Oxygen Chemisorption Compressor Study for Cryogenic Joule-Thomson Refrigeration

Jack A. Jones* and Gary D. Blue*
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

Over 20 potentially reversible heat-powered oxide reactions have been studied and/or tested to determine potential use as thermochemical oxygen compressors for cryogenic Joule-Thomson (J-T) LO_2 refrigerators. One gas-solid compound family, $Pr_{1-n}Ce_nO_x$, proved to be completely reversible with fast kinetics for all pressure ranges tested below 650°C. With a heat-powered charcoal/methane physical adsorption upper stage and a $Pr_{1-n}Ce_nO_x$ chemisorption lower stage, temperatures should be attainable in the 55–80 K range for less power and over five times less weight than for charcoal/nitrogen sorption refrigeration systems. Total system power requirements with a hydride chemisorption lower stage (10–7 K minimum) are about three times less than *any* mechanical refrigerator, and spacecraft refrigeration weights are about 20 times less. Due to the lack of wear-related moving parts in sorption refrigerators, life expectancy is at least 10 years, and there is essentially no vibration.

Introduction

SORPTION refrigeration systems have no moving parts, other than very long-life check valves, and thus could eventually have a potential lifetime of decades operating with virtually no vibration. Sorption compressor systems operate by physically or chemically sorbing low-pressure gas to solids at various temperatures. When the gas-solid combinations are heated an additional 100–200°C, the gas becomes greatly pressurized and is vented from the solid. The high-pressure gas is then precooled and expanded through a Joule-Thomson (J-T) valve, where the gas is partially liquefied. The liquid is boiled by absorbing heat from electronics, e.g., infrared detectors, and the resulting low-pressure gas is eventually reabsorbed by the solid sorbent.

The most well-known sorption refrigeration system was first developed in the Netherlands in 1972[1] and later developed and endurance-tested at the Jet Propulsion Laboratory (JPL).[2] For this system, which is shown in Fig. 1, low-pressure hydrogen is chemically absorbed into $LaNi_5$ at about room temperature. When heated to 100°C, the hydrogen is pressurized from 1 to 40 atm and then vented. After being precooled with LN_2 at 80 K, the high-pressure hydrogen is expanded to 1 atm at 20 K. The precooling at about 80 K is necessary in order for the hydrogen to be significantly below its inversion temperature of about 200 K and thus provide significant refrigeration when expanded. If a high-pressure gas is expanded when it is *above* its inversion temperature, *heating* will actually occur instead of cooling.

Before this present study, the only known means to obtain sorption refrigeration in the 80 K range was by physically adsorbing nitrogen to charcoal at temperatures of about 225 K.[3] Unfortunately, this type of physical adsorption requires relatively large amounts of power that have to be rejected by a radiator at 225 K. The resulting radiator sizes for most Earth-orbital missions are extremely large and often impractical. In order to improve upon the relatively large power requirements and low heat rejection temperatures of physical adsorption systems, a search for chemical absorption systems was initiated for F_2, CO, N_2, O_2, Ar, He, and Ne.

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*Member of Technical Staff, Mechanical and Chemical Systems Division.

Thermochemical Analysis

For the gas/solid combinations, the equilibrium vapor pressure of the gas with the solid is described by Fast.[4] According to Fast, the equilibrium pressure for chemical reactions of solids with a singular increase in oxide (or fluoride, nitride, etc.) level can be represented by

$$\log P = 2x\left(\frac{\Delta H^\circ_{298} - \Delta G^\circ_{298}}{4.576 \times 298} - \frac{\Delta H}{4.576 \times T}\right)$$

where P is the gas pressure (atm), ΔH°_{298} the enthalpy of the solid at 298 K (cal/deg mole), ΔG°_{298} the Gibbs free energy of the solid at 298 K (cal/deg mole), and T the gas-solid equilibrium temperature (K).

By thoroughly examining these values for many thousands of possible gas-solid reactions,[5–16] a number of conclusions have been drawn regarding the feasibility of using certain gases as chemisorption compressors. Gas-liquid reactions have not been studied due to the difficulty of residual multicomponent vapor freezeout in the J-T circuit and zero-g separation problems.

