

Oxygen Recovery Systems for Manned Space Flight

J. J. KONIKOFF

THE PROBLEM of supplying man with his oxygen requirement and uncontaminated air during prolonged confinement is receiving considerable research attention. In particular, the recovery of oxygen using biological specimens as the mechanism for converting carbon dioxide into oxygen plus other materials has been the subject of many papers recently.

There can be no doubt concerning the need for a regenerative system that will produce oxygen from man's respiratory wastes for space application. Any cursory examination of the weight involved in storing man's oxygen requirement, whether for long duration space flight or submarine submergence, reveals that after some point in time it becomes economically justifiable as well as operationally important to manufacture this necessary material *in situ*.

Of course, this premise also holds for water and food. Obviously any procedure that will permit the complete regeneration of man's needs from his wastes, resulting in a closed ecological system, will be most useful for space vehicles. However, present technology is limited insofar as means for the manufacture of food are concerned. Water can be recovered successfully, as has been demonstrated in an earlier paper.¹³ This paper is concerned with the purification of air and the regeneration of oxygen.

Problems to be Solved.—The major problem areas are:

1. Atmospheric purification: Because of the small sealed volume enclosed by a space vehicle or submarine or any other confined area, air

purification becomes an immediate and continuous problem. The air will be depleted of oxygen at a rate of about $1\frac{3}{4}$ pounds per man-day with an approximate equivalent mole quantity of water and carbon dioxide being formed in its place. In addition, certain noxious gases from flatus and body surface will be present. Body perspiration and sebaceous gland excretions will also enter the atmosphere and require removal. Considering carbon dioxide only, it can be shown by simple calculation that in a sealed volume of 100 cu. ft. per man the CO_2 content of the atmosphere will reach 3 per cent within three to four hours if no purification is attempted. Man's capability for useful work is seriously impaired at this value of CO_2 content.

2. Oxygen regeneration: The major difficulty associated with the storage of oxygen is the additional weight and volume of the containers. Because of oxygen's low boiling point, storage as a liquid requires good insulation while storage as a gas requires strong, heavy tanks. For extended trips of perhaps a month or longer, the $1\frac{3}{4}$ lb. per man-day requirement will become a substantial weight problem. It therefore becomes advantageous to recover oxygen from man's waste products for reuse. Used oxygen is found primarily in water and carbon dioxide. A lightweight, safe, and reliable system for regenerating oxygen from these sources is needed.

Current Status.—

1. The purification of the atmosphere is concerned with the control of three constituents, carbon dioxide, humidity and noxious gases and odors. In current practice for short term space flight, the CO_2 is removed by adsorption on a solid such as anhydrous lithium hydroxide. This method is satisfactory for relatively short

Presented at the Annual Meeting of the Aerospace Medical Association, Miami, Florida, May 11, 1960.

From the Missile and Space Vehicle Department, General Electric Company, Philadelphia, Pa.

term flight inasmuch as one pound of LiOH will adsorb 0.8 pounds of CO₂. Reuse of the desiccant becomes important as flight time increases if one considers the weight relationships involved. For example, on a daily basis, man produces about 2.0 lb. of CO₂; to absorb this quantity requires about 2.5 lb. of LiOH. In this manner, for a thirty-day flight, a total of 75 lb. of LiOH are required in addition to the container weight. If it becomes necessary to remove the CO₂ from the LiOH in order that the hydroxide may be reused, a high temperature is required. The lithium carbonate formed is decomposed at a temperature of 1200° F.

Submarine practice is advanced in that the newer type of vessels use a system in which the CO₂ is removed by monoethanolamine which is then freed of CO₂ by heating to a moderate temperature and is thus ready for reuse. This is an application of a regeneration system and is advantageous primarily because of the extended submergence periods modern nuclear powered submarines can maintain.

Another possible approach to the regeneration system is through the use of a molecular sieve. This material is now under study and shows promise because little energy is required for its regeneration. Heating to a temperature of 95°C will suffice at one atmosphere. At reduced pressures, a lower temperature is required although it has been shown that some heat is necessary even at pressures of 15 mm. Hg in order that all of the CO₂ be driven off.²

Humidity has been controlled by means of one of several methods. Freeze and dew point condensation techniques have proven feasible and, in the case of condensation, valuable in submarine applications. This technique is applicable in space use, because of the need for a cabin air conditioner which furnishes the cold surface necessary for the condensation to take place. A second approach is through the use of a desiccant such as lithium chloride or silica gel. The use of LiCl appears suitable for regeneration purposes since water can be recovered by heating the material to 300°F.

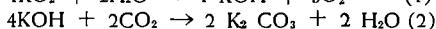
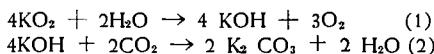
The use of activated charcoal for the removal of odorous material from the air appears quite feasible since mass requirements are small.

