AN ENGINEERING ANALYSIS ON
CONTROL OF BREATHING ATMOSPHERES
USING ALKALI METAL SUPEROXIDES

PHASE I

under Omnibus Contract Number
N00612-79-D-8004 for
Delivery Order Number HR-43

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January 15, 1982
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ABSTRACT

A search of the literature indicates potassium superoxide is a proven choice as a reliable air revitilization chemical. Sodium superoxide must be cooled to prevent the unexpected release of carbon dioxide by the thermal decomposition of sodium bicarbonate. Calcium superoxide and the alkali metal ozonides are not available as pure commercial products and the kinetics for oxygen production are unknown.

The effect of pressure on the chemical equilibria is very small; at 25°C the bicarbonate phase is heavily favored by the equilibria at depths to 1000 feet. Most of the reliable kinetic data are available for potassium superoxide tablets and spheres. Particles of small diameter (<10 mesh or 2 mm diameter) give high rates of oxygen evolution but suffer from excessive pressure drop and "dusting". With suitable control of humidity, KO₂ particles of 2 - 4 mesh (5 to 8 mm diameter) will give acceptable, but low, rates of oxygen evolution (~2 lb O₂/man-day). A rippled plate configuration of the superoxide is promising but more kinetic reaction data are needed.

The preferred KO₂ cannister inlet conditions established by our studies are: 3 mm Hg < P CO₂ < 11 mm Hg and 15 mm Hg < P H₂O < 20 mm Hg at a temperature of 25°C. These conditions over an adequate potassium superoxide bed will produce initial oxygen evolution rates of 1.75 to 2 pounds O₂/man-day. It is desirable to control the inlet humidity independent from the inlet partial pressure of carbon dioxide to the superoxide bed. Upstream carbon dioxide scrubbing of the breathing gases is indicated for optimum utilization of the potassium superoxide.
The theoretical superoxide bed loading for an eight hour mission, assuming 1.87 pounds of oxygen are needed for one man-day, and 60% of the theoretical KO$_2$ utilization, is three pounds. The kinetics for revitilizing humid air, $P_{H_2O} = 15$ to 20 mm Hg, demand 3 to 4 pounds superoxide bed if the volumetric gas flowrate is 20 liters per minute. The correlated rate equation used in predicting these bed loadings is based on initial rate data; we expect the "aged" KO$_2$ beds will show reaction rates lower, by a factor of 3, than our predictions. The superoxide exit carbon dioxide partial pressure is predicted at less than 0.3 mole percent, surface equivalent.

For the preferred potassium superoxide cannister inlet conditions, supplemental carbon dioxide scrubbing in the amount of 0.8 to 1.7 lb. CO$_2$/man-day must be provided for the total air revitilization system to cleanse 2.21 lb. CO$_2$/man-day. Soda-sorb, lithium hydroxide, etc., are possible scrubbing agents. The steady state gas temperature can be controlled to less than or equal to 35°C with heat exchange to the environment using less than 8 ft$^2$ of area assuming the "worst" case for heat transfer.

Additional kinetic measurements are necessary to document the effect of pressure to 30 atmospheres and the effect of temperature upon the reaction rate.
SECTION I

INTRODUCTION

Any sort of enclosed space for which human activity is to be sustained for some period of time, necessitates a means of life support. Usually this situation results any time man is subjected to a hostile environment, such as beneath the water, in space, or in the presence of a hazardous atmosphere. Pressurized oxygen in cylinders had been the acceptable means of air revitalization for many years in several applications. However, the weight and volume of such systems has precluded its efficient use required by the technology for submarines, aircraft, space vehicles, and even portable breathing apparatus.

There have been a variety of different atmosphere regeneration techniques developed in the past several decades. These include using some sort of umbilical method, cryogenic oxygen (both supercritical and subcritical), high pressure oxygen storage, electrochemical methods, and chemical methods. Depending on the type of application, each of the aforementioned systems can perform air revitalization either alone or in concert with another system. Each has its advantages and disadvantages. Three factors of consideration to the design of a life support system are weight, volume (space occupied), and energy requirements. Other criteria may be the need for sophisticated controls or the ease of 'recharging' the system. The design of life support systems for space and marine vehicles share some common problems, primarily in weight and volume requirements. Table 1 summarizes the advantages and disadvantages in the evaluation of life support systems for space exploration (Prince, 1970).

Despite some of its disadvantages, chemical methods (i.e., the use of
superoxides, etc.) for total air revitilization, both production of oxygen and removal of carbon dioxide, offer an attractive alternative to other methods. Chemical carbon dioxide absorbents have already been the primary means for carbon dioxide control in many life support systems. There are several chemical compounds which will release oxygen under moderate conditions. Combinations of these compounds or chemicals which can perform both functions of air revitilization simultaneously, have been developed, studied, and successfully used in many applications. Of course, those compounds best suited for use in life support systems will be light, contain a maximum amount of releasible oxygen per molecule, and have a high carbon dioxide absorbing capacity.

Chemical systems possess many comparative advantages over other types of systems. Generally, the chemicals are relatively light and occupy little space. As has been necessary in the development of life support systems for space vehicles, weight and volume limitations dictate severe restrictions for the air revitilization system. So are the same requirements for marine vehicles and even more so for a portable one-man back pack. Whereas, an electrochemical system may be possible for a small submersible, the same is not probably true for the one-man portable system. Chemical agents use a minimal amount of energy, if any; most are demand operating to meet varying requirements without sophisticated controls. Lastly, the chemicals are usually easily recharged, often by merely replacing a cannister containing the chemical.

In this report, we begin by presenting a general overview of air revitilization compounds, their chemistry, properties, manufacture, and practical use. The literature survey narrows down to an in-depth look of a specific compound, potassium superoxide, which we deem to be the most
viable choice for a chemical air revitalization system. This choice is substantiated by a wealth of information that is presented on specific mechanisms, past history, and engineering applications of potassium superoxide. The subject of subsequent sections is the specific analysis of the physical performance of potassium superoxide, both theoretical and actual (based on data accumulated from the literature search). Three such sections are given on the thermodynamics and equilibrium, kinetics, and thermal behavior of the chemical system. The approach in each of these analyses is to elucidate the effects of a number of variables in the superoxide system, principally an interpretation of given information to determine performance with varying depth (pressure), temperature, carbon dioxide and water vapor concentrations. Additional sections deal with the practical design of a superoxide system with respect to chemical loading, required inlet conditions, and pressure drop. The end result is a set of predicted working guidelines in which to base preliminary design considerations. Finally, we advocate a proposal for continued research and experimentation.
In the early 1960's, when there was a large impetus for designing efficient life support systems by the National Aeronautics and Space Administration, close scrutiny went into the analysis and development of various types of chemical compounds for air revitilization. Some of these chemicals had already been utilized in other applications, principally as emergency oxygen suppliers or auxiliary carbon dioxide absorbers. The space program in this period increased the variety of available chemical systems by funding a large host of studies, most of which are used as the supporting data in this report. The types of chemicals that were reviewed can be placed in three categories:

1) oxygen producing compounds
2) carbon dioxide removing compounds
3) total air revitilization compounds

Clearly the last category of chemical compounds was most carefully reviewed as this class was found to be the most versatile and holding the greatest potential for revitilization efficiency. In this report, we follow that example making only a brief mention of the first two categories, and looking at the third in much greater depth. Sources of information for this literature survey came from the following abstract services:

1) Chemical Abstracts (1945 - present)
2) National and Technical Information Service (1960 - present)
3) Scientific and Technical Aerospace Reports (1960 - present)
4) International Aerospace Abstracts (1968 - present)
Oxygen Producing Compounds.

Many oxygen containing compounds will decompose to yield oxygen when heated under the proper conditions. Primarily, Alkali Metal Halates which include alkali metal chlorates and perchlorates have been successfully employed as emergency oxygen supplies in aircraft (Thompson, 1975), submarines (Smith, 1960), and in portable breathing apparatus (Martin, 1971). Two such halates, sodium chlorate and lithium perchlorate, have found extensive use for such purposes. A continuous source of heat is necessary to sustain the thermal decomposition reactions which liberate the oxygen. As a result of this requirement, the practical use of alkali metal halates is in the form of a 'candle', so called due to the shape and characteristics of the fabricated form. The composition of the candle includes a fuel for this purpose. Also incorporated into the mixture are additives for binding the candle composition and to control burning quality.

Though well proven in practice, these candles suffer from some disadvantages which would prevent their efficient use in closed environments for extended periods of time. As a consequence of the need for a fuel, two problems occur. First of all, in burning to decompose the halate, some of the produced oxygen is consumed (Schechter et al., 1950); secondly, the fuel or for that matter any additive makes the chemical less weight efficient. Additives and any contamination of the candle composition can give rise to a number of impurities in the gas stream (Litman, 1969). And because halates contain chlorine, the production of chlorine gas can occur if the composition of the candle is not carefully controlled (Maustellar, 1970). Halate candles produce oxygen at a specified rate proportional to the rate of burning; they are not demand-type chemicals. Controlling the rate of burning for varying demand can be difficult (Litman, 1969).
Obviously, in lieu of the several disadvantages cited, halate candles are inadequate for the marine application considered here. Where such devices may be employed, as emergency or secondary oxygen sources, the real purpose for which they were designed. Furthermore, chlorate candles have been extensively used to provide quick starting features for superoxide cannisters in portable breathing apparatus (Bovard, 1960).

Carbon Dioxide Absorbents.

There are several types of chemical carbon dioxide absorbents for different applications. Many absorb carbon dioxide under standard conditions without the need of a catalyst, the addition of heat, or any auxiliary device. Used in conjunction with an oxygen producing compound or a revitilization chemical, a carbon dioxide absorbent can provide the desired control or revitilization of respired gases. Most absorbents are solids, which lend themselves to ease of application in bed fabrication and cannisters, and also have more absorbing capacity per pound of chemical.

Typically the compounds utilized are alkali metal oxides, hydroxides, and carbonates, or mixtures of same. As with any revitilization compound, the lightest are the best; with alkali metal compounds, the obvious choice is lithium, if the compound has other properties which do not preclude its efficient use. The mechanisms of carbon dioxide absorption are simple. For example, lithium hydroxide ($LiOH$) removes carbon dioxide predominately by the following reaction:

$$\text{(1) } 2\text{LiOH} + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$$

Other reactions for lithium hydroxide and other alkali metal absorbents are multistep involving a hydrated species or some other intermediate, such as below:
(2) LiOH + H₂O = LiOH·H₂O  
(3) 2LiOH·H₂O + CO₂ = Li₂CO₃ + 3H₂O

Carbon dioxide absorption is usually enhanced by increasing water vapor concentration in the gas stream (Martin, 1971).

A knowledge of alkali metal absorbents is important, not only for their potential in supplementing revitilization chemicals, but the reactions they undergo can clarify some of the reactions that occur for carbon dioxide absorption by total revitilization chemicals. This is particularly true for the hydroxide absorbents as they are intermediates for superoxide and ozonide systems. By studying a simple system of hydroxide carbon dioxide absorption, some important information can possibly be obtained for more complex revitilization systems.

Air Revitilization Chemicals.

Air revitilization chemicals possess the ability to produce oxygen and absorb carbon dioxide. It is this feature that makes this class of compounds a superior material for life support systems, assuming the air revitilization can deliver the desired amount of oxygen and remove the required amount of carbon dioxide to meet human respiratory needs.

The ratio of the volume of carbon dioxide absorbed to the volume of oxygen released by a chemical is known as the system respiratory quotient (SRQ). Similarly, the ratio of the volume of carbon dioxide released to the volume of oxygen required by a human being is called a man's respiratory quotient (MRQ). Depending on the environmental conditions and the amount of physical activity, the MRQ typically varies between 0.76 and 1.00; the most generally accepted average is 0.82 (Kunard and Rogers, 1962). This number is usually set as a goal for a chemical air revitilization system.
Theoretically, a series of chemical reactions can be controlled to provide the desired stoichiometry at equilibrium conditions. However, the ease with which the system respiratory quotient is satisfied at the desired value, varies with compound groups, and in some cases the RQ\(^1\) is not met despite elaborate controls and catalytic additives. It is the goal to develop a chemical system for air revitilization which is light and easy to control. This may necessitate the combination of different chemical systems.

Of the types of compounds considered as air revitilization chemicals, there are generally three classes: peroxides, superoxides, and ozonides. The last two represent unnatural oxidation states of the respective metals, in that they are thermodynamically unstable with respect to standard oxides and peroxides. Several references are available on the chemistry of these compounds (Vannerberg, 1962; Vol’nov, 1966, and Shanley, 1967). Other literature relates to the applications of these chemicals as air revitilization compounds in life support systems (Bovard, 1960; Petrocelli and Capotosto, 1964; Petrocelli and Wallman, 1969; and Maustellar, 1970). Each class of compounds is discussed below.

**Peroxides.**

The most simple peroxide is hydrogen peroxide. Alone hydrogen peroxide cannot be a total air revitilization chemical since it does not combine with carbon dioxide chemically. It does release oxygen via the decomposition reaction:

\[
(4) \quad \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 0.5\text{O}_2
\]

which is believed to be an ancillary step in alkali metal peroxide

---

\(^1\)RQ is an abbreviation for Respiratory Quotient. RQ is used interchangeably with SRQ and MRQ which when discussed in this report, are synonymous with a value of 0.82.
atmospheric air regeneration (Markowitz and Dezmelyk, 1964). Schmauch and Bailey (1966) showed the feasibility of using hydrogen peroxide as an oxygen supplier. Though hydrogen peroxide has the highest theoretical capacity for oxygen evolution of any peroxide, it is of no practical importance as an air revivification compound since it will not absorb carbon dioxide. This is not true for the other peroxides considered here.

The peroxides release oxygen and absorb carbon dioxide according to the general reaction:

\[ M_{2}O_{2} + CO_{2} + H_{2}O \rightarrow M_{2}CO_{3} + 0.5 O_{2} \]

where \( M \) represents an alkali metal from Group IA of the Periodic Table. In this study, alkali metals will be limited to lithium, sodium, and potassium, the lightest elements of this group. It would also seem that the same stoichiometry would be applicable to the alkaline earth metals of Group IIA (Beryllium, Magnesium, Calcium, Strontium, and Barium) according to the reaction:

\[ M(II)O_{2} + CO_{2} = M(II)CO_{3} + 0.5 O_{2} \]

However, the chemistry of this group of peroxides does not permit the above reaction to occur readily, and many of the lower weight alkaline earth metal peroxides that would be of interest as air revivification compounds are difficult to prepare or do not exist (Vol'nov, 1966).

**Lithium Peroxide.** Lithium peroxide has found more use as a carbon dioxide absorbent, but it also produces oxygen concurrently in the reaction with water and carbon dioxide. Nevertheless, only 0.35 pound of oxygen per pound of lithium peroxide can be produced theoretically. On the other hand, lithium peroxide has the capacity to absorb 0.96 pound of carbon dioxide per pound of chemical to yield a theoretical respiratory quotient for the peroxide of 2.0. Lithium peroxide does have a 4% greater capacity, theoretically, for carbon dioxide absorption than lithium hydroxide. On this basis,
lithium peroxide would be useful in a mixed, active chemical system as an
auxiliary carbon dioxide scrubber where its higher carbon dioxide absorp-
tion capacity could be applied and it could also provide supplemental
oxygen.

The overall reaction stoichiometry of this process is:

\[
(7) \quad \text{Li}_2\text{O}_2(s) + \text{CO}_2(g) = \text{Li}_2\text{CO}_3(s) + 0.5 \text{O}_2(g)
\]

Markowitz and Dezmelyk (1964) performed a study which confirmed the above
reaction, however, the evolution of oxygen lagged behind the absorption of
carbon dioxide. To explain this result, the researchers postulated the
evolution of oxygen and the carbon dioxide absorption process were occurring
by two different reaction mechanisms. In the first reactions, lithium
peroxide reacts with water vapor to form active carbon dioxide absorbents,
lithium hydroxide and lithium hydroxide monohydrate.

\[
(8) \quad \text{Li}_2\text{O}_2(s) + 2 \text{H}_2\text{O}(g) = 2 \text{LiOH}(s) + \text{H}_2\text{O}_2(l)
\]

\[
(9) \quad \text{LiOH}(s) + \text{H}_2\text{O}(g) = \text{LiOH} \cdot \text{H}_2\text{O}(s)
\]

Then, carbon dioxide is absorbed by the reactions listed below:

\[
(10) \quad 2 \text{LiOH}(s) + \text{CO}_2(g) = \text{Li}_2\text{CO}_3(s) + \text{H}_2\text{O}(l)
\]

\[
(11) \quad 2 \text{LiOH} \cdot \text{H}_2\text{O}(s) + \text{CO}_2(g) = \text{Li}_2\text{CO}_3(s) + 3 \text{H}_2\text{O}(l)
\]

It is conjectured that the slow decomposition of hydrogen peroxide is respon-
sible for the oxygen release to lag behind the carbon dioxide uptake reaction.
Thermodynamically, hydrogen peroxide has a very high equilibrium constant
for its formation (log \(K = 48.7\)) and thus its decomposition is not favored.
Markowitz and Dezmelyk (1964) proposed the stability of hydrogen peroxide,
that is its failure to decompose rapidly to release oxygen, could be attri-
buted to the formation of a lithium peroxide/hydrated hydroxide solid
mixture; these studies seem to strengthen the following hypotheses of the
Russians.

Selezneva (1960) has investigated the reaction of lithium peroxide with
water vapor and carbon dioxide at various temperatures. He found that up to 200°C, lithium peroxide did not react with dry carbon dioxide. However, at higher temperatures (above 200°C), some active oxygen (oxygen which is available by stoichiometry) was evolved and carbon dioxide was absorbed to form lithium carbonate. As expected, this activated oxygen evolution and carbonate formation reaction was increased in rate for increasing temperatures. The reactions eventually stopped after about an hour because of the diffusion resistance caused by a barrier of carbonate crust layer. A difference in the reaction rates was noted for different crystalline structures of lithium peroxide; alpha and beta phases. The phase transition temperature occurs between 225 and 250°C.

Selezneva (1960) drew three major conclusions from the interaction of lithium peroxide with carbon dioxide in the presence of water vapor. At room temperature, the species lithium peroxide monohydrate is formed.

\[
\text{(12)} \quad \text{Li}_2\text{O}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{Li}_2\text{O}_2\cdot\text{H}_2\text{O}(s)
\]

Some of the hydrate formed can decompose to the hydroxide:

\[
\text{(13)} \quad \text{Li}_2\text{O}_2\cdot\text{H}_2\text{O}(s) \rightarrow 2\text{LiOH}(s) + 0.5\text{O}_2(g)
\]

A secondary reaction may also take place, that being the formation of lithium hydroxide monohydrate.

\[
\text{(14)} \quad \text{LiOH}(s) + \text{H}_2\text{O}(g) \rightarrow \text{LiOH}\cdot\text{H}_2\text{O}(s)
\]

Above 200°C, lithium peroxide reacts appreciably with water vapor to form lithium hydroxide only and to liberate oxygen. The amount of oxygen evolution at 200°C is 70.3% of the theoretical capacity; carbon dioxide absorption is 68% of the theoretical. At 300°C, thermal decomposition occurs in addition to the chemical decomposition of the peroxide. Lithium peroxide does not completely liberate all of its oxygen until the reaction temperature is between 315 to 342°C (Vol'nov, 1966).

Several methods of preparation are available; on the commercial scale,
concentrated hydrogen peroxide is added to lithium oxide hydrate (Bach and Boardman, 1962). Other methods involve the oxidation of lithium metal amalgam (Huhn, 1954) and the reaction of lithium nitrate with sodium superoxide in liquid ammonia at low temperatures (Schechter and Kleinberg, 1954). Lithium peroxide must be stored in hermetically sealed containers to prevent the formation of a carbonate crust on the external surfaces.

Other peroxides. Like lithium peroxide, sodium peroxide has been used as an auxiliary carbon dioxide scrubber. Sodium peroxide ($\text{Na}_2\text{O}_2$) along with potassium superoxide have been the most frequently used chemicals in portable breathing apparatus (Clarke, 1956). Sodium peroxide is often used in combination with a superoxide (Kunard and Rogers, 1962) and occasionally in special air revitilization mixtures (Sanders, 1970). Sodium peroxide of 95% purity is manufactured on a large scale by burning sodium in air (Hardie, 1955) among other methods. Higher purity sodium peroxide is obtained by reducing low quality peroxide with sodium followed by oxidation to a peroxide in a rotary furnace (Tadler and Coleman, 1957).

Potassium peroxide is not readily made; its oxygen capacity per pound of peroxide does not warrant its production as an atmosphere regeneration material. The same is true for the heavier molecular weight peroxides of the alkali metals. For the alkaline earth metals, beryllium peroxide does not exist and attempts to prepare magnesium peroxide have been unsuccessful (Markarov and Vol'nov, 1954). Calcium peroxide has a higher active oxygen content than sodium peroxide, but the application of the calcium compound as an air revitilization chemical is doubtful because of its low reactivity to form oxygen and also its low solubility (Vol'nov, 1966).

Efforts have been undertaken to enhance the revitilization capabilities of the more promising peroxides, lithium and sodium. Both have been evaluated as total air revitilization compounds and were found to be better suited as
carbon dioxide absorbents. The addition of catalysts such as copper oxychloride, manganese dioxide, and other metal oxides failed to lower the SRQ below its practical value of 3.0 to the theoretical value of 2.0 as shown by Copotosto and Petrocelli (1968). The lowest values of the SRQ were only obtained in gas stream humidities near 100%. Boryta (1975) developed solid granules of catalyzed lithium peroxide containing a non-oxidizable, hydroscopic agent for use in closed cycle life support systems. These granules in 100% relative humidity were able to increase oxygen production to give a SRQ of 1.97 after two hours of use. Large scale use of this method is doubtful, however. For sodium peroxide, similar results were obtained by Petrocelli et al., (1966). However, manganese dioxide did show increased decomposition of the peroxide at an elevated temperature of 250°C. This decomposition was found to be dependent on surface area. Still, the results of the above studies demonstrate the inability of alkali metal peroxides to perform as total air revitilization compounds.

Superoxides.

Superoxides are the only one of the three classes of air revitilization chemicals which may be controlled to match a MRQ of 0.82. The general chemistry governing superoxide evolution and carbon dioxide absorption is described by the following reactions where M represents an alkali metal cation:

\[
\begin{align*}
(12) & \quad 2 \text{MO}_2 + \text{H}_2\text{O} = 2 \text{MOH} + 1.5 \text{O}_2 \\
(13) & \quad 2 \text{MOH} + \text{CO}_2 = \text{M}_2\text{CO}_3 + \text{H}_2\text{O}
\end{align*}
\]

Often these equations, equations (12) and (13), are generalized into a single reaction:

\[
(14) \quad 2 \text{MO}_2 + \text{CO}_2 = \frac{\text{M}_2\text{CO}_3 + 1.5 \text{O}_2}{\text{H}_2\text{O}}
\]
From equation (14), one may calculate a theoretical SRQ of 0.67. The control of the SRQ of this system is achieved via a competing reaction of carbon dioxide with the hydroxide to form the bicarbonate:

\[(15) \quad \text{MOH} + \text{CO}_2 = \text{MHCO}_3\]

Taken together, reactions (12) and (15) can be represented as:

\[(16) \quad 2 \text{MO}_2 + \text{H}_2\text{O} + 2 \text{CO}_2 = 2 \text{MHCO}_3 + 1.5 \text{O}_2\]

In this case, the theoretical SRQ is 1.33. Therefore, depending on the mode of carbon dioxide absorption, the SRQ for a superoxide system can be either 0.67 or 1.33 or some value between. This of course brackets the desired SRQ of 0.82. It logically follows that a combination of carbon dioxide absorption by the formation of the carbonate and by the formation of the bicarbonate in the proper proportions would yield a SRQ of 0.82.

