Oxygen Recovery by the Catalytic Dissociation of Carbon Dioxide

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IN A PREVIOUS paper,[1] the problems concerned with oxygen recovery systems for manned space flight were examined. A procedure was described which led to the purification of the atmosphere and at the same time, permitted the two major atmospheric contaminents, CO_2 and H_2O, to be collected for further use as warranted. It was suggested that the oxygen content of the entrapped water become available by the process of electrolysis. The remainder of the paper concerned itself with methods for the recovery of O_2 from CO_2. Although many techniques were mentioned, six were described in detail. These six include:

1. Fischer-Tropsch synthesis
2. Reverse water-gas reaction
3. Other hydrogenation reactions
4. Alkali-metal reactions
5. Photochemical decomposition
6. Thermal dissociation at reduced pressure

A ranking of these techniques was presented, using a set of arbitrary criteria which inferred the superiority of the Fischer-Tropsch synthesis. However, additional work recently completed has reversed this ranking, placing thermal dissociation at reduced pressures at the top of the list. This present report presents the justification for this decision.

THEORETICAL ANALYSIS

The computed ranking established in the previous paper was based upon two major con-

siderations: (a) energy requirement and (b) complexity.

The energy requirement is computed as the total theoretical energy input needed to recover the full O_2 content contained in 903g. of CO_2 (a value approximately equal to one man's normal daily gas exchange rate based on a respiratory quotient of 0.81). This results in a total theoretical yield of 656g. O_2 which is equal to about 81 per cent of the daily O_2 required by man.

The theoretical electrical energy required to decompose one gram mole of CO_2 into carbon and oxygen is given by the equation:

$$CO_{2(g)} \longrightarrow C_{(s)} + O_{2\,(g)}$$

for which 94,030 cals are required; thus, to produce 32g. of O_2 requires 94,030 cals. The total stripping of O_2 from CO_2 requires 1930K cal or 2.2Kwh.

Complexity is derived from the number of reactions necessary to completely strip O_2 from CO_2. Additionally, the requirement is placed upon each process wherein all materials needed for the reaction are obtained by regenerative methods.

With these criteria established, the following equations indicate the major reaction and the necessary sub-reactions required to obtain all useful components.

Fischer-Tropsch synthesis   (1)
(a) $CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$
(b) $2H_2O \longrightarrow 2H_2 + O_2$
(c) $CH_4 \xrightarrow{\text{cat.}} C + 2H_2$
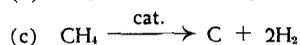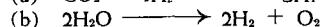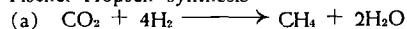
Reverse water-gas shift reaction   (2)
(a) $CO_2 + H_2 \longrightarrow CO + H_2O$
(b) $2H_2O \longrightarrow 2H_2 + O_2$
(c) $2CO \xrightarrow{Fe_3C} C + CO_2$
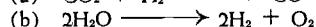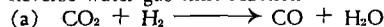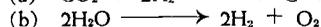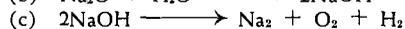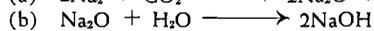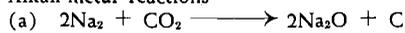
Hydrogenation   (3)
(a) $CO_2 + 2H_2 \longrightarrow C + 2H_2O$
(b) $2H_2O \longrightarrow 2H_2 + O_2$

Alkali-metal reactions (4)
(a) $2Na_2 + CO_2 \longrightarrow 2Na_2O + C$
(b) $Na_2O + H_2O \longrightarrow 2NaOH$
(c) $2NaOH \longrightarrow Na_2 + O_2 + H_2$

Photochemical decomposition (5)
(a) $2CO_2 \longrightarrow 2CO + O_2$
(b) $2CO \xrightarrow{Fe_3C} C + CO_2$