2. The problem of obtaining oxygen from man's metabolic wastes has received considerable attention in recent years. Primary emphasis has been on the approach that utilizes the photosynthetic ability of chlorophyll-containing plants to synthesize food and oxygen from carbon dioxide and water in the presence of sunlight, or other light in the visible region of the spectrum. Several excellent reports are available concerning the results of studies using algae as the photosynthetic device.^{1,4,17,18} Basically, a seemingly ideal relationship may be formed between a man and an algal plant. The algae will absorb the CO₂ expired by man and with water and the proper energy input (light in the visible spectrum) produce a carbohydrate plus oxygen, using chlorophyll as a catalyst. The carbohydrate is used by the plant whereas the oxygen is, of course, needed by man. It has been estimated that 2.2 kilograms of algae will support the O₂ requirements for one man.¹⁷ Although this value is probably subject to revision downward, one must remember that a quantity of water, amounting to from twenty times, to perhaps 100 times the weight of algae must be added to the over-all system weight. In addition, a fundamental problem has arisen concerning the non-equivalence of the CO₂/O₂ production rate (the respiratory quotient (R.Q.) for animal and the assimilatory quotient (A.Q.) for plants.) It has been found that the A.Q. for algae, although an apparent function of its nitrogen source, is lower than the R.Q. for animals. Hence, an oxygen overproduction results which enriches the atmosphere if left without adequate controls. However, in spite of this difficulty, it is quite obvious that the algae can support animal life by converting carbon dioxide into oxygen to meet the animal's oxygen requirement. Still, many other problems exist that require a solution prior to its widespread acceptance and use as a source of oxygen for space flight. Weight, volume, and

energy input requirements are quite high if lamps are the light source as currently contemplated. Another extremely important point that must be resolved is the reliability of a biological system. This point must be investigated before a realistic evaluation can be made. To date, little has been done in this particular area.

A second approach toward obtaining an adequate supply of oxygen using regeneration methods makes use of inorganic chemistry.

The use of potassium superoxide is attractive for this purpose since this material will react with the moisture in the air to produce oxygen and an hydroxide which will react with the CO₂ in the air, forming a carbonate:



This reaction is currently under study by several agencies. One point that requires further investigation before this system is completely acceptable is the difference in the oxygen production rate and the CO₂ consumption rate. These values do not balance with the R.Q. of man (Chemical R.Q. = 0.67, Man R.Q. = 0.82). Hence, an inhibitor or other means, i.e., mechanical bleed, etc., must be built into the system to equate the two quotients. This approach, strictly speaking, cannot be considered a regenerative method because the superoxide must be prestored in quantities proportioned to flight time. Weight estimates of a system embodying this technique indicate that the approach, while an improvement over the basic prestorage method, does not compete with regenerative techniques utilizing man's wastes as the raw materials.

Studies concerning the possibility of obtaining oxygen from carbon dioxide have also received attention. Konikoff¹² and Foster and McNulty⁸ have examined this problem and came to the same conclusion; namely, the hydrogen reactions with carbon dioxide are potentially important and, with proper care, recovery of essentially all of the oxygen contained in the carbon dioxide can be accomplished.

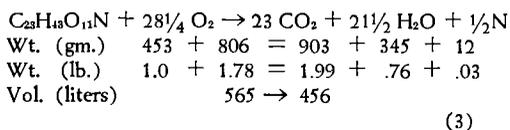
Improved Techniques.—The approach considered here is based upon the fact that man's intake of water and oxygen is equaled by his output of these materials, although they may be in another form. Of great importance and difficulty are the techniques of collection and processing that are required so that these materials, normally referred to as metabolic wastes, may be presented to him in a form suitable for his ingestion and inhalation.

As a basis for the statement made previously concerning the equivalence of man's input and output, consider first his metabolic process. Assuming that a daily diet totaling K cal. and composed of

- 52 per cent carbohydrate (glucose—C₆H₁₂O₆)
- 32 per cent fat (palmitin—C₃₁H₆₄O₆)
- 16 per cent protein (meat—C_{2.1}H_{6.4}O_{1.4}N)

is suitable, then the weight of this dehydrated food becomes 454 gm. (1 lb.) per day. By simple manipulation, a hypothetical food molecule may be derived from this combination of C-H-O-N. This food molecule has the form of C₂₃H₄₃O₁₁N.

The trace elements, i.e., S, Fe, I, P, etc., have been ignored in this analysis, since their total weight is small in comparison with that of any of the major constituents. Since the process of metabolism is basically one of oxidation (combustion), we may write equation 3 from which we obtain the stoichiometric O₂ requirement and also the quantity of CO₂ and H₂O produced.



$$\text{R.Q.} = \frac{\text{CO}_2 (\text{Vol})}{\text{O}_2 (\text{Vol})} = \frac{456}{565} = 0.81$$

The 903 gm. of CO₂ contain $\left[\frac{32}{44} \times 903 \right]$

gm. of O₂ or 656 gm. and 345 gm. of H₂O contain 306 gm. of O₂. Therefore, if it is possible to extract all the oxygen contained in

these two waste materials, a total of 962 gm. of O_2 are made available for respiration. This quantity is greater than the required amount (806 gm. derived from equation 3 because some of the oxygen from the food is converted to CO_2 and H_2O and hence recovered.)

It should be pointed out at this time that the above analysis is simplified and is, at best, an approximation of the complicated process involved in human metabolism.

For example, it can be argued that a waste molecule ($C_mH_nO_2N$) should appear in place of the N in equation 3. However, the effect of this molecule on the O_2 uptake and CO_2 production is negligible in this approximate analysis.

This hypothetical reaction does serve to indicate the general chemical reactions involved and, with a fair degree of accuracy, reports on the required quantities.

