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OXYGEN COMPLEXES FORMED AT 4°K?

by

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OXYGEN COMPLEXES FORMED AT 4°K?

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SUMMARY

A recent U.S. Patent claimed that oxygen could be complexed so that it would be stable in the solid form at relatively high temperatures. To test the patent claims, three component gases were tested for their ability to form such complexes; these were nitrogen tetroxide, Freon-22, and carbon dioxide.

Oxygen and the component gas were quickly solidified in a cryogenic chamber at 4.2°K. The resultant product was slowly heated, and the temperature and quantity of gas evolved from the product were continuously measured.

It was found that oxygen was not complexed by the nitrogen tetroxide, Freon-22, or carbon dioxide. These findings lend doubt to this proposed method for the storage of oxygen.

INTRODUCTION

On all manned space missions and for all non-manned
missions involving experiments with living matter, some means
must be provided to store or produce oxygen. In the former
class, supercritical oxygen has been employed though, in the
future, regenerative oxygen-carbon dioxide-oxygen cycles will
probably be used. In the latter case, high-pressure oxygen
gas usually supplies the small requirements.

There is a real weight and volume gain if liquid oxygen
could be employed for missions where any sizeable amount of
oxygen must be carried. To attain the high liquid densities,
oxygen must be cooled below -297°F (at one atm.) thus storage
vessels must be well insulated. In addition, even if liquid
were stored, there are problems in measuring, separating, and
handling a mixture of gas and liquid under weightless conditions.

Thus it was with considerable interest that we noted a
U.S. Patent 3,378,351, April 16, 1968, which proposed a new
method of storing oxygen. This patent is appended to this report
but it is summarized as noted in the first paragraph of the
patent: "... it relates to a method of combining oxygen gas with
other compounds and solidifying the product into a blend much
more stable than solidified oxygen itself."

In essence, oxygen gas and another gas (nitrogen dioxide,
water vapor, isobutylene, or ethylene) were co-condensed rapidly
to a solid mixture at liquid helium temperatures. It was claimed
that the solid mixture contained "combined oxygen" which would
not be evolved until temperatures higher than the oxygen satura-

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tion temperatures were attained.

For example, with nitrogen dioxide, the solid "had to be heated above -297°F" (the normal boiling point of oxygen) to evolve all of the oxygen. Some oxygen was still being generated at -250°F, almost 50°F higher than one would have expected if the nitrogen dioxide-oxygen solid were purely a physical mixture. The oxygen evolved at temperatures higher than -297°F amounted to a complex containing 1 mole of oxygen to 6.6 moles of NO_2.

With these few results to guide us, we have duplicated the experimental apparatus and condensation technique outlined in the patent and have tested N_2O_4, Freon-22, and carbon dioxide as "complexing agents." The experiments are described in detail below. The object was to determine from these few tests whether or not this proposed scheme might have promise in space missions as an oxygen storage technique wherein oxygen, complexed in the solid state, could be stored at relatively high temperatures and generated at any desired rate by varying the temperature rise rate of the solid complex.

We were reluctant to accept the patent claims a priori since we could see no reason why oxygen should complex in a chemical manner with gases of the type noted above. True, there may be a very intimate physical mixture formed with some possible trapping of oxygen in an inert matrix, but this, upon heating, would then not behave as described in the patent. With such conflicting thoughts, we then initiated the experimental program.

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EXPERIMENTAL PROGRAM

A Brief Description   (Refer to Figure 1)

Oxygen and the complexing gas were added separately and allowed to mix in the main chamber. The temperature and pressure of each gas could be measured and, since the volume of the main chamber was known, the initial composition could be determined using the gas laws. After equilibration of the gases with the surroundings, the main chamber was connected to the cryogenic chamber which had been immersed in liquid helium at 4.2°K. The gases were rapidly cryopumped from the main chamber and solidified out in the cryogenic chamber.

The temperature(s) at which the solidified product decomposed and the quantity of the gases which were evolved at this temperature(s) were measured.

Detailed Description of Salient Features of Apparatus

Cryogenic Chamber (Figure 2)

The cryogenic chamber consisted of a Pyrex container fitted with a closed internal annulus through which warm helium gas flowed. This acted as a warm sheath to prevent premature deposition of solids in the upper regions of the chamber. The lower part of the chamber was surrounded by a liquid helium bath which was, in turn, immersed in a Dewar of liquid nitrogen to minimize boil-off rates of helium. The temperature of the
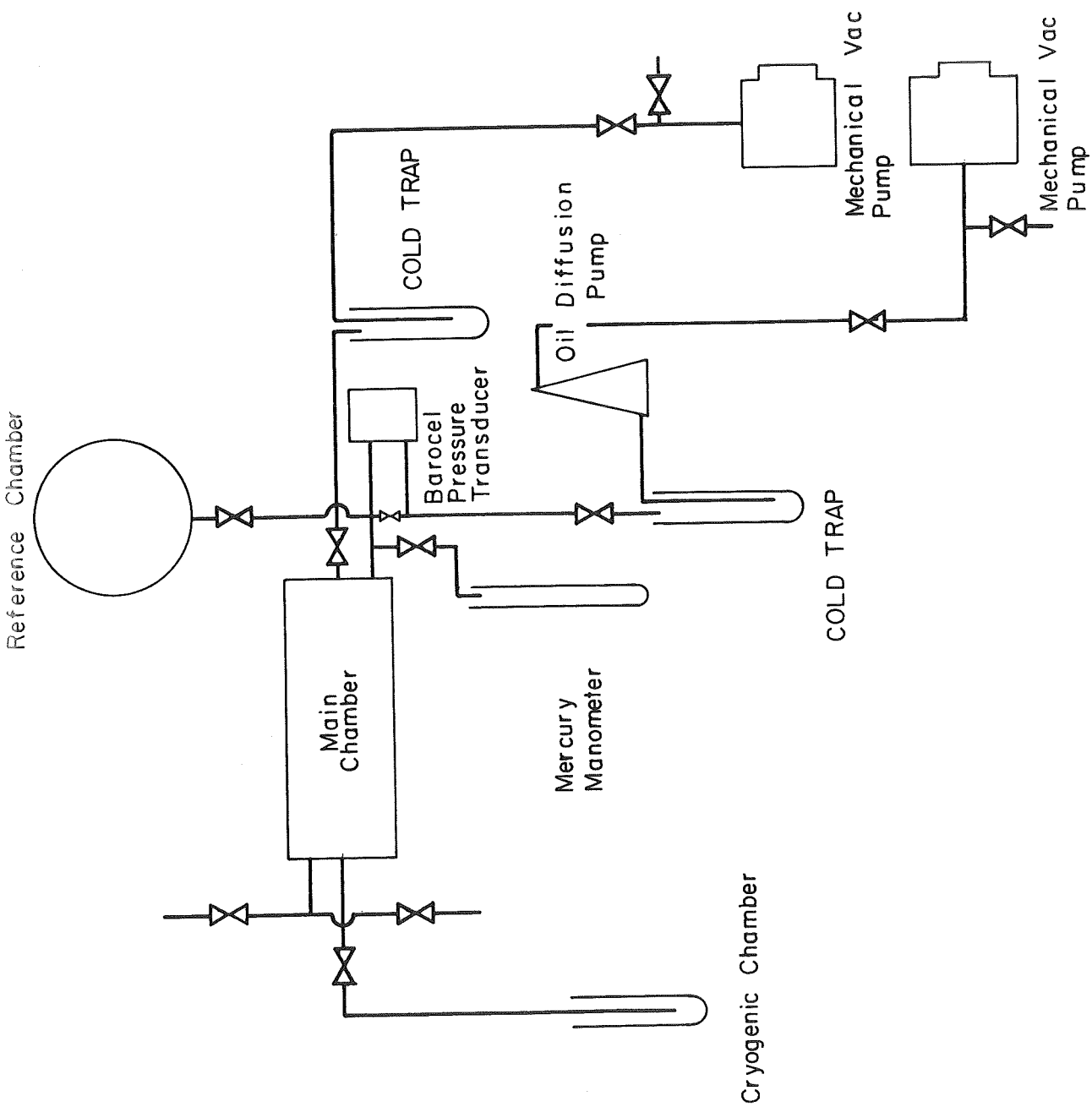
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FIGURE I   EXPERIMENTAL APPARATUS

solid(s) deposited at the bottom of the chamber was measured
by a copper-constantan thermocouple probe made with 0.002
inch diameter wire.

