INVESTIGATION AND DESIGN OF A REGENERABLE SILVER OXIDE SYSTEM FOR CARBON DIOXIDE CONTROL

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FOREGROUND

This report was prepared under Air Force Contract No. AF 33(657)-10928 under Project No. 6373, "Equipment for Life Support in Aerospace," Task No. 637302, "Respiratory Support Equipment."

The experimental program was carried out between April 1, 1963 and March 31, 1964 at the Chemical Division Laboratory of Denver Research Institute, University of Denver, Denver, Colorado 80210. Mr. W. J. Culberston, Jr., served as principal investigator and project supervisor and was assisted by Mr. Dave Jordan.

Mr. C. M. Meyer, Respiratory Equipment Branch, Biotechnology Division, Biomedical Laboratory, Aerospace Medical Research Laboratories, was the contract monitor.

The author wishes to acknowledge the contributions to this program made by Mr. Gavin Mallett for X-ray diffraction work and Mr. Francis Bonomo for infrared absorption work.

This technical report has been received and is approved.

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ABSTRACT

Precipitated silver carbonate was investigated using test tube samples to establish the merits of this approach to an Ag₂O solid system for CO₂ removal. Moisture catalyzes transport of CO₂ or Ag⁺ through an Ag₂CO₃ layer protecting the Ag₂O from conversion to Ag₂CO₃. At above 2½% CO₂ in the air CO₂ is adsorbed and displaces surface H₂O enough to inhibit conversion. Below 1% CO₂ reduced CO₂ driving force slows conversion. At the optimum 1 to 2½% CO₂ over 24 hours are required for good yields, even at 100% humidity. Humidities of 50% result in even slower absorption.

Regeneration to Ag₂O may be accomplished in moist partial vacuum at 125°C within 2 hours. H₂O must reach the decomposing Ag₂CO₃ by penetrating a protective Ag₂O layer countercflow to the outflowing CO₂. Moisture is not necessary with Y⁺⁺⁺ catalyst at 150°C.

Absorption is speeded 2-3 fold with Y⁺⁺⁺ catalyst. At 1% CO₂ and 50% humidity 75% yield is attained within 16 hours. Y⁺⁺⁺ dissolved in the cation lattice is believed to induce Ag⁺⁺⁺ vacancies in Ag₂CO₃ and increase Ag⁺⁺⁺ transport through the Ag₂CO₃ layer. H₂O may catalyze by supplying OH⁻ which dissolves in the anion lattice inducing Ag⁺⁺⁺ vacancies. Y⁺⁺⁺ may also induce Ag⁺⁺⁺ vacancies and/or strain in the Ag₂O causing increased absorption rates at between 1-2½% CO₂ where diffusion through the Ag₂CO₃ layer is less limiting than the reaction mechanism at the Ag₂O - Ag₂CO₃ interface.

Preliminary work on several other metal oxides showed Zn and Pb to be most promising of these as a substitute for the short-lived Ag₂O.
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I. INTRODUCTION

A. REGENERABLE CO₂ ABSORBENTS

Although removal of carbon dioxide from manned space capsule atmospheres can be accomplished by absorption with, say, anhydrous lithium hydroxide to form lithium carbonate, this is not easily reversible and for long missions a large supply of such a nonregenerable absorbent would be required. Thought has therefore been directed to development of an absorbent which can be regenerated periodically by ejecting the previously captured CO₂.

Previous work under sponsorship of the Biomedical Laboratory at Wright-Patterson Air Force Base has included that reported by T. L. Willard (ref 1) on a study of the Linde-type 5A molecular sieve for reversible adsorption of CO₂ and that reported by Chandler et al (ref 2) on work on both the Linde-type 5A molecular sieve and on the hopefully reversible silver oxide-silver carbonate system. Silver oxide as a CO₂ absorber had previously been studied and reported by Northwestern University (ref 3) under sponsorship of the U. S. Navy, but a heavy inert carrier was used and there was also difficulty in regeneration.

Denver Research Institute issued a proposal September 16, 1962, in response to an Air Force Request for Proposal. A certain amount of prior work on the silver oxide system reported in the normal literature was discussed, especially that of Spencer and Topley (ref 4, 5). Unfortunately, the absorptions performed by these workers were at elevated temperatures and although in one place reference is made to 90 successive cycles these cycles were to a yield of only about 10% of theoretical. There appears to be no previous reference to the absorption of CO₂ by Ag₂O at room temperature except in Mellor (ref 6) wherein absorption of CO₂ by aqueous suspensions of Ag₂O and by moist Ag₂O is mentioned. The work reported by Chandler et al (ref 2) had not been published nor was that of Northwestern University (ref 3) available.

The work herein reported demonstrates the existence of two types of absorption of CO₂ by Ag₂O, one at elevated temperatures (above about 50°C) and the other at room temperature. Both require the presence of moisture in the air, but a difference in the two types of absorption is believed to lie in the difference in modes of the
catalysis of the CO₂ absorption by water. Physically adsorbed surface moisture may be said to catalyze the room temperature absorption whereas chemisorbed moisture catalyzes the high temperature absorption of CO₂. The room temperature absorption has been more extensively studied.

With metallic oxide-carbonate systems as regenerable CO₂ absorbers, the heat of dissociation of the carbonate represents the major heat requirement (15,000 - 22,000 cal per gm mol CO₂) and this is relativelyunchanging for a variety of metals. For the molecular sieve the heat requirement is about equally split between the heat of desorption of CO₂ (33,000 cal per gm mol CO₂) and the sensible heat to heat the sieve. From a heat requirement standpoint there is an advantage in using a metallic oxide rather than a molecular sieve.

An advantage from a weight standpoint in using a metallic oxide rather than a molecular sieve is also apparent since at 100% conversion to carbonate Ag₂O contains 19.0% CO₂ whereas Linde 5A molecular sieve can contain only about 5.2% CO₂ in equilibrium with 0.5% CO₂ containing air.

A table showing a comparison of a molecular sieve and of several metallic oxides from a bed weight and total heat of regeneration standpoint for various assumed numbers of cycles completed is presented in Table IV, pg. 72, in this report.

Metallic oxides have a further advantage over a molecular sieve since the latter avidly adsorbs moisture which tends to displace any adsorbed CO₂. The sieve must therefore be protected from moisture by a dehydration bed. Also, any adsorbed moisture on the sieve must be driven off by rather high temperatures (175 to 260°C). Silver oxide does not absorb water to any great extent in normal operation, and although saturated air is preferable because of the catalytic action of water, half saturated air is workable, especially if a rare earth catalyst is used. Lead oxide allows 50% rather than 100% relative humidity air to be used resulting in less loss of absorption rate than silver oxide, although H₂O is believed to enter the lattice.

The design, fabrication, and testing of a laboratory working model using silver oxide was postponed because of difficulty in obtaining good yield after more than 10 or 15 cycles from either the pure silver system or the best catalyzed silver systems. As a result more time for study of other possible catalysts and for limited study of a
zinc oxide system (which preliminary work had shown to hold promise as a lighter absorbent than the silver oxide system) was provided. Discovery of a moist vacuum method of regeneration of the pure silver system has revived hopes of longer lifetimes with the silver oxide system under cyclical-operation and further testing is justified.

Originally it was planned to prepare silver oxide specimens by several methods. However, early relative success with precipitated or "amorphous" (rather than more coarsely crystalline) silver carbonate, its high surface to volume ratio, and reports that it behaved (refs 4, 5, 7) kinetically like the synthetic or reformed Ag₂CO₃ formed in cyclical operation, caused standardization on precipitated carbonate. Other methods originally proposed were (1) calcination of silver nitrate to silver followed by oxidation to Ag₂O and (2) precipitation of Ag₂O by alkali hydroxide.

B. CYCLICAL SYSTEMS UTILIZING REGENERABLE CO₂ ABSORBENTS

Any practical closed-cycle or even open-cycle life support system probably must contain a device that concentrates the 0.5 to 2% CO₂ maintained in the space capsule air to nearly 100%. With the closed-cycle system any chemical reactor converting CO₂ to C and/or O₂ should probably be fed CO₂ containing as little diluent air as possible in order to increase the reaction rate and to reduce side reactions such as C + O₂ → CO₂. With the open-cycle system wherein CO₂ is simply concentrated and ejected to space any air diluent obviously would be wasted to space.