Air Purification.—Since the CO_2 and H_2O are the sole sources of oxygen, the first task in this study—the removal and collection of these contaminants from the expired air—becomes evident. By passing the air over a purification train consisting of a suitable desiccant or freeze trap for water removal and then through a molecular sieve, diethanolamine scrubber, or other suitable means for CO_2 removal, this task can be resolved with no major problems. A "suitable" desiccant is one which will permit regeneration with a reasonably low energy input. In addition, the energy input should be of a rather low-grade form. For example, the use of LiOH for CO_2 absorption is quite attractive because, weight-wise, the relationship is roughly 1 to 1. However, to recover the carbon monoxide from the carbonate is a difficult task requiring initially a temperature of about $600^\circ C$ in order that the Li_2CO_3 be reduced to Li_2O which must then be hydrolyzed to form LiOH. A question exists as to the feasibility of such a procedure.

On the other hand, the use of a molecular sieve, while not as efficient a collector, requires energy at a temperature of only about $95^\circ C$ for regeneration and hence appears more desirable

than the LiOH system since the energy requirements should be kept to a minimum. In addition, the regeneration process is relatively simple. More recent work has indicated the feasibility of the removal of CO_2 from a molecular sieve by means of vacuum technology. Early results² show that the CO_2 can be recovered by applying moderate vacuum to the sieve (15 to 20 mm. Hg) while maintaining the sieve at or near normal room temperature ($15^\circ C$). The use of an activated charcoal bed appears suitable as a means for the removal of odors.

Oxygen Recovery from Water.—Once the CO_2 and H_2O have been recovered from the contaminated air, the extraction of O_2 from these materials can begin. The most direct method for the recovery of O_2 from H_2O is by electrolysis.

The decomposition of water by electrolysis is a process that has long been understood and practiced. Since pure water is a poor conductor, some substance is usually added to increase conductivity. In practice, a dilute solution of sulfuric acid or sodium or potassium hydroxide is usually employed.

Theoretically, the decomposition proceeds as follows:



This shows that an expenditure of 136.5 K calories is required to obtain one mol. (22.4 liters at S.T.P.) of O_2 . Hence, since 565 liters are required per man per day, the total energy requirement becomes 3445 K cal./manday. This assumes complete conversion. Using a standard laboratory type electrolysis cell (Hoffman type, Cenco improved Electrolysis apparatus, model 81240) and H_2SO_4 as the electrolyte, it was found that an energy input of 24.8 K cal./l. of O_2 was required indicating an efficiency of 24.6 per cent.

Use has been made of a General Electric fuel cell that combines O_2 and H_2 to produce energy, water being the by-product.²⁰ This cell is unique in that it contains a hydrophilic resin

membrane containing a molecularly anchored, ionically active functional group as the electrolyte. This permits an essentially self-regulating action. Thus, water is automatically rejected from the resin as it is formed in the cell reaction. In addition, the electrolyte cannot be leached from the membrane by the water. Reversing the action of this ion-exchange solid-membrane electrolytic fuel cell results in an electrolysis cell having these advantages:

1. Since the electrolyte is incorporated in the membrane, pure water may be decomposed by electrolysis with no additional substance required to improve conductivity.

2. The membrane also serves as a dividing wall for the O_2 and H_2 chambers.

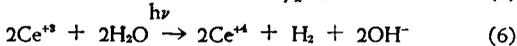
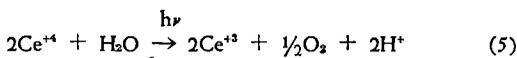
3. Energy input is considerably below that of the laboratory model cell reported upon above. Test data yielded a value of 8.14 K cal./l. of O_2 resulting in an efficiency of 74.9 per cent.⁸

Using the efficiency value cited above the total energy requirement shown previously now becomes 4600 K cal./man-day.

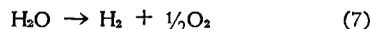
Although the decomposition of water by electrolysis is a simple and well understood phenomenon, it has a requirement for a high grade energy input. Admittedly, solar energy is available in space; however, the conversion of this energy into electricity is a relatively inefficient process. With the present techniques an efficiency of 10 per cent can be expected at best. Thus this approach is relatively costly.

Another method for recovering O_2 from water involves the photo-decomposition of water. It is an intriguing problem made important by possible space application because of the abundance of solar irradiation in space. The major problem is to find a catalyst that will be capable of sensitizing the decomposition in a more energetically abundant region of the solar spectrum. This is necessary because water is transparent down to about 1800 Å. Heidt⁹ has demonstrated that a photosensitized decomposition of water takes place in perchloric acid solutions of cerous

and ceric perchlorates. The reaction scheme may be as follows:

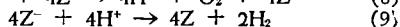
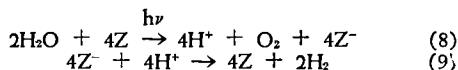


Net reaction:

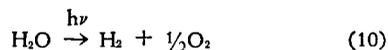


This reaction was studied at the 2537 Å line of a high intensity mercury arc. In direct sunlight, the reaction has a very low efficiency. After several days' illumination in sunlight, a formation of about 10^{-8} moles of hydrogen was collected.