Main Chamber

The main chamber was made of a brass cylinder with an
approximate length and diamter of 30 and 14 cm respectively.
The volume of the main chamber was 3.87 liters.

Pressure Measurement

Pressures less than 100 mm Hg were measured with a Barocel
electronic manometer, Type 511, with the reference port connected
to the inlet of an oil diffusion pump. Pressure readings were
believed accurate to ±0.5 microns.

Pressures exceeding 100 mm Hg were measured with a mercury
manometer, and readings were taken with a cathetometer and levels
estimated to ± .05 mm Hg.

Temperature Measurement

The main chamber temperature was measured using a 30 gauge
(0.01 inch) copper-constantan thermocouple probe with ice-water
as a reference junction. A Honeywell portable potentiometer was
used to read voltages to ± .005 millivolts (±0.05°C).

Temperatures in the bottom of the cryogenic chambers were
measured using a 50 gauge (0.002 inch) copper-constantan thermo-

Helium gas out

Helium gas in

Inner annulus

Thermocouple
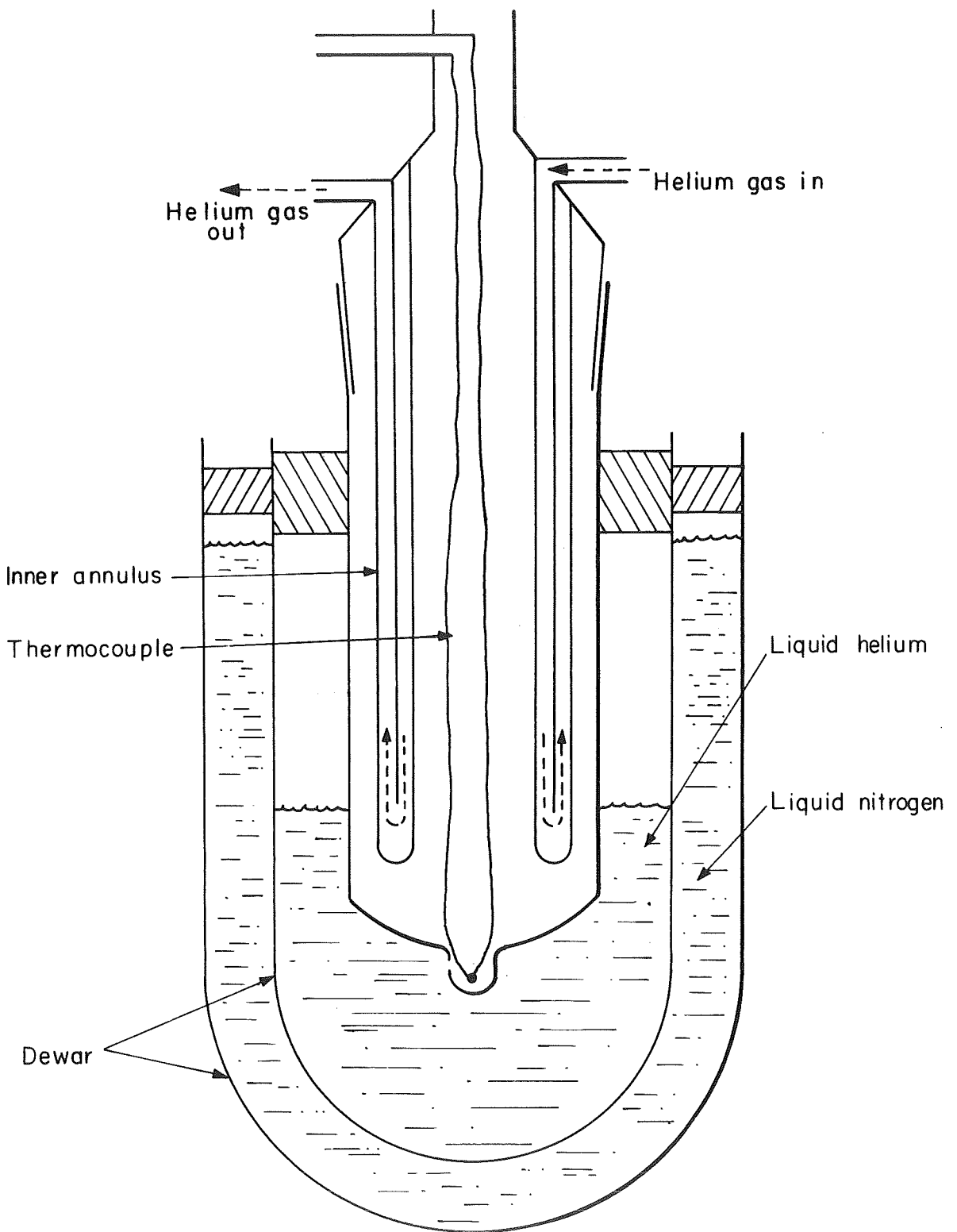
Liquid helium

Liquid nitrogen

Dewar

FIGURE 2. CRYOGENIC CHAMBER

couple probe with a liquid nitrogen reference junction. A Leeds and Northrup Type K potentiometer was used in the readout to measure voltage within ±5 microvolts (±0.2°C).

Run Procedure

The detailed procedure carried out during each run is given in Appendix II.

Design Considerations

Thermocouple Size

The thermocouple which was positioned in the cryogenic
test chamber was set in place at the very bottom with a small
helical wire coil above it to allow heat-stationing. The wire
size was determined from a heat-transfer analysis which assumed
(conservatively) that no heat-stationing coil was present and
the thermocouple received energy by conduction from the vertical
leads. By assuming various wire sizes, the predicted temperature
errors between the measured and true cryogenic test chamber could
be determined. A 2-mil wire was finally selected; the maximum
heat-leak error for this size is only $0.3°K$. With the heat-
stationing coil, the actual error would be much less.

Mixing Time in Main Chamber

When making up the desired gas composition in the main
chamber, each gas was metered in separately. However, a homo-
geneous gas mixture was desired before expanding these gases
into the cryogenic chamber.

The time for the gases to be completely mixed can be estimated
by assuming that the gases are initially separated from each other
by an impermeable partition which divides the main chamber in
half. The partition is then removed and the gases interdiffuse.
The time for complete mixing of the gases, based on the above
model, is then overestimated, since, in the feeding of the gases

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into the main chamber, there is some turbulence which would reduce the time for complete mixing.