When regenerable CO₂ absorbents are used, the degree of concentration achieved depends little on the absorption step but primarily on the regeneration step of the process. For maximum concentration of the CO₂, the ratio of void space to charged bed CO₂ capacity should be a minimum to minimize air trapped in the bed after absorption. Such air would be mixed with the CO₂ charge driven from the bed on regeneration. This is something of a problem with a molecular sieve (Linde 5A) in which the interstitial porosity of the gross particles is about 55% ¹ and the ratio of the air trapped to the CO₂ charge (about 5.2 wt % CO₂)

¹ Particle density or apparent specific gravity is 1.1 gm per cc and the bulk density is 45 lb per cu ft (see ref 7 and ref 8).
is about 1.8 wt % or 2.7 mol %. This is less troublesome with an oxide absorbent such as Ag₂O where the CO₂ charge may approach a theoretical 19%. Oxides are no less dense.

Where purge gas is desirable because moisture is required in the gas above the regenerating bed for catalytic action this gas should be pure recycled CO₂. This avoids mixing of air and CO₂ in the regenerating bed. Use of moist purge gas under reduced pressure is possible if higher CO₂ partial pressures suppress regeneration unduly. An alternate is to use vacuum in which moisture is introduced. In general, recycle purge must complicate the apparatus and require more heat and power hence is to be avoided if possible.

Certain rare earth and other catalysts allow the silver oxide system to be regenerated in vacuum without special attention to water catalysis (as is desirable almost to the point of necessity with the pure silver oxide system). The zinc oxide and lead oxide systems may be regenerated in a vacuum although there is undoubtedly some loss of water from the solid during regeneration which must be ejected with the CO₂ (not necessarily a disadvantage for a short mission) if the CO₂ is ejected to space. However, such loss of water during regeneration would not be serious if the CO₂ is merely being concentrated and lead to a reactor in a closed-cycle system.
II. EXPERIMENTAL PROGRAM

A study of the basic chemistry of the Ag₂O-CO₂ system has been attempted, since many variables were unexplored by previous workers. The basic apparatus has been a recording balance and differential thermal analysis apparatus (DTA). Several alternate mechanisms of absorption and one mechanism of regeneration have been proposed which may form an aid to further research with the pure Ag₂O system, especially in regard to cation catalysis. Practical information on the effect of the main variables in space capsule application of the Ag₂O-CO₂ system has also resulted. Other metal oxides-CO₂ systems have also been studied in the same apparatus.

Close study of changes in the solid involved in solid-gas reactions usually involves (1) progressive analysis of the solid as reaction proceeds or (2) progressive analysis of the gas plus a material balance as reaction proceeds. The latter is complicated by the amount of data required. The former, which is carried out by ordinary sampling and destructive analysis disturbs the geometry and the quantity of the specimen. When only one species is absorbed by the solid, as in the Ag₂O + CO₂ reaction, gravimetric monitoring of the reaction is also available. This can be conveniently done with a recording balance and has been the present approach.

In monitoring the reaction by the recording balance to obtain data suitable for correlation any gradual change occurring in a given solid sample from run to run could make comparison of an earlier run with a later one not strictly valid. To avoid this problem the split-run method, in which conditions (such as temperature or gas composition) are quickly changed in a given run so that any change in rate noted is due to the change in these rather than in any slow change of the nature of the solid or its reactivity as reaction progresses, was often used. This split-run method was found to be inapplicable to the room temperature absorption reaction (although apparently applicable for regeneration and high temperature absorption) because slow replacement of catalytic H₂O in or on the solid by CO₂ occurs as the CO₂ is increased and time is required for kinetic equilibrium to be established.

Testing of various possible solid catalysts with the silver system was encouraging since in several cases both the rate of absorption and rate and extent of regeneration in vacuum could be considerably increased. Particularly effective were Y+++ and certain rare earth cations with apparent ionic radii similar to that of Ag++. 

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Considerable difficulty in regeneration of the silver system to completion without catalysts was encountered until moisture was used with the vacuum. Even moist inert purge regeneration was relatively slow. Once complete regeneration was available valid effects of variables on the rate of absorption were obtainable.

A common method of testing adsorbent or absorbent materials is to pack them in a bed and observe the length of time required for the absorbed species to break through with the exit gas. From the concentration of the species in the exit gas vs time curve it is possible to determine the length of the mass transfer zone (MTZ) of the bed. This is a very practical test but it does not allow study of changes in the rate of absorption by the solid as influenced by the degree of saturation of the solid nor does it allow collection of much fundamental data. The recording balance program allowed collection of such data.

Within limits, the reaction rates determined on the recording balance are easily convertible to MTZ bed data for the following reasons: (a) It has been found that the superficial gas film resistance to diffusion is a minor contributor to overall reaction resistance of a sample in the recording balance apparatus. This leaves CO₂ concentration as the only remaining variable important at a given stage of absorption. (b) The rate of absorption as a function of CO₂ concentration at given stages of absorption (see Figures 25 and 26) has been obtained. A problem of variable H₂O vapor concentrations does not exist since so little change in the concentration should occur through the reaction zone, although the rate at the given fixed H₂O concentration must be known. To use the above assumptions it must be assumed that heat of absorption is carried away and that the bed operates isothermally since a small increase in temperature above room temperature drastically reduces the absorption rate.

The main experimental program will be discussed starting with the recording balance work on the pure Ag₂O system and will progress through the study of the influence of catalytic cations on the Ag₂O system by differential thermal analysis and recording balance and on to a short study of ZnO, PbO, and other oxides.

A. COMPOSITION AND PREPARATION OF THE MATERIALS STUDIED

Isomet Corporation (ref 2) found better absorption of CO₂ by Ag₂O was obtained by starting with Ag₂CO₃ coprecipitated with alumina
than with Ag$_2$O coprecipitated with or precipitated on various materials. They concluded that in preparing Ag$_2$O by thermal decomposition of Ag$_2$CO$_3$ the decomposition perhaps served to develop porosity and perhaps also served to condition the Ag$_2$O to reabsorption of CO$_2$. Spencer and Topley (ref 5) previously had reported results on high temperature partial absorption of CO$_2$ by Ag$_2$O formed by thermal decomposition of crystalline Ag$_2$CO$_3$ and amorphous-like recarbonated Ag$_2$CO$_3$. In view of the relative success of preliminary work in the present program with precipitated "amorphous" Ag$_2$CO$_3$ this was standardized as the starting material for work with the silver oxide system.

1. **Precipitation of "Amorphous" Silver Carbonate.**

Precipitation was accomplished by adding with stirring a nitrate solution of the silver with the catalyst cation, if any, to 0.2 M sodium carbonate solution. Addition was normally stopped while there was yet 10 to 20% excess of sodium carbonate. The precipitated material was washed two or three times with distilled water on a sintered glass Buchner funnel or in a large centrifuge tube. The color of freshly precipitated silver carbonate is light yellow but this darkened after drying and exposure to heat or light. The precipitation was carried out in subdued light since darkening is most likely to occur at the time of precipitation rather than during washing. The finely divided silver carbonate precipitate is crystalline to X-ray diffraction, but corresponds to the "amorphous" preparations mentioned in the literature (refs 4, 9).

2. **Avoidance of Calcination of the Silver Carbonate.**

First experiments run on the recording balance were with materials prepared by the drying and calcining procedure tried by Isomet Corporation. In this procedure the Ag$_2$CO$_3$ (with any coprecipitated Al$_2$O$_3$·nH$_2$O) was dried at 120°C and 1 atmosphere in air for 16 hours. Following the drying, the silver carbonate was decomposed to silver oxide by heating to 170-175°C for 16 hours at 2 mm Hg pressure followed by heating at 200°C for 6-9 hours at 2 mm Hg pressure.

X-ray diffraction work has shown that these heating conditions are probably too drastic for treatment of either an ordinary silver system containing no alumina or of one that does contain alumina. Visual examination of the final preparations showed some surfaces, edges, and even entire particles had turned white, both in the ordinary silver system and in a system containing 20% alumina. X-ray diffraction proved
the white material to contain mostly metallic silver. Even the bulk of the material which was nominally black Ag₂O contained finely divided metallic silver. (Although black material from the 26% alumina containing preparation and also from a pure silver system was found by X-ray diffraction to possibly contain a small amount of Ag₂O₃, the identification is not considered certain.) Therefore it became standard practice to not calcine the carbonate to oxide before placing it in the recording balance furnace but to decompose the carbonate in the balance furnace just before starting running. This allowed good control of the decomposition temperature and pressure and allowed continuous monitoring of the extent of decomposition to avoid over-calcination.

3. Drying the Silver Carbonate

Since silver carbonate does not contain "water of crystallization" and is easily dried to a reasonable degree most samples were dried at 120°C for 1 or 2 hours at 1 atmosphere pressure. Even drying at room temperature for a day or so in room air was found satisfactory. X-ray diffraction studies of some of the dried samples containing catalyst metals were made in order to observe any indication of solid solution or other change in the X-ray pattern. Considerable influence of 1% yttrium on the normal carbonate X-ray Debye pattern was noted with much low-angle scattering apparent. Other possible catalysts did not alter the pattern much, if at all, but rare earths of similar apparent ionic diameter to yttrium have not yet been studied by X-ray.