Still another approach to the photodecomposition of water concerns the Hill Reaction.¹⁰ This is the photo-oxidation which occurs in nature whereby the photolysis of water by chloroplasts in the presence of some electron acceptor Z results in the formation of H_2 and O_2 . The reactions are:



Net reaction:

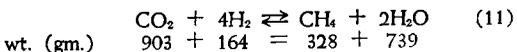


In laboratory study of this reaction, the electron acceptor most frequently used is ferricyanide. The reduction of ferricyanide to ferrocyanide is exergonic, hence the light energy used to energize the reaction is not stored but lost. Thus, the over-all efficiency is quite low.

Oxygen Recovery from CO_2 .—

1. Fischer-Tropsch Synthesis: The direct removal of O_2 from CO_2 presents a more difficult problem. It is well known that the decomposition of CO_2 into C and O_2 under usual conditions requires an extremely high energy input, and yields are quite low.

Therefore, it becomes desirable to find another manner in which the O_2 can be recovered. One logical approach would be to reduce the CO_2 to a form from which it is relatively easy to recover O_2 . The Fischer-Tropsch synthesis is such a reaction and is shown in equation 11.



OXYGEN RECOVERY SYSTEMS—KONIKOFF

This reaction is feasible and is certainly a desirable one since all of the O₂ is removed from the CO₂ and converted into water. By electrolysis, a total of 656 gm. of O₂ (462 liters) is obtained.

An interesting by-product in equation 13 is solid carbon which, under proper conditions, may be activated in the presence of hydrogen.

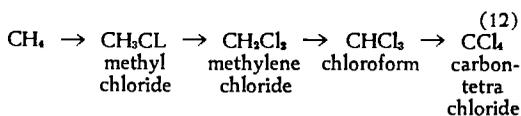
It should be pointed out at this time that the reactions shown above (equations 11 to 14,

TABLE I. THE HEAT OF REACTION FOR THE REACTIONS OF EQUATIONS 11 AND 15 AND THE FREE ENERGY AS A FUNCTION OF TEMPERATURE

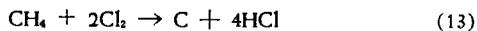
Reaction	Temperature							
	H, K-Cal.				F° K-Cal. (approx)			
	0°C	127	227°C	327°C	0°C	127°C	227°C	327°C
Equation 11	-39.4	-40.6	-41.8	-42.8	-28	-22	-19	-12
Equation 15	-9.8	-9.7	-9.5	-9.3	-8	-7	-6.5	-5.0

The methanation reaction shown in equation 11 is strongly exothermic. In fact, this entire series of Fischer-Tropsch reactions involving H₂ and CO₂ or CO (equation 15) are exothermic. Table I lists the heats of reaction for the reaction of equations 11 and 15 and also the free energy as a function of temperature.⁷

The second product formed by this reaction, methane, appears to be quite useful in an overall system concept for several reasons: (a) It is a fuel having a caloric value of 1067 Btu/cu. ft. and, hence, could be useful as a secondary energy source. (b) When methane is treated with chlorine, its hydrogen is replaced step by step in the production of useful chlorinated hydrocarbons:



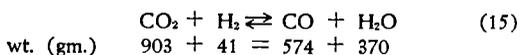
or by treating with hydrogen, acetylene (C₂H₂) is formed, which can then be treated to yield acetic acid. There are many other reactions which will yield useful products resulting from the treatment of methane. Thus, an interesting *in situ* regenerating plant may result. (c) Methane may be treated with chlorine to yield hydrochloric acid which, upon decomposition, releases hydrogen. In this manner there is no loss of this element.



inclusive) concerned with the further treatment of the by-product CH₄ are not easily accomplished. Considerable experimental work is required before they can be applied. Also of interest is the recovery, for reuse, of the chlorine.

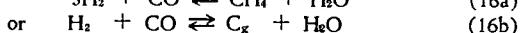
Of course, a final suggestion is to collect the methane, and dump it overboard.

2. Reverse Water-Gas Reaction: A second approach, reverse water-gas shift reaction, is somewhat similar to the Fischer-Tropsch synthesis. The major difference is that the CO₂ is initially reduced to CO only. Thus, only one atom of O₂ is recovered for each molecule of O₂ in the CO₂.



It is easily seen, comparing this reaction with that of equation 11, that just one-half of the water is produced. This reaction must take place at elevated temperatures. At temperatures below 800°C the equilibrium very much favors the reactant side.²² At a temperature of 1500°C over an iron chromate catalyst, however, the equilibrium has shifted so that about 60 per cent of the CO₂ is removed in a single pass.

In order that the remainder of the O₂ be recovered, it is necessary to treat the CO formed in equation 15. Many possibilities exist. The most direct appears to be the hydrogenation of carbon monoxide:



The water is then electrolyzed, yielding the required O_2 .

These reactions^{7,22} have been carefully studied. As mentioned earlier, both reactions are greatly exothermic and heat must be removed. Table II shows data for reaction of methane. It proceeds best at lower temperatures with a decreasing value for the equilibrium constant as the temperature increases.

3. Other CO_2 Hydrogenation Methods: Still a third attractive reaction between CO_2 and H_2 is:

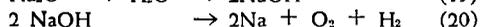
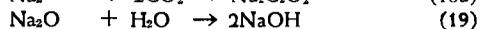
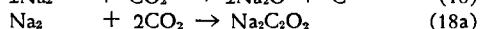
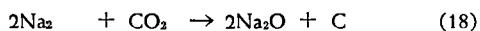


This reaction, while theoretically feasible, requires further study in order that it may be more fully understood.