For an equal molar mixture of gases (refer to Figure 4), the problem can be described mathematically

$$\frac{\partial C}{\partial \theta} = D \frac{\partial^2 C}{\partial X^2}$$

With the boundary conditions:

at $\theta = 0$, $0 < X < L/2$, $C = C_0$

$\theta > 0$, $X = 0$, $\frac{\partial C}{\partial X} = 0$

$\theta > 0$, $X = L/2$, $C = \frac{1}{2} C_0$

The solution is

$$C = \frac{C_0}{2} + \frac{2}{\pi} C_0 \sum_{n=0}^{\infty} \frac{(-1)^r}{2n+1} \; e^{-D(2n+1)^2 \pi^2 \theta / L^2} \cos\frac{(2n+1)\pi X}{L} \qquad (2$$

Figure 3a is a diagrammatic representation of the concentration profiles, in various times. Figure 3b is a plot of the degree of mixing, i.e.,

$$\frac{C_{initial} - C_{final}}{C_{final}} \; X \; 100 \qquad \text{at } x = 0$$

against time of mixing in minutes for a typical case of nitrogen - CO_2. After 45 minutes, the gases are completely mixed. Similar calculations for other gas mixtures indicate that this time of 45 minutes would suffer to allow essentially complete diffusive mixing of all gas mixtures used in the work.

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(a) Concentration profiles as a function of time in main chamber
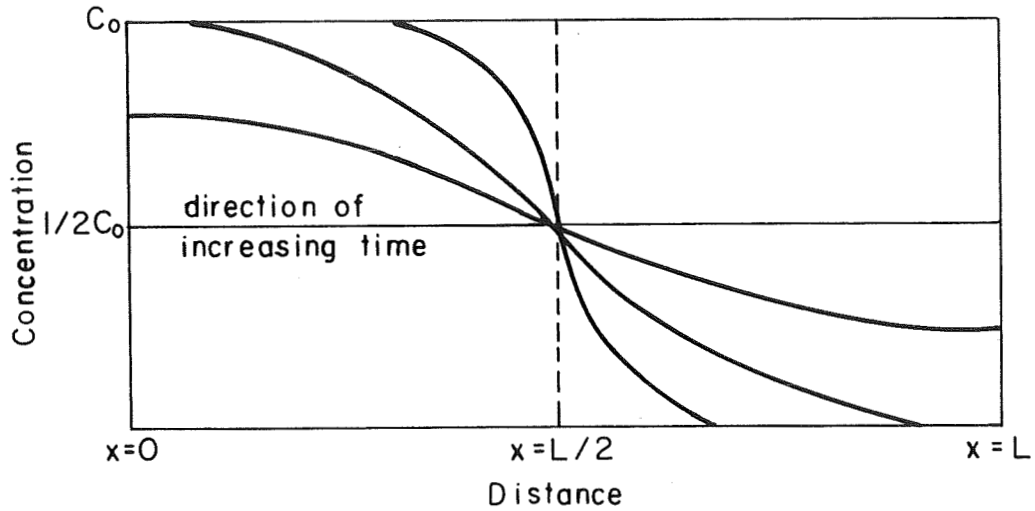
(b) Percentage of completion of the concentration at the wall (i.e. degree of mixing) vs. time of mixing

$$50/50 \ N_2 / CO_2$$

$$D_{AB} = 0.167 \ cm^2/sec$$
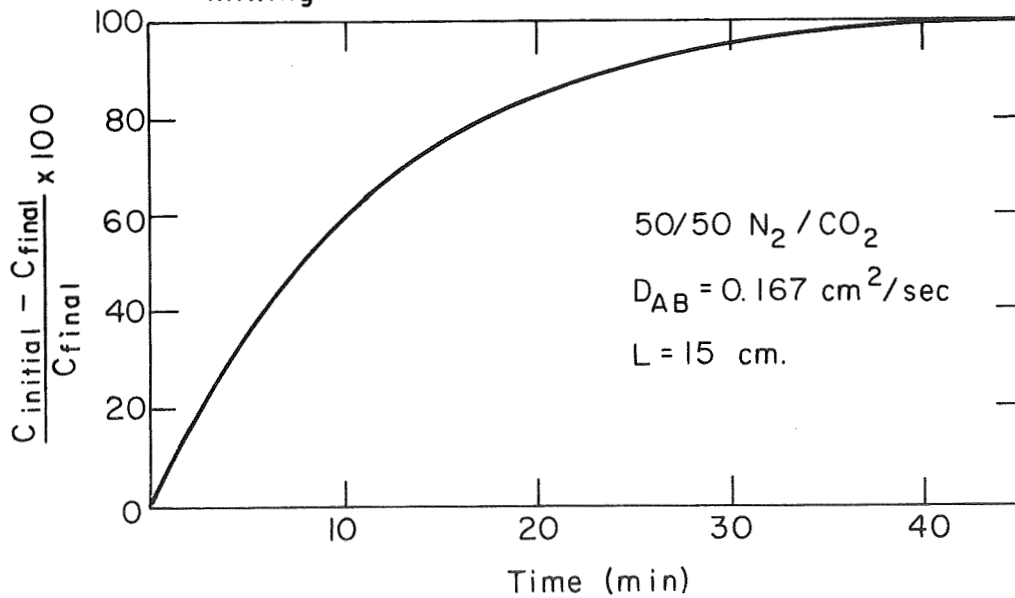
$$L = 15 \ cm.$$

FIGURE 3

RESULTS

Three component gases were tested for their ability to
'complex' with oxygen at low temperatures - nitrogen tetroxide,
Freon-22, and carbon dioxide. Nitrogen tetroxide was tested
as it was one of the gases stated in the patent which would
complex oxygen; Freon-22 was chosen because it is a good
advent (as a liquid) for oxygen; and carbon dioxide was select-
ed because it freezes a temperature so much higher than oxygen
and, hence, might be more able to 'trap' oxygen.

When nitrogen tetroxide was tested, the experimental
apparatus and procedure were modified. Since nitrogen tetroxide
is highly corrosive, the electronic barocell was detached from
the system, the volume of the system remaining unchanged.
Pressures were measured only with the mercury manometer; between
readings, the manometer was isolated from the system since
nitrogen tetroxide also reacts slowly with the mercury.

Three gas mixtures of nitrogen tetroxide and oxygen were
studied. Each had the same initial composition (i.e. refer to
Table I). In the first experiment, the cryogenic temperature
and pressure were measured continuously from 4.2 (i.e. normal
boiling point of liquid helium) to 110°K, and a final reading of
pressure was taken when the cryogenic chamber was at room temper-
ature; the second experiment was carried out from 4.2 to 155°K,
and the third experiment from 4.2 to ambient temperature
(i.e. 295°K).

Table I also contains the compositions of the Freon-22 and carbon dioxide gas mixtures. Each gas mixture, with approximately the same gas compositions, was tested twice to verify the reproducibility of the experimental results.