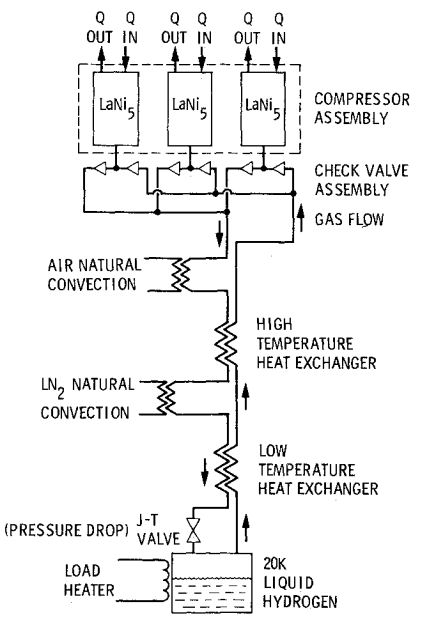

Fig. 1 $LaNi_5$ hydride sorption refrigerator schematic.

An upper temperature limit of 650°C has been assumed, as the strength of high-temperature alloys, e.g., inconel, decreases rapidly above this temperature.[17] Inconel has a 50,000-h yield strength of 50 ksi at this temperature and can last many hundreds of thousands of hours at 25-ksi pressure. All compressors sized for this study assume a maximum oxide compressor stress of 12.5 ksi.

It should be noted that the following preliminary conclusions are drawn based entirely on thermodynamic considerations of the bases examined. In order to confirm long-term gas-solid reversible kinetic behavior for any particular system, actual tests would be required under pressure and temperature conditions similar to those expected during operation.

The study shows that the inert gases, Ar, He, and Ne, can provide sorption refrigeration with physical adsorption only. Unfortunately, fluorides and nitrides tend to have binding energies that are too high to provide reversible chemisorption in the temperature range of interest (below 650°C for materials strength purposes).

Compounds that form with carbon monoxide (CO), i.e., carbonyls, have a somewhat different problem, however. Many carbonyls are liquid or gas at room temperature, e.g., $Ni(CO)_4$, and most carbonyls have binding energies that are too high. Unfortunately, the carbon-oxygen bond is such that if the binding energy of the CO molecule to a solid is low enough, the CO tends to pick up an extra oxygen atom and desorb as CO_2.[18] A classic example of this is the platinum catalysis of CO to CO_2 in automobile exhaust systems. Primarily because of this fact, there are no reversible carbonyls that will suffice for the chemisorption behavior sought in our particular ranges of interest.

The only gas, other than hydrogen, that was found to potentially form reversible chemical compounds applicable for our proposed use was oxygen. A listing of some potential oxide reactions discussed in the following sections include:

$$3\,F-CoSaEnO_x + 1/2\,O_2 = 3\,F-CoSaEnO_{x+1}$$

(fluomine cobalt chelate)

$$2\,Ag + 1/2\,O_2 = Ag_2O$$

$$Li_2O + 1/2\,O_2 = Li_2O_2$$

$$Na_2O + 1/2\,O_2 = Na_2O_2$$

$$K_2O_2 + 1/2\,O_2 = K_2O_3$$

$$K_2O_3 + 1/2\,O_2 = K_2O_4$$

$$Rb_2O + 1/2\,O_2 = Rb_2O_2$$

$$Cs_2O + 1/2\,O_2 = Cs_2O_2$$

$$BeO + 1/2\,O_2 = BeO_2$$

$$MgO + 1/2\,O_2 = MgO_2$$

$$CaO + 1/2\,O_2 = CaO_2$$

$$SrO + 1/2\,O_2 = SrO_2$$

$$BaO + 1/2\,O_2 = BaO_2$$

$$Sc_2O_2 + 1/2\,O_2 = Sc_2O_3$$

$$Y_2O_2 + 1/2\,O_2 = Y_2O_3$$

$$La_2O_2 + 1/2\,O_2 = La_2O_3$$

$$CuCrO_3 + 1/2\,O_2 = CuCrO_4$$

$$SrCrO_3 + 1/2\,O_2 = SrCrO_4$$

$$V_2O_4 + 1/2\,O_2 = V_2O_3$$

$$PbO + 1/2\,O_2 = PbO_2$$

$$Pr_6O_{11} + 1/2\,O_2 = Pr_6O_{12}$$

$$Ce_6O_{11} + 1/2\,O_2 = Ce_6O_{12}$$

$$Pr_{1-n}Ce_nO_x + y/2\,O_2 = Pr_{1-n}Ce_nO_{x+y}$$

A NASA patent is pending on the overall oxide compressor refrigeration process.[19]

Test Hardware

Some of the oxides listed in the previous section were eliminated as a result of an extensive literature search of previous testing. Most of the oxides, however, were eventually tested at JPL by using a Dupont Model 951 Thermo-Gravimetric-Analyzer (TGA) instrument in order to determine basic low-pressure reversibility (1-atm maximum). The TGA consists of a quartz beam microbalance that can detect very small changes in weight as a function of temperature.