TABLE II. REACTIONS OF METHANE

Temperature °C	K _{eq}
27	24.677
227	10.060
427	3.571

4. Alkali Metal Reactions: An interesting, and possibly useful technique for CO_2 reduction is that concerning the reaction of the alkali with CO_2 . For example, using sodium, the theoretical yields are high and energy inputs are reasonably low.



The actual yield of the oxide formed in equation 18 approaches 98 per cent.¹⁵ Expected conditions for the reaction would be a temperature of under $300^\circ C$. Although the speed of the reaction is known, previous work has indicated it is not impractical from the time sense. After the formation of the oxide, it is combined with H_2O (equation 19) forming sodium hydroxide. The electrolysis of $NaOH$ is a commercial process which, for many years, has been carried out in the Castner Cell.¹¹ The process is quite simple and proceeds as shown in

equation 20 where $NaOH$ at $320^\circ C$. is fed at a current density of 2.0 amps/cm² with a current efficiency of 80 per cent. Cell voltage of 8V gives a high yield.²¹ During electrolysis of the $NaOH$, the actual reactions are:



The water diffuses to the cathode and is decomposed to H_2 and $NaOH$. It is estimated that a yield of 50 per cent per pass is feasible.

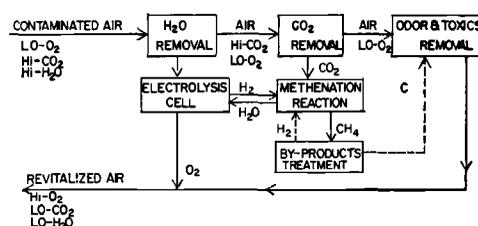


Fig. 1. Schematic flow diagram for Fischer-Tropsch synthesis for oxygen recovery.

Equation 18a shows the reaction involving the other two per cent of the total input in equation 18. The sodium oxalate may be treated to eventually yield the metal (Na) and CO which can then be recycled or it may be discarded.

Another interesting product of this reaction is carbon. Equation 18 shows that an appreciable quantity of C is formed, amounting to $(12/44 \times 1.99 \times .98) = 0.52$ lbs. per day, approximately. Reactivating this solid carbon in the presence of hydrogen may be possible, hence permitting a further step toward a closed ecology.

Figure 1 is a schematic flow diagram illustrating the inter-relationship of the methanation reaction (equation 11). By simple substitution of the water-gas reaction (equation 15) in its appropriate place, the diagram still holds. The block marked "By-product Treatment" may include any of the reactions shown in equations 12, 13, 14, 16a and 16b. Figure 2 illustrates the alkali metal reaction.

5. Decomposition of CO_2 at High Temperatures and/or Reduced Pressures: Another approach that is of possible interest is a thermal

decomposition method as expressed by the equilibrium reaction:



This reaction has been reported in the literature by Nernst and Von Wartenberg¹⁹ and

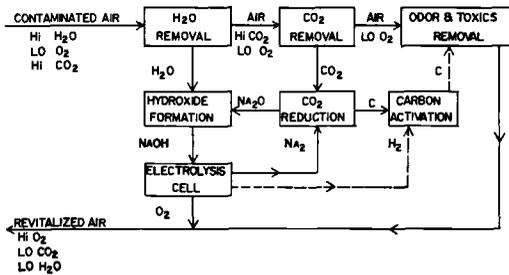


Fig. 2. Schematic flow diagram illustrating alkali reduction of carbon dioxide for oxygen recovery.

by Langmuir.¹⁴ The former have demonstrated that high yields can be attained by passing CO₂ through a heated zone at reduced pressures. Ordinarily, the decomposition of CO₂ by the application of high temperature is quite low; at 2000° C. less than 2 per cent of the CO₂ is decomposed. However, by reducing the ambient pressure, the reaction is greatly accelerated toward completion. Their results show the following per cent of decomposition per pass as a function of pressure at a temperature of 2500° C.

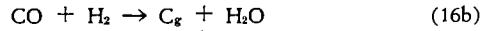
Pressure, atm.	10.00	1.00	0.10	0.01
CO ₂ decomposition, per cent	7.08	15.80	30.70	53.00

Langmuir also studied this reaction using a somewhat different experimental technique. He passed the CO₂ at atmospheric pressure over a small diameter platinum wire uniformly heated over its entire length of about 31 cm. His results indicated a very strong dependence of the decomposition rate upon the temperature, particularly at the higher values as seen in Table III.

It can be seen that at 3000° (abs.) 48.5 per cent decomposition can be attained at atmospheric pressure. An interesting conjecture con-

cerns the possible decomposition rate when both high temperatures and low pressures are used.

Pursuing this general approach appears promising since the other product, CO, can be further acted upon either to go to C and H₂O or CO₂. These reactions are (theoretically):



Equation 22 would require Fe₃C as a catalyst. It is of interest to note that the carbon deposited out speeds the catalytic reaction. This reaction (equation 22) proceeds at a rather low temperature (450° C.) for the maximum yield of CO₂.