Kunard and Rogers (1962) wrote the required stochiometry of the combined reactions for such an occurrence:

\[(17) \quad 2 \text{MO}_2 + 1.23 \text{CO}_2 + 0.23 \text{H}_2\text{O} = 0.77 \text{M}_2\text{CO}_3 + 0.46 \text{MHCO}_3 + 1.5 \text{O}_2\]

It would be extremely fortunate if getting a SRQ of 0.82 for a superoxide air revitilization system could be achieved by merely controlling alkali metal carbonate and bicarbonate formation. The superoxide-water vapor-carbon dioxide system includes several other possible reactions. In the chemical equilibria of the system are reactions of the products in hydrations and some of these can also react with carbon dioxide. There is also the thermal decomposition of the superoxide to be considered:

\[(18) \quad 2 \text{MO}_2 + \text{heat} = \text{M}_2\text{O} + 1.5 \text{O}_2\]

Each alkali metal has a different set of secondary reactions which accompany the evolution of oxygen and the absorption of carbon dioxide. One additional condition is the decomposition of the products, particularly the bicarbonates since their decomposition would lead to the decreased
overall absorption of carbon dioxide.

Other than alkali metal superoxides, the alkaline earth metal superoxides also have potential for use as air revitilization materials. The generalized reaction for alkaline earth metal superoxides is:

\[(19) \quad \text{M(II)O}_4 + \text{CO}_2 \rightarrow \text{M(II)CO}_3 + 1.5 \text{O}_2\]

However, for the purposes of this study, we will limit our discussion to calcium superoxide, since other alkaline earth metal superoxides either do not exist, have inadequate reactivity, or are not weight efficient chemicals. Of the alkali metal superoxides, only the three lightest are reviewed: lithium, sodium, and potassium superoxides. Other superoxides of the heavier metals are not weight efficient in so far as to the production of oxygen.

**Lithium Superoxide.** On the basis of theoretical oxygen production per pound, lithium superoxide is the most efficient superoxide. In comparison to the well used potassium superoxide, lithium superoxide will yield 80% more oxygen and absorb 81% more carbon dioxide on a per pound basis. However, until recently, few claims were received of its actual existence. In the past, lithium superoxide was found only by indirect evidence such in the absorption spectra of liquid ammonia solutions of metallic lithium (Davidson and Kleinberg, 1953). Molecules of lithium superoxide have been isolated in oxygen matrices by Raman spectroscopy which indicate successful synthetic techniques (Hatzenbuhler and Andrews, 1971). Several years before, the Russian scientist Shatunia (1957, 1959) was able to prepare small amounts of lithium superoxide of very low purity (7 to 9 weight percent) in an admixture of lithium peroxide and hydroxide. Attempts to synthesize lithium superoxide by other conventional superoxide preparation methods have failed (Vol'nov, 1966).

The stability of pure lithium superoxide has been studied by several
groups. Vannerberg (1962) postulated that it could not exist as a stable compound due to the small radius of the lithium ion (0.60 Å); he hypothesized the critical cation radius is between 0.66 and 1.15 Å for a stable superoxide to exist. Other researchers have studied the thermodynamics of lithium superoxide. Snow (1965) calculated the free energy of the compound relative to the free energies of other lithium oxides as a function of temperature. He found that between 100 and 300 K, the lithium superoxide was unstable by +15 kcal/mole, and this instability in the free energy increased with temperature. D'Orazio and Wood (1965) confirmed this analysis with similar conclusions regarding the stability of lithium superoxide. Bell and Sadhukhan (1974) have postulated that lithium superoxide may be grossly unstable as predicted by equilibrium thermodynamics; but by some unknown means, the kinetics of its decomposition reaction prevent whole scale destruction of the compound.

**Sodium Superoxide.** Sodium superoxide was first synthesized in 1949 by the oxidation of sodium peroxide at an oxygen pressure of 289 atmospheres and a temperature of 490 °C for a reaction period of 100 hours (Kazarnovskii, 1949; Stephanou et al., 1949). Improvements in this process have yielded products which are almost pure (Schechter and Shakely, 1957; Cunningham, 1959). Another method employs the self-oxidation of benzophenone with metallic sodium dissolved in tetrahydrofuran (LeBerne and Godsuen, 1962). Today, sodium superoxide is manufactured on a commercial scale in the Soviet Union. There is also some production in the United States. A small percentage of the sodium peroxide produced commercially contains sodium superoxide (George, 1955).

Sodium superoxide follows the general chemistry described for superoxide air revitilization compounds. At temperatures below 10 °C however, only the superoxide oxygen in liberated:
Furthermore, under the same conditions, Mel'nikov and Firsova (1961) found sodium peroxodicarbonate (Na$_2$C$_2$O$_6$) is formed in the presence of water vapor and carbon dioxide. To rationalize these results, the following reactions were proposed:

(21) \[ 2 \text{NaO}_2 + 8 \text{H}_2\text{O} = \text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O} + \text{O}_2 \]

(22) \[ \text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O} + 2 \text{CO}_2 = \text{Na}_2\text{C}_2\text{O}_6 + 8 \text{H}_2\text{O} \]

Overall,

(23) \[ 2 \text{NaO}_2 + 2 \text{CO}_2 = \text{Na}_2\text{C}_2\text{O}_6 + \text{O}_2 \]

The stoichiometry indicates a much larger amount of water is necessary to 'catalyze' the revitilization process. Additionally, less oxygen is produced with a resulting theoretical SRQ of 2.0. The same chemists noted that sodium superoxide does not react with dry carbon dioxide.

Another study was performed for the sodium superoxide-water vapor-carbon dioxide system by Petrocelli and Capotosto (1965). In their work, the relative humidity was increased to 100% and the oxygen production rate increased proportionally according to first order kinetics. The carbon dioxide absorption rate was observed to increase with first order kinetics as well.

The sodium system is characterized by a large number of reactions compared to other superoxide systems (See Tables 3 through 6). Hydrates of the hydroxides, carbonate, and bicarbonate products are possible; many more than for the potassium system. Also, a small amount of sodium peroxide is usually present in sodium superoxide, and this peroxide may also be involved in the reaction scheme.

Potassium Superoxide. The most widely used chemical for air revitilization over the past 40 years has been potassium superoxide. Primarily, it has been used in conjunction with a carbon dioxide absorbent, or alone
in portable, one-man breathing apparatus, used by miners, firefighters, and military personnel (Bovard, 1960a; Li et al., 1976; Stein, 1976; Orner and Audet, 1971). Potassium superoxide has also been employed in small submersibles, 'Star III' by General Dynamics (Presti et al., 1967) and 'Deep Quest' manufactured by Lockheed (Li, 1980). A Russian diving apparatus which appeared to use potassium superoxide as part of the life support system was captured during the Vietnam War (Kelly et al., 1968). However, the predominance of research activity has centered around the development of potassium or sodium superoxide life support systems for spacecraft (Keating et al., 1960; Kunard and Rogers, 1962; McGoff, 1965; McGoff and King, 1966). Superoxide systems have actually been used in the Vostok and Voshkod space capsules in the Soviet space program (Petrocelli, 1965; Jaax, 1973).

Although superoxides have been used in submersibles, the pressure of the breathing atmosphere inside the submersible was maintained near atmospheric pressure.

Perhaps the primary reason that potassium superoxide is used so widely is due to the ease of its commercial manufacture. There are five major routes for the production of potassium superoxide (Bell and Sadhukhan, 1974):

1) Oxidation of potassium metal in dissolved in liquid ammonia (Lux, 1959)
2) Direct oxidation of the metallic vapor (Jackson, 1946)
3) Oxidation of a lower oxide, for example, potassium oxide (Kohlmuller, 1959)
4) Oxidation of potassium hydroxide (Kroger, 1945)
5) Disproportionation of a peroxide-peroxyhydrate

In the latter method, the synthesis of potassium superoxide is via an unusual compound, potassium peroxide dihydroperoxidate ($K_2O_2 \cdot 2H_2O_2$). Kazarnovskii and Neiding (1952) devised the method so that this compound
could be kept without decomposing at the temperature of frozen carbon dioxide. At higher temperatures, it would disproportionate into the superoxide and water:

\[ K_2O_2 \cdot 2H_2O_2 = 2 KO_2 + 2 H_2O \]  

On an industrial scale, potassium superoxide is produced by the second of the five listed methods (Vol'nov, 1966). The direct oxidation of a metallic vapor process is a fairly economic one in comparison to the other methods and to most other air regeneration materials. The most expensive parts of the process are the heating of the metal and the need for highly corrosion resistant equipment. Figure 1 shows a diagram of the commercial apparatus. Sadhukhan and Bell (1978) propose an alternate to the molten potassium process, in which potassium hydroxide is subjected to a radio frequency discharge in an oxygen atmosphere. The technique has been used with a great deal of success resulting in a purer product and using less expensive starting materials. Interestingly enough, this same process was applied to the synthesis of other superoxides with the preparation of only sodium superoxide being possible. For both lithium and calcium, the peroxides are created in lieu of the superoxides.

The chemistry of potassium superoxide as an air revitilization chemical has been studied extensively. Mel'nikov et al. (1962) showed the reaction between carbon dioxide and potassium superoxide required the presence of water vapor. Like sodium superoxide, below 10°C, the reaction of the system evolves only superoxide oxygen:

\[ 2 KO_2 = K_2O_2 + O_2 \]

Similarly, a neutral salt of peroxodicarbonic acid (K₂C₂O₆) is formed in the reaction of potassium superoxide with carbon dioxide in the presence of water vapor under these conditions.

\[ 2 KO_2 + n H_2O = K_2O_2 \cdot nH_2O + O_2 \]
\[(27) \quad K_{2}O_{2} \cdot nH_{2}O + 2CO_2 = K_2C_2O_6 + nH_2O\]

In this case, 'n' is unknown since the investigators were unable to isolate the potassium peroxide hydrates. Again, a higher theoretical SRQ of 2.0 is represented by the above stoichiometry. At higher temperatures, all of the active oxygen is evolved and potassium hydroxide is formed as in the general superoxide reaction (equation 12). With sufficient water, the potassium hydroxide will react with the water to form hydrates in addition to combining with carbon dioxide:

\[(28) \quad KOH + 0.75H_2O = KOH \cdot 0.75H_2O\]
\[(29) \quad KOH + H_2O = KOH \cdot H_2O\]
\[(30) \quad KOH + 2H_2O = KOH \cdot 2H_2O\]

Above 50°C, all active oxygen is evolved and both potassium carbonate and bicarbonate are formed. The potassium carbonate can further react with water vapor to form two hydrates, \(K_2CO_3 \cdot 0.5H_2O\) and \(K_2CO_3 \cdot 1.5H_2O\). The extent and significance of these additional reactions is discussed in the next section on superoxide thermodynamics and equilibrium.

Kunard and Rogers (1962) confirmed the above results showing that dry carbon dioxide did not react with the superoxide. At ambient temperatures, water vapor alone will react to form the hydroxide and hydrated hydroxide with the evolution of oxygen as by reaction (31) and (32) below:

\[(31) \quad 2KO_2 + H_2O = 2KOH + 1.5O_2\]
\[(32) \quad 2KO_2 + 3H_2O = 2KOH \cdot H_2O + 1.5O_2\]

In regard to the reactions of potassium superoxide with carbon dioxide in the presence of water vapor, Kunard and Rogers (1962) concluded:

1) As the reaction proceeded, the oxygen production rate decreased while the water absorption rate remained essentially constant.

2) The absorption of carbon dioxide increased directly as
the concentration of water increased in the gas system.
The significance of the former statement is that hydration of the products
competes with the hydration of the superoxide. With the formation of the
hydrates, it becomes more difficult for the superoxide to react with the
water vapor since a coating of the hydrates forms over the active surface
of the chemical bed. From the second conclusion, is the observation that
carbon dioxide absorption continues after the evolution of oxygen ceases.

**Calcium Superoxide.** Most of the calcium superoxide research over the
past ten years has been connected with its preparation. Calcium superoxide
has an oxygen storage capacity which is 37% greater than potassium super-
oxide and 7% greater than sodium superoxide on a weight basis. The melting
melting point of calcium hydroxide is much higher than the hydroxides of
potassium and sodium (Calcium hydroxide - 580°C; Potassium hydroxide -
360°C; Sodium hydroxide - 318°C) and the air revitilization reactions with
calcium superoxide show the smallest heat of reaction of the superoxides.
Though not previously discussed, these factors can be important in the
consideration of a superoxide system since some fusing of the chemical
surface can limit efficiency. Despite these advantages, the utilization
of calcium superoxide is limited by the fact that it cannot be prepared
in high purities.

The lack of success in producing pure calcium superoxide is attributed
to its instability; Brosset and Vannerberg,(1965) speculate that where
calcium superoxide is actually produced, it exists as oxygen anions (O₂⁻)
in a matrix of lower oxides. The stability of calcium superoxide was
estimated in a similar manner as described earlier for lithium superoxide;
the free energy of calcium superoxide was compared to the free energies of
other calcium oxides as a function of temperature (Bell and Sadhukhan, 1975;
Sadhukhan and Bell, 1979). These calculations show that calcium superoxide
is unstable to the lower oxides for the entire temperature range of 100 to 500°K.

The preparation methods used in the synthesis of other superoxides, for example, the direct oxidation of a metallic vapor, are ineffective for the synthesis of calcium superoxide. Vol'nov et al., (1957) successfully prepared calcium superoxide by a process involving the disproportionation of calcium peroxide diperoxide hydrate (CaO₂·2 H₂O₂) which resulted in a product with a purity of 16% by weight of the superoxide. Refinement of the reaction conditions and other parameters, such as reactant surface area, improved purities to 54.4% (Vol'nov and Shatunia, 1966). However, many of the results obtained by Vol'nov and Shatunia, and other Russian scientists (Vol'nov and Chamova, 1960; Vol'nov et al., 1959) were not reproducible. The disproportionation reaction involved in these studies is given below:

\[
\begin{align*}
(33) \quad 2[\text{CaO}_2\cdot2\text{H}_2\text{O}_2] & \rightarrow \text{Ca}(\text{O}_2)_2 + \text{Ca(OH)}_2 + 3\text{H}_2\text{O} \\
& + 1.5\text{O}_2
\end{align*}
\]

The maximum possible purity that can be obtained for calcium superoxide by the equimolar disproportionation reaction is 58.4% by weight.

Petrocelli and Capotosto (1965) attempted to prepare calcium superoxide by the reaction of calcium peroxide with ozone which produced a product of only 3-10% purity. Other methods of preparation have included the reaction of aqueous hydrogen peroxide with an inorganic or organic calcium compound; the highest yields using this technique were obtained with the hydroxide and 50-80% aqueous hydrogen peroxide at 0°C to give a product of 35-60% purity. The attempted scale-up of the process to produce commercial amounts of the superoxide was frustrated by lower product purity and inconsistent (unreproducible) results. The introduction of the catalysts, CdO and TiO₂, had no effect on product purity but did help to give more consistent results. Jackson (1966) and Rewick et al. (1972) further
investigated the use of ozone in the preparation of calcium superoxide with no success in bettering the purities obtained by the disproportionation process.

Recent studies have focused on the variation of temperature, pressure, particle size, reactant purity, transport and reaction control techniques, which may help in obtaining higher and more consistent yields. Ballou et al. (1977) prepared calcium superoxide at sub-ambient temperatures with purities of 61%, which is above the theoretical maximum claimed for the disproportionation reaction. More investigation revealed consistent yields with purities in the range of 59 to 61% (Ballou et al., 1978a; Ballou et al., 1978b); the technique may be amenable to commercial scale-up. The latest studies have involved the use of a fluidized bed to contain the reactants in a radio frequency discharge similar to the method reported with high success for potassium superoxide production (Sadhukhan and Bell, 1978). Purities up to 67% have been obtained from this method (Wydeven et al., 1979; Wood et al., 1980). Active research continues in this area with an eye towards large scale production of the calcium product.

Due to the inability to prepare a pure sample, the chemistry of calcium superoxide is not well characterized. Some work has been done however. Like alkali metal superoxides, it would be expected that calcium superoxide follow the general reaction, equation (12), in an analogous form for alkaline earth metals:

\[(34) \ M(II)O_4 + H_2O = M(II)[OH]_2 + 1.5 O_2\]

For Calcium, this would simply be:

\[(35) \ Ca(O_2)_2 + H_2O = Ca(OH)_2 + 1.5 O_2\]

Kinetic studies of the reaction of calcium superoxide with water vapor were conducted by Petrocelli and Capotosto (1965). The results they obtained were different than expected. The visible product following the
reaction was a white, powdery and dry-looking solid. This was in contrast to concentrated hydroxide solution resulting from the reaction of potassium superoxide with water vapor. This result was anticipated due to the relatively high heat of fusion for calcium hydroxide. Also, surprising was that the oxygen evolved did not match the stoichiometry of the reaction (35). From the analysis of the data, two different interactions with water vapor were proposed:

\begin{align*}
(36) \quad \text{Ca(O}_2\text{)}_2 + 2 \text{H}_2\text{O} & = \text{Ca(OH)}_2 + \text{H}_2\text{O}_2 + \text{O}_2 \\
(37) \quad \text{Ca(O}_2\text{)}_2 + n \text{H}_2\text{O} & = \text{CaO}_2\cdot n \text{H}_2\text{O} + \text{O}_2
\end{align*}

Reaction (36) was seen as the least plausible because the formation of hydrogen peroxide was inconsistent with the dryness of the chemical bed after the reaction. An analysis of the bed confirmed this belief and pointed to reaction (37) as a more likely reaction. This result was also documented by Ballou et al. (1977) with one slight modification:

\begin{align*}
(38) \quad \text{Ca(O}_2\text{)}_2 + n \text{H}_2\text{O} & = \text{CaO}_2\cdot n \text{H}_2\text{O} + (n - x) \text{H}_2\text{O} + \text{O}_2
\end{align*}

In fact, it was this same reaction that was believed to sometimes interfere with the preparation of calcium superoxide.

The reaction of calcium superoxide with carbon dioxide and water vapor has also been investigated by Petrocelli and Capotosto (1965). Experiments were carried out at room temperature and various relative humidities. It was found that there was a considerable lag in carbon dioxide absorption with respect to oxygen evolution. The measured SRQ varied between 0.71 and 1.38 for 50% relative humidity. At saturated conditions, the SRQ was observed to be about 1.00 (average). The following modes of carbon dioxide absorption were proposed:

\begin{align*}
(39) \quad \text{CaO}_2\cdot n \text{H}_2\text{O} + x \text{H}_2\text{O} & = \text{Ca(OH)}_2 + 0.5 \text{O}_2 + (n+x-1) \text{H}_2\text{O} \\
(40) \quad \text{Ca(OH)}_2 + \text{CO}_2 & = \text{CaCO}_3 + \text{H}_2\text{O}
\end{align*}
If the three reactions of the mechanism were added together (Reactions 37, 39, and 40), a similar overall reaction would be obtained as for the alkali metal superoxides (reaction 14). The only differences in this overall reaction and that for alkali metals are the intermediate hydrated peroxide species and the uncertainty in the required stoichiometry for water. Therefore, a theoretical SRQ of 0.67 would be predicted for this system as has been generalized for all superoxides. What would be affected is perhaps the kinetics of the calcium superoxide system, since another reaction is introduced. However, this is mere speculation at this point in time without a thorough review of the system.

It is also possible that carbon dioxide would be absorbed by the calcium peroxide hydrate by the reaction below:

\[
Ca(O_2)nH_2O + CO_2 \rightarrow CaCO_3 + nH_2O + 0.5O_2
\]

In either case, the SRQ would be 0.67. In the calcium superoxide system, unlike alkali metal superoxides, the bicarbonate species does not exist. Moreover, no common hydrates of either the carbonate or hydroxide would be possible with this system. Therefore, there probably is only one route of carbon dioxide absorption. The higher SRQ's from the subsequently cited experiments must be interpreted cautiously, because as stated by the authors themselves, the samples were not pure. Both calcium hydroxide and peroxide existed at significant levels in the tested chemicals during the study. Side reactions of water vapor and carbon dioxide with the impurities in the sample may have possibly given misleading results.

Ozonides.

Ozonides have the highest oxygen storage capacity of all known air revitalization chemicals. Lithium ozonide, for example, has the theoretical
capacity to evolve 0.73 pound of oxygen per pound of chemical as compared to the 0.43 lb O\textsubscript{2}/lb and 0.34 lb O\textsubscript{2}/lb chemical for sodium and potassium superoxides, respectively. The general chemistry of ozonide oxygen production/ carbon dioxide absorption is similar to that for the superoxides; (M represents an alkali metal cation)

\begin{align*}
(42) \quad 2 \text{MO}_3 + \text{H}_2\text{O} &= 2 \text{MOH} + 2.5 \text{O}_2 \\
(43) \quad 2 \text{MOH} + \text{CO}_2 &= \text{M}_2\text{CO}_3 + \text{H}_2\text{O}
\end{align*}

the overall reaction being:

\begin{align*}
(44) \quad 2 \text{MO}_3 + \text{CO}_2 &= \text{M}_2\text{CO}_3 + 2.5 \text{O}_2
\end{align*}

The SRQ describing the carbonate scheme is theoretically, 0.4; for the competing bicarbonate formation in carbon dioxide absorption, the SRQ is calculated to be 0.8.

\begin{align*}
(45) \quad 2 \text{MOH} + 2 \text{CO}_2 &= 2 \text{MHCO}_3
\end{align*}

In this case, the overall reaction is:

\begin{align*}
(46) \quad 2 \text{MO}_3 + \text{H}_2\text{O} + 2 \text{CO}_2 &= 2 \text{MHCO}_3 + 2.5 \text{O}_2
\end{align*}

The combination of the carbonate and bicarbonate reactions will produce a SRQ between 0.4 and 0.8. This would mean a carbon dioxide absorbent is necessary to supplement any ozonide system. This is not because the ozonide system does not absorb enough carbon dioxide; it absorbs the same amount as a superoxide would. It is a case of oxygen overproduction. In this paper, only the three lightest ozonides are described (lithium, sodium, and potassium).

**Lithium Ozonide.** Attempts to synthesize stable lithium ozonide of any purity have failed. Vol'nov (1973) has obtained unstable lithium ozonide from the reaction of lithium peroxide with ozone in Freon-13 at -100°C. The ozonide decomposed rapidly and its existence was indirectly detected by EPR (Electron Paramagnetic Resonance) spectra. The difficulties in preparing lithium ozonide are believed to be analogous to those observed
for preparing lithium superoxide (Nikol'skii et al., 1951; Smith, 1956). A related compound, the tetra ammoniate of lithium ozonide (Li[NH$_3$]$_4$O$_3$) has been prepared (Kacmarek et al., 1962) but the compound has no utility as an air regeneration chemical.

Sodium Ozonide. A great deal of success has been achieved in synthesizing sodium ozonide compared to lithium ozonide. In 1951, Nikol'skii et al. (1951) reported the preparation of sodium ozonide using anhydrous sodium hydroxide and 8 to 9 percent ozone in oxygen at -50°C in liquid ammonia. Further work resulted in the preparation of a product of 90 wt.% sodium ozonide that was soluble in liquid ammonia, but unstable at room temperature; it decomposed in 53 hours to sodium superoxide and oxygen. At about the same time, Whaley and Kleinberg (1951) prepared a high purity sodium ozonide that was quite stable at room temperature, and insoluble in liquid ammonia. The preparation of this latter method was conducted at room temperature as opposed to the sub-ambient temperature used in the Russian technique. Soloman and Kacmarek (1960) attempted to reconcile this discrepancy of these two results by hypothesizing the existence of two stable crystalline forms or phases of the ozonide. This theory has not enjoyed wide acceptance and the apparent discrepancy between the characteristics of the two differently prepared compounds remains unresolved.

Petrocelli and Capotosto (1964) attempted to prepare sodium ozonide using the same method as Nikol'skii (1951). They obtained sodium ozonide in a solution of liquid ammonia. However, they failed in trying to isolate the material; upon vacuum evaporation, a white solid, sodium hydroxide was obtained. Using the method of Whaley and Kleinberg (1951) a low purity product was obtained which could not be purified by extraction techniques. It was concluded that until a new method of preparation is developed, sodium ozonide is not a potential air revitalization chemical.
Potassium Ozonide. The same preparation method that is used to synthesize sodium ozonide is used for producing potassium ozonide (Kazarnovskii and Nikol'skii, 1949). A large latitude on the synthesis temperature is allowed for the potassium ozonide production (Maharov and Sohovnin, 1960). Most recent methods of preparation involve the reaction of potassium superoxide with ozone in Freon-12 (Vol'nov and Tokareva, 1977). For the evaluation of potassium ozonide as an air revitalization chemical, Petrocelli and Capotosto (1964) prepared the compound via ozonization of potassium hydroxide at -10°C to +15°C to establish yields up to 7% and a product purity of 88 to 97% after extractions with ammonia.