Thermal dissociation at reduced pressure (6)
(a) $2CO_2 \longrightarrow 2CO + O_2$
(b) $2CO \xrightarrow{Fe_3C} C + CO_2$
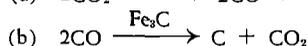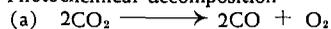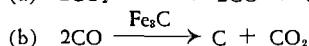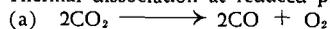
The first three techniques are all essentially hydrogenation reactions. The basic requirements include H_2, CO_2, and a catalyst, Fe, Ni, or Pt. By judicious selection of the catalyst and the thermal energy level, various carbon compounds are formed in addition to water. Basically, water is the desirable product since, by electrolysis, O_2 is obtained for breathing purposes. Hydrogen, the second product of the electrolysis, is also needed to continue the basic hydrogenation of the CO_2. This is a basic drawback because of the need for a high-grade energy source (electricity) for electrolysis. The second product of the basic reaction, CH_4 or CO or C, respectively, also require treatment since, with the exception of carbon, these materials cannot be discarded because they contain H_2 and/or O_2. Thus, means must be found for their complete recovery. In the Fischer-Tropsch synthesis the methane produced as a by-product necessitates further treatment to make available the hydrogen required for the basic reaction. The decomposition of methane requires a large energy input at high temperatures ($\approx 1400°C$). As a result, the total energy input is high because of the two decompositions required.

The reverse water-gas reaction basically requires a high temperature (1500°C) before the equilibrium shifts in the direction of the reaction arrow. In addition, electrolysis of the water formed increases the energy input requirement. The third reaction, hydrogenation, suffers from a lack of clearly defined products shown in the equation (3a). Consequently, to regenerate all materials completely for re-use is difficult.

The alkali-metal reaction, although interesting, also suffers from the need for a great input of electrical energy needed for the electrolysis of the hydroxide as shown in equation 4c.

The photochemical decomposition also suffers from high energy input requirements in addition to low yields. It appears that until a photocatalyst is discovered which will greatly enhance the quantum yield, this approach cannot be considered as being in the same state as the others.

The final reaction shown, thermal dissociation, appears desirable because it bypasses several of the objections of the other techniques. For example:

1. It does not require the electrolysis of H_2O.

2. The other product formed is easily treated to result in a more amenable material.

3. It does not require reactants to reduce the CO_2.

This reaction will proceed with a yield approaching 50 per cent per pass if the proper catalyst is heated to elevated temperatures. In addition, reducing the ambient pressure has been found to increase the degree of dissociation. This reaction results in the production of gaseous oxygen and carbon monoxide. Obviously, since the oxygen is already in the form which may be immediately used by man, this technique is more desirable than a reaction in which the oxygen is obtained only after a further decomposition of some by-product, for example, water.

Table I presents the computed ranking of these techniques. Based upon energy requirements, the thermal dissociation is first. Considering complexity only, hydrogenation, photochemical, and dissociation share first place, although the photochemical reduction is still in the realm of theory only.

DISCUSSION

The selection of the dissociation reactions for oxygen recovery is predicated upon the low

energy requirement, the rather low complexity, and the fact that the reaction proceeds well at reduced pressures. The basic experimental

ture. Table III, after Langmuir, demonstrates this relationship.

Bjerrum[4] also studied the dissociation of car-

TABLE I. COMPUTED RANKING

Technique	THEORETICAL ENERGY REQUIREMENTS					
	(1) Remove O_2 from CO_2 K cal/man day	(2) Obtain O_2 gas K cal/man day	(3) Total K cal/man day	(4) Efficiency (1) Percent	(5) Complexity Factor	(6) Ranking
Dissociation	1390	1250	2640	73.0	1	1
Fischer Tropsch Synthesis	-874	4600	3726	51.8	2	2
Reverse Water Gas Shift	-1402	4600	3198	60.5	2	3
Hydrogenation	-880	4600	3720	51.8	1	2
Alkali Metal Reaction	-3633	13000	9370	20.6	4	4
Photochemical Decomposition	1390	1250	2640	73.0	1	5

(1) Computed by $\dfrac{1930 \text{ K cal}}{\text{col (3) K cal}} \times 100$

TABLE II

Pressure (Atm.)	Percent of Dissociation of CO_2
10.00	7.08
1.00	15.80
0.10	30.70
0.01	53.00

TABLE III

Temperature, °K	Percent of Dissociation of CO_2
1000	2.0×10^{-5}
1500	4.36×10^{-2}
2000	1.84
2500	15.60
3000	48.50