TABLE III. TEMPERATURE AND CARBON DIOXIDE DECOMPOSITION RATE

Temperature Absolute	CO ₂ Decomposition Per Cent
1000	2.0 x 10 ⁻⁵
1500	4.36 x 10 ⁻²
2000	1.84
2200	5.00
2500	15.6
3000	48.5

6. Photo-chemical Decomposition of CO₂: Over the years investigators have periodically published experimental data concerned with the decomposition of CO₂ in ultraviolet light. Cline and Forbes⁶ describe their experiments in which CO₂, purified from water vapor and saturated with mercury vapor, was rapidly decomposed when radiation at wave length of 1840 Å was admitted. Quantum yields of 0.8 were realized. Jucker and Rideal¹⁰ also reported on the photo-decomposition of CO₂. These workers used Xenon 1470 Å radiation and found quantum efficiencies of 1.9. In both studies, the decomposition reaction was:



In the case of the mercury vapor saturation, the O₂ reacted with the Hg and formed yellow mercuric oxide.

Unfortunately, this over-all approach, while scientifically feasible, is primarily one of low

efficiency. In fact, it appears that any reaction of the type described above is inherently inefficient and hence may not prove suitable for space flight where energy utilization is of paramount importance.

DISCUSSION

The several techniques described above are but a few of the many approaches available for the removal of oxygen from carbon dioxide. They do, however, represent a sample of each method having a high probability of success. Each approach is attractive from at least one point of view.

The Fischer-Tropsch synthesis (equation 11) is a member of a family of reactions that has been carefully studied (information is available on the energy, catalysts, temperatures and pressure requirements, etc.). The fact that the reaction will proceed at a pressure of one atmosphere is advantageous. Yields are high and the by-product, CH_4 , is useful should the requirement exist insofar as utilization of all waste.

To a great extent, the reverse water-gas shift reaction (equation 15) has attributes similar to the Fischer-Tropsch synthesis. The point of departure, however, is the fact that only one half of the O_2 is removed in the reaction. Hence, the by-product, CO , must be decomposed in order that the necessary O_2 requirement can be met. Fortunately, many reactions are feasible for the extraction of O_2 from CO , although some may not be direct. However, as shown in equations 16a and 16b, the CO can be effectively decomposed.

The hydrogenation reaction shown in equation 17 is an interesting one and should be the subject of additional study. Some data concerning this reaction are available in the overall wealth of information concerning the Fischer-Tropsch reactions.^{8,22}

The reactions of the alkali metals are of interest primarily because of the large body of data available concerning the electrolysis of the eutectic mixture of the carbonates, i.e., Li_2CO_3 or the hydroxide, NaOH . Unfortunately, while

these reactions may result in the release of sufficient O_2 gas, the fundamental premise of a complete independence of prestored materials for O_2 supply is not met by this technique. The alkali metal in sufficient quantities for a specified voyage must be initially stored.

The direct decomposition of CO_2 is usually considered to be a difficult reaction because of the energy requirements. While this is still a valid objection, the description of the techniques of Nernst, Von Wartenberg and Langmuir are scientifically intriguing and should be subjected to continued study. The results, showing 50 or more per cent dissociation per pass, are a remarkable achievement. It would be interesting to examine this reaction under the combined action of high temperature, platinum wire catalyst, and reduced pressure.

The photochemical decomposition of CO_2 falls into the category of the previous technique. By nature, it is a low efficiency reaction with present knowledge; of utmost importance here would be the discovery of a photocatalyzer which would upgrade the reaction and energy utilization.

Another important factor in the discussion of the several techniques that require attention is the energy requirement. Obviously, at present, it becomes mandatory to specify a technique which will use the minimum quantity of energy. In addition, the technique should use energy in a form most easily obtained. For example, if thermal energy is required, the sun is an excellent source and merely using a lens or concentrator (parabolic reflector) will permit almost a 100 per cent conversion efficiency. Should the required energy be in the electrical form however, a serious loss due to conversion efficiency is immediately noted if we wish to utilize the sun as our source of energy. Here, using available solar cells, a conversion efficiency of 10 per cent is available with the possibility that perhaps 12 per cent cells may shortly become available.

Each of the techniques described earlier requires energy. Also, each requires both the thermal and electrical forms.

OXYGEN RECOVERY SYSTEMS—KONIKOFF

Table IV is a listing of the computed energy requirements of these techniques. The total energy is obtained by determining any or all of the heats of formation, reactions, decompositions, electrolysis, etc., that are necessary in

ture control. The total energy shown, 9916 K cal./man-day, is a reasonable value considering a photosynthetic efficiency of 25 per cent. It should be pointed out that this energy value is a realistic appraisal based on empirical

TABLE IV. COMPUTED RANKING TECHNIQUES FOR THE RECOVERY OF OXYGEN FROM CARBON DIOXIDE

Technique	Theoretical Energy Requirements			Complexity Factor	Ranking
	Remove O ₂ From CO ₂ K-Cal./Man-Day	Obtain O ₂ Gas K-Cal./Man-Day	Total K-Cal./Man-Day		
Fischer-Tropsch synthesis	-874	4600	3726	1	1
Reverse water gas reaction	-1402	4600	3198	2	2
Hydrogenation	-880	4600	3720	2	3
Decomposition	1390	1250	2640	2	3
Alkali metal reaction	-3633	18000	9370	3	4
Photosynthetic gas exchange		—	9916	—	—

order that the end product be oxygen in a sufficient quantity for one man per day as determined by equation 3. Since the reactions generally remove the oxygen molecule from CO₂ and combine it with hydrogen, forming water, the energy computations are twofold. First is the amount of energy added or extracted from the reaction (endothermic or exothermic) and second, the electric energy required to electrolyze the H₂O. The total energy is simply the algebraic sum. Practically, this is difficult to justify since it is unrealistic to presume that all of the heat generated in the exothermic reactions will be recovered and reused elsewhere. However, for the intended use, it is acceptable since we are interested in ranking the techniques based upon these analytical considerations only.