A few of the most promising oxide reactions were then tested in a specially fabricated high-temperature/high-pressure vessel system. The sorbent was placed in an inconel tube and heated by a radiant heater. As the temperature was increased from 20 to 700°C maximum, the corresponding pressure was measured. Complete isotherm data could be taken as a function of oxygen loading by "burping" a small amount of oxygen into a control volume, as measured by another pressure transducer. All temperature and pressure data were recorded on a Fluke 2285 Data Logger.

Oxide Chemisorption Study Results

Cobalt Chelates

Cobalt chelate oxide has been used extensively for high-altitude fighter aircraft oxygen recirculation.[20] The cabin air is circulated over the chelate, wherein the oxygen is chemically absorbed. The carbon dioxide is then exhausted overboard, and the chelate oxide is heated. The desorbed oxygen is then pumped back to the pilots for rebreathing. The system can be used for up to 300 h and is considerably lighter than bringing aboard heavy, high-pressure oxygen bottles. Unfortunately, there is a noticeable degradation of absorption with time, and the absorptive capacity after 300 h is only about half as much as the original.[20,21] Thus, this compound was not considered for further testing.

Silver

One well-known, fully reversible oxygen reaction is disilver-oxide,

$$2\,Ag + 1/2\,O_2 = Ag_2O$$

This reaction is used in the important production of ethylene-oxide from ethylene and oxygen.[21] Ethylene and oxygen are mixed and forced over silver catalysts. The silver readily combines with the oxygen and then releases the oxygen atom to the ethylene, thus producing ethylene-oxide. The pressure-temperature characteristics are such that at about 450 K (177°C), the equilibrium vapor pressure of oxygen with silver is about 0.3 atm. At this pressure, high temperatures produce Ag and O_2, while at lower temperatures, the entire stoichiometric mixture becomes Ag_2O.[22] The reaction, however, is strictly a surface reaction, as are most solid oxides. Thus, for large amounts of oxygen to react, very large silver surface areas are required.

By supporting silver on very high-surface area silicas or aluminas, silver surface areas as high as 100 m^2/g have been attained.[23,24] By heating (desorbing) and cooling (absorbing) a series of high-surface area silver canisters, it may then be possible to produce a continuous flow of high-pressure oxygen.

It should be noted, however, that repeated cycling of the silver/oxygen system has never been attempted at such high temperatures and pressures. In fact, there is reason to believe that sintering, or agglomeration, of the silver may occur to effectively reduce this surface area. Such sintering has occurred in somewhat lower-temperature tests conducted by Czanderna[25] and Presland et al.[26] Considerable success has recently been obtained by Geus[27] in producing high silver area catalysts with high sintering resistance. Geus has been able to produce silver catalysts that have a surface area of 50 m^2/g and that are resistant to sintering even at 800°C. Also, doping with certain alkaline earth compounds has proven to increase total oxygen reactivity and resistance to sintering.[22]

In order to further examine the silver-oxygen system, a high-surface area NH_4 Y zeolite was coated with a small amount of platinum and silver in a manner similar to Ref. 27. The resulting material, which has a 5% Pt loading and a 15.5% Ag loading (by x-ray diffraction analysis) was then placed in the TGA

apparatus and heated to 400°C to drive off all the oxygen. When cooled to 170°C, however, very little oxygen was reabsorbed. Somewhat larger amounts were absorbed at 100 and 50°C, however, and are more likely due to physical adsorption (well-known for zeolites) than chemical absorption. The actual amount adsorbed at 50°C is still far less than necessary for this high-void volume material to function as a chemisorption compressor for a J-T refrigerator.

Scanning electron microscope (SEM) analyses were performed on the before and after samples in order to determine if gross silver sintering resulted from heating to 400°C. The results show no gross difference in the before and after appearance, although submicroscopic changes may still have occurred (300 Å resolution).

An x-ray diffractometer pattern of the reduced zeolite showed a 20–25% reduction in the crystallinity of the zeolite, thus indicating some type of amorphous transition. That is, there may have been some basic submicroscopic breaking down of the zeolite structure.