TABLE IV

Temperature, °K	Per cent of Dissociation of CO_2		
	at 0.1 atm.	at 1.0 atm.	at 10 atm.
1000	5.3×10^{-5}	2.5×10^{-5}	1.1×10^{-5}
1500	0.1040	0.0483	0.0224
2000	4.35	2.05	0.960
2500	33.5	17.6	8.63
3000	77.1	54.8	32.2
3500	93.7	83.2	63.4
5000	99.6	98.7	96.1

work has been reported in literature by Nernst and Von Wartenberg[2] and by Langmuir.[3] The former have demonstrated that high yields may be obtained by passing carbon dioxide through a heated zone at reduced pressures. Ordinarily, the dissociation of carbon dioxide by application of high temperatures is quite low; however, by reducing the ambient pressure, the reaction is greatly accelerated towards completion. Their results show the per cent of dissociation per pass as a function of pressure at a temperature of 2500°K (Table II).

Langmuir also studied this reaction, using a somewhat different experimental technique. He passed the CO_2 (at atmospheric pressure) over a small diameter platinum wire uniformly heated over its entire length of about 37 centimeters. His results also indicated a very strong dependence of decomposition rate upon tempera-

bon dioxide at very high temperatures and arrived at an empirical equation in which the degree of dissociation can be computed as a function of pressure and temperature. Using this equation, dissociations of greater than 50 per cent may be obtained at reaction pressures on the order of one-tenth of an atmosphere. The temperatures for this reaction are between 2500°K and 3000°K. Table IV, derived from Bjerrum's empirical equation, demonstrates the pressure dependence.

Further analysis of this process illustrates its apparent desirability for space utilization. Speculatively, it appears that in practice the

Pursuing this approach further appears promising since the other product, carbon monoxide, can be treated in a straightforward

$$2\,CO_2 \longrightarrow 2\,CO + O_2 \qquad (1)$$

$$903g \;=\; 575g + 328g$$

$$2\,CO \longrightarrow C \;+\; CO_2 \qquad (2)$$
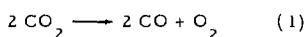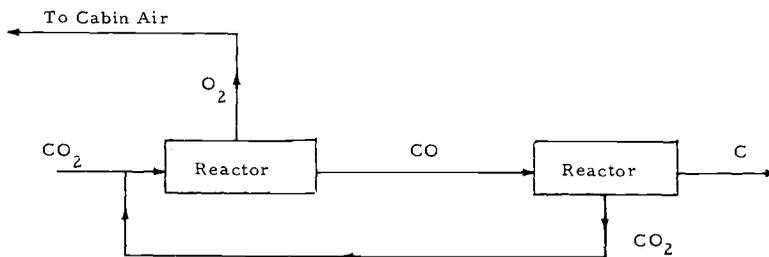
$$575g \;=\; 123g + 452g$$

Fig. 1. Schematic flow diagram of thermal dissociation at reduced pressure.

system be connected to the space vacuum in order that the system pressure be reduced to a value which will yield a high degree of dissociation at a reasonable temperature level.

The fundamental reaction has been studied, using pure platinum for the catalyst. This material melts at $2032°K$; thus, the practical operating temperature for this material is perhaps $1700°K$. At atmospheric pressure, the percent dissociation is about 0.8. However, at 0.1 atm. this value becomes 1.7 or two times as great.

Thus it becomes important to investigate further the dissociation as a function of pressure. Of course, it is also important to obtain a material which will act as a catalyst for this reaction and still remain solid at temperatures greater than $2000°K$. Some possible candidates and their melting points are:

TABLE V

Tungsten	$3643°K$
Ruthenium	$2763°K$
Rhodium	$2223°K$
Osmium	$2963°K$
Iridium	$2706°K$

fashion to obtain carbon and water or carbon dioxide. These reactions are:

$$CO + H_2 \longrightarrow C + H_2O \qquad (7)$$

$$2CO \xrightarrow{\;Fe_3C\;} C + CO_2 \qquad (8)$$
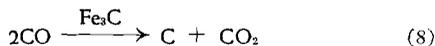
Reaction 7, in which the monoxide reacts with hydrogen to form carbon and water, is a relatively simple and well known reaction and would result in the need for the electrolysis of water so that the oxygen is made available. However, the advantage to this would be that the hydrogen, also made free by the electrolysis, could be re-used in the basic carbon monoxide reaction.

