

RATE OF DECREASE OF PEROXIDE TO BASE RATIO FOR THE DECOMPOSITION OF SODIUM PEROXIDE PEROXYHYDRATES TO SODIUM SUPEROXIDE AT 25°C AND 3 MM PRESSURE



Considerably more data were necessary to elucidate more clearly the complex mechanism whereby the peroxyhydrates were converted to superoxides as a result of spontaneous oxidation-reduction within the crystals. More data were also necessary to ascertain the effects of calcium chloride.

At any rate, the above results showed that two methods of preparing $Na_2O_2 \cdot 2H_2O_2$ were of extreme importance. The one method prepared crystals that were quite stable. This stable product could be stored, preferably at a low temperature such as 0° C., and shipped for use as a bleaching agent or other sources of oxygen. The second method prepared crystals that were easily converted to superoxide. This method would be used to prepare $Na_2O_2 \cdot 2H_2O_2$ to be used for the preparation of NaO_2. The advantage of NaO_2 over $Na_2O_2 \cdot 2H_2O_2$ as a source of oxygen is, obviously, its excellent stability at ordinary temperatures in the absence of water or carbon dioxide. An additional advantage is that NaO_2 contains 43.6% available oxygen while $Na_2O_2 \cdot 2H_2O_2$ contains 32.9%. Therefore, 75.6 parts by weight of NaO_2 correspond to 100 parts of $Na_2O_2 \cdot 2H_2O_2$.

An additional factor that appeared to be very important in the preparation of NaO_2 by the above procedure was shown by a decrease in the superoxide content for Runs S15 and S16. This factor increased the complexity involved in the mechanism whereby the superoxide formed because it showed that while superoxide continued to form decomposition must have

started. This decomposition tended to decrease the rate and also the yields. Several factors may have tended to cause this decomposition.

First of all, a small amount of decomposition was caused by contacting the samples with small amounts of water vapor and carbon dioxide when the samples were removed for analyses. Rigorous precautions were not exercised in removing samples; however, the desiccator was filled with dry oxygen and the samples were removed to a dry box before removing small samples for analysis.

The second factor that may have caused decomposition may have been due to dissociation of the superoxide according to reaction (28).

$$2\ NaO_2 \longrightarrow Na_2O_2 + O_2 \qquad (28)$$

The resulting product would have been sodium peroxide and the peroxide to base ratio would have remained constant. Decomposition at constant Z values was shown to be the case for Runs S15 and S16 at the end of the reaction.

From the fact that sodium superoxide forms from sodium peroxide and oxygen at very high pressure (90 atmospheres) at temperatures of the order of 300° C., it appeared that the dissociation pressure at 25° C. would have been very low and, therefore, the rate of decomposition should have been very slow. At this time sufficient data were not available to show more clearly the cause of decomposition. At any

rate the decomposition of the NaO_2 appeared to be very important in preparing NaO_2 by the above procedure. This decomposition, undoubtedly, was more effective where the rate of formation of the superoxide was slow.

From the data and results tabulated in Table VIII the composition of almost all of the NaO_2 samples was calculated assuming the presence of only NaO_2, $Na_2O_2 \cdot 2H_2O_2$, NaOH, and water. These calculations are tabulated in Table XI.

The above results showed that the NaO_2 samples consisted mainly of NaO_2 and NaOH with not much water. The assumption that the excess base was NaOH was, undoubtedly, incorrect in that the material balance showed negative water in several cases. This showed that water was removed quite readily and that someof the base was left as sodium monoxide. This corresponds to the mechanism predicted for the decomposition of NaOOH. It was expected that if Na_2O formed along with the NaO_2 and water, the water would react preferably with the superoxide.

The above results showed that sodium superoxide formed under very moderate conditions from the peroxyhydrates of sodium peroxide. The only other methods available for the preparation of NaO_2 involve very high pressure and moderately high temperature oxidation with oxygen or oxidation in liquid ammonia of sodium metal as previously discussed. The advantages of NaO_2 over KO_2 include: (1) NaO_2 reacts less rapidly with water and carbon dioxide, (2) A 78.5% NaO_2 product is