TABLE I

Component Gas	Figure No.	Expt. No.	Initial Fraction of O_2 in Gas Mixture
Nitrogen Tetroxide	4	A-1	0.49
		A-2	0.49
		A-3	0.48
Freon - 22	5	B-1	0.50
		B-2	0.51
Carbon Dioxide	6	C-1	0.51
		C-2	0.51

The results are plotted as 'fraction of initial solid evolved as gas' versus the cryogenic temperature and are shown in Figures 4, 5, 6. This fraction represents the total moles of gas in the cryogenic and main chambers divided by the initial total moles of both gases used.
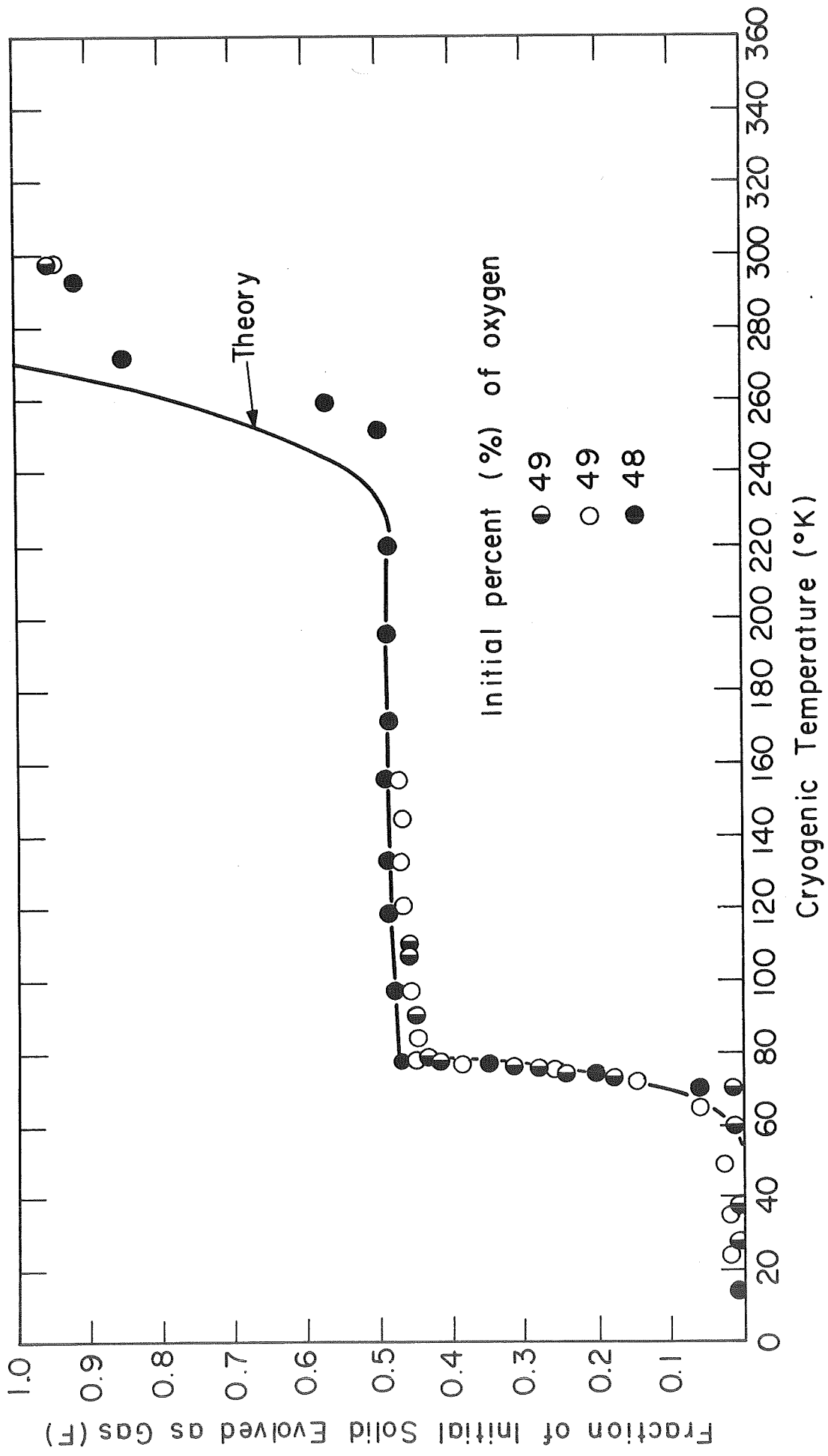
FIGURE 4. FRACTION OF INITIAL SOLID EVOLVED AS GAS versus CRYOGENIC TEMPERATURE — SYSTEM OXYGEN-NITROGEN TETROXIDE
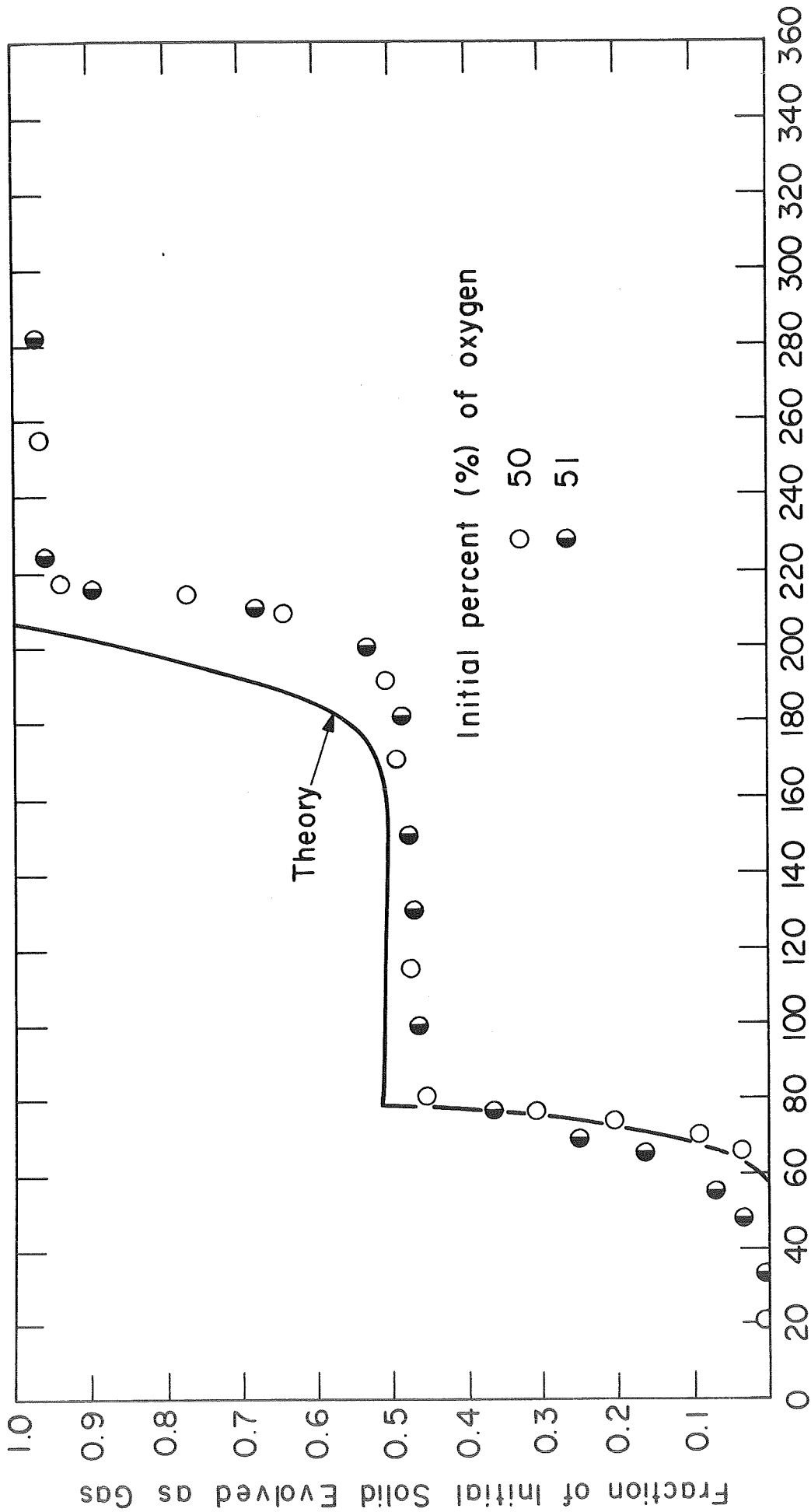
FIGURE 5. FRACTION OF INITIAL SOLID EVOLVED AS GAS versus CRYOGENIC TEMPERATURE — SYSTEM OXYGEN — FREON 22
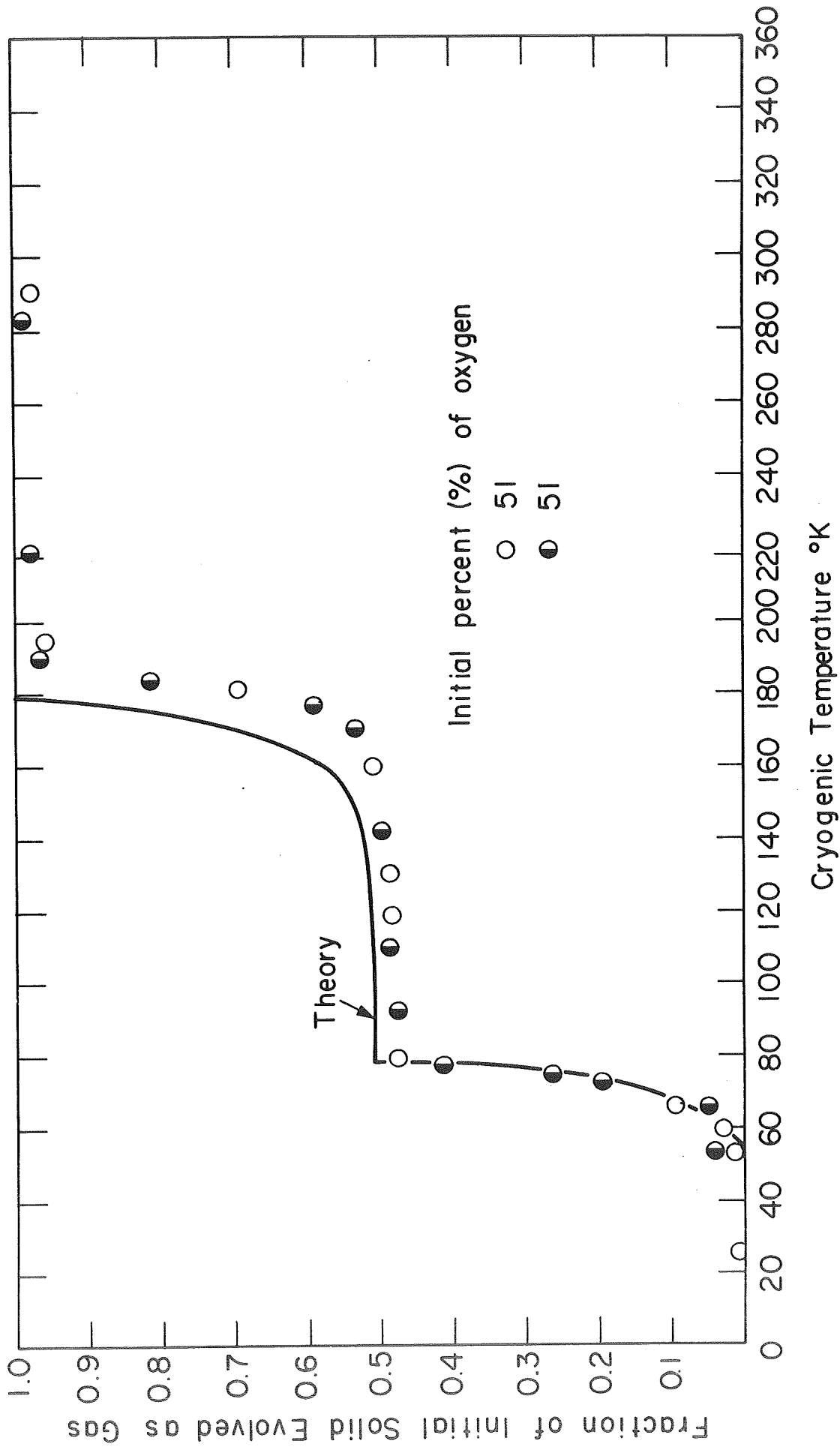
FIGURE 6. FRACTION OF INITIAL SOLID EVOLVED AS GAS versus CRYOGENIC TEMPERATURE-SYSTEM OXYGEN -CARBON DIOXIDE