The reactions of potassium ozonide with water vapor and carbon dioxide have been investigated by Petrocelli and Capotosto (1964). The kinetics of the reaction of potassium ozonide with water vapor at different relative humidities revealed an increase of the average rate of oxygen evolution for increasing humidity. For example, at 50% relative humidity, the oxygen production was 10.9 ml/gm. ozonide/hr.; at 100% humidity, the rate nearly tripled to 29.6 ml/gm. ozonide/hr., and the total reaction time for this oxygen evolution decreased (30 to 22 minutes, respectively). At 37°C, the reaction time and oxygen production rate were affected in a similar manner. Like superoxides, potassium ozonide did not react with dry carbon dioxide. Reactions with carbon dioxide at various water vapor concentrations generally yielded low SRQ's. In one case a SRQ of 0.63 was measured; taking into account the impurities in the potassium ozonide sample (hydroxide), the predicted SRQ was 0.48 for carbon dioxide absorption by carbonate formation only. If bicarbonate alone was formed, the SRQ expected would be 0.80. The result is that a large amount of bicarbonate is formed in these reactions, this being confirmed by potentiometric titrations with hydrochloric acid.

Firsova et al. (1967) obtained similar results for the response of the
ozonide system with the water vapor concentration and reaction temperature. However, it was determined that potassium hydroxide dihydrate (KOH·2 H₂O) was formed initially which in turn reacts with carbon dioxide to form potassium carbonate and water by the following reactions:

\[
\begin{align*}
(47) \quad \text{KO}_3 + 2 \text{H}_2\text{O} & \rightarrow \text{KOH} \cdot 2 \text{H}_2\text{O} + \text{O}_2 \\
(48) \quad 2 \text{[KOH} \cdot 2 \text{H}_2\text{O]} + \text{CO}_2 & \rightarrow \text{K}_2\text{CO}_3 + 5 \text{H}_2\text{O}
\end{align*}
\]

The formation of the dihydrate results in a volume increase since its density is 2.21g/cc compared to 1.62 g/cc for potassium ozonide. This in turn causes a barrier to water diffusion and can limit the efficiency of the reaction.

In order to elucidate the actual reaction mechanism for the potassium ozonide-water vapor-carbon dioxide system, a study of isotopic exchange of oxygen was carried out by Kazarnovskii and Lipikkin (1956). Based on their experiments, they proposed the following reaction scheme:

\[
\begin{align*}
(49) \quad \text{KO}_3 + \text{H}_2^{18}\text{O} & \rightarrow \text{K}^{18}\text{OH} + \text{OH} + \text{O}_2 \\
(50) \quad 2\text{OH} & \rightarrow \text{H}_2\text{O} + 0.5 \text{O}_2 \\
(51) \quad 2\text{OH} & \rightarrow \text{H}_2\text{O}_2 \\
(52) \quad \text{OH} + \text{H}_2^{18}\text{O} & \rightarrow ^{18}\text{OH} + \text{H}_2\text{O} \\
(53) \quad 2^{18}\text{OH} & \rightarrow \text{H}_2^{18}\text{O} + 0.5 \text{O}_2
\end{align*}
\]

From their observations, an entirely different reaction mechanism was submitted. Yet other research would be necessary to justify their proposal.

**Special Air Revitalization Chemical Mixtures.**

Traditionally, superoxides must be supplemented by some form of a carbon dioxide absorption system since adequate control of the revitilization system is difficult for maintaining the proper SRQ with a single chemical. These 'auxiliary' absorption systems have included sodasorb, lithium
hydroxide, and lithium peroxide. In the past years, there have been patents granted for combined systems to approximate the SRQ to the MRQ. A single uniform mixture of two chemicals, for example, potassium superoxide and lithium hydroxide is often proposed rather than two cannisters each containing one of the chemicals.

Sanders (1970) reports one such mixture having a composition of 21 wt. % sodium peroxide, and 79% potassium superoxide. He proposed the following chemical equation of stoichiometry to achieve a desired SRQ:

\[
(54) \quad (1.5 \ RQ - 1) \ Na_2O_2 + (2 - RQ) \ KO_2 + RQ \ CO_2 = O_2 + (1.5 \ RQ - 1) \ Na_2CO_3 + (1 - 0.5RQ) \ K_2CO_3
\]

Application to other mixtures of oxides, peroxides, and superoxides were given by Sanders (1970). Some examples are sodium superoxide and potassium peroxide and the mixture potassium superoxide and lithium oxide. The patent also called for the introduction of 0.1 to 2% decomposition catalysts in the formulation (such as platinum, manganese dioxide, ferric chloride, or copper oxychloride).

More sophisticated air revitilization compositions have been reported by Gustafson (1977a, 1977b) with the purpose of creating a total air revitilization chemical which is resistant to surface fusion, to the formation of hydrates, and to diminish the need for rapid heat dissipation. In the former patent (1977a), Gustafson proposed an admixture of the following composition:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight Pct.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous Calcium Sulfate</td>
<td>3 - 8</td>
</tr>
<tr>
<td>Silicon Dioxide</td>
<td>0 - 2</td>
</tr>
<tr>
<td>Lithium monoxide</td>
<td>2 - 10</td>
</tr>
</tbody>
</table>

or:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight Pct.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium monoxide</td>
<td>2 - 10</td>
</tr>
<tr>
<td>Lithium metaborate</td>
<td>5 - 10</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>0 - 2</td>
</tr>
</tbody>
</table>
The remaining amount of the mixture was potassium superoxide. The results of these various compositions was high oxygen evolution and carbon dioxide absorption rates. The effects of the added materials was to increase the observed capacity of the materials on a per pound basis in spite of the weight penalty.

In another patent (1977b), Gustafson advanced a different chemical formulation to meet the same objectives of air revitilization. The generalized formula was:

\[ \text{A} \text{Z} \quad (D \quad O \quad H) \quad m \quad n \quad x \quad y \quad z \quad \rho \]

where:

A - a base having an alkaline earth or alkali metal cation and an oxide, hydroxide, peroxide, superoxide, or ozonide anion. (Typically lithium, sodium, potassium, or calcium hydroxide, potassium peroxide, calcium oxide, or magnesium superoxide). The base acts to increase the effectiveness of carbon dioxide absorption.

Z - any cation or mixed cation which can combine chemically with the DOH group.

D - boron, zirconium, or titanium.

O - oxygen having any valence but at least one oxygen in the DOH group has a valence greater than (-2), e.g. (-1).

H - hydrogen

m - an integer from 0 to 1

n - an integer from 1 to 4

p - an integer either 1 or 2

x - an integer from 1 to 3

y - an integer from 2 to 13

z - an integer from 0 to 3

Examples of effective compositions are: Ca2ZrO8, Ca(OH)2Ca(O2)2NaBO5, (LiOH)Li2O2Li3P3O13, (Li2O2)Li2B2O8, and (LiOH)LiBO5. It was recommended that admixtures of the above compositions with potassium
superoxide could be employed.

While total air revitilization chemical mixtures may seem attractive, often such mixtures may be difficult to prepare and sometimes costly. They also may be somewhat inflexible to respiratory demands of changing conditions which may be handled by a dynamic, two chemical system. Some chemical additives can find application in superoxide systems and are discussed in a later subsection.

Comparison Of Air Revitilization Chemicals.

The question of which air revitilization compound is most suitable depends on a number of factors dictated by the application to be considered. For our purposes, that is the development of a chemical system for either a small submersible or one-man back pack, we have established the following criteria in making our recommendation:

1) Theoretical and practical oxygen generation and carbon dioxide absorption per unit mass and volume.
2) Current preparation techniques for large yields with high purity; commercial availability and relative costs.
3) Chemical characterization (existing data).
4) Ambient temperature stability.
5) Reliability as demonstrated by un-manned and manned testing.

There are also other features that can be deemed valuable in selecting the most appropriate compound, for example, the ability to remove noxious and toxic airborne contaminants. Such characteristics, however, are secondary to the selection standards listed above. It is also important to recognize that combinations of chemicals or special mixtures can also meet this criteria. But because of the vast number of potential chemical combinations that exist, the comparison is limited to single chemicals.
Theoretical Considerations. The most important criterion is the chemical's ability to evolve oxygen and absorb carbon dioxide. On a pound oxygen evolved (or carbon dioxide absorbed) per pound chemical basis, the lithium compound of each chemical group (peroxides, superoxides, and ozonides) would have the highest capacities. Overall, lithium ozonide would be the most weight efficient chemical. Also significant is the ratio of these capacities or the chemical's SRQ. Peroxides, as previously discussed, have low oxygen evolution per pound, and thus a relatively high SRQ. Just on this theoretical basis, the peroxides are not suitable as total air revitalization chemicals. Their only usefulness may be as supplemental carbon dioxide scrubbers. Of the two remaining chemical groups, the ozonides are more weight efficient, but the superoxides have a SRQ closer to the desired value of 0.82. The data for all compounds is presented in Table 2.

Chemical Reactivity and Control. The reactions between the compound of interest, water vapor, and carbon dioxide comprise the reaction system for each chemical. Generally, simple systems with a small number of reactions are more efficient, because there are fewer reactions occurring to produce unwanted products or effects in the reaction system. The proposed reaction systems for all superoxides and potassium ozonide are given in Tables 3 to 7. The potassium superoxide and ozonide reactions are very similar, the only difference being the stoichiometry of the first reaction with respect to oxygen released. The greatest differences are seen between different metal cations for the superoxide series; in order of increasing complexity (increasing number of reactions) are lithium, calcium, potassium, and sodium. Of course, not all of the proposed reactions may occur. These are simply reactions which are possible for each system. To discern the most important reactions from those which occur at insignificant levels, both the equilibrium and kinetics of the system must be analyzed. Even
supposing a small number of possible reactions, the types of products must also be reviewed. Some products may be unstable to increasing temperatures and release carbon dioxide back into the system lowering the air revitilization chemical's efficiency in removing carbon dioxide. Some products may also have low melting points and fuse the chemical surface. As can be seen from the preceding examples, a complete comparison of air revitilization chemicals requires a thorough characterization of the chemicals.

Most investigators have found supplemental carbon dioxide scrubbing must be provided for the air revitilization compounds. Even superoxides which theoretically can achieve a desirable SRQ, have a practical need for extra carbon dioxide scrubbing ability. Taking this into account, predictions for the amount of two different carbon dioxide absorbents (Lithium hydroxide and peroxide) are given in Figure 2. Therefore, if one wanted to determine efficiency on the basis of weight alone, the mass of the absorbent must be included. The variation in the amount of absorbent that must be provided gives an indication of the relative "control" that a revitilization chemical has in regenerating air.

Preparation, Purity, and Commercial Availability. The most practical consideration is the availability of the chemical in a usable form. So far, up to this point, all superoxides and ozonides are potential candidates for air revitilization. Yet both lithium superoxide and ozonide have not been prepared and because of their inherent instability; little likelihood is seen for their synthesis in coming years. For sodium ozonide, little research has been conducted in the last ten years, at which point preparation techniques yielded inconsistent results and typically low purities. Extraction methods for potassium ozonide have given purities in the range 83 - 97% (Petrocelli and Capotosto, 1964), but the laboratory techniques are not suitable for large scale production of the chemical. Calcium superoxide preparation
has received the greatest attention in the past few years. However, the highest reported purity is 67% (Wood, et al. 1980). There is a chance that continued research will bring about a commercially feasible process with high purities. Yet in actually, the only chemicals that are easily prepared and are commercially produced in the United States are potassium and sodium superoxides.

A factor that might be considered with these other revitalization compounds, is the relative oxygen evolution and carbon dioxide absorption based on compound purity. For example, on the basis of oxygen yield per pound chemical (theoretical), 85% purity calcium superoxide would yield as much oxygen as 100% pure potassium superoxide; 93% pure calcium superoxide is equivalent to pure sodium superoxide in oxygen evolution. Figure 3 shows these relative capacities as related to pure sodium and potassium superoxides.

**Compound Stability.** All of the air revitalization compounds must be protected from ambient conditions. They must be sealed in air tight containers with dry atmospheres to prevent hydration of the chemical. Many of the available compounds will eventually decompose if left at room temperature, especially the ozonides. Both sodium and potassium superoxide are relatively stable and have long shelf lives (on the order of months and years, respectively) at ambient conditions, when protected from humidity.

**Chemical Testing and Reliability.** Most of the research and development of air revitalization compounds has involved either sodium or potassium superoxide. Since the compounds are prepared easily and stable for long periods of times, the chemistry and engineering applications of these chemicals has been well studied. This is not the case for any of the other air revitalization compounds; research on actual performance has been limited, if at all. Table 8 gives a list of many of the test programs conducted for
potassium and sodium superoxides. The most extensive of these tests was the NASA sponsored study of Kunard and Rodgers (1962). Much of the practical chemistry for potassium and sodium superoxide in closed atmospheres was emphasized with related considerations such as aggregate state, bed design, reaction products, and rate of heat release. More sophisticated engineering studies concentrating on cannister/bed design, aggregate state and passive versus dynamic systems were conducted by the Mining Safety Appliances Research Corporation on NASA contracts (McGoff, 1965; McGoff and King, 1966). In the early 1970's when electrochemical techniques became viable means for life support systems, NASA sponsored research was curtailed. Nevertheless, a number of studies have been conducted by other organizations in conjunction with miner safety, aviation, and submarine applications (Li, 1980).

Large chamber studies involving humans (Keating et al, 1960; Boeing Co., 1964; and Ducros, 1970) and/or metabolic simulators (Kunard and Rodgers, 1962; McGoff, 1966; and Ganas, 1969) have demonstrated the feasibility of using either potassium or sodium superoxide as an air revitilization chemical. The test by Boeing Company (1964) in the development of an environmental system for NASA demonstrated that five men could survive for 30 days in a closed, self-sustained, environment using a life support system employing cannisters of sodium superoxide and lithium hydroxide.

The system of Kunard and Rodgers (1962) measured 129 cubic feet and operated between 0.5 and one atmosphere using potassium superoxide cannisters connected in series. Ducros et al. (1970) used potassium superoxide for a two man test lasting 13 hours. Satisfactory control of the oxygen and carbon dioxide partial pressures were maintained for ten of those hours using only 4 kilograms of the superoxide.

The Boeing study used a chamber of 2400 cubic feet at atmospheric
pressure and 76°F. The respiratory control system used six superoxide beds giving a 4.8 day margin in excess of the theoretical requirements. During the test, the average oxygen concentration was 20.9% with a range between 19 and 22.8%; for carbon dioxide, the average was 0.72% with a variance between 0.30 to 0.87%. The carbon dioxide concentration was kept at or below the maximum (0.75%) limit for 91.5% of the time. The overall efficiency of the superoxide beds with respect to oxygen production was measured at 96.7%, with a corrected SRQ value found at 0.83.

**Sodium and Potassium Superoxide.** Based on the established criteria, only sodium and potassium superoxide can qualify as suitable air regeneration chemicals. Principally it is a choice based on availability, but the most favorable argument is the success with which each chemical has been used. In comparing potassium superoxide to sodium superoxide, the sodium compound does yield more oxygen per pound (0.43 lbs oxygen versus 0.34 pounds), release more heat per liter oxygen evolved (2.46 kcal vs. 2.27 kcal); however, these effects which are beneficial to deep diving are outweighed by other considerations. Sodium superoxide costs about ten times as much as potassium superoxide. There are a larger number of reactions for the sodium system (See Tables 5 and 6) that compete for the reactants, water and carbon dioxide. The solid products of the superoxide reactions impede the progress of superoxide conversion by forming a crust on the exterior of the particles; the sodium system probably forms this crust faster than the potassium system since sodium hydroxide has a lower fusion temperature than potassium hydroxide (318°C vs. 360°C). Increased bed pressure drop has also been attributed to crust formation. The thermal stability of the bicarbonates of sodium and potassium (Figure 4) shows the potassium compound to be favored in applications where superoxide bed temperature may exceed 60°C; the sodium bicarbonate decomposes at temperatures lower than potassium bicarbonate thus
releasing carbon dioxide into the gas stream. In cannister studies involving sodium superoxide (Kunard and Rodgers, 1962), the oxygen over production compared with carbon dioxide was confirmed, and significant amounts of water generation verified the decomposition of sodium bicarbonate. These reasons together with the fact that potassium superoxide is well characterized, make it the best choice for a marine application.

**Improvement of Potassium Superoxide Performance.**

With the chemistry of potassium superoxide nearly established, engineering practice has taken over to find the best ways for using the chemical in various applications. Investigation of methods for improving superoxide performance has taken primarily two forms. Both are aimed at the same objective—full utilization of the compound. The first category involves different ways of physically modifying the chemical to provide better contact with the reactants. The second is a matter of chemistry, principally with the addition of catalysts for the purpose of achieving complete decomposition of the chemical to the desired products or increasing the reaction rate. A third subject deals with realizing potassium superoxide’s full potential in regard to its purifying characteristics.

**Changes in Aggregate State.** Superoxide, for use as an air revitilization chemical, is employed in a myriad of forms. It can be used as a powder, in granular form, in shaped forms (pellets or blocks), and in several "configurations". The object is to create an aggregate state with a large surface area to volume ratio in order to have maximum utilization of the chemical. A related consideration is the pressure drop across a bed or cannister; the flow through the superoxide is related to the imposed pressure drop in as much as low flows (low convective mass transport) are the result of high pressure
drop. Finely divided powders are somewhat inefficient in application to air revitilization when used in packed beds; the "dusting" of these beds may be hazardous to the users of one-man back packs having the powdered chemical, in addition to the resulting high pressure drop.

Specific testing for particle size effects by Kunard and Rodgers (1962) was conducted with large mesh particles (2 - 4 mesh) and small mesh particles (4 - 8 mesh). The problem of large pressure drops caused by fusion of the particles was partially alleviated by 'shaping the bed', i.e., large granules were used along the centerline of the cannister with small granules used on the perimeter. Such 'shaping' of the bed will decrease the amount of bypassing the bed as the porosity of the bed decreases due to fusion of the particles. Other researchers have devised similar bed geometries in an attempt to completely utilize the superoxide (Bovard, 1959; McGoff and King, 1966; Staub, 1976).

Shaping potassium superoxide into pellets or other solid forms has been used with some success. Usually the pellets are packed into a cannister with fiberglass filters on the ends and a spring device to hold the assembly in place. The geometry of the pellet can influence the efficiency of utilization by affecting bed porosity. Ganas (1969) reports flattened cylinders of 9 mm diameter to be the optimum size for use in portable life support systems. Rio (1972) demonstrated the use of a shaped cylinder with convex sides, 7 - 10 mm in diameter and 4 - 6 mm thick; these pellets were pressed under a pressure of 80 - 120 kg/cm² and had a porosity of 43 - 47%.

The particle density is an important variable in affecting the rate of diffusion through the pellet. The Japanese Fire Research Institute in Tokyo (Satoshi, 1976) investigated the reaction characteristics of porous, tableted, and granulated potassium superoxide. Porous superoxide which had been compacted at a force of 120 kg/cm² and then crushed was found to be the best
aggregate form for use in portable breathing masks. Ganas (1969) reported of the mediocre reactivities of pellets having less than 45% porosity and the poor mechanical strength for pellets having porosities greater than 50%. McGoff and King (1966) showed a compacting force of 120 kg/cm$^2$ produced a tablet having a particle density of 0.88 g/cm$^3$; these tablets demonstrated superior capacity for oxygen generation and carbon dioxide absorption than tablets pressed at 320 kg/cm$^2$ and a pellet density of 1.01 g/cm$^3$. The dense pellets exhibited a 45% lower rate for oxygen evolution and a 40% lower rate for carbon dioxide removal than the less dense pellets (0.88 g/cm$^3$).

The density or porosity of superoxide forms is also important in terms of structural strength. The ability for a pellet or form to withstand disintegration can have some impact on superoxide performance. Powdering of pellets can lead to increased pressure drop, but more significantly, this "dusting" if not properly filtered can provide irritation to users, especially in the close contact of a one-man back pack. As expected, the average shear stress that can be withstood by a superoxide form increases with compacting force (McGoff and King, 1966). At a standard compacting force of 105 kg/cm$^2$, the shear stress limit for potassium superoxide was 3.5 kg/cm$^2$; for sodium superoxide, a value of 0.7 kg/cm$^2$ was obtained, and for a mixture of 75% KO$_2$ and 25% LiOH, it was 2.5 kg/cm$^2$. At a higher compacting pressure, the differences between potassium superoxide and the other chemicals were much larger. Clearly, another advantage of potassium superoxide over sodium superoxide is greater structural strength.

Geometric shapes other than pellets have been reported by McGoff and King (1966). The goal of this research was to develop the optimum geometry of a non-granular superoxide material to minimize total weight of the chemical and containment structure. A passive system utilizing potassium superoxide in the form of disks (3.75 inches in diameter by 0.25 inches
wide) having a one inch diameter hole in the middle showed a chemical efficiency of 93% for oxygen evolution whereas the granules of potassium superoxide gave a maximum efficiency of 90.5%. The assembly of disks showed 33% less dusting compared to high density 4 - 8 mesh superoxide granules; some of the decrease in dusting may be attributed to the inherently less severe hydrodynamic conditions of the passive system.

McGoff and King (1966) tested other rigid geometries including disks having patterns of holes along the cylinder axis, corrugated plates, rippled plates, and diagonal rippled plates of the superoxide. For different 'mission' lengths, different plate designs were reported to have greater oxygen production and carbon dioxide absorption per unit mass of the chemical than the disc patterns. For long mission lengths, the disks were found to be more suitable. In applications where pressure drop is of prime importance, as in the one-man back pack, the diagonal plate design of potassium superoxide is best.

Two novel approaches in superoxide utilization involve radically different methods of contacting the superoxide with other reactants. In the first technique, Manganaro (1970) has used pellets of potassium superoxide which are added directly to a water or saline solution. This results in a rapid oxygen evolution at a rate much greater than previously described methods (21.3 cm$^3$ O$_2$/sec-in$^2$), and a alkaline (hydroxide) solution that can be used in a countercurrent absorption system for the absorption of carbon dioxide. Bolles et al. (1966) developed a microcontactor in which high-density potassium superoxide in the form of a block is ground at a controlled rate and then brought in intimate contact with a dynamic air stream. The grinding provides finely divided superoxide particles which allow complete utilization of the chemical. This together with a reaction-filtration zone accrue many advantages: 1) storage volume is reduced by a factor of three,
2) superoxide utilization is nearly 100%, 3) control of oxygen evolution and carbon dioxide absorption can be controlled by the rate of grinding the block, and 4) a lower pressure drop results. One the disadvantage of this system is the degree of complexity of its design. Also, though compact, such a device would probably not be adaptable for a portable life support system.

Catalysts and Additives. Catalyzed potassium superoxide shows enhanced yields of oxygen in the range of 90 to 95% of theoretical oxygen evolution. The beneficial effect of these catalysts is realized more for short term missions where high rates of oxygen evolution are necessary; in long term missions where slow and constant oxygen evolution is required, the use of catalysts is less desirable and in some cases not beneficial. Ducros et al. (1970) showed that potassium superoxide of 81% purity with 0.15 to 0.30 wt.% cupric oxychloride (CuOCl₂) liberated 91.0% of theoretical oxygen whereas unpromoted superoxide liberated only 64.3% in short term tests. Kunard and Rodgers (1962) confirmed the increased oxygen generation of the copper catalyzed superoxide samples; they attributed the beneficial effects of the catalyst either to increased surface area (0.6 m²/g versus 0.4 m²/g) or to the inherent effects of the catalyst itself (i.e., the immediate release of oxygen from the copper oxychloride). Beyer et al. (1966) also reported the increased oxygen evolution from copper catalyzed potassium superoxide at a loading of 10 wt. % in short tests.

McGoff and King (1966) evaluated the effect of several additives to improve the carbon dioxide absorption for the superoxide plate configurations in short term tests (2 to 8 hours). In separate tests, lithium hydroxide, sodium peroxide, and sodium hydroxide were blended with the superoxide. Lithium hydroxide did not enhance carbon dioxide absorption and actually reduced the oxygen generation efficiency for both granular (McGoff,
1965) and disk configurations. Similarly, a mixture of potassium superoxide and sodium peroxide (20 wt. %) showed little improvement in carbon dioxide absorption. With low concentrations of sodium superoxide blended with the potassium superoxide, the oxygen evolution and carbon dioxide absorbing capacity increased from 56.3% to 60.7% for the ten percent mix and from 56.3% to 66.7% for the five percent mixture. Mixtures with sodium hydroxide showed no beneficial effect. The addition of 1 wt.% copper oxychloride to potassium superoxide demonstrated a 12% improvement in oxygen efficiency over the unpromoted superoxide in short term tests. The beneficial effects of the copper catalysts were not realized in tests longer than four hours, in which the promoted and unpromoted superoxide liberated the same amount of oxygen.