Table XI

Approximate Composition of NaO_2 Samples

Basis: One gram

Run No.	Time days	Base meq.	Peroxide meq.	NaO_2 gm.	$Na_2O_2 \cdot 2H_2O_2$ gm.	NaOH gm.	H_2O gm.
S15	4	17.7	20.4	0.366	0.334	0.261	0.039
	7	17.9	17.9	0.442	0.239	0.262	0.057
	28	18.9	11.5	0.612	0.010	0.308	0.070
	115	18.4	18.4	0.672	0	0.266	0.062
S16	3	15.5	33.2	0.107	0.764	0.125	0.004
	24	17.6	28.9	0.281	0.577	0.182	---
	37	17.5	23.7	0.446	0.380	0.168	0.006
	45	16.8	21.0	0.494	0.292	0.153	0.061
	44	17.5	16.5	0.670	0.104	0.155	0.073
	112	18.3	10.4	0.722	0	0.206	0.072
	130	18.0	10.0	0.665	0	0.234	0.101
S17	--	21.6	6.4	0.403	0	0.572	0.034
S18	--	19.4	17.8	0.161	0.362	0.500	---
S19	40	15.4	35.3	0.068	0.830	0.160	---
	72	17.3	29.2	0.169	0.635	0.220	---
	90	18.5	20.4	0.312	0.358	0.317	0.003
	100	18.9	21.1	0.294	0.382	0.332	---
S20	39	23.6	4.3	0.093	0.064	0.843	0.0
S21	33	18.1	28.6	0.100	0.652	0.295	---
	56	20.6	18.8	0.243	0.300	0.485	---
	65	22.9	12.9	0.289	0.185	0.603	---
S23	17	13.8	36.3	0.065	0.854	0.082	0.0
S24	33	19.4	21.8	0.203	0.441	0.397	---
	64	22.8	5.1	0.277	0.004	0.646	0.063
S26	15	15.3	28.7	0.145	0.635	0.171	0.049
	33	12.6	20.2	0.220	0.391	0.326	0.063
	43	19.5	13.6	0.290	0.202	0.432	0.076
S31	5	16.9	34.1	0.087	0.793	0.180	---
	7	17.7	27.6	0.184	0.590	0.250	---
	10	18.6	23.3	0.296	0.435	0.295	---
S32	5	16.8	33.8	0.025	0.810	0.206	---
	7	17.4	31.6	0.079	0.735	0.234	---
	10	17.8	28.3	0.174	0.610	0.252	---

equivalent to a 100% KO_2 product in available oxygen, and (3) Sodium superoxide will serve as a source of oxygen in the same manner that KO_2 serves while it does not require the valuable potassium.

The overall reaction for the preparation of NaO_2 from NaCl is given by reaction (29). All intermediate reactions were carried out at room temperature.

$$2\ NaCl + 3\ O_2 + 4\ CH_3OH \longrightarrow 3\ Cl_2 + 4\ NaOCH_3 + 2\ NaO_2 + 2\ H_2O \qquad (29)$$

The inexpensive materials, sodium chloride, oxygen or purified air, and methyl alcohol were converted to valuable chlorine, sodium methylate, and superoxide.

IV. SUMMARY

Recently, emphasis has been placed on the oxidation with purified air or gaseous oxygen of certain easily oxidizable organic materials such as anthraquinone and hydrazobenzene as a means of producing peroxide oxygen. One such cyclic process was described whereby: (a) sodium amalgam and methyl or ethyl alcohol were used to reduce azobenzene dissolved in the alcohol and benzene to give hydrazobenzene and the sodium alcoholate and (b) oxidation of the hydrazobenzene to split off hydrogen peroxide which was precipitated as sodium hydroperoxide (NaOOH), sodium peroxide octahydrate, sodium hydroperoxide monohydrate ($NaOOH \cdot H_2O$) or as anhydrous sodium peroxide. Sodium peroxide formed only when the alcohol concentration was highly reduced in which case the reduction step was quite slow. These compounds were all relatively unstable when prepared under the conditions used.

(1) A mercury electrolytic cell, mercury circulating system and an electrical power source consisting of a transformer and a selenium bridge rectifier, has been constructed for the preparation of sodium amalgam of uniform strength in a continuous manner. The technique of the operation of this unit has been perfected. The amalgam was used to carry out the above well-known reduction.

(2) When calcium chloride was added to the reduced solution it was found that insoluble, gelatinous calcium methyl-

ate and sodium chloride formed. When the hydrazobenzene was oxidized with oxygen in the presence of the calcium methylate, the oxidation was incomplete and hydrogen peroxide decomposition resulted on the surface of the calcium methylate.

(3) Sodium peroxide diperoxyhydrate ($Na_2O_2 \cdot 2H_2O_2$) was made in a new cyclic process with a yield of over 90% based on the amount of reduction. The product made was about 98% pure $Na_2O_2 \cdot 2H_2O_2$, a compound which is equivalent to 70% hydrogen peroxide and is an excellent potential source of peroxide oxygen.

(4) The pure sodium peroxide diperoxyhydrate was crystalline and very easy to filter and wash. The dry product was easy to handle and could be poured on the dry skin without causing undue burning.