Lithium

The lithium-oxide reaction, $Li_2O + 1/2\ O_2 = Li_2O_2$, is one of the most interesting due to its potentially very high usable oxygen loading capacity (35% by weight). Furthermore, Li_2O has a very high melting temperature (1843 K) and should thus be fairly resistant to sintering problems. Thermochemically, it should have an oxygen equilibrium pressure of 1 atm at 400 K and 100 atm at 525 K. It has been used for air regeneration by means of absorbing CO_2 and H_2O and then releasing oxygen,[28] but has never been used as an oxygen absorber directly.

For this chemical, both bulk and high-surface area compounds were tested. Although over 35% of the original material was liberated by heating, almost none was reabsorbed. Unfortunately, tests on the high-surface area lithium zeolite also showed very little reabsorbed oxygen when maintained at 100°C.

A further test was run for the bulk Li_2O_2 in the high-pressure apparatus. The oxygen was first driven off at 400°C and then held at 100°C and 7 atm pressure for 2 h. Very little oxygen was reabsorbed, even for this elevated pressure condition.

Sodium, Potassium, Rubidium, Cesium

No tests were performed on the $Na_2O + 1/2\ O_2 = Na_2O_2$ system, as the required temperature levels were above 700°C. The materials container strength and life become a major problem at high oxygen pressures when temperatures are above about 675°C.

Potassium, rubidium, and cesium, on the other hand, have oxygen equilibrium temperatures within reason. These chemicals were rejected because they all form low melting point oxides that are highly corrosive. A TGA test for Ce_2O_2 shows boiling occurring at about 950°C. The resulting fumes were so reactant that they reacted with portions of the TGA apparatus in the immediate vicinity, and several parts had to be replaced.

Berryllium, Magnesium, Calcium

Although these three compounds have oxygen equilibrium temperatures at 1 atm below 675°C, they are known not to form reversible oxides. Of these three, calcium should have the easiest reversibility due to its larger crystalline structure relative to oxygen, thus providing greater mobility. Tests on the calcium oxide system, however, showed that even after six days at 50 atm O_2 pressure and 100°C, less than 0.17% of CaO had reconverted to CaO_2.[29]

Strontium

Extensive testing has been performed on strontium oxide, as it has been shown by Mullhaupt and Stern[30,31] at Union Carbide to react reversibly for air separation purposes. Union Carbide has used this patented process to manufacture catalyzed (doped) SrO_2 such that it absorbs O_2 when air is passed over it at a temperature below 360°C. The nitrogen passes on through the powder, and when the powder is heated, it liberates the oxygen.

The equilibrium oxygen pressure for the system $SrO + 1/2\ O_2 = SrO_2$ is shown in Fig. 2. Oxygen can be absorbed at 1 atm at about 360°C and can be compressed to about 100 atm at about 650°C.

By adding small amounts of dopants such as Na, Co, Ag, and Ni to SrO_2, Mullhaupt and Stern were able to increase the rate of reformation of SrO_2 by over 500 fold. They relied heavily on small amounts of hydroxide formation, $Sr(OH)_2$, in order to expedite the oxygen reabsorption process. Differential scanning calorimetry (DSC) analysis at JPL revealed that the hydroxide melted at about 500°C. Unfortunately, this melting resulted in extensive sintering of the material. Mullhaupt and Stern were able to operate their air separation system below 500°C and were thus able to avoid this problem, but in order to obtain the very large O_2 pressures required for efficient J-T expansion, SrO_2 temperatures of about 650°C are required.

It should also be mentioned that they found that even for temperatures below 500°C, the hydroxide eventually sublimed with extensive cycling and had to be replenished by adding trace amounts of water to the SrO_2. Over a period of 7000 cycles (approximately 7000 h), trace amounts of water were added 15 times in order to maintain high reaction speeds.

The SrO_2 powder manufactured by JPL produced results generally similar to those in Refs. 30 and 31, in that the oxygen was absorbed very well at 330°C and was vented quickly at 420°C. In the high-pressure apparatus, the equilibrium O_2 curve of Fig. 2 was confirmed from 1–10 atm, but extensive sintering resulted above this temperature. A second high-pressure SrO_2 canister was fabricated, and an attempt was made to completely remove the hydroxide components. With a high-vacuum bakeout at 10^{-7} Torr at 400°C for 3 h, it was concluded that most of the hydroxide component should have been removed. For extra margin, the canister was slowly heated to 700°C while maintaining the high vacuum. When cooled, however, the powder did not reabsorb oxygen, and postmortem analysis revealed that extensive sintering had again occurred. X-ray analysis of the residue revealed that about 60% of the residue was SrO and 17.7% was $Sr(OH)_2$, while the remainder was not identified. It is interesting to note that the hydroxide amounts measured before and after baking out remained essentially the same. It is possible, however, that the hydroxide could have been decomposed during the bakeout and then reformed during the brief x-ray analysis in air.