The reaction shown in equation 8 requires a Fe_3C catalyst. The reaction proceeds at approximately $450°C$ for a maximum yield of carbon dioxide. (It is of interest to note that the carbon deposited out during this reaction speeds the catalystic reaction.) Once the carbon dioxide is obtained, it is then passed back into the original reaction chamber for dissociation.

This latter reaction appears desirable since the over-all energy required is considerably re-

duced by the complete elimination of the process of electrolysis.

Figure 1 is a schematic flow diagram illustrating a desired pathway for this process.

The freeze point of CO_2 is $-78°C.$, $CO = -199°C$ and $O_2 = -183°C$. Thus, by chilling the product gas flow below $-78°C$ but higher than $-183°C$, the CO_2 can be simply removed.

MOLECULAR SIEVE TYPE 4A
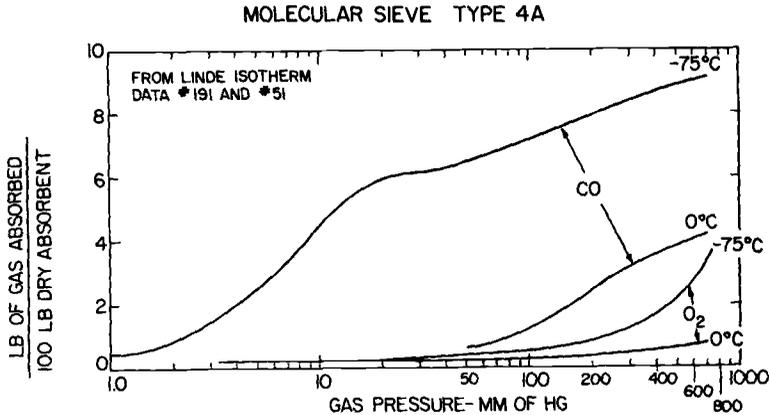
Fig. 2. Molecular sieve Type 4A.

PROBLEMS TO BE SOLVED

Several problems exist before this technique may be considered suitable for space flight. Initially, the investigation must include studies of the catalytic activity of various high temperature materials. It is obvious that the proper combination of pressure and temperature will result in the optimum yield of CO and O_2 per pass. If complete reliance is placed on the low pressure effects at the expense of temperature, then the gas through-put (flow velocity) is greatly restricted because of the need to maintain a reduced pressure. The reverse is also a poor approach because of the difficulties that result when materials are stressed by maintaining them at temperatures approaching their melting points.

A second problem that will require resolution involves the separation of the products. As a result of the reaction, CO, O_2 and CO_2 will be produced. The CO_2 must be collected and piped back to the reaction chamber. The CO must also be collected so that it can be further operated upon. The O_2 should be piped into the cabin air supply. The separation of CO and O_2 presents some difficulties whereas the removal of the CO_2 is relatively simple.

A Linde type 4A molecular sieve appears suitable for a partial separation of the remaining two gases. Figure 2 plots the adsorption data for CO and O_2 at $0°C$, $-75°C$ (CO) and $-80°C$ (O_2). It can be seen that the sieve will adsorb about ten times as much CO as O_2 at the lower temperature (this temperature is fortuitously about the same as the freeze point of carbon dioxide). A simple computation indicates that if 575g. (1.269 lbs.) of CO are produced per day then 18.5 lbs. of M.S. material are required for adsorption. This quantity of sieve will adsorb 33.6g. (0.074 lbs.) of O_2 per day. Since the total O_2 content of the CO_2 is 656g. (1.48 lbs.) this is roughly equivalent to a five per cent loss of oxygen per day.

Another separation approach that requires investigation is the reaction of CO and water which result in the formation of formic acid:

$$CO + H_2 \longrightarrow HCOOH \qquad (9)$$

The formic acid may then be dehydrated by the action of concentrated sulfuric acid or ferro cyanide thus recovering the CO.

FUTURE WORK

As the result of the revised ranking shown on Table I, it appears that the recovery of O_2

from CO_2 may most efficiently be affected by a process of thermal dissociation at a reduced pressure. To this end a research program is presently underway to determine maximum yields, optimization of over-all operating efficiencies, studies of carbon monoxide reduction methods, and gas separation techniques. Additionally, the application of this technique to space flight is of overriding importance. As such, the utilization of the space environment (solar energy, vacuum) will be integrated into the final results.

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