(5) Since in a cyclic process producing $Na_2O_2 \cdot 2H_2O_2$ only one-third of the sodium methylate was removed, new methods were developed to remove the excess methylate from the reduced solution. The one method involved the precipitation of calcium methylate which gave the advantage of producing highly anhydrous systems because of the removal of the water as calcium hydroxide. A second method recovered the valuable sodium methylate as a pure product containing at least 98.8% $NaOCH_3$.

(6) A new cyclic process has been developed for the preparation of potassium peroxide diperoxyhydrate ($K_2O_2 \cdot 2H_2O_2$) in good yields. The product was considerably

less stable than $Na_2O_2 \cdot 2H_2O_2$. Its stability was increased considerably when stored at temperatures below 0° C.

(7) Lithium chloride was converted to lithium peroxide monoperoxyhydrate ($Li_2O_2 \cdot H_2O_2$) in a new cyclic process in good yields.

(8) By substituting ethyl alcohol in the reduced system the lithium chloride was converted to anhydrous lithium peroxide (Li_2O_2) in yields considerably above 90% based on the amount of reduction. However, the product contained about 92% Li_2O_2.

(9) The above processes represent the only economically feasible method available for the preparation of the above-mentioned anhydrous peroxide compounds.

(10) By an entirely new reaction a sodium superoxide product containing about 70% NaO_2 was prepared from $Na_2O_2 \cdot 2H_2O_2$. Reaction mechanisms have been postulated and the experimental results compared favorably with the theory.

(11) When $Na_2O_2 \cdot 2H_2O_2$ was prepared by utilizing calcium chloride to remove sodium methylate and water, it was found that its conversion to NaO_2 was less efficient, being of the order of 15 times slower than the conversion when the $Na_2O_2 \cdot 2H_2O_2$ was prepared by other methods not utilizing calcium chloride to remove water and sodium methylate.

(12) Correspondingly, it was shown that the decomposition of the $Na_2O_2 \cdot 2H_2O_2$ when stored in closed containers at 6° C. was about 15 times greater when calcium chloride was

not used prior to the oxidation to remove water.

(13) When $Na_2O_2 \cdot 2H_2O_2$ and NaOOH, prepared in the above manner, were stored at 6° C. 2% to 3% decomposition resulted in four weeks. Pure sodium peroxide diperoxyhydrate prepared from an extremely anhydrous medium lost less than 3% available oxygen when stored 13 weeks at 6° C. The same preparation lost less than 10% available oxygen when stored at room temperature for a period of two weeks compared to 80% decomposition for samples less carefully prepared.

(14) Sodium superoxide formed more rapidly from sodium peroxide diperoxyhydrate when ultra-violet light and heat were applied. However, too much heat caused undesirable decomposition.

(15) Evidence was presented that indicates that lithium peroxide monoperoxyhydrate exists as $Li_2O_2 \cdot H_2O_2$ while sodium peroxide diperoxyhydrate exists as $H_2O_2 \cdot 2NaOOH$.

(16) A small amount of lithium superoxide (LiO_2) was prepared from the $Li_2O_2 \cdot H_2O_2$. The existance of LiO_2 had previously not been proven.

(17) Potassium peroxide diperoxyhydrate was very readily converted to a potassium superoxide product containing about 70% KO_2.

(18) It was predicted that the yield of both NaO_2 and KO_2 could have been increased in the newly developed methods used by improvement in operating techniques.

(19) It was found in working with alcoholates that ethylenediamine dihydrochloride stabilized the various alcoholates from oxidation to resinous materials.

V. BIBLIOGRAPHY

1. Anon, Chem. Eng. News, 23, 1516 (1945).

2. Conroy, J., J. Chem. Soc., 26, 808 (1873).

3. Cunningham, G. L., U. S. Patent 2,083,691 (Sept. 29, 1936).

4. D'Ans, J. and Friederich, W., Z. anorg. Chem., 73, 325-59 (1911).

5. deForcrand, R., Compt. rend., 130, 716-718 (1900).

6. Ibid., 158, 991-4 (1914).

7. Ibid., 144, 920 (1900).

8. Ibid., 130, 1465 (1900).

9. Doptoglon, D. D., M. S. Thesis, University of Cincinnati (1953).

10. Fairley, T., J. Chem. Soc., 31, 125 (1877).

11. Fischer, F., and Ploetze, H., Z. anorg. Chem., 75, 10 (1912); 75, 30 (1912).

12. Foregger, R., and Philipp, H., J. Soc. Chem. Ind., 25, 298-302 (1906).

13. Furman, N. H. "Scott's Standard Methods of Chemical Analysis," Vol. II, p. 2180, New York: D. Van Nostrand Company, Inc., 1939.