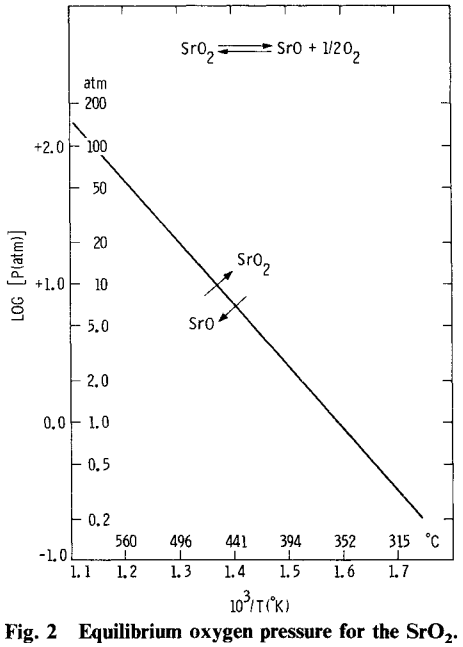

Fig. 2 Equilibrium oxygen pressure for the SrO_2.

Barium

The Brin process,[32] which utilizes the following reaction,

$$BaO + 1/2\ O_2 = BaO_2$$

was used commercially for air separation from about 1880 until it was displaced by the distillation of liquid air in the 1920's. Various chemical dopants have recently been found to enhance the formation of BaO_2 without changing the dissociation equilibrium pressures.[33]

Unfortunately, very high temperatures are required for the Brin process to work. For absorption at 1 atm pressure, temperatures of 800°C are required, and for desorption at 100 atm pressure, a temperature of about 1250°C is required. Unless materials are found that can operate under high pressure for long periods at these temperatures, barium will have to be bypassed for now.

Scandium, Yttrium, Lanthanum

Because of their larger crystal lattice sizes and thus greater oxygen mobility, both La_2O_3 and Y_2O_5 were tested in the TGA apparatus for oxide decomposition. Unfortunately, less than 0.5% of the oxides decomposed during both runs, and this family of oxides was thus eliminated.

Copper Chromate, Strontium Chromate, Vanadium

All three of these chemicals have reportedly been used for air separation,[34] and thus TGA tests were run to ascertain their potential uses. Both the copper chromate and V_2O_5 resulted in liquid phase production at the higher temperatures and had to be eliminated due to likely sintering and/or caustic reaction problems.

The strontium chromate, however, had no apparent phase change and resulted in liberating about 2% of its weight. Unfortunately, attempts to reabsorb the oxygen resulted in less than 0.5% reabsorption.

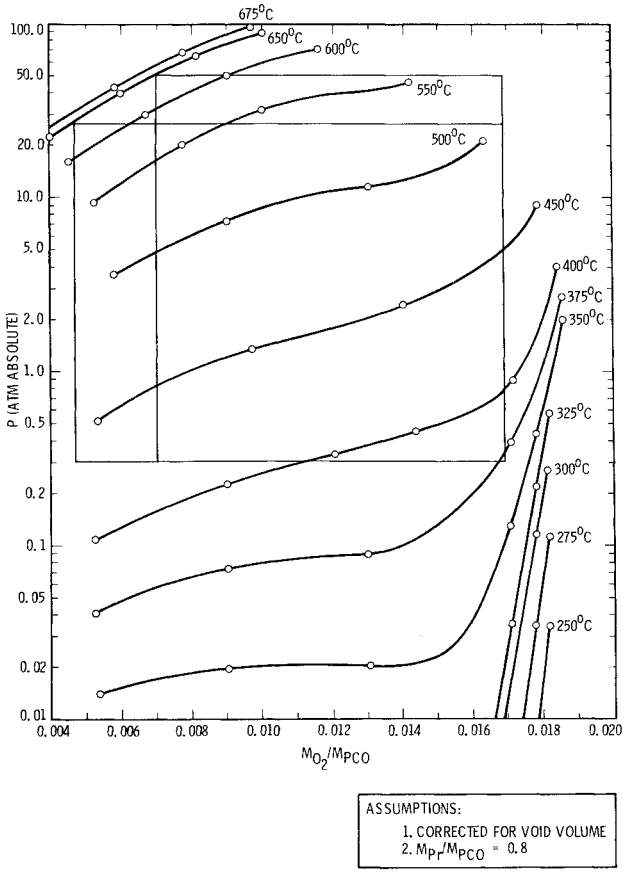

Fig. 3 $P_rC_eO_x$ (PCO) isotherms.