Long term testing (McGoff and King, 1966) of potassium superoxide blended with sodium superoxide, lithium peroxide, lithium chloride, and potassium permanganate showed little or no improvement in oxygen generation and or carbon dioxide absorption. In fact, penalties were incurred for blends of superoxide with sodium superoxide (poor structural integrity), and with lithium peroxide (3.5 to 10 wt.% - poor oxygen evolution and carbon dioxide absorption). Some improvement in air revitilization was reported for molded plates of potassium superoxide impregnated with 5% by weight asbestos fiber; the role of the asbestos was to increase porosity, hence permeability, of the plates to gaseous reactants. Other beneficial effects were the control of overheating the superoxide plates and increased structural strength of the plate (Beyer et al., 1966; Gustafson, 1977a).

The recently discovered health hazards associated with asbestos will preclude its use in any type of life support system.

A study of catalysts for the thermal decomposition of sodium superoxide in dry environments (Petrocelli et al., 1966; Marriot et al., 1968)
may shed light on the mechanism of oxygen generation in potassium superoxide systems. Eleven metal oxides and two polymeric copper compounds were evaluated at a concentration level of 10% by weight. Successful catalysts were noted to accelerate the rate of decomposition by a multistep reaction scheme as given below: (M represents an alkali metal cation)

\[
\begin{align*}
(55) & \quad 2 \text{MO}_2 = \text{M}_2\text{O}_2 + \text{O}_2 \\
(56) & \quad \text{M}_2\text{O}_2 = \text{M}_2\text{O} + 0.5 \text{O}_2
\end{align*}
\]

This of course meant increased oxygen evolution. Manganese dioxide and the copper catalysts were effective in facilitating the decomposition of the superoxide (reaction 55) but not the peroxide (reaction 56). Two oxides of vanadium (III and V) also accelerated superoxide decomposition, but only vanadium (III) oxide also increased peroxide decomposition. These studies were conducted at a temperature of 160°C; but at higher temperatures (250°C) the catalysts had no effect. These studies may suggest additional studies of promoters in wet environments to simulate potassium superoxide air revitilization reactions and the effects of catalysts.

**Removal of Airborne Contaminants.** Although not the result of any design improvement, potassium superoxide has been found effective in removing bacteria and certain chemicals from air streams; these bacteria and chemicals are given off in the respiration system and from the body. Kunard and Rodgers (1962) demonstrated how nose and throat bacteria were completely removed from an air stream in contact with potassium superoxide. Similar tests showed that canisters of potassium hydroxide were also effective in removing the same bacteria thus confirming the sterilization effect to be the result of chemical causticity.

Certain odoriferous compounds are released as waste products of human metabolic activity. In short term missions, accumulation of chemicals from sweat or even 'bad' breath may produce an irritating atmosphere in a diving
suit or submersible vehicle. Kunard and Rodgers (1962) investigated the ability of potassium superoxide in removing such compounds. Skatole, indol, and p-cresol in concentrations of 13 to 155 ppm were completely removed by the superoxide. Optimum efficiencies were realized for longer contact times and smaller particle sizes. Both methanol and hydrogen sulfide were removed to major extent by superoxide; acetylene was not, and very high concentrations of hydrogen sulfide (1000 ppm) were not. The effectiveness of potassium superoxide in these tests was attributed to its strong oxidizing nature.

**Summary.**

We have discussed the basic chemistry and applications of several chemicals which have been considered for air regeneration. All superoxides and ozonides were shown to have potential theoretically. However, due to practical constraints, many were eliminated from consideration either because of their inherent instability or failure to be produced in high enough purities. With the exception of sodium and potassium superoxides, only calcium superoxide shows any promise as ongoing research continues. Potassium superoxide was found superior to sodium superoxide for a number of reasons including reaction system simplicity, product stability, and greater structural strength. Innovations in air revitilization system design have improved potassium superoxide performance with various aggregate states and the addition of catalysts. Further characterization, design, and development of potassium superoxide systems will attain success in application to the marine environment in deep diving.
SECTION III

POTASSIUM SUPEROXIDE SYSTEM THERMODYNAMICS AND EQUILIBRIA

Our first approach in evaluating the performance of potassium superoxide has been a look at the thermodynamics in its reactions with water vapor and carbon dioxide. This is a fundamental but not necessarily accurate way of viewing the problem, because the methods involved only allow predictions for the theoretical potential of the system. A thermodynamic analysis, however, can be a starting point and offer reasonable estimates of the effects of both temperature and pressure. Taken together with a kinetic evaluation of observed data, a reliable understanding can be gained to allow preliminary design calculations for the potassium superoxide air revitilization system.

The word 'system' is often used in this report and therefore requires definition. Initially, the system comprises potassium superoxide and a gas mixture of carbon dioxide, water vapor, oxygen, and helium. With time, reactions between the various components (except helium) occur, so that the system in addition contains the reaction products. For given depths, the gas constituent concentrations vary with pressure, yet the partial pressure of carbon dioxide, water vapor, and oxygen are to be maintained constant. Thus, with depth, the helium partial pressure is increased to have the total pressure inside the submersible (or diving suit) match the hydropressure outside the vehicle (or suit). The specifications for the system are as follows:

1) Temperature varies between 30 and 100°F (-1 to 38°C)
2) Pressure varies between 1 atm and 30 atm. (0 to 1000 ft depth)
3) Oxygen partial pressure is set at 160 mm Hg.
Specifications continued:

4) Carbon dioxide partial pressure is set at 3 mm Hg.

5) Water partial pressure is set at 5 mm Hg.

Previous Investigations. One of the major questions submitted to this study has been 'what is the effect of pressure and temperature on the potassium superoxide system?' A review of the literature shows no previous evaluation of the system thermodynamic equilibria. Some work has been done on simple thermodynamics (Todd, 1953; Coughlin, 1954; Gilles and Margrave, 1956) but this has been primarily in the measurement of thermodynamic properties. Instead studies have been oriented towards actual measurements of system behavior, but these have been limited and therefore provide little information for the specifications that are of interest in this study. For example, temperature dependence has been investigated by Kunard and Rodgers (1962). This information is presented in Section IV.

Even more scant is the amount of work done on pressure effects. Some limited research has been done under hypobaric (low pressure) conditions by Kunard and Rodgers (1962) and McGoff and King (1966). Both found that reduced pressure did not alter oxygen generation and carbon dioxide absorption. Only one study has involved high pressures in superoxide systems. Ducros et al. (1973) investigated potassium superoxide performance from pressures of 4 to 30 atm finding no observable change in system reaction rates with changes in pressure. These conclusions, however, must be viewed skeptically since no data was included in the article. Another high pressure study of related interest, involved barylyme and sodasorb. Cook (1972) found decreasing efficiency of the absorbents with decreasing temperature (31 to -3°C) and increasing pressure (2 to 4 atm). Since these absorbents comprise hydroxides, the effects may be relatable to the hydroxide product and its carbon dioxide absorbing ability in the potassium superoxide system.
Nevertheless, a lack of sufficient data and confirmation in both the studies by Ducros et al. (1973) and Cook (1972) do not provide enough foundation to base any conclusions. This leaves a thermodynamic analysis as the best means to presently evaluate these effects.

Gas Phase Ideality. Thermodynamically, when gases are subjected to high pressures and low temperatures, they typically become non-ideal depending on the actual conditions and the physical properties of the gas. The significance of the non-ideality of the gas, is connected to the toxicity limits which are determined at low pressure conditions where gases behave ideally. In addition, if the gas is non-ideal, this can complicate some of the models to evaluate system efficiency. The toxicity limits are determined by the thermodynamic pressure exerted by the gases on the human body; carbon dioxide and oxygen are known to poison the body functions when the partial pressures of these gases are outside the nominal ranges as determined experimentally on human subjects.

The partial pressure of a gas at room conditions (25°C and 1 atm) is an excellent measure of the thermodynamic pressure. In the limit of the ideal gas behavior, the partial pressure becomes identical to the thermodynamic pressure, known as fugacity. Under conditions of non-ideal gas behavior, the partial pressure and the fugacity of a gas phase constituent may be different by as much as one order of magnitude. In all calculations of chemical equilibria, the fugacity is the proper quantity to characterize the system. In terms of gas equilibria with a human body to result in toxic poisoning, the question of proper toxicity limits for a human in a high pressure environment must be considered.

Two types of calculations were preformed to characterize the gas phase non-ideality at the conditions of interest to this study. We chose the most extreme conditions at which to make the calculations: 30°F and 30 atm.
For comparison, additional calculations were made at 1 atm and 10 atm at a temperature of 30°F. A measure of the non-ideality of gases in a chemical equilibria is the thermodynamic partial property—the fugacity coefficient. Under ideal gas conditions, it has a value of unity. Deviations from unity indicate non-ideality of the gas phase. Using the Redlich-Kwong equation of state, the fugacity coefficients were calculated as a function of reduced temperature and pressure, and the accentric factor:

\[
\varphi_{iv} = \exp \left\{ \frac{(Z - 1) \frac{B_{ii}}{B}}{2} - \ln (Z - B) - \frac{2 (A_{ii})^{0.5}}{A^{0.5}} - \frac{B_{ii}}{B} \ln \left( \frac{Z + B}{Z} \right) \right\}
\]

The compressibility factor \(Z\), is found by solving the cubic equation:

\[
Z^3 - Z^2 + Z \left( A - B - B^2 \right) - AB = 0
\]

where the parameters, \(A\), \(A_{ii}\), \(B\), and \(B_{ii}\) are virial coefficients which are determined by correlations with reduced pressure and temperature, component mole fraction, and accentricity.

The results of the calculations are shown in Table 9. As expected, there is little non-ideality at the conditions of 1 and 10 atm.; the largest deviation is for water at 3.6% at 10 atm. At 30 atmospheres, both water and carbon dioxide deviate to a minor extent (water 10%; carbon dioxide 3.9%). These calculations were confirmed using the Principle of Corresponding States and Kay's Law. These results may imply a need to re-evaluate the toxicity criteria for high pressure work (at 1000 feet), but the ideal gas law should still offer reasonable estimates when used in modelling superoxide efficiency.

**Thermodynamic Data.** In order to calculate the equilibria of the system, it is necessary to know the thermodynamic functions of the chemical species involved. This proved difficult; even for the well-studied potassium superoxide system, much basic data was unavailable. The largest problem was the
lack of tabulated free energies for some compounds, primarily the hydrates of hydroxide and carbonate. The free energies are important in determining the equilibrium constant by the following relationship:

$$\ln \left( K_a \right) = -\frac{\Delta G_{\text{rxn}}^0}{RT}$$

where:

$$K_a = \text{equilibrium constant based on component activities}$$

$$\Delta G_{\text{rxn}}^0 = \text{standard Gibbs free-energy change of reaction (sum of product free energies minus sum of reactant free energies in stoichiometric proportions), in cal/mole}$$

$$R = \text{gas constant (1.986 cal/mole-}^\circ\text{K})$$

$$T = \text{temperature (value used is } 298^\circ\text{K})$$

For all compounds, the heat of formation ($\Delta H_f^{\text{o},298}$) was known. The missing thermodynamic properties could be evaluated using known thermodynamic properties (heat of formation and entropy) in the Gibbs-Helmholtz Law or by empirical correlations of various sources (Latimer, 1951; Maslov, 1960; and Gorbunov, 1971). Reasonable values were obtained for nearly all compounds (with missing thermodynamic properties) using these methods. Thermodynamic data for the potassium superoxide system is presented in Table 10.

The most questionable value was the free energy yielded for potassium bicarbonate. The free energy was found to be -221.4 kcal/mole. This value is fairly close to the compound's heat of formation ($\Delta H_f^{\text{o}} = -229.3$), which is unusual for a chemical of this type. For an analogous compound, sodium bicarbonate, the heat of formation is listed as -226.5 kcal/mole and the free energy as -203.6 kcal/mole (Lange, 1979). Unfortunately, free energies for other alkali metal bicarbonates are not available. However, heat of formation data is, and a comparison of this data show values that range from -231.7 (lithium bicarbonate) to -226.5 (sodium bicarbonate). This seems to indicate that the free energy values should also be fairly close
together as well. Similarities in thermodynamic properties often exist for compound types (i.e., bicarbonates) of the same periodic group. This is the case for the carbonates, hydroxides, and peroxides of potassium and sodium.

From the pattern of other compound types, a value for potassium bicarbonate could be assigned, but extreme caution must be exercised since a small difference in the compound free energy could have significant effects on the equilibrium constant of a reaction involving that chemical. Instead, it was decided to use potassium bicarbonate decomposition data to directly find the free energy. For ideal conditions, the equilibrium constant can be calculated in terms of partial pressures or mole fractions instead of activities. Thus, for the decomposition of bicarbonate in the reaction given below:

\[
2 \text{KHCO}_3 \rightarrow \text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}
\]

the equilibrium constant can be represented as follows:

\[
K_a = K_p = \frac{(P_{\text{CO}_2}) (P_{\text{H}_2\text{O}})}{P_{\text{decomp}}}
\]

For the decomposition pressure, \(P_{\text{CO}_2} = P_{\text{H}_2\text{O}} = P_{\text{decomp}}\). Using a decomposition pressure at a given temperature, relationships (57) and (59), together with the following equation, the free energy can be found.

\[
\ln (K) = \ln (K_1) - \frac{\Delta H_{\text{xn}}}{R} \left[ \frac{1}{T} - \frac{1}{T_1} \right]
\]

For a decomposition pressure of 5 mm Hg at 80°C, the free energy is found to be -207.1 kcal/mole. For other decomposition pressures and temperatures, an average value of -207.0 kcal/mole is obtained.

**Reaction System.** Several reactions have been proposed to describe the equilibria for the potassium superoxide system (Bovard, 1960; Kunard and Rodgers, 1962; Lui et al., 1980). Many other possible reactions can exist. Thermodynamic laws show only the set of independent reactions need be considered to fix the chemical equilibria of the reactions (Aris, 1969).
Thus, reactions that are linear combinations of others can be eliminated from further consideration only insofar as the equilibria is concerned. For example, below are three possible reactions in the potassium superoxide system:

(61) \[ 2 \text{KO}_2 + \text{H}_2\text{O} = 2 \text{KOH} + 1.5 \text{O}_2 \]
(62) \[ 2 \text{KOH} + \text{CO}_2 = \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \]
(63) \[ 2 \text{KO} + \text{CO}_2 = \text{K}_2\text{CO}_3 + 1.5 \text{O}_2 \]

If reaction (61) is added to reaction (62), the result is reaction (63). Thus reaction (63) is said to be a linear combination of reactions (61) and (62). The independent reactions of the potassium superoxide system are given in Table 11 along with the thermodynamic functions for each listed reaction.

For each reaction there is an associated heat of reaction, free energy change and equilibrium constant. Each piece of thermodynamic data can give an indication of which reactions will be more likely to occur than others. In the potassium superoxide system, the first three reactions listed in Table 11 are considered the primary reactions, all have large positive free energy changes and equilibrium constants compared to the other five reactions. Usually, when a reaction has a large positive equilibrium constant on the order of \(1 \times 10^3\) or larger, this is an indication that the reaction will go to completion. However, since there are several reactions, most competing for the same reactants, this is not necessarily true; the system as a whole must be evaluated.

Qualitatively, a number of things can be determined from the reaction scheme. For example, water must react with superoxide to form hydroxide and allow carbon dioxide absorption. There are two modes of carbon dioxide absorption that can be followed—either carbonate or bicarbonate formation. Yet, water also competes with the carbon dioxide in reaction with the
hydroxide for form three possible hydrates. Even though not shown in the reaction scheme, these hydroxide-hydrates can in turn absorb carbon dioxide (such reactions are linear combinations of reactions [2] and [4] or [5] or [6] as listed in Table 11). Thus there are actually five routes for carbon dioxide absorption, two that are direct ([2] and [3] in Table 11), and three which are indirect through hydroxide-hydrate intermediates. The role of water as a reactant can also be traced in the reaction system. Other than the reaction with superoxide which begins the reaction sequence, water is involved in the formation of two hydrates of the carbonate. These hydrates together with the carbonate and bicarbonate are believed to form the crust that is sometimes observed to form on the chemical bed. Fusing of the hydroxide can also contribute to this 'diffusion' barrier.

The physical meaning of the equilibrium constant is the product of product activities over the product of reactant activities. Individual or product and reactant activities are raised to the power of their stoichiometric coefficients. Activities of solids can be taken as unity leaving only gas activities remaining in the equilibrium expression (for the reactions considered here). Activities can be replaced by gas partial pressures or mole fractions with pressure terms for ideal conditions. The latter form is preferred since pressure effects on a reaction can be determined.

The equilibrium constant for reaction [1] in Table 11 can be represented as follows:

\[ K_y = \frac{Y_{O_2}^{1.5} P^{0.5}}{Y_{H_2O}} = 3.25 \times 10^9 \]

where:

- \( K_y \) = equilibrium constant in terms of mole fractions and pressure
- \( Y_{O_2}, Y_{H_2O} \) = mole fractions of oxygen and water respectively
- \( P \) = pressure in atmospheres
Equilibrium expressions of the same form are listed in Table 11 for each independent reaction. In the given example, the pressure effect is to the square root. A simple way to determine the pressure effect in a reaction, is to observe the change in moles of the gas phase. The pressure term will be raised to this power in the equilibrium equation. For $\Delta n_{\text{gas}} = 0$, there is no effect of pressure on the reaction.

At a given temperature, the equilibrium constant will remain the same for changes in pressure. What will change are the mole fractions of the reactants or products. For the example, an increase in pressure will tend to favor the reactants (water) over products (oxygen). In carbon dioxide absorption by carbonate formation (reaction [2] in Table 11), there will be no pressure effect. But in the bicarbonate reaction [3], the pressure term is raised to the first power, and increases in pressure will favor the product. In all five hydration reactions ([4] through [8]), products will also be favored. Therefore from a qualitative standpoint, it would appear that the reaction system could change significantly with increasing pressure both by increased carbon dioxide absorption by the bicarbonate mode over the carbonate route, and with the formation of more hydrated products.

**Equilibrium Calculations.** Calculation of the equilibria for a system yields the 'extents' of the reactions involved. The extent of a reaction is the degree of completion it undergoes or by strict definition the change in moles of a reactant or product over its stoichiometric coefficient. If the extents for all reactions are known, then the equilibrium concentrations of all system components can be determined. Knowing this information for the potassium superoxide system, parametric studies of temperature and pressure effects can be conducted.

In the first interim report, we presented equilibrium calculations for a two reaction system involving two primary reactions ([1] and [2], Table 11).
A variable 'x' (extent of reaction) was defined for each reaction, $x_1$ the molar extent of reaction [1] and $x_2$ the molar extent for reaction [2].

Equilibrium concentrations were determined in terms of these molar extents as given below:

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>INITIAL MOLES</th>
<th>EQUILIBRIUM MOLES</th>
<th>EQUILIBRIUM MOLE FRACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>3</td>
<td>$5 - 0.5x_1 - 0.5x_2$</td>
<td>$(5 - 0.5x_1 - 0.5x_2)/S$</td>
</tr>
<tr>
<td>Water</td>
<td>5</td>
<td>$3 - 0.5x_2$</td>
<td>$(3 - 0.5x_2)/S$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>160</td>
<td>$160 + 0.75x_1$</td>
<td>$(160 + 0.75x_1)/S$</td>
</tr>
<tr>
<td>Helium</td>
<td>592</td>
<td>592 (inert)</td>
<td>592/S</td>
</tr>
</tbody>
</table>

$S = 760 + 0.25x_1$

which gave the following equilibrium expressions:

$$K_1 = \frac{[(160 + 0.75x_1)/S]^{1.5} P^{0.5}}{(5 - 0.5x_1 - 0.5x_2)/S}$$

$$K_2 = \frac{(5 - 0.5x_1 - 0.5x_2)/S}{(3 - 0.5x_2)/S}$$

Manipulating these expressions gave the following:

$$E_2 = \frac{E_1 + 2(Y_{CO_2}^0 K_2 - Y_{H_2O}^0)}{1 + K_2}$$

$$E_2 = 2 Y_{CO_2}^0 - \frac{2 (Y_{O_2}^0 + 0.75 E_1)^{1.5} P^{0.5}}{K_1 K_2}$$

where,

$E_1 = \frac{x_1}{N_T}; \quad E_2 = \frac{x_2}{N_T}$

$P = \text{pressure in atmospheres}$

$N_T = \text{total number of moles in the gas phase (initially)}$

$Y_{i}^0 = \text{initial mole fraction of component 'i'}$

$K_1$ and $K_2$ are the equilibrium constants for the reactions
Normally, the procedure would be to select values of $E_1$ and plot the corresponding values of $E_2$ from expressions (64) and (65). The point at which the two curves intersected would be the solution (giving values $E_1$ and $E_2$ and thus the molar extents of reaction). However, in this case, the equilibrium constants were very large in comparison to the other variables: $K_1 = 3.25 \times 10^8$ and $K_2 = 4.21 \times 10^{24}$. The result of these relationships was to show that the extents $E_1$ and $E_2$ were very close to unity and that the effect of pressure in the first reaction [1], was eclipsed by its large equilibrium constant.

A second simple set of reactions considered were the two direct modes of carbon dioxide absorption, reactions [2] and [3]. Some practical work was done by Kunard and Rodgers in attempting to determine which product (carbonate or bicarbonate) prevailed in the potassium superoxide system, but no strong conclusions were reached. These reactions were set up in equilibrium equations in the same way as in the previous example. The resulting expressions were:

\[
\begin{align*}
(66) \quad E_3 &= \frac{K_3 P (Y^{O_2}_1 - E_2) - 1}{K_3 P - 1} \\
(67) \quad E_3 &= 1 - \frac{K_3}{K_2} (Y^{O}_1 + E_2)
\end{align*}
\]

where:

\begin{align*}
E_2 &= \frac{x_2}{N_T}; \quad E_3 = \frac{x_3}{N_T} \\
P &= \text{pressure in atmospheres} \\
N_T &= \text{total number of moles in the gas phase (initially)} \\
Y^{O}_1 &= \text{initial mole fraction of component 'i'} \\
K_2, K_3 &= \text{equilibrium constants for reactions [2] and [3]}
\end{align*}

Again there is no need to plot the results. Inspection of the equations and recognizing the magnitudes of the equilibrium constants ($K_2 = 4.21 \times 10^{24}$,
$K_3 = 1.58 \times 10^{16}$ show that the equations yield unity as the molar extent for reaction [3]; the molar extent for reaction [2] is very close to zero. There is a loss of significance in the numerical answers which results in the assignment of the values of 1 and 0. Changing the pressure in the system will have little effect as seen in equation (66). Interpretation of these results points to bicarbonate formation alone with minimal pressure effect.

The preceding analyses of simple two reaction systems can be solved algebraically with little effort. Such is not the case for multi-reaction systems like that for potassium superoxide with the eight listed independent reactions. The next step in determining superoxide equilibria was to use all three reactions considered thus far. The system was set up in a similar fashion as for the two reaction analyses, but solution required the employment of numerical methods on the computer. Several methods were considered (Brinkley, 1947; Kandiner, 1950; and Naphtali, 1961), however these techniques were not adaptable to our system. We tried two methods for solving non-linear equations simultaneously: the Newton-Raphson Method (Carnahan et al., 1969) and Brown's Method (Brown and Dennis, 1971).

Both techniques failed to give solutions. In each case, singularity of the matrix occurred in which the pivot element in the matrix either becomes infinitely large or small. It is believed that the reason for this phenomena were the extremely large equilibrium constants which dwarf the other variables in the set of equations. Attempts to bypass this problem also failed. It was hoped to model the equilibria of eight system reactions. Nevertheless, some of the two reaction system analyses can give reasonable estimates of system behavior in reaching equilibria.