4. Other Metal Carbonates

The yttrium, lead, cadmium, bismuth, and zinc carbonates used for study of these systems were precipitated, washed and dried at 120°C in the same way as for the silver system.

B. THE RECORDING BALANCE APPARATUS

Figure 1 is a sketch of the recording balance apparatus. The recording balance used was Ainsworth type BV coupled to a type AU-2 dual pen recorder. One pen records the temperature of the sample furnace tube by means of a thermocouple while the other pen simultaneously records the sample weight. A sample of about 1 gram of carbamate of approximately 0.08 inch diameter extruded worms or similar diameter particles was placed in a conical basket made of a spiral winding of chromel thermocouple wire which was hung on the left side of the balance.
Figure 1. Recording Balance Apparatus
beam. A similar empty counterpoise basket was hung on the right side of the balance beam. Each basket was hung in a steel furnace tube below the table level of the balance. Both furnace tubes were immersed in a stirred air bath within a heavy aluminum walled furnace and were connected at the bottom to coiled steel air preheating tubes, also in the aluminum walled furnace. The identical sample basket and furnace tube on each side of the beam allowed considerable cancellation of buoyancy effects and upward friction drag caused by upward moving air in the two furnace tubes. A standard air rate of about 675 ml per minute was generally used in each furnace tube.

The aluminum walled furnace temperature was programmed so it could be electrically heated to a predetermined regeneration temperature and cooled by air jets to a predetermined absorption temperature. The regeneration could be accomplished in a vacuum of 2 mm Hg, as was usually the case, or it could be accomplished in a stream of purge air or other gas with or without water saturation. The absorption could be accomplished in a stream of air containing any desired concentration of CO₂ and saturated, partially saturated, or dry. For standardization, during absorption, the CO₂ had been usually set at 2% and the water concentration had usually corresponded to saturation at about 25°C.

The absorption or purge air supply was obtained from an 80 psig compressor source. The air was reduced to pressure to 5 to 10 psig and lead through about 5 ft of length of silica gel in four steel pipe drying tubes. The air stream was split and one stream saturated at room temperature by a porous bubbler stone in a quart and a half jar of water while the other was by-passed around the bubbler to allow selection of partially saturated air. Each stream was controlled by a needle valve and metered by a rotameter. CO₂ was injected downstream of the bubbler and also controlled by a needle valve and metered by a rotameter.

The bottle containing water for moist vacuum regeneration was used only in the last phases of the program. When it was used a vacuum of about 10-15 mm was obtained and the water in the bottle slowly boiled at room temperature.

C. THE DIFFERENTIAL THERMAL ANALYSIS APPARATUS

A Deltherm differential thermal analysis (DTA) apparatus was used in a study of the decomposition of various carbonates containing various catalyst cations. Special pressure-vacuum sample blocks
sealed by copper gaskets were built by the supplier and were used in obtaining both atmospheric pressure and vacuum DTA curves. Four samples could be run at a time in the apparatus. Heating rates were standardized at 3°C per min.

A different DTA apparatus constructed at Denver Research Institute was also used in certain studies. This apparatus had but one channel but the sample containers were small and fitted on the thermocouples with an easily removable slip fit. In this way sample weight could be determined initially and at given quench points during a run.
III. EXPERIMENTAL RESULTS AND DISCUSSION

A. THE PURE Ag₂O SYSTEM

1. Rate of Regeneration

Study of the regeneration of amorphous or synthetic recarbonated Ag₂CO₃ to Ag₂O is made difficult by two complicating phenomena. (1) There is a more or less reversible transition in Ag₂CO₃ at 185°C and the resulting high temperature form of the Ag₂CO₃ surprisingly decomposes more slowly than the low temperature form. (2) The presence of moisture in the gas phase above the solid catalyzes the decomposition of the low temperature form of Ag₂CO₃.

a. Effect of the 185°C transition in Ag₂CO₃ on its decomposition.

Figure 2 shows a recording balance run consisting of a series of alternate vacuum regenerations and absorptions in which regeneration was attempted at too high a temperature. The 200°C temperature used for the regeneration was higher than the 185°C transition of Ag₂CO₃. The sluggishness of the regenerations (after a brief spurt at rapid rate before transition had occurred) was the main cause of apparent sluggishness of the absorptions. This resulted because of the lack of sufficient Ag₂O present to adsorb very rapidly the CO₂. Although there was a considerable amount of undecomposed Ag₂CO₃ left throughout the run it slowly decreased as more cycles were run. The X-ray diffraction pattern from a sample taken at the end of the run showed no metallic silver but a mixture of silver oxide and carbonate.

In Figure 3 the great improvement obtained in regeneration and absorption when vacuum regeneration is carried out at a temperature below the transition temperature of Ag₂CO₃ is shown.

Figure 4 shows a plot of the decomposition rate in vacuum of a 0.863 gm sample of "amorphous" Ag₂CO₃ precipitated in excess K₂CO₃ as a function of temperature obtained by the split-run method by quickly increasing or decreasing the temperature and noting the percentage change in rate. Several such changes allow establishment of a plot. Figure 5 shows a similar plot starting with a 0.915 gm sample of Ag₂CO₃ recarbonated from previously formed Ag₂O. The higher rate with the second sample is due to the mode of precipitation rather than the fact that it was recarbonated, as was demonstrated by other runs.
Figure 2. Runs at Too High a Regeneration Temperature

Figure 3. Run with Regeneration Temperature Below Transition Temperature of Ag₃CO₃
Figure 4. Decomposition of Precipitated $\text{Ag}_2\text{CO}_3$

Figure 5. Decomposition of Recarbonated $\text{Ag}_2\text{CO}_3$
In both Figures 4 and 5, there is evident a rapid increase in decomposition rate up to about 185°C. Above this temperature the rate decreases considerably but increases again on cooling due, apparently, to reversibility of a carbonate transition. It was found that some time was required in establishing the lower rate (about 15 minutes) on proceeding to, for example, 190°C. This is because of slowness in the transition reaction of the carbonate. The similarity of the heating and cooling curves in Figure 4 indicates good reversibility of the transition.

DTA, with the special Denver Research Institute constructed apparatus at atmospheric pressure, produced the curve shown in Figure 6. The sample was contained in a small cup and the weight loss could be obtained at any place on the curve after quickly quenching the specimen by removing the DTA furnace from around it. By quenching at just above the first endothermic reaction appearing at 185°C negligible weight loss was found. Cooling and repeating the DTA run on the same specimen gave nearly as strong an endotherm; again at 185°C. Furthermore, thermo-gravimetric analysis (TGA) in 1 atm of CO₂ gave the weight vs. heating curve shown in Figure 7. Here again, there is no weight loss at a temperature of 185°C.

One possible explanation of the transition is that at 185°C the CO₃⁻ anion attains a greater degree of freedom, perhaps because of full rotation. Attempts to obtain infrared absorption of the Ag₂CO₃ above 185°C failed because of the formation of an opaque surface layer of metallic silver at this temperature, either in vacuum, in an inert CO₂ stream, or in air. Traces of organic vapors may be to blame for the formation of silver. X-ray diffraction work below and above the presumed transition temperature would be very enlightening but the hot stage in the Metallurgy Division was inoperative.

Evidence that the 185°C transition of Ag₂CO₃ is responsible for the reduced regeneration rate at high temperature is rather circumstantial because of uncertainties in fixing the exact temperature at which the rate is reduced on heating or increased on cooling. This must be a problem because of slowness of any transition reaction at near the transition temperature. However, with an Ag₂CO₃ specially precipitated with saturated K₂CO₃ solution the rate effect was especially sharp and could be established within about ±15°C.

Summarizing, the low temperature form of Ag₂CO₃ decomposes more rapidly than the high temperature form and the effect is reversible.
Figure 5. Atmospheric Pressure DTA of Precipitated Ag₂CO₃

Figure 7. TGA of Precipitated Ag₂CO₃ in CO₂
- that is, not only can the rate be lowered drastically by increasing the temperature above 185°C but it can be increased by dropping the temperature below 185°C. A certain amount of time is necessary for the effect to occur in either direction.

b. Catalysis of $\text{Ag}_2\text{CO}_3$ decomposition by moisture-purge regeneration

Evidence of the catalysis of regeneration by moisture is seen in Figure 8. This shows a typical switch-over from vacuum regeneration to absorption. Regeneration progressed at a rate much faster than during the vacuum period itself after atmospheric pressure air saturated at 25°C with moisture (and containing 2% CO$_2$) had been started past the sample but before the temperature had cooled appreciably. The rapidity with which the rate increased indicates that the regeneration may be catalyzed by surface moisture rather than by moisture in the lattice of the $\text{Ag}_2\text{O}$ or $\text{Ag}_2\text{CO}_3$. The time requirement for moisture to diffuse into the interior of the particles seems to be greater than the short time required to note the greatly increased regeneration rate. The rapid increase in regeneration rate in switching is, of course, not observed with purge regeneration.