14. Helms, A., and Klemm, W., Z. anorg. allgem. Chem., 241, 97 (1939); 242, 201 (1939).

15. Holt, W., and Sims, W. E., J. Chem. Soc., 65, 432 (1849).

16. Holtermann, C. B., Ann. chim., 14, 121-206 (1940).

17. Jackson, C. B., and Miller, R. R., Abstract of Papers Presented at A. C. S., Atlantic City, New Jersey, Sept. 18 to 23, p. 80P (1949).

18. Kazarnovskii, I. A., and Neiding, A. B. (Karpov. Phys. Chem. Inst., Moscow). Doklady Akad. Nauk. S.S.S.R., 86, 717-20 (1952); C.A. 47, 9548 (1953).

19. Kleinberg, J., Stephanou, S. E., Schechter, W. H., and Argersinger, W. J., Jr., J. Am. Chem. Soc., 71, 1819 (1949).

20. Kraus, C. A., and Whyte, E. F., J. Am. Chem. Soc., 48, 1781 (1926).

21. Krell, A., and Herzog, E., U. S. Patent 2,211,235 (1938).

22. Manchot, W., and Hersog, J., Annalen, 316, 331 (1901).

23. Mellor, J. W., and Parkes, C. D. "Mellor's Modern Inorganic Chemistry," p. 553, New York: Longmans, Green and Company, 1939.

24. Miller, U. S. Patent 3,414,116 (1947).

25. Mitteau, R., Chimie et industrie 63, 138-46 (1950).

26. Moeller, T. "Inorganic Chemistry," p. 506, New York: John Wiley and Sons, Inc., 1952.

27. Ibid., p. 510.

28. Partington, J. R. "General and Inorganic Chemistry," p. 381, London: MacMillan and Company, 1949.

29. Ibid., p. 682.

30. Pfeiderer, G., U. S. Patent 2,158,525 (1935).

31. Ibid., U. S. Patent 2,215,856 (Nov. 10, 1936).

32. Riesenfeld, E. D., and Nottebohm, W., Z. anorg. Chem., 89, 405 (1914).

33. Robinson, R. S., U. S. Patent 2,437,272 (March 9, 1948).

34. Schechter, W. H., and Kleinberg, J., J. Chem. Education 24, 302-3 (1947).

35. Schechter, W. H., Sisler, H. H., and Kleinberg, J., J. Am. Chem. Soc., 70, 267 (1948).

36. Schechter, W. H., Thompson, J. K., and Kleinberg, J., J. Am. Chem. Soc., 71, 1816 (1949).

37. Seyb, E., and Kleinberg, J., Analytical Chem., 23, 115-17 (1951).

38. Thorne, P. C. L., and Roberts, E. R. "Inorganic Chemistry," 5th Edition, p. 422, New York: Interscience Publishers, Inc., 1948.

39. Traube, W., and Schulze, W., Ber., 54, 1626 (1921).

40. Vining, U. S. Patent 2,474,021 (1941).

41. White, L. M., Chem. Eng. News 23, 1626 (1945).

VI. APPENDIX

A. Run No. 47, Preparation of $Na_2O_2 \cdot 2H_2O_2$.

Reduction solution:

64 grams azobenzene

480 cc. of thiophene-free benzene

320 cc. of methanol

Azobenzene reduced in reduction vessel; 10 cc. of this solution required 66.7 cc. of 0.1042 N hydrochloric acid. 815 cc. used for oxidation.

$NaOCH_3$ in reduced solution:

$815(0.1042)6.67 = 566$ meq.

$CaCl_2$ (96%) to remove one-half of the methylate:

$(566/2)(0.0555/0.96) = 16.4$ grams

The calcium chloride was added and the solution was stirred for one hour, filtered, and washed. Ten cc. of 895 cc. collected required 29.8 cc. of acid.

$NaOCH_3$ in oxidation solution:

$895(2.98)0.1042 = 278$ meq.

$f = (278/566) = 0.49$

Solution was placed in oxidizer in ice bath and oxygen was passed into the solution with stirring. At various time intervals 10 cc. of the well-agitated slurry was removed, filtered, and the precipitate washed with a cold solvent consisting of 60% benzene and 40% methanol. The precipitate was added to ice water and analyzed for base and peroxide.

The filtrate was analyzed for base. The rate of peroxide precipitated as $Na_2O_2 \cdot H_2O_2$ is tabulated in Table XII.