SIMPLE THEORETICAL PREDICTION

If the solids in the cryogenic chamber consisted only of a physical mixture of oxygen and a less volatile complexing gas, then it is relatively easy to predict the fraction of solids evolved as the temperature of the cryogenic chamber is increased.

At the very low condensation temperature (circa 4.2°K), the vapor pressure of both oxygen and the complexing gas are essentially zero. Thus, initially, the entire system's pressure is too small to be measured. As the temperature in the cryogenic chamber is raised, oxygen begins to vaporize though, in most cases, the complexing gas vapor pressure remains close to zero since it is so much less volatile.

At any given temperature, let the system pressure be P. Assume that the temperature is sufficiently low that one can neglect the effect of the presence of the complexing gas in the vapor. Then P should be the vapor pressure of oxygen and the fraction of gas evolved would equal $(PV/R\overline{T})/N_T$. The value V represents that for the combined cryogenic and main chambers. R is the gas constant, N_T, the <u>total</u> moles condensed, and $\overline{T}$ an average temperature based on the relative volumes and actual temperatures of various portions of the system. This quantity is plotted in Figures 4, 5, and 6 and at low temperatures agree well with the data. When this fraction accounts for all the oxygen theoretically present (i.e., that which was added), when one would expect no change in pressure with temperature (except

that due to gas expansion) until the complexing gas vapor
pressure becomes measurable. Repeating the calculations, a
theoretical curve can be drawn and compared with the data.
As noted in Figures 4, 5, and 6, the theoretical curves agree
well with the experimental data points indicating that little
or no complexing occured in any run.

CONCLUSIONS

Oxygen is not complexed by the nitrogen tetroxide at 4.2°K. This conclusion is in direct contradiction to the claim of the patent.

Oxygen is not complexed by Freon -22 and carbon dioxide.