Figure 9 shows a comparison between regeneration using air saturated with moisture at 25°C as purge and that using 2 mm Hg vacuum. Both regenerations were performed at 200°C on precipitated "amorphous" silver carbonate from the same batch. Regeneration in which moisture is introduced is much more rapid for the high temperature form of $\text{Ag}_2\text{CO}_3$. That regeneration is faster using purge air saturated with moisture than in vacuum for the low temperature form of $\text{Ag}_2\text{CO}_3$ also may be seen from Figure 10 for the precipitated silver carbonate at 170°C.

c. Effect of moisture concentration on purge regeneration of $\text{Ag}_2\text{CO}_3$

A series of purge regenerations at around 150°C with air, nitrogen, and oxygen demonstrated rather than an effect of oxygen an effect of moisture due to various methods of drying or moistening the gases.

Figure 11 shows the effect of moisture concentration on air purge regeneration of re-carbonated $\text{Ag}_2\text{CO}_3$ at 130°C determined by
Figure 8. Regeneration to Absorption Switch-Over

Figure 9. Purge vs Vacuum Regeneration at 200°C
Figure 10. Purge vs. Vacuum Regeneration at 170°C

Figure 11. Effect of Moisture Concentration on Air Purge Regeneration Above and Below 185°C
the split-run method. At this temperature the \( \text{Ag}_2\text{CO}_3 \) is in its low
temperature form. Also shown in Figure 11 is the effect of moisture on purge regeneration of \( \text{Ag}_2\text{CO}_3 \) in its high temperature form at 205°C. There is a saturation effect at the lower temperature such that at the higher water concentrations little increase in rate is obtained on further increase in concentration.

Typical moisture saturated air purge decompositions at several temperatures for reformed \( \text{Ag}_2\text{CO}_3 \) are shown in Figure 12. These are similar to decompositions of precipitated \( \text{Ag}_2\text{CO}_3 \).

d. Activation energy of regeneration of low temperature form of \( \text{Ag}_2\text{CO}_3 \) in vacuum and with purge

In Figure 13 is plotted the log of the rate vs \( 1/\tau \) for decomposition of the low temperature form of \( \text{Ag}_2\text{CO}_3 \) in vacuum, 10% relative humidity purge, and 100% relative humidity purge. Dotted lines are for precipitated \( \text{Ag}_2\text{CO}_3 \), solid lines are for reformed \( \text{Ag}_2\text{CO}_3 \). Since the rate tends to slow down and is continually changing with time it is necessary to use the split-run method - and note several percentage changes in rates. The rates were compared to a reference rate at a reference temperature for the particular sample in the recording balance. There appears to be little trend in the slope of the lines with respect to humidity. Thus moisture may not catalyze regeneration through the classical formation of an intermediate or through a low activation energy path. This is also true with moisture catalyzed absorption discussed later in which the activation energy does not appear to be changed by moisture although the frequency factor is increased.

For convenience, the mean activation energy of the lines in Figure 13 of 20.2 K cal per mole is shown on the plot of Figure 14 along with others discussed later. Spencer and Topley found 23.4, 24.8, and 22.5 K cal per mole in the absence of \( \text{CO}_3 \).

e. Activation energy of regeneration of high temperature form of \( \text{Ag}_2\text{CO}_3 \) in vacuum and with purge

Regeneration rates of the high temperature form of \( \text{Ag}_2\text{CO}_3 \) as a function of temperature in vacuum have been measured by the split-run method and activation energies so determined are 26.3 to 31.2 K cal per mole.

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Figure 12. Saturated Air Purge Regenerations at Various Temperatures
Figure 13. Log Regeneration Rates vs 1/T

Figure 14. Regeneration Activation Energies Below 185°C

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2. Equilibrium Dissociation Pressures of Ag₂CO₃ and the Heat of Regeneration

Figure 8 shows that when the temperature has fallen sufficiently the regeneration slows down and stops and absorption commences. If H₂O adsorption is negligible and CO₂ driving energy is low enough to not cause hysteresis, the temperature at which this occurs is the dissociation temperature of Ag₂CO₃ at the CO₂ partial pressure existing in the air stream. Figure 15 shows a plot of such temperatures (circles) for the pure Ag₂O - CO₂ system run as determined by such a "kinetic method." Three equilibrium CO₂ pressures at two different temperatures are also shown (squares) as determined in a static dissociation pressure apparatus held at temperature for a long period of time. Also plotted are published dissociation pressures for Ag₂CO₃ of Spencer and Topley (ref 4), Contnerssuer and Krustinison (ref 11), Watanabe (ref 12), and Colson (ref 13). Not only is there disagreement in the position of the kinetic method line (circles) with that of the literature line but the slopes are somewhat different.

Since the static pressures (squares) agree with the literature probably the increased CO₂ pressures of the kinetic method are those required to force nucleation and growth of Ag₂O and involve surface energy of the Ag₂O. Agreement of the slopes is satisfactory for present purposes. Further work may explain the discrepancy between the kinetic data and the data of the literature. The heat of dissociation as determined by the slope of the literature log p vs 1/T plot is 17.4 K cal per mole. That calculated from thermochemical values listed in Perry (ref 15) is 18.52 and is used in present calculations.

3. Discussion of the Mechanisms of Regeneration of Pure Ag₂CO₃

The importance of whether the temperature is above or below the 185°C transition point, both for vacuum and water saturated air purge regeneration, is indication that the nature of the high temperature form of Ag₂CO₃ is strongly rate determining at above 185°C. The nature of the low temperature form of Ag₂CO₃ is not necessarily rate determining below 185°C, however, and there remains the possibility that there is a protective film of Ag₂O through which the CO₂ must diffuse that limits the rate irrespective of the nature of the low temperature form of Ag₂CO₃. In opposition to the protective Ag₂O film theory is the Pilling-Bedworth relation which states that protective films are unlikely when their molar volumes are less than that of the
Figure 15. Dissociation Pressures of Ag₂CO₃
substrate, as in the present case of Ag₂CO₃ - Ag₂O. Nevertheless, a more or less protective powdery layer is possible even if no adherent protective film exists.

a. Argument for a layer of Ag₂O powder obstructing entrance of H₂O catalyzing counter to outflowing CO₂.

Rates actually do gradually diminish, as typical with growing protective layers, in vacuum decomposition of both pure Ag₂CO₃ and some catalyst containing samples. Diminishing rates may be caused at least partly by an Ag₂CO₃ particle size and shape distribution which allows high initial rates but lower rates after the small and angular particles having high surface to volume ratio have finished reacting. But a particle size distribution can hardly explain both the early choking of the decomposition rate under certain gaseous conditions and much later choking found with other gaseous conditions, all with the same batch of Ag₂CO₃.

Decomposition in vacuum is choked unusually early with Ag₂CO₃ precipitated with saturated K₂CO₃ solution instead of the usual weak Na₂CO₃ solution. Hardly any choking is observed and a nearly linear law is obtained with Ag₂CO₃ containing 1% Y catalyst, even with temperatures resulting in rates so low that heat transfer limitation could not be a case of linearity. The contrast of these effects is not believed to be due to a greater size range of the K₂CO₃ precipitated Ag₂CO₃ than of Na₂CO₃ precipitated Ag₂CO₃ or 1% Y+++ containing Ag₂CO₃ but is believed to be due to a large particle size with K₂CO₃ precipitated Ag₂CO₃ and to drastic elimination of the effectiveness of the Ag₂O protective layer when Ag₂CO₃ containing 1% Y is used.

Spencer and Topley (ref 4) concluded that in those cases where the decomposition of crystalline Ag₂CO₃ is progressively retarded and virtually comes to an end before all the Ag₂CO₃ has decomposed, such retardation is caused by a surface layer of Ag₂O particle through which CO₂ must diffuse. They suggested that (1) outward CO₂ diffusion from the reaction zone in the center of the particle depends on adsorbed H₂O in the outer layer of Ag₂O around the particle and hence depends on the H₂O vapor concentration and that (2) there is difficulty in H₂O vapor penetrating the increasing thickness of oxide into the reaction zone. These authors hypothesized that removal of CO₂ from the reaction zone is by surface diffusion on the Ag₂O particles surrounding it and that such surface diffusion is catalyzed by the adsorption of H₂O vapor on the
Ag₂O, possibly as a surface layer of AgOH. The condition necessary for a more linear decomposition uninhibited by the overlying oxide was that CO₂ should diffuse away more rapidly than it is evolved. That, at higher temperatures, a higher concentration of H₂O vapor was required to obtain linear decompositions (indicative that diffusion was not rate-limiting) was in keeping with this latter hypothesis. The adsorption of H₂O vapor would presumably be more difficult and the interface reaction would be faster at higher temperatures.