Lead

Lead is known to have numerous oxide levels. PbO and PbO_2 have equilibrium oxygen pressures of 1 atm at about 250°C and 100 atm at 520°C. Although PbO has a melting point of 886°C, Pb itself has a melting point of only 327°C. Thus, partial melting and/or sintering is highly likely if high temperatures and pressures are attempted. Furthermore, although heat can drive PbO_2 to form PbO, the reverse process is true only for surface molecules.

Praseodymium and Cerium

Neither praseodymium nor cerium by themselves appear to be a suitable oxide-sorbent material for oxide compression. The results of CeO_2 TGA decomposition show less than 0.5% decomposition followed by a relatively low-temperature meltdown (900°C). Pr_6O_{11}, on the other hand, has a much higher-temperature phase change, but has an equilibrium pressure of no greater than 160 mm at 900°C.[35]

Oxide solid solutions of both Pr and Ce together, however, have been found by Mullhaupt[35] to be most useful as oxygen carriers in a reversible cyclic oxidation-reduction process for separating oxygen from air. Mullhaupt did extensive work with this $Pr_{1-n}Ce_nO_x$ (PCO) compound and found that the adverse effects on redox rates of contaminants in the air such as CO_2 and/or H_2O are substantially eliminated by incorporating a surface dopant such as silver into the praseodymium-ceride oxide.

A large batch of PCO carbonate compound was made according to the Mullhaupt procedure. When cycled in the TGA apparatus, the compound indeed exhibited reversible oxide chemisorption of about 1% of its actual weight. Atomic absorption spectroscopy of the compound revealed that it consisted of the following metal percentages: 80.3% Pr and 19% Ce with 0.5% Ag.

Approximately 68 g of PCO material were hammer-pressed into a high-pressure inconel canister in order to minimize void volume. The resulting density, 3.5 g/cc, is about one-half of the parent material solid density. Unfortunately, the reaction kinetics of this pressed-powder geometry were extremely slow (about 2.5 h to reabsorb O_2), and it was found necessary to drill a small oxygen distribution hole down the length of the canister. After 8 g of PCO were removed (60 g remaining), the kinetics of absorption and desorption became extremely fast and seemed to follow almost instantaneously with temperature. A complete isotherm map of the PCO compound was made from 0.01–100 atm and from 250–650°C (Fig. 3). It should be mentioned that, according to Mullhaupt,[35] variations in the Pr/Ce atomic ratio will have noticeable effects on the overall isotherm results. Lower Pr/Ce ratios will move the isotherm to higher pressures and faster kinetics, while higher Pr/Ce ratios will do the opposite. Higher Pr/Ce ratios, however, will give greater oxygen loading.

Thermodynamics of $Pr_{1-n}Ce_nO_x$(PCO) Dissociation to O_2 (Gas)

Derived thermodynamic quantities for the dissociation of $Pr_{1-n}Ce_nO_x$ to gaseous O_2 plus oxide that is more oxygen-deficient may be obtained from the isotherm data in Fig. 3 by reading off P,T values in the range of 350–350°C for each of five chosen values of the ratio $m(O_2)/m(PCO)$. When this is done, the resulting plot of log $P(O)_2$ vs $1/T$ for a given $m(O_2)/m(PCO)$ ratio is found to approximate linear behavior closely enough so that $\Delta H°_{700}$ and $\Delta S°_{700}$ values may be obtained, respectively, from the slope and intercept of the least-squares-fit to each plot. Dissociation heats and entropies obtained in this way are given in Table 1. The values tabulated are in reasonable agreement with those that may be obtained in a similar manner as previously shown, from the limited isotherm data in Fig. 1 of the Mullhaupt patent.[35]

For ease of predictive computations, all of the isotherm data used for the previous calculations (for Table 1) were treated using the method of multivariate analysis; log $P(O_2)$ was taken

Table 1 Derived thermodynamic quantities from interpolated $Pr_{1-n}Ce_nO_x$ (PCO) isotherm data[a]