April 16, 1968   R. A. RUEHRWEIN ETAL   3,378,351

METHOD OF STORING OXYGEN

Filed Oct. 24, 1961

Discharge region

Helium gas

Liquid helium

Liquid nitrogen

To pump
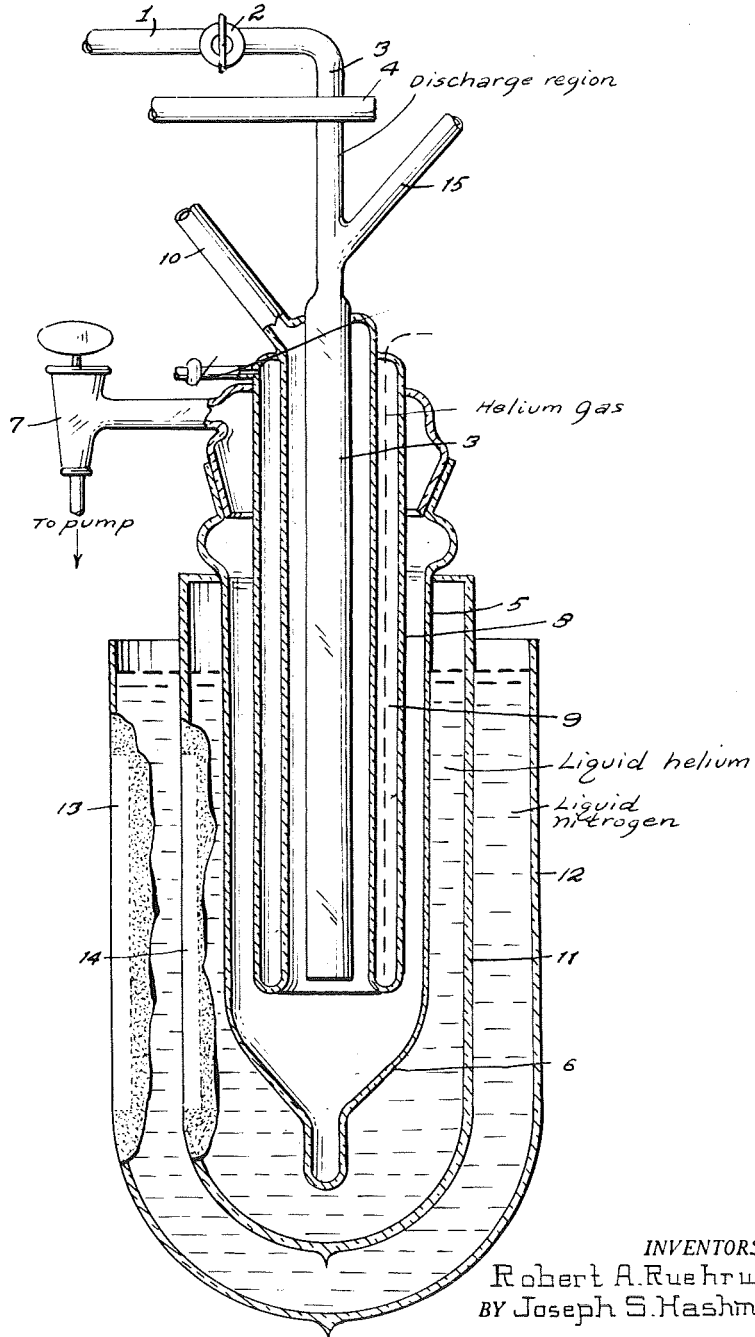
INVENTORS,
Robert A. Ruehrwein
BY Joseph S. Hashman

S. J. Rotondi, Q. J. Dupont + E. F. McKinney

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This invention relates to a process for the storage of oxygen. More particularly it relates to a method of combining oxygen gas with other compounds and solidfying the product into a blend much more stable than solidified oxygen itself.

Oxygen is conventionally stored in its liquid form. However, it cannot be stored at a temperature higher than its boiling point unless it is kept under high pressures. In order to maintain this high pressure, heavy equipment such as metal storage tanks, safety devices, etc. must be used. Since this invention requires no pressure, such equipment is eliminated.

Therefore, an object of this invention is to provide a process which will allow oxygen to be stored without the use of high pressures or the equipment necessary therefor.

A further object of this invention is to provide a means whereby oxygen may be stored in a stable manner at low temperatures.

Another object of the invention is to provide a supply of oxygen in a solid, stable form, which upon subsequent vaporization, provides a ready source of oxygen for any purpose for which it is conventionally used.

The foregoing and other objects and advantages will become apparent from the following detailed description of the invention.

In accordance with this invention, oxygen gas is blended with another gaseous material, preferably one of the following: water vapor, nitrogen dioxide (or nitrogen tetroxide) and olefins such as ethylene or isobutylene. Immediately thereafter the mixed blend is subjected to extremely low temperatures of about 4.2° K. A solidified product is formed which is a complex of molecular oxygen and another compound. The solidified product is then warmed to a temperature of from about 66° K. to about 77° K. in order to allow the uncomplexed oxygen to be pumped from the solidification zone. The remaining solid complexed material is much more stable than pure solidified oxygen and consequently may be stored indefinitely at much higher temperatures, up to 200° K. When it is desired to obtain oxygen gas from the solidified complexed material, it is merely necessary to raise the temperature of the material to a point at which oxygen gas is evolved therefrom.

The various gases used in this process are obtained from any well known source such as from commercial supplies thereof and are essentially pure.

More specifically, with particular reference to the single figure of the drawing, oxygen gas, usually obtained directly from a cylinder (not shown), is introduced through a supply tube 1 and controlled by means of a stopcock 2. It is throttled into a Pyrex tube 3 open at its lower end and having a Y connection with another supply tube 15. The oxygen gas flows out of the lower end of tube 3 into the lower part 6 of a Pyrex cylinder 5. The lower part of this cylinder is immersed in liquid helium. It is also equipped with a vacuum pump connection 7 which may be in turn connected with a vacuum pump (not shown) when it is desired to remove gases from the cylinder 5. The lower part 6 of Pyrex cylinder 5 which has been immersed in liquid helium acts as a trap or condenser by freezing out all gases and thus constitutes, in effect, a high speed pump for maintaining the flow of gas toward it.

Surrounding the Pyrex tube 3 is another Pyrex tube 8,

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also open at its lower end and having hollow walls 9. The additional gas with which it is desired to blend the oxygen gas is supplied from a source (not shown) through either tube 10 or tube 15. If the additional gas is supplied through tube 10, it is then drawn down tube 8 into the lower part 6 of cylinder 5 by the vacuum created therein by the action of the liquid helium constantly freezing out all gases. The blending of the oxygen gas and the additional gas then takes place in the lower part 6 of cylinder 5 wherein it is almost immediately solidified. When the additional gas is supplied through tube 15 it is blended with the oxygen gas at the Y connection of Pyrex cylinder 3 and tube 15. The two gases together then are drawn down Pyrex cylinder 3 and out the lower end thereof into the lower part 6 of Pyrex cylinder 5 wherein they are solidified.

In order to prevent condensation or solidification of the gases at temperatures much above 4.2° K., Pyrex tubes 3 and 8 are kept at a relatively high temperature, for instance, room temperature. This temperature is maintained by forcing a relatively warm gas such as helium or nitrogen into the hollow walls 9 of tube 8. The introduction of such a sheath of warm gas extending considerably below the liquid helium level causes but a slight heat input. However, by this means the gases pass abruptly from a relatively high temperature to the extremely low temperature of the lower part 6 of Pyrex cylinder 5 and accumulate in solid form in this area.

The liquid helium bath may be insulated from the outside temperature by an additional bath of liquid nitrogen in order to reduce the amount of liquid helium required to maintain the lower part of cylinder 5 at a very low temperature. The helium and nitrogen baths are contained in Dewar flasks 11 and 12, respectively, which can be raised and lowered by means of a screw elevator (not shown) in order to vary the temperature in the lower end of cylinder 5. The silvered Dewar flasks 11 and 12 are provided with strip windows 13 and 14, respectively, to allow observation of the solidified material which is deposited at the bottom of Pyrex cylinder 5. The level of the liquid helium is maintained around the lower end of Pyrex cylinder 5 by slowly raising the Dewar flasks as the helium boils away. This prevents unnecessary excessive cooling of the Pyrex entrance tubes 3 and 8.

Following the blending of the oxygen gas with an additional gas and the subsequent solidification thereof, the lower end 6 of cylinder 5 is warmed to a temperature of from about 66° K. to about 77° K. by lowering the Dewar flasks 11 and 12. Control of the elevation of the Dewar flasks gives very good temperature control and it is possible to warm or cool the solidified product at will or hold it at any desired temperature for hours. As the solidified product is warmed to the aforementioned temperature, the uncomplexed oxygen becomes gaseous again and is removed by a vacuum pump (not shown) through connection 7. This oxygen gas may be recovered and then returned to the original oxygen supply in order to be used in the process again. The remaining solid material is, of course, the complex of solidified oxygen and an additional solidified gaseous compound. The oxygen may be conveniently stored in the complex for an indefinite period as long as its temperature remains below the decomposition point thereof. A ready supply of oxygen gas is obtained by merely raising the temperature of the solid complexed product above its decomposition point.