Evidence contradictory to Spencer and Topley's views is the difference between the activation energy of vacuum regeneration above and below 185°C. In the present work between 26.3 to 31.2 K cal per mole activation energy was found above 185°C and 20.2 K cal per mole below 185°C. This indicates that CO₂ surface diffusion over Ag₂O is not an important rate limiting step but that some property of Ag₂CO₃ changed by its transition is involved in the rate limiting mechanism. The rate limiting mechanism must involve the reaction sites (the interface reaction) at the Ag₂CO₃ rather than poor CO₂ diffusion out from the Ag₂CO₃ over Ag₂CO₃ surfaces.

The hypothesized Ag₂O protective layer around the unreacted Ag₂CO₃ may simply obstruct entrance of H₂O catalyst to the Ag₂CO₃ interface. The gradually increasing rate limiting action of such an Ag₂O protective layer as reaction proceeds would simply be due to the increased distance H₂O vapor would have to penetrate to the reaction sites at the Ag₂CO₃ interface counterflow to outflowing CO₂. The outflowing CO₂ from the decomposition of Ag₂CO₃ would continually tend to sweep H₂O catalyst away from the reaction interface and a continuing need would exist for entrance of H₂O catalyst.

That lack of H₂O catalyst at the Ag₂CO₃ reaction interface rather than at the surface of Ag₂O is rate limiting is not disputed by the fact that both vacuum regenerations and regenerations with air purge at 100% relative humidity (all below 185°C) give the same activation energy of about 20.2 K cal per mole (see Figures 13 and 14). If lack of H₂O catalyst at the scattered atomic sites of the reaction interface were rate limiting the activation energy would be relatively constant irregardless of the humidity and the resulting number of such sites. Rates would vary mainly with the frequency factor in the Arrhenius rate equation. If H₂O catalyzed by adsorbing on the surface of Ag₂O thereby allowing more rapid surface CO₂ diffusion the activation energy possibly would be gradually lowered by gradually greater quantities of adsorbed H₂O. It is not certain.
b. Rate determining step in presence of ample H₂O catalyst.

As proposed above, H₂O catalyzes decomposition below 185°C by assisting at the reaction interface. It catalyzes a former limiting step of 20.2 K cal activation energy but the new limiting step also has about the same activation energy. The increase of rate is secured by increase of the frequency factor rather than by lowering of the activation energy if the new rate limiting reaction is still the same as the old. However, if a different mechanism other than the old limits the reaction, it may or may not be one involving water catalysis.

The activation energy of 20.2 K cal per mole of the limiting step of the water catalyzed decomposition of Ag₂CO₃ is similar to the 18.6 K cal per mole of the electric conductivity of Ag₂CO₃. This suggests that a volume property of Ag₂CO₃ may have a role in the new limiting step. That the activation energy of electrical conductivity of Ag₂O is much lower at 14.5 K cal per mole perhaps precludes it as important in the new step. It must be admitted, however, that the conductivity of both Ag₂CO₃ and Ag₂O may be composed of a much greater electronic part than ionic part. Although there are direct relations between ionic conductivity and ionic diffusion (see ref 10) the activation energies of electrical conduction actually measured of 18.6 and 14.5 may primarily be caused by the electronic part and have no significance in the above argument. Even though electronic conduction predominates, however, what relatively small ionic conduction and associated diffusion that exists may be absolutely large and of great kinetic significance. The ionic conduction activation energy, of course, may be different from the activation energy of electronic conduction.

c. Explanations of apparent negative temperature coefficient of regeneration.

Spencer and Topley felt that lack of adsorbed H₂O (which facilitated CO₂ diffusion past the Ag₂O layer as mentioned above in Section III A 3 a) provided a possible explanation of the negative temperature coefficient found by Centnerszewski and Brzes (ref 9) for the decomposition of amorphous Ag₂CO₃ between 240° and 260°C. At these temperatures the amount of H₂O vapor required might be considerable yet none
was added. As the temperature was increased to 260°C the relative dryness of the material was increased and the reaction became slower because of poor H₂O catalysis. As the temperature was further increased above 260°C the exponential increase of reaction rate with temperature again outweighed the effect of dryness; hence, the "apparent anomaly of a temperature coefficient being first positive, then negative, then again positive."

The transition at 185°C in Ag₂CO₃, and the slowness of decomposition of the high temperature form compared to that of the low temperature form, leads to an alternate explanation of the negative temperature coefficient to that hypothesized by Centnerszewer and Bruss. The discrepancy between the temperature at which the minimum decomposition rate occurs of 185 - 200°C of the present work and that of 240 - 260°C found by Centnerszewer and Bruss may be due to their working with a larger mass of material through which the resistance to heat transfer was sufficient to cause the true temperature of the interior of the mass to be lower than that registered in the furnace.
4. Difficulties and Recommendations in Practical Regeneration of the Pure Ag₂O System

Studies on the regeneration of precipitated "amorphous" and re-carbonated or "synthetic" Ag₂CO₃ indicate the following disadvantageous characteristics of practical importance.

Vacuum regeneration is slow and difficult to carry to completion, probably because of lack of moisture at the site of decomposition. Temperatures above the 185°C transition in Ag₂CO₃ cause reduced regeneration rates. Temperatures as high as 250°C still give incomplete regeneration over reasonable time periods and are dangerously close to the temperature where the rate of oxide decomposition to metallic silver becomes appreciable. Once such silver is formed it is nearly impossible to re-carbonate it.

Since regeneration is accelerated by moisture in gases above the solid, conduction of moist air over it has been tried and found effective. Air saturated or half saturated at room temperature passed over the solid at 150°C has been found to give nearly complete regeneration within about 3 or 4 hours for fresh material (see Figure 12). Higher temperatures up to 185°C give faster regeneration rates.

A serious disadvantage with purge regeneration is that the CO₂ would be recovered diluted with the purge gas. This would require a CO₂ reduction reactor able to handle the air inerts, or would force loss of some air to space if the CO₂ is so ejected. The use of CO₂ itself as a purge to carry the required moisture, so eliminating inerts, is inadvisable at atmospheric pressure because to exceed the dissociation temperature of Ag₂CO₃ at 1 atm requires a temperature above the 185°C transition temperature of Ag₂CO₃. In addition, Spencer and Topley (ref 4) have shown that CO₂ partial pressures, even though below the dissociation pressure, reduce greatly the rate of dissociation of Ag₂CO₃.

A workable compromise method probably would be to regenerate using pure CO₂ purge at about 1/10 atm saturated with moisture at room temperature. The temperature required to cause dissociation would be below 185°C but a recycle pump operating at 1/10 atm would
be required. Such a system has not actually been tried and the required regeneration times are in doubt because the extent of the inhibiting effect of the high CO₂ concentration is not yet known.

An even more attractive method of regeneration, which has actually been tested, is to introduce 5 or 10 mm of H₂O vapor pressure into the system during vacuum regeneration by directly connecting a bottle of water to the dead end of the vacuum chamber so that the H₂O vapor must pass by the sample on the way out through the vacuum pump. An alternate method of introducing moisture operable in zero gravity fields would be to connect the system as above to a moist silica gel column. The vacuum pump could be replaced by the vacuum of space if the CO₂ is to be expelled to space. Complete regeneration of the pure Ag₂O system by this method is possible within 2 hours at 125°C and 1-1/2 hours at 150°C. About 20 minutes of this is required for attainment of operating temperature. The exact amount of H₂O required to expel a mole of CO₂ has not been determined but it is anticipated that less H₂O would be required than is exhaled by a man.

Another, perhaps even more attractive, method of regeneration is to use vacuum without introduction of catalyzing water and to use cation catalysts such as 1% yttrium in the solid. The cation catalysts are discussed in a subsequent section. It is uncertain whether they act as moisture reservoirs or alter the mechanism of the regeneration.