The effect of temperature on the equilibria was considered. The equilibrium constant decreases with increasing temperature for all the reactions in the superoxide system. The change in the equilibrium
constant can be predicted by relationship (60). The most dramatic changes encountered, were those for reactions [2], [3], and [6]. The overall effect of increasing temperature is to favor the reactants in each reaction. In reaction [2] for example, the equilibrium constant at 25°C is $4.21 \times 10^{24}$, but at 200°C it is lowered to $2.78 \times 10^{15}$, yet this is still very high. Figure 5 shows a plot of equilibrium constants ($\ln(K)$) versus temperature.

Summary. It was found that the gases in a closed air revitilization system would behave ideal up to pressures of 10 atmospheres, and nearly ideal to pressures of 30 atmospheres (1000 feet). This is important in setting toxicity criteria for oxygen and carbon dioxide limits and in modelling the reaction system. While assuming ideal gas behavior for modelling seems acceptable, toxicity criteria at depths over 400 feet should be scrutinized. The thermodynamics of the potassium superoxide system was evaluated with missing values assigned by thermodynamic methods or empirical correlations. For the reaction system it was noted that carbon dioxide could be absorbed indirectly by the hydroxide-hydrates. Also, eight independent reactions were found from which to model superoxide system equilibria. Attempts to solve multi-reaction equilibria failed due to matrix singularity, resulting from extremely large equilibrium constants. However, two reaction system models used on combinations of the three primary superoxide system reactions indicated that carbon dioxide absorption would take place almost solely by bicarbonate formation. The formation of carbonate was predicted to be insignificant and pressure effects were found to be minimal. Temperature had the effect of favoring reactants for all superoxide system reactions. It must be recognized, that equilibria is not necessarily reached by the superoxide system and that its predictions are highly theoretical. It is recommended that kinetics be used to determine the effects of pressure and temperature.
THE KINETICS OF THE AIR REVITALIZATION REACTIONS
OVER POTASSIUM SUPEROXIDE

A search of the literature revealed three important studies of the reactions over potassium superoxide; other studies are reported but we chose the investigations by Kunard and Rodgers (1962), Cuthrell (1970), and Mel'nikov et al. (1962) for our evaluation of the kinetics. The criteria in choosing the kinetics data are:

1) Quantity and scope of data to cover the effects of water and carbon dioxide partial pressures, temperature, and particle size.

2) Detail of experimental procedure to allow a critical evaluation of the technique.

3) Purity of the potassium superoxide product. Impure samples of the superoxide may confuse the kinetics with unexpected side reactions.

Only the report by Kunard and Rodgers (1962) satisfied all three criteria; thus, the correlations reported here are established on the kinetic data of this study. The study of McGoff and King (1968) is oriented to large chamber testing using disks and configurations of potassium superoxide. The rate data were correlated as mass transfer coefficients by modeling the superoxide bed as a packed bed absorber. These data were not included in the data base to establish the kinetics correlations since the gradients within the reactor were large.

The goal of the kinetics work-up was to establish rate correlations explicit to temperature and reactant partial pressure in the absence of diffusion and mass transfer resistances. Unfortunately, it is probable the data are somewhat "masked" by these transport effects. For most of the runs the inlet and outlet concentrations are a factor of two different,
which precludes the use of a "differential reactor analysis". We have reported the data as integral reactor rates; the reactant (product) accumulations are divided by the time of the accumulation to give a time and volume averaged rate. The reported reaction rate is not divided by the volume of the superoxide bed since the entire bed may not be effective for reaction to both reactants. This is tantamount to saying the gradients in concentration with length are different for water as compared to carbon dioxide. We report this extensive rate of reaction to emphasize the need to collect the data in the reactor which is better suited than the plug flow reactor (in collecting kinetic data). For all of the runs used in correlating these data, the weight of potassium superoxide was between 70 and 160 grams, the flow rate of the gas was between 4 to 6 liters/minute, and the temperature was 25°C.

Range of Data Base. The study of Kunard and Rodgers allowed a regression of data over ranges of composition, temperature, pressure, and particle sizes as follows:

Temperature:  25 - 60°C

CO₂ Composition:  0 - 1.5 vol %, 0 - 6.1x10⁻⁴ moles/liter

H₂O Composition:  0 - 1.5 vol %, 0 - 6.1x10⁻⁴ moles/liter

Particle Size:  2 - 6 mesh

Pressure:  1 atmosphere absolute

(NOTE: 1 vol % at 1 ATM = 7.6 mm Hg surface equivalent)

The carrier was either air or dry nitrogen for all of the runs. Oxygen evolution was calculated from an analysis of the spent superoxide for oxygen content.

Regressing the Kinetic Data at 25°C. Data were selected to fulfill the classical order of reaction tests: rate of reaction were calculated for changes in one reactant composition as all other variables were held
constant. In this manner we could cross-plot the data to obtain correlations of rates as functions of carbon dioxide and water compositions (see Figures 6 to 9). The correlating equations at 25°C are listed below.

**Rate of Heat Release:**

\[-\frac{dq}{dt} = (4270000[CO_2] + 560)[H_2O] + (0.362 + 636[CO_2]);\]

\[0 < [H_2O] < 0.0003 \text{ M}\]

\[-\frac{dq}{dt} = (1100000[CO_2] + 560)[H_2O] + (0.390 + 1533[CO_2]);\]

\[0.0003 < [H_2O] < 0.0006 \text{ M}\]

**Rate of Water Absorption:**

\[-r_{H_2O} = (0.101 - 70.5[CO_2])[H_2O]; \quad [H_2O] > 0.0001 \text{ M}; \quad \text{and}\]

\[-r_{H_2O} \leq 0.35 \times 10^{-7} \text{ moles/g-sec.}\]

**Rate of Carbon Dioxide Absorption:**

\[-r_{CO_2} = (0.0492[H_2O]) / (0.0492 + [H_2O]/[CO_2]); \quad 0 < [CO_2] < 0.0003 \text{ M}\]

\[-r_{CO_2} = [H_2O] / (1 + [H_2O](6.77 - 15100([CO_2] - 0.0003)) \times 10^4);\]

\[0.0003 < [CO_2] < 0.0006 \text{ M}\]

**Rate of Oxygen Evolution:**

\[r_{O_2} = (0.0475 - 45.573[CO_2])[H_2O] + 0.0779[CO_2]; \quad [H_2O] > 0.0001 \text{ M}\]

and \([CO_2] < 0.00061 \text{ M}\)

\[r_{O_2} = 0.0197[H_2O] + 0.0779[CO_2] \quad \text{for} \quad [CO_2] > 0.00061 \text{ M}\]

The reaction rates are reported in moles/sec, whereas the rate of heat release is given in cal./sec. All concentrations are moles/liter, M.

Care must be exercised in using these correlations to estimate reaction rates in reactors where hydrodynamics are different from plug flow. The ranges of composition are rather narrow; extrapolating to conditions of higher than \(6 \times 10^{-4} \text{ M}\) involve the ordinary risks of extrapolating out of
the range of regressed data. As an example, the rate of oxygen evolution for one of the large chamber tests by Kunard and Rodgers (1962), run #1, shows a rate of $5.36 \times 10^{-4}$ moles/sec (weight of KO$_2$ = 908 gms; [CO$_2$] = $3.39 \times 10^{-3}$ M; [H$_2$O] = $4.2 \times 10^{-3}$ M; $T_{avg}$ = 29.4°C). The predicted oxygen evolution rate at these conditions is $2.17 \times 10^{-3}$ moles/sec. For run #2 in the large chamber tests, the experimental oxygen generation rate is $7.3 \times 10^{-4}$ moles/sec for 3 pounds of potassium superoxide; the predicted rate is $1.66 \times 10^{-3}$ moles/sec. Thus, the correlated data tend to overpredict the rate of oxygen evolution of the large chamber studies.

Most investigators agree that dry carbon dioxide will not react with dry potassium superoxide, any observed oxygen generation and carbon dioxide absorption is attributed to trace quantities of water present, initially, in the system. The water absorption rate is decreased for increasing concentrations of carbon dioxide which tends to favor the reaction to form carbonate (see below) and thus liberating water.

$$2 \text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$$

The overall uptake of water is observed to decrease as the carbonate is formed.

Water will react with potassium superoxide in the absence of carbon dioxide to liberate oxygen according to first order kinetics in water concentration. In the presence of carbon dioxide at constant water concentration, the rate of oxygen evolution is increased with increasing carbon dioxide concentration. A similar increase in the rate of heat release with increasing carbon dioxide concentration at constant water concentration is observed. These findings indicate that carbon dioxide and water compete for reaction sites on the superoxide at low concentrations; possibly in the formation of hydrated compounds.

A quick check of the correlated rate of heat release shows good
agreement between theoretical and predicted heat release. In the absence of gaseous carbon dioxide, the hydrate reaction of potassium superoxide to the hydroxide are occurring with an average heat release of 15.4 kcal/mole water absorbed. The predicted heat release at $[H_2O] = 3 \times 10^{-4} M$ is 0.53 cal/sec and the predicted water absorption rate is $0.35 \times 10^{-4} M$ moles/sec. The ratio of these predicted rates gives 15.1 kcal/mole. If we include carbon dioxide absorption at $[CO_2] = 6.1 \times 10^{-4} M$, the predicted rates are: heat release - 1.7 cal/sec, carbon dioxide absorption - $0.4 \times 10^{-4}$ moles/sec, and water absorption - $0.17 \times 10^{-4}$ moles/sec. The carbonate reaction of potassium hydroxide shows a heat effect of 33.7 kcal/mole; thus, the calculated heat release is:

\[
(33.7 \text{ kcal/mole}) \times (0.4 + 0.17 \times 10^{-4} \text{ moles/sec}) + \\
(15.4 \text{ kcal/mole}) \times (0.17 \times 10^{-4} \text{ moles/sec})
\]

\[
= 2.18 \text{ cal/sec}
\]

The lack of agreement between the theoretical and correlated heat releases shows that other reactions are occurring; the most likely candidate is the bicarbonate reaction (Section I, equation 15) for which the SRQ is 1.33 as an alternative to the carbonate reaction (Section I, equation 13) with an SRQ of 0.67.

**Particle Size Effects.** A comparison of rate data over potassium superoxide beds of 2 - 4 mesh (sieve opening; 0.187 to 0.375 inches) and 10 - 20 mesh (sieve opening; 0.0331 to 0.0661 inches) at $25^\circ C$, $[H_2O] = 1 \times 10^{-4}$ moles/liter and $[CO_2] = 1.8 \times 10^{-4}$ moles/liter show increased rates of heat release (0.48 to 0.62 cal/sec), oxygen generation (0.84 to 0.93 $\times 10^{-4}$ moles/sec) and carbon dioxide absorption (0.06 to 0.076 $\times 10^{-4}$ moles/sec) for the smaller diameter particles (10 - 20 mesh). For those applications where high reaction rates are required, such as multi-man vehicles, small particle potassium superoxide is necessary to achieve the desired
rate of air revitilization. Large particles or even solid configurations of potassium superoxide will generate satisfactory reaction rates for one-man applications. The investigation of rate data for varying chemical density and different geometries was not possible because of inconsistency in the parameters affecting the reaction rate in studies of McGoff and King (1966), and Ganas (1969). In other words, variables other than the geometry or density were varied in each of the cases (such as carbon dioxide or water partial pressures) preventing a comparison for the observed effects of the desired variable.

Temperature Effects. Only a few data of Kunard and Rodgers (1962) were available to document the temperature effect upon reaction rate (Figure ). The data are so scattered, we are reluctant to report even general trends. The curves serve only to identify the data. The phenomena are very complicated in as much as both kinetic and equilibrium effects are represented in Figure 10. Without more study of the simple systems (i.e., hydration in the absence of carbon dioxide), the temperature effects are much too complicated to "unravel" in this report.

Summary. These rate correlations cover a range of operating conditions of interest to deep diving applications: temperatures from 20°C to 60°C, carbon dioxide and water concentrations from 0 to 1.5 volume percent surface equivalent, and pressures of one atmosphere. Unfortunately, the superoxide products are incompletely characterized regarding pore volume and pore size distribution; preparation method will also affect active site density, thus the reactivity of the solid. In using these correlations, we must caution of the as yet undocumented effects of total pressure upon reaction rate and the need for proper characterization of the superoxide product for intrinsic activity.
SECTION V

THERMAL ANALYSIS OF A CLOSED, AIR-REVITALIZATION SYSTEM

The purpose of this analysis is to define the steady state and transient gas temperature response for a closed, air-revitalization system in which potassium superoxide is reacting with carbon dioxide and water vapor in an oxygen-helium mixture. It is necessary to describe the steady-state gas temperature as a function of depth, humidity, and carbon dioxide partial pressure so as to design the heat exchange equipment for maintaining a comfortable breathing atmosphere. Predictions of the transient and steady state temperatures is based on a simple mathematical model of the closed recirculation system.

Description of the System.

The one-man backpack must provide a suitable diving environment for the duration of the mission. We have discussed in earlier sections of this report, the chemical reactions for revitilization of air and the associated heat effects. As the man dives to depth, the one-man backpack will accommodate the increasing hydrostatic pressure on his body by increasing the partial pressure of helium in the breathing air mixture; thus the composition and heat capacity of the breathing mixture change with depth.

Figure 11 documents these changes as a function of depth assuming the gas mixture to behave as an ideal gas with the partial pressures of carbon dioxide, water vapor, and oxygen taken as 3 mm Hg, 5 mm Hg, and 160 mm Hg respectively. Figures 12 and 13 detail the gas mixture compositions and heat capacities as a function of depth with \( P_{\text{CO}_2} \), \( P_{\text{H}_2\text{O}} \), and \( P_{\text{O}_2} \) as 11.4,
11.4, 160 mm Hg and 61, 61, and 160 mm Hg respectively. These calculations show the greatest change in mixture heat capacity to occur within 100 feet of the surface for each set of starting concentrations. At a particular depth, the heat capacity will change with initial partial pressures; for example, at the surface (0 feet depth) the mixture heat capacity increases from 5.44 to 5.94 cal/gmole-°K as the initial mixture becomes richer in carbon dioxide and water vapor. These changes in heat capacity with initial composition are insignificant at depths of 300 feet or greater.

Formulation of the Model.

The actual system for the one-man back pack is a closed loop in which the breathing air (predominately helium and oxygen) is circulated from a mask to a potassium superoxide bed followed by a capacitance volume and returned to the mask (Figure 14). A very accurate model of this system may contain elements of plug flow sections connecting in series to well-mixed volumes; however, such a model may prove mathematically intractable (White et al., 1981). We have chosen a simple tank reactor model with one inlet (from the diver's mouthpiece) and one outlet (to the diver's mouthpiece) to simulate the thermal effects in the actual system; such a model will correctly predict order of magnitude effects and will be easy to use.

The complicated gas flow pattern of the recirculation loop is modeled as a well-mixed tank (Figure 15) in which the revitilization reactions are occurring. White et al., (1981) report the conditions on which the recirculation loop reactor system may be modeled as a batch, well-mixed tank reactor. For recirculation fluxes (moles/sec.) 25 times the reaction rate (moles/sec.), the recirculation loop reactor can be modeled as a batch, well-mixed reactor. In the application of interest, the "worst case"
conditions of high reaction rates (high carbon dioxide and water vapor partial pressures) and low circulation rates (shallow depths) show a ratio of recirculation flux/reaction rate equal to 39; above the minimum criteria of 25 which confirms the validity of the tank reactor model in this application.

The first law of thermodynamics applied to the gas system (Figure 15) is:

\[
\frac{dU_{\text{system}}}{dt} = n_{\text{in}}(\tilde{H} - \tilde{H}_{\text{ref}})_{\text{in}} - n_{\text{out}}(\tilde{H} - \tilde{H}_{\text{ref}})_{\text{out}} + Q_{\text{net}}
\]

\(U_{\text{system}}\) - internal energy of the gas in volume \(V\) at temperature \(T\).
\(\tilde{H} - \tilde{H}_{\text{ref}}\) - enthalpy of gas above the reference enthalpy.
\(n\) - convective molar flow rate.
\(Q_{\text{net}}\) - net rate of heat flow.

This version of the first law assumes the kinetic and potential energy terms are negligibly small, and that no mechanical work is done by the gas on the surroundings. We have ignored the thermal influences of the solid potassium superoxide and the confinement vessels since the hardware design of the flow system is not set. The thermal effects of the solids are significant in so far as to altering the transient response (i.e., to increase the time required to reach steady state). In our model the thermal capacity of the solids may be included in the extensive heat capacity at constant volume term; see equation (70).

The first law may be reexpressed in terms of temperature:

\[
(70) \quad n_{\text{in}}^o C_v \frac{dT}{dt} = n_{\text{in}}^o C_{\text{p(in)}}(T_{\text{in}} - T_{\text{ref}}) - n_{\text{out}}^o C_{\text{p(out)}}(T - T_{\text{ref}}) + Q_{\text{rxn}}^o - Q_{\text{exc}}
\]
This equation may be cast into standard form as
\[
\frac{dT}{dt} + \frac{n^0 C_p + UA}{n_T C_v} T = \frac{n^0 C_{p,\text{in}} T_{\text{in}} + UA T_{\text{ambient}} + Q_{\text{rxn}}^0}{n_T C_v}
\]

(71) \quad \frac{dT}{dt} + \kappa T = B

where:

- \( n^0_T \) - initial number of moles in system
- \( C_p \) - heat capacity of the gas as a function of depth; assumed constant with time since the gas is mainly helium of which the heat capacity is not strongly temperature dependent.
- \( C_v \) - heat capacity at constant volume \((C_p - R)\)
- \( R \) - the ideal gas constant \((1.986 \text{ cal/mole}^0\text{C})\)
- \( Q_{\text{net}}^0 \) - net heat flow \( = -H_{\text{rxn}}^0 - Q_{\text{exchange}}^0 \) which for adiabatic cases \( Q_{\text{exchange}}^0 \) is nearly zero. For the non-adiabatic case, \( Q_{\text{exchange}}^0 = UA(T - T_{\text{ambient}}) \)
- \( n^0 \) - molar flow rate of gases to and from the tank mixer.

The solution to this first order differential equation with the initial temperature at 25\(^\circ\)C is:
\[
T = \frac{B}{\kappa} + e^{-\kappa t} (25 - \frac{B}{\kappa})
\]

If we let \( B/\kappa = a \) and \( \kappa = b/n^0_T \) then:

(72) \quad T = a + (25 - a) e^{-bt/n^0_T}

The steady state temperature is \( a \) since \( e^{-\infty} = 0 \). A measure of the transient response is the time required to attain a fraction of the steady state temperature \( a \). For example,

(73) \quad \frac{T_{ss} - T}{T_{ss}} = a - [a - (25 - a) e^{-bt/n^0_T}]

If we left the left hand side of the equation equal to 0.05 then the time required to attain 95% of the steady state temperature is

(74) \quad t^* = \frac{n^0_T}{b} \ln \frac{0.05a}{a - 25}
Parameters Used for the Prediction.

The temperature-time relationship, equation 70, requires the specification of parameters $a$, $b$, and $n^o_T$. We will justify the choice of parametric values in this subsection.

$n^o$ - molar flowrate of gases to and from the tank mixer. In reality the molar flowrate is a function of the respired volumetric flowrate ($\dot{V}$), temperature, pressure, and composition. We have demonstrated validity of the ideal gas law in Interim Report I thus removing gas composition as a factor in determining the molar flowrate. We assume the volumetric flowrate is determined by displacement volume of the diaphragm and the respiration rate; both of these parameters are assumed to be constant with depth. The choice of respired volumetric rate, 20 liters/min, is suggested by Ganas (1969) for a man expending 50 watts of energy (11.9 cal/sec.). It is assumed the gas will return to the revitilization system from the lungs at a temperature of $37^\circ$C and the total pressure of the gas will be set by the depth.

$n^o_T$ - initial number of moles in the system. The moles in the system initially is determined by the system volume, temperature, and pressure at the time at which the system is filled. Ganas (1969) shows a one-man system for use in aircraft having a volume of nearly 30 liters; we shall use 30 liters as the system volume in this study. The filling temperature is $25^\circ$C and the filling pressure will be adjusted to the depth of interest. We understand the normal procedure is to fill slightly above ambient pressure and adjust the helium partial pressure to meet the pressure at depth. For the convenience of modeling the system, we will assume the system to be filled with the proper number of moles, initially, to satisfy the pressure at depth. For each depth of interest we have set $n^o_T$ over a
range to bracket the anticipated volumes of the system.

\[ C_p \text{ and } C_v \] - heat capacities are assumed constant and equal to the values at 298 K (see figures 11 and 12). Since the gas is very rich in helium, we would expect the mixture heat capacity to change but little, over a temperature range of 100 to 200°C.

\[ T_{ambient} \] - temperature of the water at depth. We assume a temperature versus depth profile which is constant at 20°C from the surface to 90 feet. Below 90 feet, the temperature changes linearly with depth to a value of 0°C at 1000 feet.

\[ Q_{rxn} \] - rate of heat release is given by Figure 6.

\[ UA \] - rate of heat exchange. In the study we used values of UA of 0.0, 0.1, 0.5, and 1.0 cal/sec°C where the rate of heat loss is:

\[ q_{loss} = UA \left( T - T_{ambient} \right) \]

The overall heat transfer coefficient can be estimated from a knowledge of the fluid thermal properties (Prandtl number), and the fluid hydrodynamics. For the "worst case", Grashof liquid cooling and laminar flow in the gas, we estimate the overall heat transfer coefficient as approximately 0.9 Btu/hr-ft²-°F (See discussion on page 71).

Results.

Equation (71) was employed to predict the temperature histories of a closed system for depth to 1000 feet of water and for oxygen partial pressures held constant at 160 mm Hg. Tables 12 to 15 summarize these calculations for carbon dioxide partial pressure in the range of 5 to 61 mm Hg, for water vapor partial pressure in the range of 3 to 61 mm Hg, and for values of UA from 0 to 1 cal/sec°C. These conditions of partial pressure were established at the suggestions of personnel at NCSC (the lowest
partial pressures), and upon consideration of the work of Ducros et al., (1970) who used a water vapor partial pressure of 11.4 mm Hg., and the large chamber studies of Kunard and Rogers (1962) employing a water vapor partial pressure of 61 mm Hg. The highest water vapor partial pressure is somewhat high in as much as the vapor pressure of water at 298°K is below 20 mm Hg; however, the unrealistically high values are presented for the sake of comparison to the large chamber studies of Kunard and Rogers.

The table entry under the heading of $\dot{Q}(\text{cal/sec})$ is the rate of heat release to the system as correlated from the data of Kunard and Rogers, figure 6. For the sake of simplicity in modeling the system, the exothermic rate of heat release is accommodated by the model as a heat input whereas heat losses are modeled as negative, heat inputs. The rates of heat release at $p_{H_2O} = 61$ mmHg, are extrapolations out of the correlated range and should be viewed with caution. The predicted reaction rates at these high water concentrations are about 50% high compared to the rates reported in the large chamber studies by Kunard and Rogers (1962); we may infer the heat releases may be high by a similar ratio.

For non-adiabatic cases, the heat transfer constant $U_A$, was set at 0.1, 0.5, and 1.0 cal/sec°C so as to bracket the expected heat transfer rates. We related the overall heat transfer coefficient, $U$, to the gas-side, $h_i$, and water-side, $h_o$, film coefficients as:

$$U = \left[ \frac{1}{h_o} + \frac{1}{h_i} \right]^{-1}$$

These parameters were estimated from the worst possible case of laminar flow on the gas-side and Grashoff natural convection on the liquid-side. Any movement of the diver certainly will improve the liquid-side heat transfer. Estimates of $h_o$ range from 30 to 39 Btu/hr-ft²°F as the ambient water temperature changes from 0°C to 20°C; whereas $h_i$ is estimated at 0.92
Btu/hr-ft²-oF. The resulting value of U is 0.89 Btu/hr-ft²-oF. Parametric values of UA of 0.1, 0.5, and 1.0 cal/sec-°C would require surface areas of 0.8, 4.0, and 8.0 ft². These surface areas of 8 ft² and less may be obtained in the constraints of a backpack.

The predicted steady-state temperature \(T_{ss}\), reported in degrees Centigrade) corresponds to the circumstance where the net heat input to the system is balanced by the rate of heat loss to the surroundings. The numbers in this column are rounded off to the nearest integer.