Such a ranking also includes an estimate of the complexity of the process. For example, the Fischer-Tropsch synthesis will theoretically remove all of the O₂ from the CO₂ in one reaction whereas the reverse water-gas shift reaction requires two steps. Hence, the former reaction rates higher from a complexity point of view.

Also shown on the table are the energy requirements for an algal plant using the *Chlorella* strain grown under typical laboratory conditions of artificial light, proper nutrient and tempera-

data whereas the other values are based on theory only. Thus, it is probable that these other energy values will, by necessity, have to be revised upward by factors of perhaps 3 or more as experimental data are made available. Hence, it is not to be misconstrued from this tabulation that the photosynthetic gas exchange system requires considerably greater energy input than do physiochemical techniques. At this time, more information is required before valid evaluation can be made.

Inasmuch as the major premise regarding the utilization of a regenerative system for O₂ supply is weight savings, an estimate was made of the system weight of four different methods for supplying a man with oxygen during space flight. These methods are: (a) Open cycle (pre-storage), (b) Superoxide supply system, (c) Liquid oxygen supply system and (d) Regenerative system (Fischer-Tropsch synthesis).

The assumptions for each are the same and are:

- O₂ required1.78 lb./day/man
- CO₂ produced1.99 lb./day/man
- H₂O produced0.76 lb./day/man
- Odor removed by 1.0 lb. of activated charcoal.

Detailed specifications are on a daily basis for one man:

Open cycle—1. CO₂ and H₂O are absorbed

OXYGEN RECOVERY SYSTEMS—KONIKOFF

on LiOH and LiCl respectively. Required quantities are 2.5 lb. of LiOH and 1.30 lb. of LiCl. Container weight is estimated to be 2.5 per cent. 2. Liquid oxygen supplies O₂ and weighs 2.85 lbs./daily requirement.

Superoxide system (see equations 1 and 2)—
1. CO₂ and H₂O are used by the KO₂ for the production of O₂. Theoretical yields assumed, hence 5.26 lb. of KO₂ are required which will use 1.43 lb. of CO₂ eventually. Hence, 0.74 lb. of LiOH is required for the remaining 0.56 lb. of CO₂.

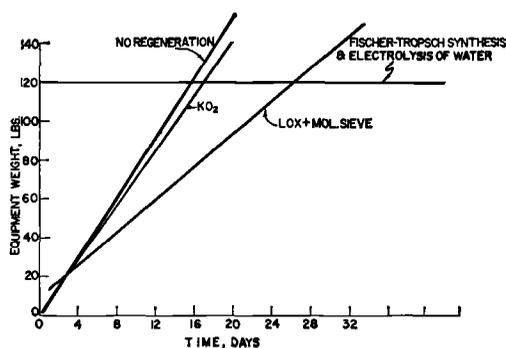


Fig. 3. Estimated breakpoint in oxygen supply systems.

LOX and regenerative CO₂ adsorber—1. CO₂ will be adsorbed on a molecular sieve system which will be regenerated hourly. Thus a total of 9.00 lb. of sieve material including spare cannister and valving is required. H₂O will be adsorbed as before in the open cycle method. 2. O₂ will be supplied as before (see open cycle method).

Regenerating system—1. The Fischer-Tropsch synthesis (equation 11) will be used and the tubing, etc., will weigh about 35 lb. 2. CO₂ will be adsorbed on a molecular sieve (see LOX and regenerative CO₂ adsorber method). 3. H₂O will be adsorbed and regenerated by heat from LiCl, or a freeze trap weighing about 1.5 lb. total. 4. H₂O will be electrolyzed by a fuel cell and, including required solar cells, the system will weigh about 85 lb.

Figure 3 presents this information. It shows the equipment weight as a function of flight time. It can be seen that a regenerative system utilizing the Fischer-Tropsch synthesis will be

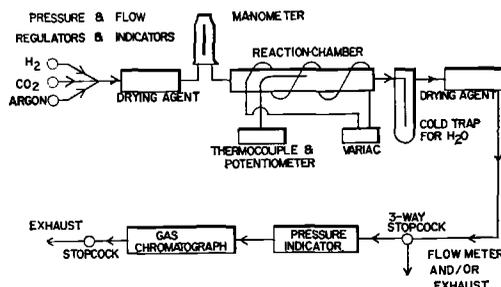


Fig. 4. Schematic flow diagram of the experimental apparatus for the reaction: $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$.

more desirable, from a weight standpoint, after a flight time of twenty-six days or perhaps, one man-month.

Since these results indicate the desirability of using the Fischer-Tropsch synthesis for oxygen recovery, an experimental program is currently underway to verify its feasibility. Figure 4 is a diagram showing schematically the experimental apparatus.