5. Rate of Absorption

The rate of absorption of CO₂ by Ag₂O left on the recording balance after regeneration was studied by passing air laden with CO₂ and/or H₂O past it at a standard rate of 675 ml per minute as described in Section II B describing the apparatus.

a. Negligible Influence of Gas Velocity and Particle Size

To observe any effects on the rate of absorption caused by such variables as temperature, moisture concentration, CO₂ concentration, and aging, it is necessary that the resistance to CO₂ mass transfer across the stagnant air film around the gross solid particles of Ag₂O contained in the sample basket of the balance not be a greatly controlling factor. This was found to be the case. For example, doubling the air velocity while maintaining the CO₂ concentration at 0.55% and the H₂O concentration saturated at room temperature yielded only a 35% increase
in rate of absorption by a typical pure $\mathrm{Ag_2O}$ sample about half reacted with $\mathrm{CO_2}$. Particle size has been generally kept at about 0.08 inch diameter. After a series of cycles in which the rate of absorption had dropped considerably the particles were crushed to about 1/5 their previous diameter and little increase in rate was noted. This indicates that there was still much internal porosity and that because of internal porosity there is relatively little effect of particle size. Further evidence that diffusion through the stagnant outer film or through internal porosity is not rate limiting to any great extent, is the fact that, on some occasions discussed later, increased $\mathrm{CO_2}$ concentration actually reduces the absorption rate.

b. Influence of temperature - high temperature vs room temperature absorption and activation energy of absorption

The reaction temperature was found to play a very important role in determining the rate of absorption of $\mathrm{CO_2}$ from gas saturated with $\mathrm{H_2O}$. The effect of temperature is shown in Figure 16 obtained by the split-run method for pure $\mathrm{CO_2}$ saturated with $\mathrm{H_2O}$ at room temperature. Curve A was for 2% $\mathrm{CO_2}$ at nearly full reaction where a thick $\mathrm{Ag_2CO_3}$ layer exists; Curve B is for a still thicker layer than Curve A at a still later time during the absorption period. There appears to be two modes of $\mathrm{CO_2}$ absorption; the one becomes increasingly rapid at temperatures above 50°C while the other becomes rapid at near room temperature. The latter is inhibited by a thick layer of $\mathrm{Ag_2CO_3}$ more than that above 50°C as comparison of Curves A and B indicate. At around 50°C neither mode is rapid and a minimum is observed. A similar minimum is obtained at 2% $\mathrm{CO_2}$. It is hypothesized in Section IV C 5 that the room temperature absorption is catalyzed by physically adsorbed water whereas high temperature absorption above 50°C is catalyzed by chemisorbed water.

Activation energies for room temperature and higher temperature absorption of pure $\mathrm{CO_2}$ have been measured by the split-run method at 100% relative humidity at room temperature and nearly zero humidity and are plotted in Figure 17. Because physically adsorbed water is so easily driven off by heat it is difficult - in fact negative values are obtained at room temperature - to interpret the energies in a conventional way at near room temperature. The activation energies at higher temperature are less influenced, however, by loss of water at each split-run temperature increase increment. That is, the decrease in frequency factor at each increment of temperature increase is less
Figure 16. Effect of Temperature on Absorption Rate of Pure CO₂ Determined by Split-Run Method

Figure 17. Activation Energies of Absorption of Pure CO₂ Determined by Split-Run Method
percentage-wise at the higher temperatures where only more avidly adsorbed water "molecules" are left. The frequency factor should be a function of the number of adsorbed water sites since only at these is an interface reaction possible, or if CO₂ or Ag⁺ diffusion limits the rate, only by vacancies caused by H₂O is diffusion possible. (These possible mechanisms are discussed in the Appendix.)

The apparent activation energies of absorption at the higher temperatures are more significant because of their probable approach to true activation energies and because of their approach to an asymptote at, perhaps, 12 or 13 K cal per mole. It was not possible to study the activation energies at higher temperatures than shown in Figure 17 because of proximity to the dissociation temperature of Ag₂CO₃. Such proximity causes abnormally low absorption rates. A pressure attachment for the recording balance was not available at Denver Research Institute and it was not possible to increase the dissociation temperature but had such been possible a discontinuity may have been found at 185°C corresponding to the transition temperature of Ag₂CO₃ if a film or layer of such is truly rate-limiting at high temperatures.

c. High temperature absorption - effect of moisture and CO₂ concentration

The high temperature absorption of CO₂ by Ag₂O is of little practical interest because of the high heating load to preheat the large amount of diluent air each pass. However, a protective Ag₂CO₃ layer probably inhibits high temperature absorption similarly as discussed in greater detail for room temperature absorption. Existence of such a layer is in agreement with the Pilling-Bedworth rule for formation of a tight layer, since the molecular volume of Ag₂CO₃ is greater than that of Ag₂O. A protective layer of Ag₂CO₃ had been hypothesized previously by Spencer and Topley (ref 5) which hindered inward diffusion of CO₂ to the unreacted Ag₂O core of a particle. Their absorptions were also at high temperature but involved pure CO₂ at various pressures with some catalytic water pressure. Alternate absorption mechanisms other than inward CO₂ diffusion (such as outward Ag⁺ diffusion) are considered in the Appendix.

In contrast to room temperature absorption, high temperature absorption does not give much lag between H₂O concentration changes and corresponding rate changes. The effect of moisture is not as critical as with room temperature absorption but this advantage is

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relatively unimportant since by the upper curve of Figure 33 only moderate temperatures are workable at 0.5% CO₂. Also space capsule CO₂ absorbents should absorb at near room temperature for lowest power requirements anyway.

In Figure 18 the effect of CO₂ concentration determined by the split-run method at 80°C and 100% relative humidity at 25°C is shown. The saturation in rate increase at high CO₂ concentrations may be due to replacement of adsorbed catalytic water by CO₂ or may be due to a reduction of point defects on or in Ag₂CO₃ by which diffusion through an Ag₂CO₃ protective layer occurs (by replacement of OH⁻ by CO₃²⁻).

d. The stages of room temperature absorption

In Figure 20 the room temperature absorptions of 2% CO₂ from H₂O saturated air after vacuum regeneration and saturated air purge regeneration are compared. The absorption after vacuum regeneration is comprised of four stages but that after moist air purge regeneration is often comprised of but three, the first stage of the former not being clearly separated from Stage 2, or present at all:

Stage 1. A rapid initial weight gain of about 1-4 mg per gram sample after vacuum regeneration (absent after bubbled air purge regeneration) is due to adsorption of CO₂. Pure CO₂ appears to give a greater initial gain, about 8 mg; 6% CO₂ about 4 mg; and 1% CO₂ no clearly separate Stage 1 but immediate onset of fairly rapid absorption of Stage 2. The upper plot in Figure 15 shows the onset of Stage 1. The plot in Figure 19 shows the onset of Stage 2 following the often slight inflection caused by slowing of Stage 1. The temperature of onset of Stage 2 is dependent on the H₂O concentration rather than the CO₂ concentration indicating the onset of the catalytic effect of H₂O with Stage 2.

Stage 2. The absorption of CO₂ while the furnace is still cooling from the regeneration temperature is rather slow for the pure silver system. However, around 50°C a small temperature increase will induce a spurt in the CO₂ absorption rate which then quickly subsides. This action is somewhat similar to that at room temperature during Stage 3 (see Discussion, g, and Figure 27) except that an ultimate fall in weight after the spurt does not occur and that it, of course, occurs only while the solid is incompletely converted to carbonate whereas the room temperature effect is most noticeable after conversion is nearly
Figure 18. Effect of CO$_2$ Concentration on High Temperature Absorption by Split-Run Method

Figure 19. Onset of Stage 2 Due to Adsorption of Catalytic Water
Figure 20. Comparison of Absorption after Vacuum and Saturated Air Purge Regeneration
finished and CO₂ pick up is very slow. The spurt may be caused by
CO₂ reacting with an Ag₂CO₃ surface or Ag₂O – Ag₂CO₃ interface supply
of Ag⁺ ions which are soon used up and but slowly replenished, or it
may be due to replacement of chemisorbed H₂O or OH⁻ by heavier
CO₂ or CO₃⁻.

The slow absorption of Stage 2 is greatly accelerated by cation
catalysis such as 1% Y⁺⁺⁺⁺ incorporated in the system during initial
precipitation of the Ag₂CO₃. These are discussed in a later section.

Stage 3. Most concern with room temperature absorption has
been with the nature of Stage 3 since for reasonable time intervals this
accounts for the greatest CO₂ weight gain. Stage 3 is a rather linear
rate law period following Stage 2. Cooling nearly completely to room
temperature (or to a temperature at which the process air is nearly
saturated with water) is desirable for the most extensive development
of Stage 3 with the pure Ag₂O system. This appears to be due to the
necessity for copious physically adsorbed water which postpones the
termination of Stage 3 and the onset of Stage 4 all due to inhibition of
diffusion through the growing Ag₂CO₃ layer.

The sensitivity to the amount of moisture in the air of the CO₂
absorption during Stage 3 before its truncation is greatly influenced by
the CO₂ concentration itself. This is illustrated in Figure 21 in which
the extent of absorption before Stage 3 is judged to be finished is plotted
as a function of CO₂ concentration for 100% and 50% relative humidity.
At 3 to 5% CO₂ the moisture content of the air has a much greater in-
fluence than at below 1-1/2% CO₂. Possibly this is due to catalytic
water adsorbed on (or absorbed in) Ag₂CO₃ being replaced by adsorbed
CO₂ causing difficult diffusion through the Ag₂CO₃ protective layer. A
great H₂O concentration increase is then necessary to maintain suffici-
ent adsorbed water in competition with the CO₂. At below 1-1/2% CO₂
relatively low H₂O concentrations are able to compete with the unde-
sirable CO₂ adsorption and mitigate diffusion resistance through the
Ag₂CO₃ layer.