The unsteady-state temperature response of the system is reported as the time required for the gas to attain 95% of the steady-state temperature \(t^*\). Tables 16 to 19 indicate this response time as a function of depth, reaction time, heat exchange rate, and number of moles of gas in the system. For the cases where the steady-state temperature is less than or equal to 25°C, no value of \(t^*\) is reported.

Discussion of Results.

One objective of this study was to define the conditions for which the recirculating loop system will attain a steady-state gas temperature in the range of 30 to 35°C. Without heat exchange to the environment, the model predictions did not show any cases for which the gas temperature was below 37°C (See Table 16). With UA = 0.1 cal/sec-°C, marginally acceptable steady-state temperatures were attained for only the lowest reaction rates \((p_{CO_2} = 3 \text{ mm Hg and } p_{H_2O} = 5 \text{ mm Hg, see Table 17})\). With UA = 0.5 cal/sec-°C, acceptable steady-state temperatures were predicted for all reaction rates except for the highest rate \((p_{CO_2} = p_{H_2O} = 61 \text{ mm Hg})\). Comfortable steady-state temperatures were predicted for the case where UA = 1.0 cal/sec-°C.
These data are summarized in figures 16 to 18; feasible operating conditions are presented as shaded areas, for required heat exchange capabilities, UA, versus heat load ($\dot{Q}_{\text{rxn}}$) to maintain the desired steady-state temperature of 25, 30, and 35°C at depths of 0, 90, 475, 1000 feet. As expected for a constant heat of reaction rate, increasing the heat exchange area (UA) decreases the steady-state temperature.

At depths of 0 to 90 feet and with the partial pressure of carbon dioxide and water less than or equal to 11.4 mm Hg, values of UA less than or equal to 1 cal/sec°C are needed to maintain the gas temperature at 25°C. At 475 feet and deeper the model shows the 25°C temperature is not attainable; moreover, a higher heat exchanger rate (0.5 versus 0.4 cal/sec°C) is needed to stabilize the temperature at 30°C for $\dot{Q}_{\text{rxn}}$ less than or equal to 2.0 cal/sec. This paradoxical result may be rationalized as follows: the molar recirculation rate increases with depth since the system inventory of gas increases with depth (respired volumetric flow rate is assumed constant). Since the temperature of the return gas from the diver's lungs is assumed constant at 37°C, increasing the circulation rate at a constant rate of heat loss (UA) will increase the rate of heat added to the system from the diver, thus increasing the steady-state temperature. The result is heat transferred from the diver's lungs to the gas system and thence to the surroundings. It may be prudent to prevent large heat exchange rates with the environment at depth to prevent the diver from losing an inordinate amount of body heat through his lungs.

Under the conditions of high reaction rate to heat exchange rate, the initial part of the dive (less than 100 feet) shows the highest temperature rises; thus the maximum heat load on the heat exchange equipment will be demanded at depths of 100 feet or less. Unfortunately, at these shallow
depths, the ambient water temperatures are the highest and the thermal driving force is the lowest. The design of the heat exchange equipment must accommodate the heat exchange demands between 0 to 100 feet; these heat exchange requirements may be met by simple exchange with the water and/or by a passive refrigeration system using replaceable cartridges of Freon refrigerant. The passive refrigeration system may be used to augment the water heat exchange system for short periods of maximum heat demand.

The transient temperature response of the system for all of the cases show the steady-state temperature is achieved within 400 seconds; the high circulation rate demanded by the respiration of the diver is responsible for the short time of the transient period. Therefore all designs should be set on the steady state conditions.

Tables 16 to 19 show the response times are drastically decreased with increasing heat exchange rate. Increasing the amount of gas in the system ($n_T^o$) will increase the time required to reach 95% of the steady-state temperature, while imposing no change in the steady-state temperature.
SECTION VI

STOICHIOMETRIC SUPEROXIDE BED LOADINGS

The stoichiometric reaction efficiencies define the necessary superoxide bed loadings of oxygen evolution and carbon dioxide scrubbing. A second constraint to define bed loading, the kinetic rates of $\text{O}_2$ evolution and $\text{CO}_2$ absorption, is defined in Section VII ("Potassium Superoxide Cannister Design Study"). In this section, we present the stoichiometric reaction efficiencies.

Based on the available literature for superoxide reaction efficiencies, Tables 20 and 21 show the theoretical bed loadings to achieve rates for oxygen evolution and carbon dioxide scrubbing equal to 1.87 and 2.11 pounds per man-day, respectively. One man-day is meant to represent the requirements of one human being for one (1) twenty-four (24) day. Theoretical loadings for other mission durations may be calculated by the appropriate ratio of mission length to 24 man-hours, multiplied by the bed loading for 24 man-hours. It should be remembered the bed loadings specified in Tables 20 to 21 do not guarantee the instantaneous rates of oxygen evolution and carbon dioxide scrubbing will meet the demands of a diver.
SECTION VII

POTASSIUM SUPEROXIDE CANNISTER DESIGN STUDY

In this section we will describe the cannister inlet conditions, potassium superoxide bed loading, and the supplemental carbon dioxide scrubber demands to give an oxygen evolution rate between 1.75 to 3.0 pounds of oxygen per man day. In this design, it is assumed that the inlet partial pressure of carbon dioxide to the potassium superoxide bed is adjusted within the limits of 3 to 11.4 mm Hg using an upstream carbon dioxide scrubber. We also assume the inlet water partial pressure is set within the limits of 5 to 45.7 mm Hg. Other design specifications are detailed in Table 22.

Model Equations. For this cannister design, a cylindrical geometry with axial symmetry is assumed. The hydrodynamics are steady, plug flow. The heat capacity and thermal conductivity of the bed and cannister are ignored; the reported temperature at the outlet is the adiabatic, gas temperature. The appropriate, one-dimensional, differential material and heat balances are:

\[
\begin{align*}
\dot{Q} \ dc_{H_2O} &= (-r_{H_2O}) \ dw \\
\dot{Q} \ dc_{CO_2} &= (-r_{CO_2}) \ dw \\
\dot{Q} \ dc_{O_2} &= (r_{O_2}) \ dw \\
\dot{\dot{\alpha}} \ C_p \ dT &= (r_H) \ dw
\end{align*}
\]

where:

- \( \dot{Q} \) = volumetric flowrate, liters/sec.
- \( r_i \) = rate of reaction for species i, moles/g-KO\(_2\)-sec.
- \( r_H \) = rate of heat release, cal/g-KO\(_2\)-sec.
- \( dc_i \) = differential change in concentration of species i, M
- \( dw \) = differential change in bed weight, grams
- \( C_p \) = average heat capacity of gas/mol-\(^\circ\)K
- \( dT \) = differential change in gas temperature, \(^\circ\)K
The balances are usually solved simultaneously between the cannister inlet and outlet conditions. For this case, the concentration of water is chosen as the integration variable; the integration is completed when the water partial pressure is below 1.9 mm Hg, the exit value. The temperature coefficient on the rate constant was not correlated with the available data, thus these design calculations will show no temperature effect on the reaction rates.

**Results.** Cases were generated for inlet conditions between 3 and 11.4 mm Hg carbon dioxide partial pressure and 5 to 45.7 mm Hg water vapor partial pressure with the inlet temperature set at 25°C (See Table 23). The data show the weight of potassium superoxide charge necessary to reduce the water partial pressure at the outlet to 1.9 mm Hg, the outlet partial pressure of carbon dioxide, the overall carbon dioxide scrubbing rate of the superoxide bed, and the overall oxygen evolution rate. From these cases, we have identified a locus of inlet humidities and carbon dioxide partial pressures which results in oxygen evolution rates between 1.75 and 3 pounds of oxygen per man-day (See Figure 19). These initial rates (i.e., rates not limited by diffusion) are probably optimistic. These results show an operating locus for the inlet conditions as follows: $P_{\text{CO}_2} = 3$ to 10 mm Hg and $P_{\text{H}_2\text{O}} = 15$ to 30 mm Hg. Since the partial pressure of the exhaled human breath is 15 mm Hg (carbon dioxide production rate is 2.21 pounds per day, respiratory volumetric rate is 20 liters/min., temperature is 37°C, and the pressure is one atmosphere), it is clear that upstream scrubbing must be provided. The rate of supplemental carbon dioxide removal (See Figure 21) is determined for the desired inlet partial pressures of carbon dioxide and water vapor to the superoxide cannister.

**Discussion of Results.** In this potassium superoxide cannister design, the important constraints are 1) overall rate of oxygen evolution from the
cannister, and 2) carbon dioxide partial pressure at the cannister exit. A specification of these design variables will set a locus of inlet humidities and carbon dioxide partial pressure on the oxygen evolution rate nomograph (Figure 19). This "operating line" together with the characteristics of the supplemental carbon dioxide scrubber will fix the carbon dioxide partial pressure to the potassium superoxide cannister inlet. That is to say, the scrubber exit $P_{CO_2}$ is equal to the superoxide inlet $P_{CO_2}$. It is assumed the humidity at the superoxide inlet can be adjusted independently of the scrubber exit humidity. These inlet conditions fix the potassium superoxide cannister charge (Figure 20), and the supplemental carbon dioxide scrubbing rates (Figure 21). The amount of potassium superoxide, the inlet conditions, and the volumetric flowrate to the cannister determines the outlet partial pressure of carbon dioxide (see Table 23).

Comparison of Model with Actual Data. The model equations were compared to data of oxygen evolution and water absorption rates in the large chamber studies of Kunard and Rodgers (1962). The inlet conditions and flowrates of the large cannister studies were entered into the model and the integration was continued until the bed loading (predicted) was comparable to the data. From the outlet conditions, the overall oxygen evolution and water absorption rates were calculated.

The model predictions are in good agreement with the data (see Table 23) when the inlet water partial pressure is less than 18.7 mm Hg and the inlet carbon dioxide partial pressure is less than 11.4 mm Hg; however, the model overpredicts the oxygen evolution rate by a factor of three (3) when the water partial pressure is greater than 30 mm Hg. For inlet conditions intermediate to these ($19 < P_{H_2O} < 30$ mm Hg and $P_{CO_2} > 11.4$ mm Hg), the error in the prediction is not documented (Kunard and Rodgers did not
Summary. A case study for the superoxide packed bed cannister design establishes inlet conditions to attain oxygen evolution rates between 1.75 and 3 pounds per man-day. These predicted rates are somewhat optimistic when the water partial pressure is greater than 20 mm Hg. The preferred inlet conditions are: $P_{CO_2} = 3$ to 11 mm Hg and $P_{H_2O} = 15$ to 20 mm Hg. It is highly desirable to control the inlet water partial pressure independent from the inlet carbon dioxide partial pressure. Supplemental scrubbing of the carbon dioxide is necessary; these rates are set to control the inlet carbon dioxide partial pressure to the superoxide cannister. With suitable design, it is possible to produce the required oxygen rate and scrub the exit gas to a carbon dioxide partial pressure that is less than 3 mm Hg. The inlet temperature is assumed to be set at $25^0C$. 
SECTION VIII

CANNISTER PRESSURE DROP CALCULATIONS

The pressure drop equation for flow through packed beds was applied to the data of Ganas (1969) to determine the effective porosity of a potassium superoxide bed at reaction conditions:

\[ \frac{-\Delta P}{L} \frac{g_c}{\rho V_o^2} D \left( \frac{\phi_s \epsilon^3}{1 - \epsilon} \right) = \frac{150 (1 - \epsilon)}{Re} + 1.75 \]

\( \Delta P \) = pressure drop across bed
\( L \) = length of bed
\( g_c \) = units conversion factor
\( \rho \) = density of gas
\( V_o \) = superficial gas velocity
\( D \) = particle diameter
\( P \) = Reynold's number of flow field
\( \epsilon \) = bed porosity
\( \phi_s \) = sphericity of particles

The Ganas data show:

\[ \frac{\phi_s \epsilon^3}{1 - \epsilon} = 1.47 \times 10^{-4} \] (dimensionless)

This factor was applied to the cannister design of this study (suggested by section VII), with:

\( \dot{V} \) = 20 liters/minute (volumetric flowrate)
\( W \) = 4 kg. (mass of potassium superoxide)
\( D_c \) = 5 inches (diameter of cannister)
\( L \) = 48 cm. (length of bed for 4 kg. of KO\(_2\))
\( \mu \) = 1.9 x 10\(^{-4}\) g/cm-sec. (viscosity of gas at 30\(^{\circ}\)C)
\( D \) = 0.76 cm. (diameter of particles; 2 - 4 mesh)
\( \rho_{gas} \) = 3.7 x 10\(^{-4}\) to 2.7 x 10\(^{-3}\) g/cc. (density of gas from 0 to 1000 feet in depth)
These parameters result in cannister pressure drops of 2 to 8 inches of water for depths of 0 to 1000 feet (see Table 25). The effect of increasing gas density (by a factor of 7) is to increase the predicted pressure drop by a factor of 4; both the friction factor and the inertial forces are altered by the change in gas density. The pressure effect on the gas viscosity is speculated to be small; the gas is predominantly helium and the reduced temperature is very high (~30). Thus the gas viscosity may be determined by the "low density" viscosity condition even though the pressure is high (reduced pressure is about 15).
A complete description of the reactions between porous potassium superoxide and gaseous carbon dioxide plus water must account for the effect of external mass transfer and diffusion within the pores on the observed reaction rate. The most complete works on air revitalization (Kunard and Rodgers, 1962; McGoff and King, 1968) do not make the proper corrections for these effects upon the observed reaction rate. It would be very risky to extrapolate these results to reactors of different configurations and/or flow fields. Furthermore, the experimental reactor configuration of these studies does not allow a cogent analysis of the rate data since there exists in the reactor large gradients in temperature and composition. There is a compelling need to measure the intrinsic reaction rates in a well-designed reactor such that the influences of mass transfer and heat transfer are absent from the data.

Proposed Work: Phase II.

The fundamentals of reaction and diffusion in porous solids together with external gradients in temperature and composition are well-established. Powerful, predictive models exist to specify global reaction rates if there is a knowledge of the rate constants, order of reaction, activation energy, heat of reaction, and a characterization of the flow field (Reynold's number and Schmidt number) together with a characterization of the solid pore structure (effective diffusivity). We propose to measure the intrinsic reaction rates (in the absence of all mass transfer resistences) over the range of variables shown in Table 26. These data on finely divided potassium
superoxide particles will be collected in a gradientless, high pressure reactor such that gradients in temperature and composition will be nearly eliminated. This part of the study will specify order of reaction, rate constants, etc. of the non-diffusion limited reaction between gas and solid potassium superoxide. Subsequent reaction rate data on large superoxide pellets (2 - 4 mesh) at selected conditions will document the effects of reaction and diffusion upon the observed reaction rates; these data will allow a description of the effective diffusivity parameter for the model of reaction and diffusion in a porous network. The potassium superoxide will be characterized for surface area and pore volume distribution by the BET technique.

With a knowledge of the intrinsic kinetics and the effective diffusivity it is possible to predict the global rates on any size pellet or slab at any point in the cannister reactor. Subsequent testing in the gradientless reactor of small slabs of potassium superoxide will document the predictions of reaction rates to superoxide configurations suffering pore and external mass transfer resistences at known values of the porosity and hydrodynamics. The superoxide slabs offer a promising alternative to tablets for a low-pressure drop configuration of the air revitilization chemical. Using the appropriate reactor design equations, overall reaction rates for the entire cannister reactor may be estimated for any type of ideal reactor including reactors which have variable rate flow field (pulsatile flow).
Potassium superoxide is produced by the oxidation of dispersed liquid potassium with air enriched with oxygen.

\[ K(1) + O_2(g) = KO_2(s) \]

Reaction conditions:
(a) 5 to 15 times theoretical air
(b) air enriched with 13 to 15% oxygen
(c) air feed temperature = 75 - 79°C
(d) reaction zone temperature = 300°C
(e) air feed pressure = 0.13 atm (excess)

INDUSTRIAL UNIT

(1) container with molten metallic potassium; (2) pipe for supplying molten potassium to sprayer; (3) sprayer; (4) pipe for supplying air to nozzle; (5) needle for controlling the supply of air and molten potassium mixture to the nozzle; (6) cylindrical superoxide container; (7) outlet for potassium superoxide.

* Reproduced from Vol'nov (1966)
FIGURE 2 COMPARISON OF AIR REVITILIZATION COMPOUND / CARBON DIOXIDE ABSORBENT MIXTURES

Lithium Hydroxide

Lithium Peroxide

Air Revitilization Compound / Absorbent System

NOTE A: Mixture amounts based on weight air revitilization compound plus auxiliary carbon dioxide scrubber needed to provide 1.87 lbs. oxygen/man-day and to scrub 2.11 lbs. carbon dioxide/man-day. Data based on theoretical properties of compounds given in Table 2 (LiOH scrubs 0.92 lb CO₂/lb chemical).

NOTE B: For lithium hydroxide mixtures, oxygen produced by air revitilization compound only; for lithium peroxide mixtures, both air revitilization chemical and absorbent provide oxygen. In latter case, amounts of each are determined by solving two equations simultaneously.

Adapted from Petrocelli and Capotosto (1963)
FIGURE 3 RELATIVE THEORETICAL PERFORMANCE AND PURITY OF AIR REVITALIZATION COMPOUNDS*

NOTE A: Pounds of oxygen evolved per pound of superoxide (lithium or calcium) or ozonide are compared with pure sodium and potassium superoxides as a function of purity. It is assumed that impurity that exists in the air revitilization chemical does evolve oxygen (i.e., peroxides). Calculations are based on theoretical data in Table 2.

*Adapted from Petrocelli and Capotosto (1963)
FIGURE 5 THE EFFECT OF TEMPERATURE ON REACTION EQUILIBRIUM CONSTANTS

NOTE A: Reaction numbers correspond to those in Table 11.
Figure 6. Rate of Heat Release over KO₂ at 25°C as a Function of Water and Carbon Dioxide Concentrations

Bed Temperature = 25°C
Contact Times = 1-5 sec
Particle size = 2-4 mesh

General Correlating Equations for Heat Release

\[-\frac{dQ}{dt} = \{2.70000[CO₂] + 560[H₂O] / 0.362 + 636[CO₂]\} \cdot 0.0003[H₂O] + \{0.362 + 636[CO₂]\} \cdot 0.0003[H₂O] \cdot \frac{[CO₂]}{[H₂O]}\]

\[-\frac{dQ}{dt} = \{1.10000[CO₂] + 560[H₂O] + \{0.390 + 1533[CO₂]\} \cdot 0.0003[H₂O] + \{0.390 + 1533[CO₂]\} \cdot 0.0003[H₂O]\} \cdot \frac{[CO₂]}{[H₂O]}\]

Water Concentration Moles/liter x 10⁴
General Correlating Equations for CO₂ Absorption

\[-r_{CO₂} = \frac{0.0492[H₂O]}{0.0492+[H₂O]/[CO₂]} \quad 0 < [CO₂] < 0.0003 \text{ M}\]

\[-[H₂O]/[1+H₂O] \{6.7715100/[CO₂]-0.0003]\} \times 10^4\]

\[0.0003 < [CO₂] < 0.0006 \text{ M}\]

\[\frac{[CO₂] \times 10^4 \text{ M}}{6.1}\]
Figure 7. Correlation of Water Absorption from KO₂ at 25°C
As a Function of Water and CO₂ Concentrations

General Correlating Equation for H₂O up-take

\[-r_{H₂O} = \left(0.101 - 70.5[CO₂]\right)[H₂O] \text{ for } [H₂O] \geq 0.0001 M\]

(Note: this equation is to be used for predicting water absorption rates no greater than \(0.35 \times 10^{-4}\) moles/sec)
Figure 9. Correlation of Oxygen Evolution from KO₂ at 25°C as a Function of Water and CO₂ Concentrations

General Correlating Equation for O₂ Evolution

\[
\tau_{O₂} = \left( 0.0475 - 45.573[CO₂]^3 \right) [H₂O] + 0.0779[CO₂]
\]

for \([H₂O] > 0.0001 M\)

Bed Temperature = 25°C
Contact Times = 1-5 sec
Particle size = 2-4 mesh

Water Concentration Moles/liter \( \times 10^{-4} \)

Rate of Oxygen Production—Moles/sec \( \times 10^4 \)
Figure 10 Correlation of Temperature Effects upon Reaction Rates
### Table: Mole Fractions at Depth

| Depth (feet) | CO₂ | H₂O | O₂ | He | Mixture Heat Capacity  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00395</td>
<td>0.00658</td>
<td>0.2105</td>
<td>0.779</td>
<td>5.438</td>
</tr>
<tr>
<td>33.9</td>
<td>0.00197</td>
<td>0.00329</td>
<td>0.1053</td>
<td>0.8894</td>
<td>5.204</td>
</tr>
<tr>
<td>135.6</td>
<td>0.00079</td>
<td>0.00132</td>
<td>0.0421</td>
<td>0.9558</td>
<td>5.0644</td>
</tr>
<tr>
<td>305.1</td>
<td>0.00040</td>
<td>0.00066</td>
<td>0.0210</td>
<td>0.9779</td>
<td>5.0177</td>
</tr>
<tr>
<td>474.6</td>
<td>0.00026</td>
<td>0.00044</td>
<td>0.014</td>
<td>0.985</td>
<td>5.0006</td>
</tr>
<tr>
<td>644.1</td>
<td>0.00020</td>
<td>0.00033</td>
<td>0.0105</td>
<td>0.989</td>
<td>4.9944</td>
</tr>
<tr>
<td>813.6</td>
<td>0.00016</td>
<td>0.00026</td>
<td>0.0084</td>
<td>0.991</td>
<td>4.9889</td>
</tr>
<tr>
<td>983.1</td>
<td>0.00013</td>
<td>0.00022</td>
<td>0.0070</td>
<td>0.992</td>
<td>4.983</td>
</tr>
</tbody>
</table>

P<sub>CO₂</sub> = 3 mm Hg; P<sub>H₂O</sub> = 5 mm Hg; P<sub>O₂</sub> = 160 mm Hg
<table>
<thead>
<tr>
<th>Depth (feet)</th>
<th>Mole Fractions</th>
<th>Mixture Heat Capacity (cal/mol-°K or Btu/mol-°R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.015 0.015 0.2105 0.759</td>
<td>5.497</td>
</tr>
<tr>
<td>33.9</td>
<td>0.0075 0.0075 0.1053 0.8797</td>
<td>5.235</td>
</tr>
<tr>
<td>135.6</td>
<td>0.0030 0.0030 0.0421 0.9519</td>
<td>5.076</td>
</tr>
<tr>
<td>305.1</td>
<td>0.0015 0.0015 0.0210 0.9760</td>
<td>5.023</td>
</tr>
<tr>
<td>474.6</td>
<td>0.0010 0.0010 0.0140 0.984</td>
<td>5.0001</td>
</tr>
<tr>
<td>644.1</td>
<td>0.0008 0.0008 0.0105 0.988</td>
<td>4.994</td>
</tr>
<tr>
<td>813.6</td>
<td>0.0006 0.0006 0.0084 0.990</td>
<td>4.989</td>
</tr>
<tr>
<td>983.1</td>
<td>0.0005 0.0005 0.0070 0.992</td>
<td>4.983</td>
</tr>
</tbody>
</table>

Figure 12: Heat Capacity of Breathing Mixture at 298°K as a Function of Depth

- $P_{CO_2} = 11.4$ mm Hg
- $P_{H_2O} = 11.4$ mm Hg
- $P_{O_2} = 160$ mm Hg

DEPTH in feet of water
Figure 13 Heat Capacity of Breathing Mixture at 298°K as a Function of Depth

<table>
<thead>
<tr>
<th>Depth (feet)</th>
<th>CO₂</th>
<th>H₂O</th>
<th>O₂</th>
<th>He</th>
<th>Mixture Heat Capacity (cal/mole-°K or Btu/#mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.08</td>
<td>0.08</td>
<td>0.2105</td>
<td>0.629</td>
<td>5.94</td>
</tr>
<tr>
<td>33.9</td>
<td>0.04</td>
<td>0.04</td>
<td>0.1053</td>
<td>0.815</td>
<td>5.457</td>
</tr>
<tr>
<td>135.6</td>
<td>0.016</td>
<td>0.016</td>
<td>0.0421</td>
<td>0.926</td>
<td>5.165</td>
</tr>
<tr>
<td>305.1</td>
<td>0.008</td>
<td>0.008</td>
<td>0.0210</td>
<td>0.963</td>
<td>5.070</td>
</tr>
<tr>
<td>474.6</td>
<td>0.0054</td>
<td>0.0054</td>
<td>0.014</td>
<td>0.975</td>
<td>5.034</td>
</tr>
<tr>
<td>644.1</td>
<td>0.004</td>
<td>0.004</td>
<td>0.0105</td>
<td>0.981</td>
<td>5.016</td>
</tr>
<tr>
<td>813.6</td>
<td>0.0032</td>
<td>0.0032</td>
<td>0.0084</td>
<td>0.985</td>
<td>5.008</td>
</tr>
<tr>
<td>983.1</td>
<td>0.0027</td>
<td>0.0027</td>
<td>0.0070</td>
<td>0.988</td>
<td>5.004</td>
</tr>
</tbody>
</table>