	$\Delta H°_{700}$ (Kcal/mole O_2)		$\Delta S°_{700}$ (cal/mole O_2-deg K)		log PO_2 (atm)
$m(O_2)/m(PCO)$	Value	Standard error	Value	Standard error	Standard error
0.008	35.472	±0.646	49.244	±0.922	±0.047478
0.010	36.983	±0.893	51.915	±1.274	±0.065585
0.012	38.127	±1.158	53.916	±1.653	±0.085067
0.014	38.741	±1.602	55.138	±2.287	±0.117703
0.016	36.965	±1.341	53.536	±1.914	±0.098521

[a] $\log PO_2(\text{atm}) = \frac{-\Delta H°_{700}}{4.576} \times \frac{1000}{T(\text{K})} + \frac{\Delta S°_{700}}{4.576}$.

Table 2 Coefficients of multiple linear regression fit to $Pr_{1-n}Ce_nO_x$ (PCO) isotherm data[a]

Regression coefficient	3-term fit[b,c]		4-term fit[d]	
	Value	Standard error	Value	Standard error
$A(0)$	10.86348	±0.18143	4.01101	±1.78838
$A(1)$	−8.14199	±0.11769	1.67446	±2.55498
$A(2)$	0	—	−3.48207	±0.90566
$A(3)$	55.33335	±5.71068	55.33335	±4.64658

[a] $\log PO_2(\text{atm}) = A(0) + A(1) \cdot \frac{1000}{T(\text{K})} + A(2) \cdot \frac{10^6}{T^2(\text{K})} + A(3) \cdot \frac{m(O_2)}{m(PCO)}$.
[b] Standard error of estimate (log PO_2) = ± 0.088470.
[c] Derived thermodynamic quantities are: $\Delta H°_{700}$ (Kcal/mole O_2)) = 37.258; $\Delta S°_{700}$ (cal/mole O_2-deg K) = 49.711 + 253.205 $[m(O_2)/m(PCO)]$.
[d] Standard error of estimate (log PO_2) = ± 0.071985.

to be a function of $1/T$ and $m(O_2)/m(PCO)$. The coefficients of such multiple linear regression fits to the $Pr_{1-n}Ce_nO_x$ (PCO) isotherm data are given in Table 2, together with footnoted values for the heat and entropy of dissociation to O_2 gas.

It should be noted that the unusual relative ease of reoxidation of the PCO compound is likely due to its nonstoichiometry, i.e., the variability of x in the formula $Pr_{1-n}Ce_nO_x$. When such a compound is heated to liberate oxygen, voids or vacancies are created in the crystal lattice, and these are readily available for oxygen occupancy when reoxidation takes place. There is no change in crystal phase, and very little change in the crystalline dimensions or axes (as revealed by x-ray diffractometer measurements). By contrast, most of the other oxides apparently formed an impervious higher oxide crust, i.e., a separate crystalline phase, on the outside of the particles, thus greatly inhibiting any subsurface oxidation.

System Design

Although the PCO compound worked extremely well in terms of kinetics and reversible oxygen sorption, the total amount of usable oxygen reacting remains at a relatively low 1%. Furthermore, with the present Pr/Ce ratio of 0.8/0.2 and a materials temperature limit of about 650°, very high pressures result in even smaller usable oxygen amounts (Fig. 3).

A computer program has been written that can readily size any gas-solid sorption system (physical or chemical) if the basic properties and isotherm data for the system are known. The program is based primarily on the equations as started by a previous SORPTION computer program developed at JPL for hydrogen and C/N_2 sorption sizing.[36] The new program, SORB, is a shortened version that is more versatile and user-friendly but eliminates pressure drop and thermoelectric cooler efficiency calculations. Using the new SORB program, it has been found that the PCO system by itself would take over 800 W of heat to generate 1 W of cooling in the 80 K temperature range (0.3 atm LO_2). This assumes that the oxygen is precooled by a thermoelectric cooler (TEC) to 185 K before the final J-T/heat exchanger circuit.