Table XII

Rate of Peroxide Precipitated

Time min.	Meq. HCl for ppt.	Meq. $Na_2S_2O_3$ for ppt.	Meq. HCl for filtrate	X	Z	Y
15	0.875	2.53	1.82	0.312*	2.90**	0.445***
52	1.34	3.91	1.323	0.504	2.92	0.72
88	1.79	5.27	1.224	0.595	2.95	0.862

* X = 0.875/(0.875 + 1.82)
** Z = 2.53/0.875
*** Y = 2.90(0.312)(0.49)

Solution was filtered, the precipitate was washed white with the 60% benzene solvent at 0° C. and dried under vacuum. No further analysis was made.

B. Run No. 59B, Preparation of $Na_2O_2 \cdot 2H_2O_2$.

Reduction carried out as in Example A.

1120 cc. reduced solution used. 747 cc. extracted with water. The benzene solution was distilled; 70 cc. collected to remove water. 70 cc. of benzene, 200 cc. of methanol, and 373 cc. of the original reduced solution added to the hydrazobenzene solution.

Oxidation was carried out at 0° C. for about two hours after which the solution was filtered and the precipitate

washed with 10% methanol in benzene then with benzene. The precipitate was dried one hour under vacuum. About 15 grams was collected, some lost.

Weight of sample for analysis:

7.1226 vial plus sample
6.3966 vial

0.7260 gram sample

Sample added to ice water; 95.6 cc. of 0.1035 N HCl required. 10 cc. of acetic acid, 40 cc. of 10% KI solution, and three drops of a saturated ammonium molybdate solution were added. 277.7 cc. of 0.1053 N sodium thiosulfate solution was required.

Meq. base per gram:

$95.6(0.1035/0.7260) = 13.67$

Meq. peroxide per gram:

$277.7(0.1033/0.7260) = 39.55$

Peroxide to base ratio:

$39.55/13.67 = 2.90$

Meq. of peroxide per gram in pure $Na_2O_2 \cdot 1.9H_2O_2$:

$(2 + 3.8)/(78 + 64.6)1000 = 40.65$

Purity of sample:

$(39.55/40.65)100 = 97.2\%\ Na_2O_2 \cdot 1.9H_2O_2$

C. Run No. 58, Preparation of $K_2O_2 \cdot 2H_2O_2$.

1080 cc. of reduced solution obtained as in Example A. 10 cc. required 79.9 cc. acid.

This solution was extracted with water. 656 cc. of hydrazobenzene solution in benzene obtained. About 10 grams $CaCl_2$ added and the solution allowed to stand over night.

$NaOCH_3$ in reduced solution:

$$1080(7.99)0.1035 = 892 \text{ meq.}$$

$KOCH_3$ solution (3.59 meq. per cc.) was added so that the $KOCH_3$ was present in an amount equivalent to one-half of original $NaOCH_3$:

$$(892/2)(1/3.59) = 124 \text{ cc.}$$

200 cc. methanol added and the oxidation carried out at 0° C. for three hours. Solution was filtered and the precipitate washed with a cold solution of 10% methanol in benzene then with benzene.

Small amount of precipitate added to ice water for analysis. 37.2 cc. of acid and 72.7 cc. of thiosulfate required.

Peroxide to base ratio:

$$72.7(0.1562)/37.2(0.1035) = 2.95$$

D. Run S30, Preparation of KO_2 from $K_2O_2 \cdot 2H_2O_2$.

$K_2O_2 \cdot 2H_2O_2$ prepared in Run No. 58, Example C.

Material was placed in desiccator at 25° C. and evacuated to about 3 mm. After 1.5 hours sample was rapidly decomposing. After 2.5 hours reaction appeared complete. Sample allowed in vacuum over night.

Weight of samples for analysis:

No. 1	No. 2	
10.3526	6.4437	vial plus sample
9.7618	6.2870	vial
0.5908	0.1567	gram sample

Peroxide and base analysis, Sample No. 2 added to ice water:

20.5 cc. of HCl

8.5 cc. of $Na_2S_2O_3$

20.5(0.1035/0.1567) = 13.56 meq. base per gram

8.5(0.1487/0.1567) = 8.08 meq. peroxide per gram

Superoxide analysis:

T = 12.5° C.

P = 741 mm.

61.9 cc. O_2 evolved

$\%KO_2$ = (61.9/0.5908)0.635(273/285.5)(741/760) = 66.2%

Material balance, Basis: one gram:

0.62/0.071 = 8.72 meq. KO_2

13.56 - 8.72 = 4.74 meq. base assumed KOH

4.74(0.056) = 0.265 gram KOH

Remaining 0.115 gram assumed water