In order that the invention may be further illustrated, the following are examples of typical embodiments of the invention.

Example I

A mixture of nitrogen dioxide gas and oxygen gas was solidified at the temperature of liquid helium (about 4.2°

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K.) in the trap formed by the lower part 6 of Pyrex cylinder 5. After warming to 77° K. and pumping off the uncombined oxygen gas, it was found that additional oxygen gas was evolved from the solidified complex product of nitrogen dioxide and oxygen at temperatures approaching and including 124° K., in a reversible manner, and in the ratio of one mole of oxygen to 0.6 moles of NO_2.

Example II

A mixture of water vapor and oxygen gas was solidified as in Example I. Again, after warming to 77° K. and pumping off the uncombined oxygen gas, it was found that additional oxygen gas was evolved from the solidified complex product of water vapor and oxygen at temperatures approaching and including 150° K. and in the ratio of one mole of oxygen to 10.5 moles of water.

Example III

A mixture of isobutylene gas and oxygen gas was also solidified as in Example I. After warming to about 72° K. and pumping off the uncombined oxygen gas, it was found that additional oxygen gas was evolved from the solidified complex product of isobutylene and oxygen at a temperature around 130° K. and in a ratio of one mole of oxygen to 27 moles of i-C_4H_8.

Example IV

A mixture of ethylene gas and oxygen gas was also solidified as in the previous examples. After warming to about 66° K. and pumping off the uncombined oxygen gas, it was found that additional oxygen gas was evolved from the solidified complex product of ethylene and oxygen at a temperature of about 86° K. in a reversible manner and in the ratio of one mole of oxygen to 7.6 moles of C_2H_4.

While the foregoing embodiments have been set forth in considerable detail, it is to be distinctly understood that many modifications and variations will naturally present themselves to those skilled in the art without departing from the spirit of this invention or the scope of the appended claims.

Having thus described the invention, what is claimed is:

1. A method for the preparation of a complex compound capable of storing oxygen at normal pressure comprising, blending oxygen gas in a vacuum with a material selected from the group consisting of water vapor, nitrogen dioxide gas, ethylene gas and isobutylene gas, solidifying by freezing the resulting blend to obtain a complexed product thereof, warming said product to a temperature between 66°–77° K. to render any uncomplexed oxygen gaseous for removal and utilizing the final solidified complexed product as a safe means of storing the complexed oxygen at normal pressure as long as the temperature of the solid product is maintained below 86° K.

2. A method of safely storing oxygen at normal pressures combined in a complex compound comprising, blending in a vacuum oxygen gas with a material selected from the group consisting of water vapor, nitrogen di-

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oxide gas, ethylene gas and isobutylene gas, solidifying the blended gas by freezing at a temperature of approximately 4.2° K. to obtain a complexed product thereof, warming said product to a temperature in a range of 66° K. to 77° K. to render any uncomplexed oxygen gaseous for removal, utilizing the solidified complex product as a safe storage of oxygen at normal pressure by maintaining the temperature below 86° K. and retrieving the oxygen for use from the solidified complex product by raising the temperature to a range of 124° K. to 150° K.

3. A solid complexed compound for the safe storage of oxygen at normal pressure and at temperatures below 86° K. consisting of a stable solidified combination formed of oxygen and a material selected from the group consisting of water vapor, nitrogen dioxide gas, ethylene gas and isobutylene gas and free of uncomplex oxygen.

4. A solid complexed compound for the safe storage of oxygen at normal pressure and at temperatures below 77° K. consisting of a stable solidified compound of solidified oxygen and solidified nitrogen dioxide gas free of uncomplexed oxygen and yielding a supply of oxygen gas at temperatures approaching and including 124° K.

5. A solid complexed compound for the safe storage of oxygen at normal pressure and at temperatures below 77° K. consisting of a stable solidified combination of frozen water vapor and solidified oxygen gas free of uncomplexed oxygen and yielding a supply of oxygen gas at temperatures approaching and including 150° K.

6. A solid complexed compound for the safe storage of oxygen at normal pressure and at temperatures below 72° K. consisting of a stable solidified combination of solidified oxygen and solidified isobutylene gas free of uncomplexed oxygen and yielding a supply of oxygen gas at temperatures approaching and including 130° K.

7. A solid complexed compound for the safe storage of oxygen at normal pressure and at temperatures below 66° K. consisting of a stable solidified combination of solidified oxygen gas and solidified ethylene gas free of uncomplexed oxygen and yielding a supply of oxygen gas at temperatures approaching and including 86° K.

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MILTON WEISSMAN, *Primary Examiner.*

ROBERT A. O'LEARY, *Examiner.*

M. L. MOORE, *Assistant Examiner.*

APPENDIX II

Detailed Description of Experimental Procedure

Start-up Procedure

1. Energize the galvonometer.

2. Fill the small dewars used as reference temperatures with ice-water and liquid nitrogen.

3. Isolate the oil diffusion pump from main system.

4. Zero the pressure meter.

5. Purge the gas feed lines.

Procedure to be Followed During Run

1. Open the cryogenic valve, reference and mercury manometer valves and evacuate the system using the mechanical vacuum pump (M.V.P.).

2. Isolate the reference pressure chamber from the main system by evacuating the vacuum cup for a few seconds and then turn the stopcock 1/2 turn. Only need to do once.

3. Turn off the main and auxiliary valves to the m.v.p. and turn off the m.v.p. Vent the pump to atmosphere.

4. Note whether the main or cryogenic chambers leak.

5. Turn off the cryogenic valve and note whether the cryogenic chamber leaks.

6. If no leaks, note the residual pressure and temperature.

7. Turn on the helium insulation line (low).

8. Immerse cryogenic chamber in liquid helium.

9. Feed in the gas mixture, one at a time, noting pressure and temperature of each component added (let gases sit for approximately 15 min) and let the final gas mixture sit for 45 minutes.

10. TURN OFF MERCURY MANOMETER VALVE.

11. Standardize the ±5 microvolts potentiometer.

12. Increase the flowrate of helium gas in insulation line.

13. Open cryogenic valve COMPLETELY.

14. Take continuous readings of pressure and temperature on main and cryogenic chambers.

15. Wait until equilibrium is attained by noting constancy of pressure. Note final pressure and temperature. NOTE: PRESSURE MUST BE LESS THAN 100 mm Hg before being able to take readings with electronic barometer.

16. Evacuate system with m.v.p. by:

    a) turning off the cryogenic valve and noting the main chamber pressure and temperature

    b) evacuate the main chamber to the lowest pressure and then close the main valve, noting the final pressure and temperature.

    c) open the cryogenic valve and wait until the main chamber pressure is constant.

    d) repeat steps (a) and (b) until gases are completely removed.

17. Lower Dewar slightly until the liquid helium level is approximately 1/2 cm from tip of cryogenic chamber.

18. Reduce helium gas flowrate.

19. Continue to remove any evolved gases.

20. After evolution ceases, lower the Dewar farther and take continuous readings of pressure and temperature (main chamber and cryogenic chamber) before and after gases begin to evolve.