Further illustration of the great sensitivity of the development
of Stage 3 to the extent of water adsorption in the 3 to 10% CO₂ region
is in its sensitivity to small changes in temperature at a given H₂O
concentration.

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Figure 21. Extent of Absorption before Stage 3 is Finished
Figure 22 shows the progress of an absorption cycle at about 7\% CO₂ and nearly 100\% relative humidity at 25°C wherein Stage 3 was terminated after about 25\% absorption. When the temperature was lowered to 20°C (at the same absolute humidity) to bring the relative humidity up to 106\%, the absorption rate became more rapid after an induction period and a further absorption was secured.

Limited rejuvenation of Stage 3 after it once has been truncated at a relative humidity less than 100\% is possible by increasing the relative humidity rather than by decreasing the temperature. This is illustrated in Figure 23 for absorption at 25°C and 9.54\% CO₂.

Stage 3 may be rather linear partly because some time is required to cool the sample furnace down to room temperature and although a very rapid rate would be expected at first when the Ag₂CO₃ protective layer is thin this is actually throttled because the water catalysis becomes only gradually effective as water gradually is adsorbed. The diffusion through the Ag₂CO₃ layer is not the only reaction resistance. The Ag₂O - Ag₂CO₃ interface reaction must also represent appreciable resistance compared to that of the Ag₂CO₃ layer in early stages of absorption when the layer is relatively thin, especially at high relative humidities and at CO₂ concentrations less than 1-1/2\% where a given thickness of Ag₂CO₃ layer presents less dimensional resistance due to less inhibition by CO₂.

Stage 4. Onset of Stage 4 appears simultaneously with truncation of Stage 3. Such onset is due to rather high diffusional resistance through the protective Ag₂CO₃ layer. The four factors which are important in determining the onset are the same ones important in prediction of the life of Stage 3: (1) Thickness of the Ag₂CO₃ layer (this is probably fixed for a given extent of absorption) (2) Relative humidity, (3) CO₂ concentration, (4) Temperature.

c. The effect of CO₂ concentration studied by the split-run method

The split-run method was first used in study of the effect of CO₂ concentration. In contrast to split runs of varied H₂O concentration, no short term induction effects were at first apparent. Variations in CO₂ concentration from about 1/2 to 7\% seemed to cause fairly proportional variation in the rate during Stage 3 as seen in Figure 24. At the higher CO₂ concentrations, however, it was found that the
Figure 22. Revival of Stage 3 by Lowered Temperature

Figure 23. Revival of Stage 3 by Increased Humidity

Figure 24. Effect of CO₂ Concentration on Absorption Rate by Split-Run Method
increased rate due to a CO₂ concentration increase would gradually disappear and the rate would drop markedly. This behavior is believed due to the gradual onset CO₂ inhibition as adsorbed H₂O is gradually replaced by adsorbed CO₂. Thus reduction of H₂O catalysis does not fully occur on short term CO₂ concentration increases although there is an increase in CO₂ diffusion through any protective Ag₂CO₃ layer due simply to the increased CO₂ concentration gradient across the layer.

f. The effect of CO₂ and H₂O concentration and absorption time studied by long-term room temperature absorptions

Figures 25 and 26 show the extent of absorption at various elapsed times as a function of CO₂ concentration at 100% relative humidity and 50% relative humidity, respectively. The termination of absorption by Stage 3 and onset of Stage 4 is indicated by the rather abrupt reduced spacing of the curves as the time is increased for a given CO₂ concentration.

An inhibition of room temperature absorption by CO₂ itself is evident at CO₂ concentrations above 1-1/2%. It appears that the absorption is enhanced by the higher relative humidity. The improvement of absorption by the higher humidity is much greater at concentrations above 1-1/2% than at those below. An optimum absorption rate appears to exist at 1% CO₂ at both humidities.

g. Discussion of previous absorption mechanism proposals

Part of the hypothesized mechanism of absorption involving a protective Ag₂CO₃ layer, catalysis by H₂O, and replacement of H₂O catalyst by CO₂ has been suggested already in Section III A 5 d.

Spencer and Topley (ref 5) found some indication of an optimum CO₂ concentration to equilibrium pressure (PCO₂ : P-equilibrium) ratio during high temperature absorption over long-term absorptions. They attributed it to too rapid nucleation of Ag₂CO₃ and to too rapid build-up of a protective Ag₂CO₃ layer thus quickly choking off CO₂ diffusion to the unreacted Ag₂O. They believed that CO₂ diffused more rapidly over Ag₂O surfaces "wetted" them more easily than over Ag₂CO₃ surfaces. Although slowing of nucleation may be valuable at higher temperatures, this is not necessarily true also at room temperature. As a matter of fact it may well be that the optimum PCO₂ : P-equilibrium ratio they
Figure 25. Extents of Absorption at 100% Relative Humidity

Figure 26. Extents of Absorption at 50% Relative Humidity
found may actually be a manifestation of the optimum CO₂ concentration at room temperature demonstrated by the present work.

Spencer and Topley also believed that adsorption of H₂O on small particles of Ag₂CO₃ forming a protective layer aggregate around unreacted Ag₂O may increase the rate of CO₂ diffusion through the layer due to increased surface diffusion over the small Ag₂CO₃ particles. It was possible during the present work to demonstrate by split-runs an increase in rate due to increased relative humidity at room or higher temperatures but ambiguous results were had with relative humidities decreasing, apparently because of a time lag in desorption of the H₂O. Apparently moisture, once adsorbed by the solid, can remain and catalyze absorption for some time after the air has been made dry or, (as commented in section III A 5c above), after the CO₂ concentration has been increased. Demonstration of an increase in rate due to increased relative humidity is perhaps best shown by comparison of Figures 25 and 26 summarizing long-term absorptions.

Substantiation of the view that CO₂ inhibition of absorption is caused by CO₂ adsorbing and replacing adsorbed H₂O is had in the fact that during room temperature adsorption runs with moisture saturated air in Stage 3 (see Figure 27) slight increases in temperature caused relatively great and rapid weight gain pips, up to 2 mg in a sample which could absorb 130 mg of CO₂ usually followed by a period of lowered absorption rate, especially if the specimen were nearly fully carbonated. This phenomenon was repeatable, but the pips were smaller at progressively higher temperatures up to about 50°C. It was repeatable for long periods during steady absorption at a given temperature level. This phenomenon may be caused by higher temperatures driving out some water (as OH⁻) from the lattice, from rifts, or from the surface of the Ag₂CO₃. The OH⁻ is replaced by the heavier CO₃⁻. The weight changes seem rather great for purely surface adsorption effects.

That there exists a slow development of the inhibition by carbon dioxide indicates the replacement of adsorbed H₂O by CO₂ to be slower than the thermal expulsion of H₂O which is then replaced by CO₂ as in generation of the above thermal pips.

h. Evidence for two modes of low temperature water catalysis - promotion of diffusion through Ag₂CO₃ layer and catalysis at Ag₂CO₃ - Ag₂O interface
Figure 27. Weight Gain Peaks Caused by Small Temperature Increases
Not only did Spencer and Topley hypothesize that adsorbed water catalyzed CO\textsubscript{2} diffusion through the Ag\textsubscript{2}CO\textsubscript{3} layer but also that adsorbed CO\textsubscript{2} at the Ag\textsubscript{2}CO\textsubscript{3} - Ag\textsubscript{2}O interface blocked reaction. They did not comment on the role of adsorbed water at the interface except to say that if it was of influence there an extremely small amount was required. They studied high-temperature absorption only, however. Possibly there is inhibition by CO\textsubscript{2} as well as water catalysis for both diffusion through the Ag\textsubscript{2}CO\textsubscript{3} layer and for the Ag\textsubscript{2}CO\textsubscript{3} - Ag\textsubscript{2}O interface reaction. Perhaps the interface reaction involves chemisorption of CO\textsubscript{2} and H\textsubscript{2}O, while the diffusion through the Ag\textsubscript{2}CO\textsubscript{3} involves physical adsorption of CO\textsubscript{2} and H\textsubscript{2}O. Further evidence for this latter view is discussed in the Section III B on cation catalysis.