P₀₂ = 160 mm Hg; P₆₁ = 61 mm Hg; P₆₂ = 61 mm Hg

DEPTH in feet of water
Figure 14 Schematic of Air Revitalization Back-Pack
(Ganas, 1971)

Figure 15 Model of Gas Flow Pattern of Back-Pack
Figure 16 Correlation of Required Heat Exchange Rate (UA) with Rate of Heat Release

\[ Q_{rxn} \text{ in cal/sec} \]

- \( T_{ss} = 25^\circ C \)
- \( T_{ss} = 30^\circ C \)
- \( T_{ss} = 35^\circ C \)

Depth = 0.0 feet
Figure 17 Correlation of Required Heat Exchange Rate (UA) with Rate of Heat Release

- $T_{ss} = 25^\circ C$
- $T_{ss} = 30^\circ C$
- $T_{ss} = 35^\circ C$

Depth = 90 feet

$Q_{rxn}$ in cal/sec
Figure 18 Correlation of Required Heat Exchange Rate (UA) with Rate of Heat Release

\[ Q_{\text{rxn}} \text{ in cal/sec} \]

Depth = 475 or 1000 feet
Figure 20 KO₂ Charge Weight as a Function of Inlet Conditions
Figure 21 Supplemental Carbon Dioxide Scrubbing Rates
<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₃ Oxygen Generators</td>
<td>Low volume, ease of resupply</td>
<td>Heat produced, reaction temperature is 1450°F, unconsummable, expendable weight</td>
</tr>
<tr>
<td>(Candles)</td>
<td>Long shelf life</td>
<td></td>
</tr>
<tr>
<td>High Pressure gas</td>
<td>Simple and reliable, no heat addition required, high flow rates available, indefinite standby capacity</td>
<td>Relatively heavy tankage, cannot be recharged from space craft</td>
</tr>
<tr>
<td>Moderate pressure gas</td>
<td>All advantages of high pressure gas</td>
<td>Large volume, heavy tankage, large unusable gas quantity.</td>
</tr>
<tr>
<td>Subcritical cryogenic</td>
<td>Low volume</td>
<td>Limited standby time, tank &amp; delivery heating required, recharging difficult</td>
</tr>
<tr>
<td>Umbilical</td>
<td>Low weight, low volume, unlimited operating time, provides tether and energy source</td>
<td>Dependency on mother vehicle, limited range reduces mobility</td>
</tr>
<tr>
<td>Absorbents</td>
<td>Easily replaced, low weight, LiOH is proven absorbent, Li₂O has high theoretical carbon dioxide capacity</td>
<td>Replacement required, non-regenerable, exothermic, Li₂O requires high humidity, low utilization efficiency, use is not well documented</td>
</tr>
<tr>
<td>Method</td>
<td>Advantages</td>
<td>Disadvantages</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Absorbents</td>
<td>Regenerable, allows indefinite operation</td>
<td>Toxic, high vapor pressure, phase separation problem, stability in oxygen not good, not well proven</td>
</tr>
<tr>
<td>(Monoethanol amine)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorbents</td>
<td>Readily regenerable, non-toxic well proven process</td>
<td>Large volume/weight, must be dry, exothermic</td>
</tr>
<tr>
<td>(regenerable)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Superoxides, Ozonides</td>
<td>Easily replaced, low weight and volume, provides oxygen in addition to removing CO₂</td>
<td>Exothermic, can have unpredictable respiration quotient, controls often required, may require auxiliary CO₂ absorbent</td>
</tr>
</tbody>
</table>

Adapted from Prince *et al.*, 1969
### TABLE 3  LITHIUM SUPEROXIDE SYSTEM REACTIONS

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta H_{\text{rxn}}^{\circ}$ $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>$2 \ \text{LiO}_2 + \text{H}_2\text{O} = 2 \ \text{LiOH} + 1.5 \ \text{O}_2$</td>
<td>-50.0 $^*$</td>
</tr>
<tr>
<td>[2]</td>
<td>$2 \ \text{LiOH} + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$</td>
<td>-22.6</td>
</tr>
<tr>
<td>[3]</td>
<td>$\text{LiOH} + \text{CO}_2 = \text{LiHCO}_3$</td>
<td>-21.8 $^*$</td>
</tr>
<tr>
<td>[4]</td>
<td>$\text{LiOH} + \text{H}_2\text{O} = \text{LiOH} \cdot \text{H}_2\text{O}$</td>
<td>-15.0</td>
</tr>
<tr>
<td>[5]</td>
<td>$2 \ \text{LiO}_2 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + 1.5 \ \text{O}_2$</td>
<td>-72.6 $^*$</td>
</tr>
<tr>
<td>[6]</td>
<td>$2 \ (\text{LiOH} \cdot \text{H}_2\text{O}) + \text{CO}_2 = \text{Li}_2\text{CO}_3 + 3 \ \text{H}_2\text{O}$</td>
<td>+6.8</td>
</tr>
<tr>
<td>[7]</td>
<td>$2 \ \text{LiHCO}_3 = \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$</td>
<td>+21.0 $^*$</td>
</tr>
</tbody>
</table>

### TABLE 4  CALCIUM SUPEROXIDE SYSTEM REACTIONS

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta H_{\text{rxn}}^{\circ}$ $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>$\text{Ca(O}_2)\text{}_2 + \text{H}_2\text{O} = \text{Ca(OH)}\text{}_2 + 1.5 \ \text{O}_2$</td>
<td>-83.5 $^*$</td>
</tr>
<tr>
<td>[2]</td>
<td>$\text{Ca(OH)}\text{}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$</td>
<td>-16.6</td>
</tr>
<tr>
<td>[3]</td>
<td>$\text{Ca(O}_2)\text{}_2 + n \ \text{H}_2\text{O} = \text{CaO}_2 \cdot n \ \text{H}_2\text{O} + \text{O}_2$</td>
<td>***</td>
</tr>
<tr>
<td>[4]</td>
<td>$\text{CaO}_2 \cdot n \ \text{H}_2\text{O} + x \ \text{H}_2\text{O} = \text{Ca(OH)}\text{}_2 + 0.5 \ \text{O}_2$</td>
<td>***</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ $(n + x - 1) \ \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>[5]</td>
<td>$\text{CaO}_2 \cdot n \ \text{H}_2\text{O} + \text{CO}_2 = \text{CaCO}_3 + n \ \text{H}_2\text{O} + 0.5 \ \text{O}_2$</td>
<td>***</td>
</tr>
</tbody>
</table>

$^1$ Reaction systems are not well characterized; these are only possible reactions.

$^2$ Values in kcal/mole

$^*$ Heat of formation data for some reaction compounds was estimated

$^{**}$ Linear combinations of other reactions

$^{***}$ Heat of formation data not available for some compounds.
TABLE 5 SODIUM SUPEROXIDE SYSTEM REACTIONS

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>( \Delta H_{rxn}^{\circ} ) 2 kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>(2 \text{NaO}_2 + \text{H}_2\text{O} = 2 \text{NaOH} + 1.5 \text{O}_2)</td>
<td>-22.4</td>
</tr>
<tr>
<td>[2]</td>
<td>(2 \text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O})</td>
<td>-52.1</td>
</tr>
<tr>
<td>[3]</td>
<td>(\text{NaOH} + \text{CO}_2 = \text{NaHCO}_3)</td>
<td>-30.1</td>
</tr>
<tr>
<td>[4]</td>
<td>(\text{NaOH} + \text{H}_2\text{O} = \text{NaOH} \cdot \text{H}_2\text{O})</td>
<td>-15.4</td>
</tr>
<tr>
<td>[5]</td>
<td>(\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O})</td>
<td>-13.7</td>
</tr>
<tr>
<td>[6]</td>
<td>(\text{Na}_2\text{CO}_3 + 7 \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 \cdot 7 \text{H}_2\text{O})</td>
<td>-93.1</td>
</tr>
<tr>
<td>[7]</td>
<td>(\text{Na}_2\text{CO}_3 + 10 \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O})</td>
<td>-128.0</td>
</tr>
<tr>
<td>[8]</td>
<td>(\text{NaHCO}_3 + 2 \text{H}_2\text{O} = \text{NaHCO}_3 \cdot 2 \text{H}_2\text{O})</td>
<td>+45.5</td>
</tr>
<tr>
<td>[9]</td>
<td>(\text{NaHCO}_3 + 3 \text{H}_2\text{O} = \text{NaHCO}_3 \cdot 3 \text{H}_2\text{O})</td>
<td>+35.7</td>
</tr>
<tr>
<td>[10]</td>
<td>(\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + 2 \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2 \text{H}_2\text{O})</td>
<td>-28.8</td>
</tr>
<tr>
<td>[11]</td>
<td>(2 \text{NaO}_2 = \text{Na}_2\text{O}_2 + \text{O}_2)</td>
<td>-60.2</td>
</tr>
<tr>
<td>[12]</td>
<td>(2 \text{NaO}_2 + 8 \text{H}_2\text{O} = \text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O} + \text{O}_2)</td>
<td>***</td>
</tr>
<tr>
<td>[13]</td>
<td>(\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O} + \text{CO}_2 = \text{Na}_2\text{C}_2\text{O}_6 + 8 \text{H}_2\text{O})</td>
<td>***</td>
</tr>
<tr>
<td>[14]</td>
<td>(2 \text{NaO}_2 + \text{CO}_2 = \text{Na}_2\text{CO}_3 + 1.5 \text{O}_2)</td>
<td>-52.1</td>
</tr>
<tr>
<td>[15]</td>
<td>(2 \left(\text{NaOH} \cdot \text{H}_2\text{O}\right) + \text{CO}_2 = \text{Na}_2\text{CO}_3 + 3 \text{H}_2\text{O})</td>
<td>-21.3</td>
</tr>
<tr>
<td>[16]</td>
<td>(2 \text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2)</td>
<td>+8.1</td>
</tr>
</tbody>
</table>

1 Listed in this table are several possible reactions that may occur for this system; others are possible. Additionally, commercial grade sodium superoxide contains sodium peroxide and oxide in significant amounts (5%) and these chemicals may enter the reaction scheme.

2 Heat of reaction values in kcal/mole

** Linear combinations of other reactions

*** Heat of formation data not available for some compounds.
<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta H_{\text{f}, \text{rxn}}^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>$2 \text{KO}_2 + \text{H}_2\text{O} = 2 \text{KOH} + 1.5 \text{O}_2$</td>
<td>-9.4</td>
</tr>
<tr>
<td>[2]</td>
<td>$2 \text{KOH} + \text{CO}_2 = \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$</td>
<td>-33.7</td>
</tr>
<tr>
<td>[3]</td>
<td>$\text{KOH} + \text{CO}_2 = \text{KHCO}_3$</td>
<td>-33.1</td>
</tr>
<tr>
<td>[4]</td>
<td>$\text{KOH} + 0.75 \text{H}_2\text{O} = \text{KOH}\cdot0.75 \text{H}_2\text{O}$</td>
<td>-16.6</td>
</tr>
<tr>
<td>[5]</td>
<td>$\text{KOH} + \text{H}_2\text{O} = \text{KOH}\cdot\text{H}_2\text{O}$</td>
<td>-20.0</td>
</tr>
<tr>
<td>[6]</td>
<td>$\text{KOH} + 2 \text{H}_2\text{O} = \text{KOH}\cdot2 \text{H}_2\text{O}$</td>
<td>-33.8</td>
</tr>
<tr>
<td>[7]</td>
<td>$\text{K}_2\text{CO}_3 + 0.5 \text{H}_2\text{O} = \text{K}_2\text{CO}_3\cdot0.5 \text{H}_2\text{O}$</td>
<td>-7.6</td>
</tr>
<tr>
<td>[8]</td>
<td>$\text{K}_2\text{CO}_3 + 1.5 \text{H}_2\text{O} = \text{K}_2\text{CO}_3\cdot1.5 \text{H}_2\text{O}$</td>
<td>-22.8</td>
</tr>
<tr>
<td>[9]</td>
<td>$2 \text{KO}_2 = \text{K}_2\text{O}_2 + \text{O}_2$</td>
<td>+17.5</td>
</tr>
<tr>
<td>[10]</td>
<td>$2 \text{KO}_2 + n \text{H}_2\text{O} = \text{K}_2\text{O}_2\cdot n \text{H}_2\text{O} + \text{O}_2$</td>
<td>***</td>
</tr>
<tr>
<td>[11]</td>
<td>$\text{K}_2\text{O}_2\cdot n \text{H}_2\text{O} + \text{CO}_2 = \text{K}_2\text{C}_2\text{O}_6 + n \text{H}_2\text{O}$</td>
<td>***</td>
</tr>
<tr>
<td>[12]</td>
<td>$2 \text{KO}_2 + \text{CO}_2 = \text{K}_2\text{CO}_3 + 1.5 \text{O}_2$</td>
<td>-43.1</td>
</tr>
<tr>
<td>[13]</td>
<td>$2 (\text{KOH}\cdot0.75 \text{H}_2\text{O}) + \text{CO}_2 = \text{K}_2\text{CO}_3 + 2.5 \text{H}_2\text{O}$</td>
<td>-0.5</td>
</tr>
<tr>
<td>[14]</td>
<td>$2 (\text{KOH}\cdot\text{H}_2\text{O}) + \text{CO}_2 = \text{K}_2\text{CO}_3 + 3 \text{H}_2\text{O}$</td>
<td>+6.3</td>
</tr>
<tr>
<td>[15]</td>
<td>$2 (\text{KOH}\cdot2 \text{H}_2\text{O}) + \text{CO}_2 = \text{K}_2\text{CO}_3 + 5 \text{H}_2\text{O}$</td>
<td>+33.9</td>
</tr>
<tr>
<td>[16]</td>
<td>$2 \text{KHCO}_3 = \text{K}_2\text{CO}_3 + \text{CO}_2 + 2 \text{H}_2\text{O}$</td>
<td>+32.5</td>
</tr>
</tbody>
</table>

---

1. Listed in this table are several possible reactions that may occur for this system; others are possible.

2. Heat of reaction values in kcal/mole

** linear combinations of other reactions

*** heat of formation data not available for some compounds.
TABLE 7  POTASSIUM OZONIDE SYSTEM REACTIONS

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>( \Delta H^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>( 2 \text{ KO}_3 + \text{ H}_2\text{O} = 2 \text{ KOH} + 2.5 \text{ O}_2 )</td>
<td>-21.6*</td>
</tr>
<tr>
<td>[2]</td>
<td>( 2 \text{ KOH} + \text{ CO}_2 = \text{ K}_2\text{CO}_3 + \text{ H}_2\text{O} )</td>
<td>-33.7</td>
</tr>
<tr>
<td>[3]</td>
<td>( \text{ KOH} + \text{ CO}_2 = \text{ KHCO}_3 )</td>
<td>-33.1</td>
</tr>
<tr>
<td>[4]</td>
<td>( \text{ KOH} + 0.75 \text{ H}_2\text{O} = \text{ KOH} \cdot 0.75 \text{ H}_2\text{O} )</td>
<td>-16.6</td>
</tr>
<tr>
<td>[5]</td>
<td>( \text{ KOH} + \text{ H}_2\text{O} = \text{ KOH} \cdot \text{ H}_2\text{O} )</td>
<td>-20.0</td>
</tr>
<tr>
<td>[6]</td>
<td>( \text{ KOH} + 2 \text{ H}_2\text{O} = \text{ KOH} \cdot 2 \text{ H}_2\text{O} )</td>
<td>-33.8</td>
</tr>
<tr>
<td>[7]</td>
<td>( \text{ K}_2\text{CO}_3 + 0.5 \text{ H}_2\text{O} = \text{ K}_2\text{CO}_3 \cdot 0.5 \text{ H}_2\text{O} )</td>
<td>-7.6</td>
</tr>
<tr>
<td>[8]</td>
<td>( \text{ K}_2\text{CO}_3 + 1.5 \text{ H}_2\text{O} = \text{ K}_2\text{CO}_3 \cdot 1.5 \text{ H}_2\text{O} )</td>
<td>-22.8</td>
</tr>
<tr>
<td>[9]</td>
<td>( \text{ KO}_3 = \text{ KO}_2 + 0.5 \text{ O}_2 )</td>
<td>-5.9*</td>
</tr>
<tr>
<td>[10]</td>
<td>( 2 \text{ KO}_2 = \text{ K}_2\text{O}_2 + \text{ O}_2 )</td>
<td>+17.5</td>
</tr>
<tr>
<td>[11]</td>
<td>( 2 \text{ KO}_3 + \text{ CO}_2 = \text{ K}_2\text{CO}_3 + 2.5 \text{ O}_2 )</td>
<td>-55.3*</td>
</tr>
<tr>
<td>[12]</td>
<td>( 2 \text{ KO}_3 + 2 \text{ CO}_2 + \text{ H}_2\text{O} = 2 \text{ KHCO}_3 + 2.5 \text{ O}_2 )</td>
<td>-54.7*</td>
</tr>
<tr>
<td>[13]</td>
<td>( 2(\text{ KOH} \cdot 0.75 \text{ H}_2\text{O}) + \text{ CO}_2 = \text{ K}_2\text{CO}_3 + 2.5 \text{ H}_2\text{O} )</td>
<td>-0.5</td>
</tr>
<tr>
<td>[14]</td>
<td>( 2(\text{ KOH} \cdot \text{ H}_2\text{O}) + \text{ CO}_2 = \text{ K}_2\text{CO}_3 + 3 \text{ H}_2\text{O} )</td>
<td>+6.3</td>
</tr>
<tr>
<td>[15]</td>
<td>( 2(\text{ KOH} \cdot 2 \text{ H}_2\text{O}) + \text{ CO}_2 = \text{ K}_2\text{CO}_3 + 5 \text{ H}_2\text{O} )</td>
<td>+33.9</td>
</tr>
<tr>
<td>[16]</td>
<td>( 2 \text{ KHCO}_3 = \text{ K}_2\text{CO}_3 + \text{ H}_2\text{O} + \text{ CO}_2 )</td>
<td>+32.5</td>
</tr>
</tbody>
</table>

1 Listed in this table are several possible reactions that may occur for this system; others are possible.

2 heat of reaction values in kcal/mole

* value of ozonide heat of formation uncertain

** linear combination of other reactions
<table>
<thead>
<tr>
<th>Year</th>
<th>Investigators</th>
<th>Chemical</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1959</td>
<td>Bovard, Mausteller &amp; Batutis</td>
<td>KO_2</td>
<td>2 man, 7 hour test</td>
</tr>
<tr>
<td>1960</td>
<td>Keating &amp; Weiswern</td>
<td>KO_2</td>
<td>1 man, 168 hour test passive system</td>
</tr>
<tr>
<td>1962</td>
<td>Ophian</td>
<td>KO_2</td>
<td>Unmanned</td>
</tr>
<tr>
<td>1962</td>
<td>Kunard &amp; Rodgers</td>
<td>KO_2 &amp; NaO_2</td>
<td>Unmanned</td>
</tr>
<tr>
<td>1964</td>
<td>Boeing Co.</td>
<td>NaO_2</td>
<td>5 men, 30 day test</td>
</tr>
<tr>
<td>1965</td>
<td>McGoff</td>
<td>KO_2 (high density)</td>
<td>Unmanned</td>
</tr>
<tr>
<td>1966</td>
<td>McGoff &amp; King</td>
<td>KO_2 (high density)</td>
<td>Unmanned</td>
</tr>
<tr>
<td>1967</td>
<td>Presti, Wallman, &amp; Petrocelli</td>
<td>KO_2</td>
<td>2 man, 5.5 hour test</td>
</tr>
<tr>
<td>1969</td>
<td>Ganas</td>
<td>KO_2</td>
<td>1 man, 3 hour, cartridge system</td>
</tr>
<tr>
<td>1970</td>
<td>Ducros</td>
<td>KO_2</td>
<td>2 man, 13 hours</td>
</tr>
<tr>
<td>Pressure (atm.)</td>
<td>Gas Component</td>
<td>Reduced Pressure</td>
<td>Reduced Temperature</td>
</tr>
<tr>
<td>----------------</td>
<td>--------------</td>
<td>------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>1</td>
<td>CO₂</td>
<td>0.0137</td>
<td>0.898</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>4.58x10⁻³</td>
<td>0.422</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>0.0201</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>0.442</td>
<td>51.94</td>
</tr>
<tr>
<td>10</td>
<td>CO₂</td>
<td>0.137</td>
<td>0.898</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>0.0458</td>
<td>0.422</td>
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<tr>
<td></td>
<td>O₂</td>
<td>0.201</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>4.42</td>
<td>51.94</td>
</tr>
<tr>
<td>30</td>
<td>CO₂</td>
<td>0.411</td>
<td>0.898</td>
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<tr>
<td></td>
<td>H₂O</td>
<td>0.137</td>
<td>0.422</td>
</tr>
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<td></td>
<td>O₂</td>
<td>0.603</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>13.27</td>
<td>51.94</td>
</tr>
</tbody>
</table>

Critical Properties Used:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Accentricity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>31.0°C</td>
<td>72.9 atm</td>
<td>0.225</td>
</tr>
<tr>
<td>Water vapor</td>
<td>374.2</td>
<td>218.3</td>
<td>0.334</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-118.4</td>
<td>50.1</td>
<td>0.021</td>
</tr>
<tr>
<td>Helium</td>
<td>-267.9</td>
<td>2.26</td>
<td>0.0</td>
</tr>
</tbody>
</table>

¹ Calculated using Redlich-Kwong equation of state

² Total of values may not add to unity due to significant figures
<table>
<thead>
<tr>
<th>Compound Formula</th>
<th>Heat of Formation*</th>
<th>Heat Capacity**</th>
<th>Entropy**</th>
<th>Free Energy of Formation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>KO₂(s)</td>
<td>-68.0</td>
<td>18.53</td>
<td>29.3</td>
<td>-57.5</td>
</tr>
<tr>
<td>KOH(s)</td>
<td>-101.78</td>
<td>15.51</td>
<td>18.85</td>
<td>-90.6</td>
</tr>
<tr>
<td>K₂CO₃(s)ₐ</td>
<td>-274.9(-177)</td>
<td>27.35</td>
<td>37.17</td>
<td>-254.4</td>
</tr>
<tr>
<td>KHCO₃(s)</td>
<td>-229.3</td>
<td>22.5</td>
<td>26.6</td>
<td>-207.0</td>
</tr>
<tr>
<td>KOH·0.75 H₂O(s)</td>
<td>-161.7</td>
<td>22.3</td>
<td>21.3(26.4)</td>
<td>-133.7</td>
</tr>
<tr>
<td>KOH·H₂O(s)</td>
<td>-179.0</td>
<td>22.3</td>
<td>23.6(28.9)</td>
<td>-148.1</td>
</tr>
<tr>
<td>KOH·2 H₂O(s)</td>
<td>-251.2</td>
<td>29.9</td>
<td>33.1(38.9)</td>
<td>-205.6</td>
</tr>
<tr>
<td>K₂CO₃·0.5 H₂O(s)ₐ</td>
<td>-311(-210.4)</td>
<td>30.7</td>
<td>38.3</td>
<td>-283.2</td>
</tr>
<tr>
<td>K₂CO₃·1.5 H₂O(s)ₐ</td>
<td>-384(-283.4)</td>
<td>39.4</td>
<td>47.7</td>
<td>-340.7</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>-57.796</td>
<td>8.02</td>
<td>45.1</td>
<td>-54.6</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>-94.0</td>
<td>8.87</td>
<td>51.1</td>
<td>-94.26</td>
</tr>
<tr>
<td>O₂(g)</td>
<td>0.0</td>
<td>7.02</td>
<td>49.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Non-subscripted values from Lange (1979)

a. Two different sets of data for the heats of formation of potassium carbonate and its hydrates have been reported. Rossini et al. (1952) gave a value of -274.9 to the carbonate and the values in parentheses to the hydrates. Maslov (1960) stated the carbonate value was too high and assigned the lower values. However, Rozenfel'd (1969) found the assumptions of Maslov (1950) to be erroneous and established the higher set of values as the true heats of formations for the carbonate compounds. The Rozenfel'd values are used in this study.


c. Entropy values not in parentheses estimated by Latimer (1951). Other values for the hydrates found by the method of Gorunov (1971). This latter method is not applicable to the hydrates of alkali metal carbonates.

d. Found indirectly by using decomposition pressure data for the compound and using thermodynamic relationships.

e. Estimated by the method of Gorbunov (1971).