Shut-down Procedure

1. Open the cryogenic and reference valves.

2. Evacuate the system to the lowest possible pressure using m.v.p.

3. Close the main and open auxiliary valves to m.v.p and turn off pump. Vent pump to atmosphere.

4. Open the by-pass valve.

5. Open the system to the oil diffusion pump.

6. Turn off the portable potentiometer and empty the reference temperature dewar.

7. Turn off ± 5 microvolts potentiometer

   a) disconnect leads to standard cell
   b) disconnect leads to one of the 3 volt battery

8. De-energize the galvanometer.

9. Turn off all gas cylinders.

10. Refill cold traps with liquid nitrogen.

11. Empty cold trap between the main and mechanical pump by venting pump to atmosphere.

APPENDIX III

Experimental Data (pressures, and temperatures in the cryogenic

and main chambers):

        Oxygen & Nitrogen Tetroxide (A)

        Oxygen & Freon-22 (B)

        Oxygen & Carbon Dioxide (C)

EXPERIMENT: A-1

Main Temperature: 24.5°C
Initial Pressure of Nitrogen Tetroxide: 215mm Hg
Initial Pressure of Oxygen: 210mm Hg

Pressure (mm Hg)	Cryogenic Temperature (°K)
1.0	38.0
4.0	59.0
47.0	70.5
69.0	72.5
94.0	74.0
110.0	75.5
124.0	75.5
163.0	77.0
169.0	78.8
174.0	81.1
174.0	84.5
175.0	86.5
175.0	89.6
179.0	93.4
179.0	94.5
179.0	106.1
180.0	109.8

EXPERIMENT: A-2

Main Temperature: 26.4°C
Initial Pressure of Nitrogen Tetroxide: 213 mm Hg
Initial Pressure of Oxygen: 208 mm Hg

Pressure (mm Hg)	Cryogenic Temperature (°K)
6.0	24.5
6.0	22.5
6.0	35.5
9.0	58.5
11.0	60.0
11.0	58.5
10.0	47.5
10.0	51.5
10.0	61.0
22.0	65.0
31.0	68.0
56.0	71.5
82.0	73.0
100.0	75.0
119.0	75.5
130.0	76.0
150.0	77.0
158.0	77.0
168.0	77.7
172.0	79.7
174.0	83.6
175.0	85.6
175.0	88.0
175.0	90.4
177.0	96.6
178.0	105.8
179.0	112.3
179.0	115.9
179.0	119.2
179.0	120.8
179.0	122.8
181.0	124.4
181.0	127.6
181.0	132.6
181.0	135.6
181.0	145.0
182.0	155.2
368.0	266.4

EXPERIMENT: A-3

Main Temperature: 24.5°C
Initial Pressure of Nitrogen Tetroxide: 218 mm Hg
Initial Pressure of Oxygen: 205 mm Hg

Pressure (mm Hg)	Cryogenic Temperature (°K)
2.0	13.5
18.0	70.5
24.0	70.0
44.0	71.5
78.0	73.5
111.0	76.5
137.0	77.0
150.0	77.0
166.0	77.0
173.0	78.5
181.0	78.8
184.0	86.5
185.0	90.1
186.0	96.8
186.0	100.5
186.0	106.3
188.0	116.7
188.0	118.7
188.0	124.5
190.0	133.8
190.0	157.5
190.0	172.6
190.0	195.5
190.0	213.5
190.0	219.6
190.0	242.2
195.0	252.0
196.0	249.6
201.0	255.2
205.0	260.0
221.0	260.6
332.0	272.0
357.0	292.8

EXPERIMENT: B-1

Main Temperature: 25.4°C
Initial Pressure of Freon -22:   208 mm Hg
Initial Pressure of Oxygen: 210 mm Hg

Pressure (mm Hg)	Cryogenic Temperature (°K)
00.0	21.0
12.9	66.0
33.5	69.5
48.5	71.0
62.8	73.0
78.5	74.0
93.5	75.0
119.0	76.5
159.0	77.0
164.0	77.0
174.0	80.6
176.0	83.0
177.0	86.2
178.0	89.2
178.0	91.5
180.0	98.9
180.0	105.
181.0	114.2
182.0	114.6
182.0	114.3
184.0	124.0
184.0	133.8
185.0	149.9
186.0	153.3
186.0	158.8
187.0	169.8
188.0	170.2
189.0	174.0
191.0	183.0
192.0	185.5
195.0	191.3
202.0	198.2
205.0	200.2
208.0	201.2
216.0	203.6
223.0	205.0
236.0	207.2
248.0	209.0
271.0	211.3

Pressure (mm Hg)	Cryogenic Temperature (^{O}K)
288.0	212.8
297.0	213.6
309.0	214.4
316.0	215.2
331.0	216.4
347.0	216.2
355.0	216.2
363.0	217.2
371.0	224.0
372.0	231.4
372.0	255.7
372.0	279.2

EXPERIMENT   B-2

Main Temperature: 25.5°C
Initial Pressure of Freon-22:   210 mm Hg
Initial Pressure of Oxygen: 215 mm Hg

Pressure (mm Hg)	Cryogenic Temperature (°K)
00.0	10.0
00.0	9.50
00.0	15.0
00.0	22.5
00.0	24.6
.706	32.5
2.6	37.0
6.9	46.0
11.8	46.0
13.5	48.0
23,0	53.0
28.5	55.0
31.5	55.6
37.0	58.5
45.5	60.0
51.7	62.0
58.0	64.0
65.5	65.0
75.0	67.0
98.0	69.2
143.	94.0
169.0	95.3
173.0	99.5
181.0	99.5
183.0	104.9
183.0	111.8
184.0	114.2
184.0	124.3
184.0	129.0
184.0	140.2
186.0	145.6
186.0	150.6
186.0	156.2
186.0	161,2
186.0	164.6
188.0	167.3
189.0	176.6
191.0	181.3

Pressure (mm Hg)	Cryogenic Temperature (°K)
193.0	185.0
195.0	191.6
203.0	197.6
208.0	200.5
216.0	203.8
244.0	208.4
266.0	211.0
314.0	214.4
336.0	215.6
350.0	216.0
358.0	216.6
373.0	224.0
373.0	229/0
376.0	281.6

EXPERIMENT: C-1

Main Temperature: $24.5\,^{\circ}C$
Initial Pressure of Carbon Dioxide: 203 mm Hg
Initial Pressure of Oxygen: 214 mm Hg

Pressure (mm Hg)	Cryogenic Temperature ($^{\circ}K$)
0.0	29.0
0.0	24.5
4.8	53.0
10.1	60.0
14.9	61.0
20.0	63.0
35.5	66.0
155.0	77.0
183.0	79.7
183.0	96.0
185.0	110.6
185.0	112.8
186.0	119.0
187.0	129.6
187.0	131.6
187.0	134.9
187.0	137.7
190.0	140.8
190.0	143.2
191.0	146.3
191.0	150.0
194.0	153.3
195.0	157.4
195.0	159.2
198.0	162.0
200.0	167.0
204.0	170.2
213.0	177.8
226.0	178.0
236.0	179.6
253.0	181.0
265.0	181.4
289.0	182.8
313.0	183.2
334.0	184.3
347.0	185.2
366.0	187.0
370.0	194.8
370.0	220.2
374.0	287.0

EXPERIMENT: C-2

Main Temperature: 25.9°C
Initial Pressure of Carbon Dioxide: 203 mm Hg
Initial Pressure of Oxygen: 213 mm Hg

Pressure (mm Hg)	Cryogenic Temperature ($^{\circ}$K)
0.07	33.5
12.0	53.5
16.1	56.0
18.6	64.5
32.2	67.5
73.5	71.5
92.0	74.0
100.0	74.5
182.0	91.8
183.0	99.2
184.0	102.8
185.0	107.6
186.0	110.2
186.0	128.4
187.0	129.8
187.0	131.3
187.0	134.7
189.0	142.4
191.0	146.5
191.0	150.0
197.0	166.4
204.0	170.5
216.0	175.2
226.0	177.0
236.0	178.8
280.0	182.0
309.0	183.6
360.0	184.6
368.0	190.6
372.0	218.8
374.0	283.4