If the oxygen is precooled by an upper stage to 140–150 K, however, it can be preliquefied at high pressure (27.5–49 atm, respectively), and the resulting J-T refrigeration is greatly enhanced. One such upper stage refrigeration system can be a charcoal/methane physical sorption system. Extensive high-pressure methane adsorption data have been taken at room temperatures by Quinn et al.[37] and Barton et al.[38] on numerous high-surface area charcoals and sarans. By using the Polanyi Potential Theory,[39] it is possible to predict complete methane isotherms at elevated temperatures. By absorbing 6.3-atm methane (CH_4) to charcoal at 275 K (2°C) and heating to 575 K (302°C), the CH_4 gas can be vented at 45-atm pressure. The high-pressure CH_4 gas can then be liquefied at 190 K by a TEC and can preliquefy the oxygen at 140 K. A sketch showing the complete $TEC/CH_4/O_2$ system cooling to 80 K is shown in Fig. 4.

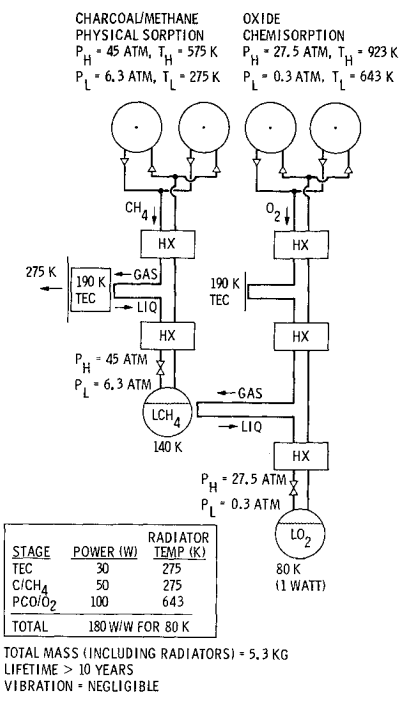

Fig. 4 Methane/oxide refrigerator schematic.

When the oxide refrigerator is combined with a liquid hydrogen (LH_2) hydride stage to 14 K or solid hydrogen hydride stage to 8–10 K,[40] its total system power and weight requirements are *far less* than any mechanical refrigeration system. It is very conceivable that temperatures below 10 K can be reached for only 600 W/W and less than 10 kg weight. The next best 10 K long-life mechanical refrigerator, i.e., the Stirling, requires 1700 W of electricity and weighs almost 200 kg.[41] Furthermore, the oxide/hydride combination can be driven entirely by heat instead of electricity, and it results in essentially no focal plane vibration of sensitive optics.

Summary and Conclusions

Chemical sorption refrigeration systems using hydrogen (20 K cooling) and physical sorption refrigeration systems using nitrogen (80–120 K cooling) have already been successfully proven. Due to their lack of wear-related moving parts, sorption refrigeration systems have potential lifetimes of decades operating with virtually no vibration. Nitrogen adsorption systems, however, require relatively large amounts of power to be rejected at low temperatures, typically 225–250 K. This results in larger, heavy radiators for most space applications. A search was thus made for possible chemical absorption systems that could reject heat at higher temperatures and cool in the 55–100 K temperature region.

Of all the gas-solid systems studied, only oxygen appeared potentially suitable. Over 20 potentially usable oxide reactions were studied and/or tested during the present program. Of these, only doped SrO_2 and $Pr_{1-n}Ce_nO_x$ (PCO) were found to be fully reversible in the 1 atm pressure range and at temperatures below 700°C (for materials strength considerations). The SrO_2 compound, which has about a 10% usable oxygen content, sintered at temperatures above about 500°C (10 atm) and could not reabsorb oxygen. Only the PCO (1% usable oxygen content) compound was found to be completely reversible in the full range of pressures (0.01–100 atm) and temperatures. By using a charcoal/methane (C/CH_4) upper stage and precooling to 140 K, a PCO refrigerator should be able to attain temperatures of 80–55 K. The total power requirements to reach 80 K are about 180 W/W, although this can be reduced to 130 W by recycling some of the PCO waste heat to power the C/CH_4 compressors. The net result of using the CH_4/PCO stage instead of a C/N_2 stage is the ability to use a 275 K heatsink instead of a 225 K heatsink. This results in about a fivefold overall refrigerator system weight decrease for space missions and can result in temperatures of 55 K instead of the 80 K practical minimum for C/N_2 systems.

When used with a hydride lower stage, total CH_4/PCO/hydride power requirements are only about 500 W/W for 14 K or 600 W/W for 8–10-K cooling. This power is about three times less than any mechanical refrigeration system, and the system weight is about 20 times less. Sorption refrigeration has the additional advantages of very long life (at least 10 years) and virtually no vibration. Furthermore, most of the sorption refrigeration power can be supplied as heat, e.g., solar or RTG waste heat, instead of heavy, inefficient electric power conversion systems.

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