ACKNOWLEDGMENTS

The author wishes to acknowledge the many important contributions made by his associates at the Space Sciences Laboratory, in particular Dr. T. K. Slawewski, M. H. Bengson, I. Brustman, and L. Lyford.

REFERENCES

1. BASSHAM, J. A.: Use of Controlled Photosynthesis for Maintenance of Gaseous Environment. University of California Report UCRL-2707, Sept., 1954.
2. BENGSON, M. G. and KONIKOFF, J. J.: Unpublished data. G.E. MSVD, Sept., 1959.
3. BRUSTMAN, I., LYFORD, L. and KONIKOFF, J. J.: Unpublished data. G.E. MSVD, Jan., 1960.
4. BURK, D., HOBBY, G. and GAUCHER, T.: Closed Cycle Air Purification with Algae, presented at International Symposium on Submarine and Space Medicine, New London, Conn., Sept., 1958.
5. CALVERT, J. G.: The utilization of the solar energy through photochemical reactions. *Ohio J. Sci.*, 53:293, 1953.

OXYGEN RECOVERY SYSTEMS—KONIKOFF

6. CLINE, J. E. and FORBES, G. S.: Mercury-sensitized decomposition in light of λ 1849 Å I. Carbon dioxide. *J. Amer. Chem. Soc.*, 61:716, 1939.
7. EMMITT, P. H.: *Catalysis*—New York: Reinhold Publishing Co., 1956.
8. FOSTER, J. F. and McNULTY, J. S.: Report on Literature Survey for CO₂ Reduction Systems. Battele Memorial Institute, Columbus, Ohio, July 31, 1959.
9. HEIDT, L. J. and McMILLAN, A. F.: Influence of perchloric acid and cerous perchlorate upon the photochemical oxidation of cerous to ceric perchlorate in dilute aqueous perchloric acid. *J. Am. Chem. Soc.*, 76:2135, 1954.
10. JUCKER, H. and RIDEAL, E. K.: Photodecomposition of carbon dioxide and of ammonia by Xenon 1470 Å radiations. *J. Chem. Soc.*, 79: 1058, 1957. (London)
11. KIRK, R. E. and OTHMER, D. F.: *Encyclopedia of Chemical Technology*. Vol. I. New York: Interscience Publishing Co., 1952.
12. KONIKOFF, J. J.: A Partially Closed Cycle Life Support System for Long Term Space Flight—4th Symposium on Ballistic Missile and Space Technology, Los Angeles, California, Aug., 1959. Also G.E. MSVD Report TIS R59SD443, Oct., 1959.
13. KONIKOFF, J. J. and BENGSON, M. H.: Recovery of Potable Water from Man's Metabolic Wastes—137th National Meeting, A.C.S., Cleveland, Ohio, April 12, 1960. Also G.E. MSVD Rpt. TIS R60SD341, March, 1960.
14. LANGMUIR, IRVING: The dissociation of water vapor and carbon dioxide at high temperatures. *J. Amer. Chem. Soc.*, 28:1357, 1906.
15. LEMARCHANDS, M. and ROMAN, H. L.: Action of anhydrides on metals. *Compt. Rend.*, 192: 1381-3, 1931.
16. MARCUS, R. J.: Photochemical Conversion Reactions and the Storage of Energy as Hydrogen. Transactions of the Conference on the Use of Solar Energy—Vol. IV. Tuscon, Arizona: The University of Arizona Press, 1958.
17. MYERS, J.: Basic Remarks on the Use of Plants as Biological Gas Exchangers in a Closed System. *J. Aviation Med.*, 25:407, 1954.
18. MYERS, J.: Study of Photosynthetic Gas Exchange as a Method of Providing for the Respiratory Requirements of a Human in a Sealed Cabin. USAF SAM Publ. 58-117, Nov., 1958.
19. NERNST, W. and VON WARTENBERG, H. V.: The dissociation of carbon dioxide. *Z. Physikal Chem.*, 56:548, 1906.
20. NIEDRACH, L. W.: The Ion Exchange Membrane Fuel Cell. 13th Power Sources Conf., Atlantic City, N. J., April 28-30, 1959.
21. POTTER, E. C.: *Electrochemistry*. New York: Macmillan Publishing Co., 1956.
22. STORCH, H. H., GOLUMBIC, N. and ANDERSON, R. G.: *The Fischer-Tropsch and Related Synthesis*, New York: John Wiley and Sons, Inc., 1951.

Food and Absorption of Vitamin B₁₂

D. J. DELLER, M.B., H. GERMAR, M.D., and L. J. WITTS, M.D.
Radcliffe Infirmary, Oxford, England. *Lancet*, 1:574-577, 1961

Administration of a fasting dose of radioactive vitamin B₁₂ is not a reliable method of determining absorption of the vitamin in patients with partial gastrectomy. When the test dose is given with a meal free of vitamin B₁₂, absorption of the vitamin is significantly enhanced. In partial gastrectomy patients with grossly subnormal absorption, the effect of food sometimes is comparable to that of intrinsic factor. Doses of vitamin B₁₂ labeled with cobalt 58 were given under fasting conditions and with food to patients with partial gastrectomy or pernicious anemia and to healthy persons. Absorption was enhanced by food in the partial gastrectomy group only.—*Modern Medicine*, 1961.