* values in kcal/mole  ** values in cal/mole-°K
<table>
<thead>
<tr>
<th>No.</th>
<th>Independent Reaction</th>
<th>ΔH°&lt;sub&gt;rxn&lt;/sub&gt;</th>
<th>ΔG°&lt;sub&gt;rxn&lt;/sub&gt;</th>
<th>ΔS°&lt;sub&gt;rxn&lt;/sub&gt;</th>
<th>ln(K&lt;sub&gt;a&lt;/sub&gt;)</th>
<th>Equilibrium Expression&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 KO&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O = 2 KOH + 1.5 O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-9.4</td>
<td>-11.6</td>
<td>+7.5</td>
<td>19.6</td>
<td>$K_Y = \frac{(Y_{O_2})^{1.5} P^{0.5}}{(Y_{H_2O})}$</td>
</tr>
<tr>
<td>2</td>
<td>2 KOH + CO&lt;sub&gt;2&lt;/sub&gt; = K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-33.7</td>
<td>-33.6</td>
<td>-6.5</td>
<td>56.7</td>
<td>$K_Y = \frac{(Y_{H_2O})}{(Y_{CO_2})}$</td>
</tr>
<tr>
<td>3</td>
<td>KOH + CO&lt;sub&gt;2&lt;/sub&gt; = KHCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-33.1</td>
<td>-22.1</td>
<td>-43.3</td>
<td>37.3</td>
<td>$K_Y = 1.0/(Y_{CO_2})P$</td>
</tr>
<tr>
<td>4</td>
<td>KOH + 0.75 H&lt;sub&gt;2&lt;/sub&gt;O = KOH·0.75 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-16.6</td>
<td>-2.2</td>
<td>-31.4</td>
<td>3.7</td>
<td>$K_Y = 1.0/(Y_{H_2O})^{0.75} P^{0.75}$</td>
</tr>
<tr>
<td>5</td>
<td>KOH + H&lt;sub&gt;2&lt;/sub&gt;O = KOH·H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-20.0</td>
<td>-2.9</td>
<td>-40.4</td>
<td>4.9</td>
<td>$K_Y = 1.0/(Y_{H_2O})P$</td>
</tr>
<tr>
<td>6</td>
<td>KOH + 2 H&lt;sub&gt;2&lt;/sub&gt;O = KOH·2 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-33.8</td>
<td>-5.8</td>
<td>-76.1</td>
<td>9.8</td>
<td>$K_Y = 1.0/(Y_{H_2O})^2P^2$</td>
</tr>
<tr>
<td>7</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; + 0.5 H&lt;sub&gt;2&lt;/sub&gt;O = K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;·0.5 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-7.6</td>
<td>-1.5</td>
<td>-21.4</td>
<td>2.5</td>
<td>$K_Y = 1.0/(Y_{H_2O})^{0.5} P^{0.5}$</td>
</tr>
<tr>
<td>8</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; + 1.5 H&lt;sub&gt;2&lt;/sub&gt;O = K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;·1.5 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-22.8</td>
<td>-4.4</td>
<td>-57.1</td>
<td>7.3</td>
<td>$K_Y = 1.0/(Y_{H_2O})^{1.5} P^{1.5}$</td>
</tr>
</tbody>
</table>

<sup>1</sup>Values of ΔH°<sub>rxn</sub> and ΔG°<sub>rxn</sub> in kcal/mole; values of ΔS°<sub>rxn</sub> in cal/mole·°K; ln(K<sub>a</sub>) dimensionless

<sup>2</sup>Equilibrium expressions assuming ideal behavior using component mole fractions and pressure term
Table 12: Summary of Model Predictions for Temperature-Time Excursions of a Breathing Air Mixture in Contact with KO₂

<table>
<thead>
<tr>
<th>Depth, feet</th>
<th>P_water (mm Hg)</th>
<th>P_CO₂ (mm Hg)</th>
<th>Q, cal/sec</th>
<th>T_ss, °C</th>
<th>Temperature Equation Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>48</td>
<td>47.96, 0.0216</td>
</tr>
<tr>
<td>90</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>40</td>
<td>40.2, 0.0816</td>
</tr>
<tr>
<td>475</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>37</td>
<td>37, 0.340</td>
</tr>
<tr>
<td>1000</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>37</td>
<td>37, 0.694</td>
</tr>
<tr>
<td>0</td>
<td>11.4</td>
<td>11.4</td>
<td>2.08</td>
<td>65</td>
<td>65.3, 0.0216</td>
</tr>
<tr>
<td>90</td>
<td>11.4</td>
<td>11.4</td>
<td>2.08</td>
<td>45</td>
<td>45.2, 0.816</td>
</tr>
<tr>
<td>475</td>
<td>11.4</td>
<td>11.4</td>
<td>2.08</td>
<td>39</td>
<td>39.1, 0.340</td>
</tr>
<tr>
<td>1000</td>
<td>11.4</td>
<td>11.4</td>
<td>2.08</td>
<td>38</td>
<td>37.8, 0.694</td>
</tr>
<tr>
<td>0</td>
<td>61</td>
<td>61</td>
<td>19.3</td>
<td>261</td>
<td>261.4, 0.0216</td>
</tr>
<tr>
<td>90</td>
<td>61</td>
<td>61</td>
<td>19.3</td>
<td>98</td>
<td>97.5, 0.0816</td>
</tr>
<tr>
<td>475</td>
<td>61</td>
<td>61</td>
<td>19.3</td>
<td>56</td>
<td>55.9, 0.034</td>
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<tr>
<td>1000</td>
<td>61</td>
<td>61</td>
<td>19.3</td>
<td>46</td>
<td>46.1, 0.694</td>
</tr>
</tbody>
</table>

\[
\frac{dT}{dt} + \frac{bT}{n_T} = \frac{a}{n_T} \quad ; \quad T(°C) = a + [25-a] \exp(-bt/n_T) ; \quad UA = 0.0 \text{ cal/sec}^{-°C}
\]
Table 13 Summary of Model Predictions for Temperature-Time Excursions of a Breathing Air Mixture in Contact with KO₂

<table>
<thead>
<tr>
<th>Depth, feet</th>
<th>$P_{\text{water}}$</th>
<th>$P_{\text{CO}_2}$</th>
<th>$Q$, cal/sec</th>
<th>$T_{\text{ss}}, °\text{C}$</th>
<th>Temperature Equation Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>32</td>
<td>31.84, 0.051</td>
</tr>
<tr>
<td>90</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>35</td>
<td>34.56, 0.1139</td>
</tr>
<tr>
<td>475</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>36</td>
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\[
\frac{dT}{dt} + \frac{bT}{n_T} = \frac{ab}{n_T}; \quad T(°\text{C}) = a + [25-a]\exp(-bt/n_T); \quad UA = 0.1 \text{ cal/sec-°C}
\]
Table 14  Summary of Model Predictions for Temperature-Time Excursions of a Breathing Air Mixture in Contact with KO₂

<table>
<thead>
<tr>
<th>Depth, feet</th>
<th>P_water (mm Hg)</th>
<th>P_CO₂ (mm Hg)</th>
<th>Q, cal/sec</th>
<th>T_ss, °C</th>
<th>Temperature Equation Constants</th>
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\[
\frac{dT}{dt} + \frac{bT}{n_T} = \frac{ab}{n_T}; \quad T(°C) = a + [25-a] \exp(-bt/n_T); \quad UA = 0.5 \text{ cal/sec-°C}
\]
Table 15 Summary of Model Predictions for Temperature-Time Excursions of a Breathing Air Mixture in Contact with KO₂

<table>
<thead>
<tr>
<th>Depth, feet</th>
<th>P_{water} mm Hg</th>
<th>P_{CO₂} mm Hg</th>
<th>Q, cal/sec</th>
<th>T_{ss}, °C</th>
<th>Temperature Equation Constants</th>
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<td>0.804</td>
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<td>25.19 1.029</td>
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<td>23.1 0.316</td>
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<td>2.08</td>
<td>25</td>
<td>25.11 0.404</td>
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<td>2.08</td>
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<td>26.13 0.674</td>
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<td>19.3</td>
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<td>39.13 0.277</td>
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<td>19.3</td>
<td>39</td>
<td>38.75 0.393</td>
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<td>34.65 0.674</td>
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<td>61</td>
<td>19.3</td>
<td>35</td>
<td>35.31 1.025</td>
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</tbody>
</table>

\[
\frac{dT}{dt} + \frac{bT}{n_T^a} = \frac{ab}{n_T^a} ; \quad T(°C) = a + [25-a] \exp(-bt/n_T^a) ; \quad UA = 1.0 \text{ cal/sec}^*°C
\]
Table 16  Summary of Model Predictions for Temperature-Time Excursions of a Breathing Air Mixture in Contact with KO₂

<table>
<thead>
<tr>
<th>Depth, feet</th>
<th>P&lt;sub&gt;water&lt;/sub&gt; (mm Hg)</th>
<th>P&lt;sub&gt;CO₂&lt;/sub&gt; (mm Hg)</th>
<th>Q&lt;sub&gt;t&lt;/sub&gt;, cal/sec</th>
<th>n&lt;sup&gt;e&lt;/sup&gt; &lt;sub&gt;T&lt;/sub&gt; moles</th>
<th>t* in seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>0.25; 0.5; 1.</td>
<td>26.3; 52.5; 105.1</td>
</tr>
<tr>
<td>90</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>2.; 4.; 8.</td>
<td>49.8; 99.5; 199.</td>
</tr>
<tr>
<td>475</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>10.; 15.; 25</td>
<td>55.; 82.5; 137.5</td>
</tr>
<tr>
<td>1000</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>20., 40., 60.</td>
<td>53.9; 107.8; 161.7</td>
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<td>11.4</td>
<td>2.08</td>
<td>0.25; 0.5; 1.</td>
<td>29.2; 58.3; 116.7</td>
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<td>11.4</td>
<td>2.08</td>
<td>2.; 4.; 8.</td>
<td>53.9; 107.8; 215.7</td>
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<tr>
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<td>11.4</td>
<td>11.4</td>
<td>2.08</td>
<td>10.; 15.; 25</td>
<td>58.2; 87.4; 145.6</td>
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<td>11.4</td>
<td>2.08</td>
<td>20., 40., 60.</td>
<td>55.3; 110.7; 166.</td>
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<td>19.3</td>
<td>0.25; 0.5; 1.</td>
<td>33.6; 67.1; 134.3</td>
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<td>19.3</td>
<td>2.; 4.; 8.</td>
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<td>10.; 15.; 25</td>
<td>70.9; 106.3; 177.2</td>
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<td>61</td>
<td>19.3</td>
<td>20., 40., 60.</td>
<td>64.; 128.; 192.</td>
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</table>

\[
\frac{dT}{dt} + \frac{bT}{n_T^e} = \frac{ab}{n_T^e} \quad T(°C) = a + [25-a] \exp(-bt/n_T^e) \quad UA = 0.0 \text{ cal/sec}°\text{C} \\
t* = -n_T^e / b [\ln(0.05a/(a-25))]
Table 17 Summary of Model Predictions for Temperature-Time Excursions of a Breathing Air Mixture in Contact with KO₂

<table>
<thead>
<tr>
<th>Depth, feet</th>
<th>P_{water} mm Hg</th>
<th>P_{CO₂} mm Hg</th>
<th>Q, cal/sec</th>
<th>n_T moles</th>
<th>t* in seconds</th>
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</thead>
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<td>0.25; .5; 1</td>
<td>7.1; 14.2; 28.4</td>
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<td>3</td>
<td>0.804</td>
<td>2; 4; 8</td>
<td>30.; 60.; 90</td>
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<td>475</td>
<td>5</td>
<td>3</td>
<td>0.804</td>
<td>10; 15; 25</td>
<td>47.9; 71.8; 119.7</td>
</tr>
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<td>3</td>
<td>0.804</td>
<td>20; 40; 60</td>
<td>49.3; 98.6; 197.2</td>
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<td>2.08</td>
<td>0.25; .5; 1</td>
<td>9.7; 19.4; 38.8</td>
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<td>2.08</td>
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<td>33.9; 67.7; 135</td>
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<td>11.4</td>
<td>2.08</td>
<td>10; 15; 25</td>
<td>49.5; 74.2; 123.7</td>
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<td>11.4</td>
<td>2.08</td>
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<td>14.4; 30.4; 60.4</td>
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<td>2; 4; 8</td>
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<td>61</td>
<td>19.3</td>
<td>10; 15; 25</td>
<td>63.2; 95.0; 158.</td>
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<td>61</td>
<td>19.3</td>
<td>20; 40; 60</td>
<td>59.7; 119.; 179.</td>
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</table>

\[
\frac{dT}{dt} + \frac{bT}{n_T^*} = \frac{ab}{n_T^*} ; \quad T(°C) = a + [25-a]exp(-bt/n_T^*); \quad UA = 0.1 \text{ cal/sec} °C
\]

\[
t^* = -n_T^*/b \left[ \ln(0.05a/(a-25)) \right]
\]
Table 18  Summary of Model Predictions for Temperature-Time Excursions of a Breathing Air Mixture in Contact with K0,  

<table>
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<th>Depth, feet</th>
<th>P&lt;sub&gt;water&lt;/sub&gt;</th>
<th>P&lt;sub&gt;CO₂&lt;/sub&gt;</th>
<th>Q, cal/sec - n°</th>
<th>n&lt;sub&gt;T&lt;/sub&gt; moles</th>
<th>t* in seconds</th>
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<td>--;--;--</td>
</tr>
<tr>
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<td>3</td>
<td>0.804</td>
<td>2;4;8</td>
<td>--;--;--</td>
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<td>3</td>
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<td>10;15;25</td>
<td>22.7;34.;56.7</td>
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<td>11.4</td>
<td>2.08</td>
<td>2;4;8</td>
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<td>11.4</td>
<td>2.08</td>
<td>10;15;25</td>
<td>25.5;37.9;63.1</td>
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<td>11.4</td>
<td>2.08</td>
<td>20;40;60</td>
<td>30.2;60.5;90.7</td>
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<td>61</td>
<td>19.3</td>
<td>0.25;0.5;1.0</td>
<td>4.; 8.; 16.</td>
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<tr>
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<td>61</td>
<td>19.3</td>
<td>2; 4; 8</td>
<td>19.8; 39.6; 79.2</td>
</tr>
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<td>61</td>
<td>19.3</td>
<td>10; 15; 25</td>
<td>50.5; 75.7; 126.</td>
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<td>61</td>
<td>19.3</td>
<td>20; 40; 60</td>
<td>47.6; 95.2; 143.</td>
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</tbody>
</table>

\[
\frac{dT}{dt} + \frac{bT}{n^*} = \frac{ab}{n^*}; \quad T(°C) = a + [25-a] \exp(-bt/n^*_T); \quad UA = 0.5 \text{ cal/sec-°C} \\
t^* = \frac{-n^*_T}{b \ln(0.05a/(a-25))}
\]
Table 19 Summary of Model Predictions for Temperature-Time Excursions of a Breathing Air Mixture in Contact with KO₂

<table>
<thead>
<tr>
<th>Depth, feet</th>
<th>P&lt;sub&gt;water&lt;/sub&gt; mm Hg</th>
<th>P&lt;sub&gt;CO₂&lt;/sub&gt; mm Hg</th>
<th>Q, cal/sec</th>
<th>n&lt;sub&gt;T&lt;/sub&gt; moles</th>
<th>t* in seconds</th>
</tr>
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<td>3</td>
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<td>0.25; 0.5; 1.1</td>
<td>--; --; --</td>
</tr>
<tr>
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<td>3</td>
<td>0.804</td>
<td>2.4; 8</td>
<td>--; --; --</td>
</tr>
<tr>
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<td>3</td>
<td>0.804</td>
<td>10; 15; 25</td>
<td>--; --; --</td>
</tr>
<tr>
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<td>5</td>
<td>3</td>
<td>0.804</td>
<td>20; 40; 60</td>
<td>--; --; --</td>
</tr>
<tr>
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<td>11.4</td>
<td>2.08</td>
<td>0.25; 0.5; 1.1</td>
<td>--; --; --</td>
</tr>
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<td>11.4</td>
<td>2.08</td>
<td>2.4; 8</td>
<td>--; --; --</td>
</tr>
<tr>
<td>475</td>
<td>11.4</td>
<td>11.4</td>
<td>2.08</td>
<td>10; 15; 25</td>
<td>--; --; --</td>
</tr>
<tr>
<td>1000</td>
<td>11.4</td>
<td>11.4</td>
<td>2.08</td>
<td>20; 40; 60</td>
<td>--; --; --</td>
</tr>
<tr>
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<td>61</td>
<td>19.3</td>
<td>0.25; 0.5; 1.0</td>
<td>1.8; 3.6; 7.2</td>
</tr>
<tr>
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<td>61</td>
<td>19.3</td>
<td>2.4; 8</td>
<td>9.9; 19.8; 39.6</td>
</tr>
<tr>
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<td>61</td>
<td>19.3</td>
<td>10; 15; 25</td>
<td>25.1; 37.6; 62.7</td>
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<tr>
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<td>61</td>
<td>19.3</td>
<td>20; 40; 60</td>
<td>34.9; 69.8; 105.</td>
</tr>
</tbody>
</table>

\[
\frac{dT}{dt} + \frac{bT}{n_T} = \frac{ab}{n_T} ; \quad T(°C) = a + [25-a]e^{-bt/n_T} ; \quad UA = 1.0 \text{ cal/sec-}°\text{C}
\]

\[
t^* = \frac{-n_T^*}{b \ln(0.05a/(a-25))}
\]
TABLE 20

Theoretical Oxygen Evolution Efficiencies for Superoxides

Evolution efficiencies are expressed as pounds of chemical needed to generate 1.87 pounds of oxygen per man day (24 hours). The quantity 1.87 pounds of oxygen is the requirement of one human being during a 24 hour day. These calculations are based on the stoichiometric equations to form the alkali metal hydroxide from the alkali metal superoxide.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pounds of Chemical Needed for Generating 1.87 pounds of Oxygen per man-day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Utilization of Chemical 100% 90% 80% 70% 60%</td>
</tr>
<tr>
<td>KO₂</td>
<td>5.5 6.2 6.9 7.9 9.2</td>
</tr>
<tr>
<td>NaO₂</td>
<td>4.3 4.8 5.4 6.1 7.1</td>
</tr>
</tbody>
</table>

TABLE 21

Theoretical CO₂ Scrubbing Efficiencies for Superoxides vs. Alkali Hydroxides.

Scrubbing Efficiencies are expressed as pounds of chemical needed to absorb 2.11 pounds of carbon dioxide per man day (24 hours). The quantity 2.11 pounds of carbon dioxide is equal to the production rate of one man in a 24 hour day. These calculations are based on the theoretical uptake of a stoichiometric amount of carbon dioxide to form the carbonate of the metal. To allow for incomplete utilization of the chemical, these tabular results are given for 70 to 100% utilization (complete reaction with the chemical.) Thus the pounds of potassium superoxide at 70% utilization (9.7 pounds of KO₂) may be compared to the pounds of sodalime at 100% efficiency needed for absorbing the 2.11 pounds of CO₂ (4.22 pounds of sodalime).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pounds of Chemical Needed for Absorbing 2.11 pounds of carbon dioxide per man day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Utilization 100% 90% 80% 70%</td>
</tr>
<tr>
<td>KO₂</td>
<td>6.8 7.5 8.5 9.7</td>
</tr>
<tr>
<td>Ca(O₂)₂</td>
<td>5.0 5.6 6.3 7.2</td>
</tr>
<tr>
<td>Sodalime¹</td>
<td>4.2 4.7 5.3 6.0</td>
</tr>
</tbody>
</table>

¹ Sodalime is a mixture of NaOH & CaOH
Table 22  Design Specifications for KO₂

Cannister

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumetric Flowrate</td>
<td>20 liters/minute</td>
</tr>
<tr>
<td>Average Gas Heat Capacity</td>
<td>5.4 cal/g-mole—°K</td>
</tr>
<tr>
<td>KO₂ Tablet Size</td>
<td>2-4 mesh</td>
</tr>
<tr>
<td>Cannister Inlet Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Exit Water Partial Pressure</td>
<td>1.9 mm Hg</td>
</tr>
<tr>
<td>Total pressure</td>
<td>1 atm.</td>
</tr>
<tr>
<td>Inlet O₂ Partial Pressure</td>
<td>0.0 Hg</td>
</tr>
</tbody>
</table>
Table 24  Comparison of Cannister Predictions with Large Chamber Data of Kunard & Rodgers

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Q 1/min</th>
<th>([\text{H}_2\text{O}])</th>
<th>([\text{CO}_2])</th>
<th>Weight of (\text{K}_2\text{O}_3), grams</th>
<th>Water Absorbed, g</th>
<th>(O_2) Evolved, moles</th>
<th>Test Length, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>440</td>
<td>6.9 E-4</td>
<td>6.1 E-4</td>
<td>1816</td>
<td>2424</td>
<td>162</td>
<td>181</td>
</tr>
<tr>
<td>10(\checkmark)</td>
<td>308</td>
<td>9.3 E-4</td>
<td>6.1 E-4</td>
<td>1816</td>
<td>2276</td>
<td>173</td>
<td>175</td>
</tr>
<tr>
<td>20(\checkmark)</td>
<td>60</td>
<td>1.0 E-3</td>
<td>6.1 E-4</td>
<td>1989</td>
<td>2002</td>
<td>72</td>
<td>170</td>
</tr>
<tr>
<td>13 A</td>
<td>117</td>
<td>1.6 E-3</td>
<td>6.1 E-4</td>
<td>4540</td>
<td>5205</td>
<td>477</td>
<td>896</td>
</tr>
<tr>
<td>28</td>
<td>24</td>
<td>3.5 E-3</td>
<td>6.1 E-4</td>
<td>1802</td>
<td>1754</td>
<td>198</td>
<td>89.5</td>
</tr>
<tr>
<td>19</td>
<td>25</td>
<td>4.0 E-3</td>
<td>6.1 E-4</td>
<td>7945</td>
<td>7945</td>
<td>890</td>
<td>1256</td>
</tr>
</tbody>
</table>

Note: In these predictions the \([\text{CO}_2]\) was set at 6.1 E-4 M even the actual test conditions showed higher concentrations. The carbon dioxide order data would not allow an extrapolation to higher \(\text{CO}_2\) concentrations.

For all these tests the inlet temperature was set at 25°C in the model,
### TABLE 25 PREDICTED CANNISTER PRESSURE DROP

<table>
<thead>
<tr>
<th>Depth (ft.)</th>
<th>Gas Density (g/cm$^3$)</th>
<th>$\Delta P$ (in. H2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$3.7 \times 10^{-4}$</td>
<td>2.0</td>
</tr>
<tr>
<td>135</td>
<td>$6.9 \times 10^{-4}$</td>
<td>2.8</td>
</tr>
<tr>
<td>475</td>
<td>$1.4 \times 10^{-3}$</td>
<td>5.2</td>
</tr>
<tr>
<td>1000</td>
<td>$2.7 \times 10^{-3}$</td>
<td>8.0</td>
</tr>
</tbody>
</table>

### TABLE 26 RANGE OF EXPERIMENTAL VARIABLES

Pressure: 0 feet (1 atm.) to 1000 feet (30.5 atm.)

Temperature: 0°C to 50°C

Humidity: 5 mm Hg to 46 mm Hg (dewpoints: 32°F to 98°F)

Carbon Dioxide Partial Pressures: 3 mm Hg to 26 mm Hg

Oxygen Partial Pressures: about 160 mm Hg
REFERENCES