Apparently Ag\textsuperscript{+} diffusion could be involved in either the interface reaction step or in diffusion through the Ag\textsubscript{2}CO\textsubscript{3} protective layer (rather than CO\textsubscript{2} as previously tentatively assumed, following Spencer and Topley). At the interface Ag\textsuperscript{+} diffusion from the interior of Ag\textsubscript{2}O to its surface may be involved. In the protective layer Ag\textsuperscript{+} would diffuse through Ag\textsubscript{2}CO\textsubscript{3} or over its surface. Strong evidence for Ag\textsuperscript{+} diffusion is the fact that cation catalysis is possible.

If the reaction sites at the Ag\textsubscript{2}O - Ag\textsubscript{2}CO\textsubscript{3} interface are Ag\textsuperscript{+} ions (or clusters) their concentration will depend on the rate of diffusion of the Ag\textsuperscript{+} from the interior of the Ag\textsubscript{2}O to its surface. Thus there will be two rate controlling factors in the interface reaction, (1) the presence of H\textsubscript{2}O catalyst at the Ag\textsuperscript{+} ions and (2) the number Ag\textsuperscript{+} ions exposed to CO\textsubscript{2}. If both H\textsubscript{2}O and CO\textsubscript{2} are necessary at a given Ag\textsuperscript{+} ion for reaction, and if they compete for adsorption, there should be an optimum CO\textsubscript{2} concentration at a given H\textsubscript{2}O concentration. Such an optimum is found but it is ambiguous in that it may be due to an optimum in diffusion of CO\textsubscript{2} or Ag\textsuperscript{+} through a protective Ag\textsubscript{2}CO\textsubscript{3} layer as discussed above or to an optimum in the interface reaction rate.

6. Difficulties in Use of the Pure Ag\textsubscript{2}O System for Absorption of CO\textsubscript{2}

The main difficulty in practical room temperature absorption of CO\textsubscript{2} by the pure Ag\textsubscript{2}O system is caused by the necessity to keep adsorbed catalyzing water present in the solid. Too high a temperature, as little as 15°C above the dew point of the air, with 2% CO\textsubscript{2}, is also sufficient to greatly reduce the rate and extent of carbonation. The water catalyzes (1) possibly the Ag\textsubscript{2}O - Ag\textsubscript{2}CO\textsubscript{3} interface reaction if
such is a rate limiting step, (2) possibly Ag⁺ diffusion out from the Ag₂O through the Ag₂CO₃ protective layer, and (3) possibly CO₂ diffusion inward through the protective Ag₂CO₃ layer.

The water is easily lost from the solid by (1) too low a relative humidity in the air or (2) by too low a ratio of H₂O concentration to CO₂ concentration. A relative humidity of 50% instead of near 100% is sufficient to appreciably reduce the rate of absorption at all CO₂ concentrations. More work is needed to delineate which of these two conditions is operative in the above three modes of catalysis. Possibly below 1% CO₂ concentration where CO₂ does not inhibit absorption the relative humidity is definitive but above 3% where CO₂ does inhibit the H₂O to CO₂ ratio is important.

The decay of room temperature absorption yields on repeated cycling has been examined wherein the weight of CO₂ absorbed per absorption cycle is plotted for runs with vacuum and saturated air purge regeneration. The useful life appears to be about 15 cycles for both cases. Examination of the solid after running indicated much size contraction or sintering. Similar results were found with the 1% Y containing system. More work on system life is needed since relative humidities other than 100% on absorption have not been investigated and only moist air purge regeneration of the pure Ag₂O system and 150°C vacuum regeneration of the 1% Y containing system have been tried. Especially desirable is testing of the moist vacuum, 125°C regeneration of the pure Ag₂O system.

B. THE ADDITION OF CATION CATALYSTS TO THE Ag₂O SYSTEM

The catalytic action of cations incorporated in the silver system has also been studied. These were added through co-precipitation of carbonates from aqueous solution. Several rare earth catalysts which accelerate both regeneration and absorption have been discovered. For regeneration and absorption the ultimate criterion has been trial on the recording balance to determine absorption rates at various stages of the absorption cycle. Regeneration catalysis has, however, also been evaluated through the use of DTA.

We originally suggested that the catalytic action of impurities could be expected to act in three possible ways during absorption, the
more difficult part of the cycle: (1) facilitation of nucleation and growth in the first stages of the reaction, (2) facilitation of the oxide-carbonate-CO$_2$ interface reaction, and (3) facilitation of diffusion of CO$_2$ through the Ag$_2$CO$_3$. All these possibilities were based on the hypothesis of Spencer and Topley of CO$_2$ diffusion through the carbonate to the oxide.

Apparently (1) above, is unimportant, practically, because ordinarily observed absorption induction periods are rather short. Mechanism (2) assumes diffusion of CO$_2$ through the Ag$_2$CO$_3$ to the Ag$_2$O by surface diffusion over and around each component particle making up the aggregate of the Ag$_2$CO$_3$ protective layer, as hypothesized by Spencer and Topley. Mechanism (3) as a rate limiting step and also (2), both assume CO$_2$ diffusion through the carbonate to the oxide.

To these possibilities of catalysis of the mechanism of absorption of Spencer and Topley we must add catalysis of the four alternative mechanisms discussed in the Appendix which involve diffusion of ions through the silver carbonate lattice. Particularly desirable is consideration of the first two alternates which involve the diffusion of Ag$^+$. If vacancies in the silver lattice of the silver carbonate can be introduced by doping with multivalent impurities the diffusivity of silver through the carbonate should be increased. Such an increase would result in an increased rate of absorption of CO$_2$ if either or both of the first two of the four alternate mechanisms proposed are valid.

Absorption catalysis by impurities in the silver oxide could also possibly result from strain of the silver oxide structure if the rate of absorption is limited by Spencer and Topley's interface reaction or if alternate mechanisms three and four which involve reaction of species at the Ag$_2$O interface are important. Possibly, also, Ag$^+$ diffusion through Ag$_2$O (see Section III A 5 b) limits the rate in some way and is catalyzed by doping.

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1 Experience with regeneration of the pure silver system in the laboratory to date indicates that regeneration in an ordinary vacuum is actually rather difficult to bring to completion, although air purge containing moisture or vacuum containing moisture has been found to increase the regeneration rate. Cation catalysis during regeneration thus would be helpful during regeneration as well as during absorption.

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In contrast to the pure silver system, that containing 1/2 - 4% yttrium or certain other rare earths has been found to:

1. Rapidly regenerate to completion in vacuum at 130-150°C, somewhat lower a temperature than required for incomplete regeneration in vacuum with the pure Ag system.

2. Absorb more rapidly in all temperature regions, and absorption stages.

3. Much more rapidly adsorb CO₂ during the cooling down period or Stages 1 and 2 of the absorption cycle.

1. Comparison of Vacuum DTA with Recording Balance Results

Early limited success with a 1% yttrium catalyst in the silver system encouraged trials of other possible catalysts. It had been thought that the possible diameter of catalyst cations would be within 15% either way of the Ag⁺. Some thirty ions between Ti⁺ (1.49 Å radius) and Ca⁺⁺ (0.80 Å radius) have been studied (see Table 1) in more or less detail as catalysts.

X-ray diffraction powder patterns of most of the original dried precipitates (except for Mn and La for which patterns have not yet been made) and for Y which showed drastic modification, showed the carbonate lines to appear little if any altered in position by the foreign cations. This does not necessarily indicate lack of partial or complete solution of the cations in the silver carbonate (since back-reflection cameras were not used to show small changes in lattice parameters). X-ray studies do not give information about any vacancies generated in any case.

Probably most of the cations selected did dissolve in the silver carbonate to some extent. This is indicated by the drastic effects noted in most of the regeneration rates, and if not there, in the absorption rates and/or DTA curves.

Screening the catalysts has been facilitated by use of vacuum differential thermal analysis (vacuum DTA) which indicates the onset of thermal decomposition as the sample temperature is progressively increased. It also indicates the ratio of easy carbonate decomposition at low temperature to difficult carbonate decompositions at higher
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<td>Fair</td>
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<td>Poor</td>
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</tbody>
</table>
Contrails

temperature. Usually indicated when present, although sometimes
masked by the easy carbonate decomposition, is a transition from a low
temperature carbonate phase to a high temperature carbonate phase at
about 185-200°C. The vacuum DTA results correlate with vacuum
balance rates of absorption at various concentrations for a given cation
and within the rare earths for various cations. This allows rapid
screening of many concentrations on the DTA. Usually the best con-
centration only has been further tested on the recording balance over
several actual regenerations and absorptions.

Vacuum and atmospheric DTA runs are collected in Appendix
II. In general little difference was found in the range 1/2 to 4 or 8%
cation and in such cases the curve for 1% is presented. Where ap-
preciable differences were noted the other concentrations are also
presented.

Results of the DTA screening performed to date (see Table 1)
seem to indicate that it is common for a foreign ion to catalyze re-
generation. But only those ions which tend to suppress the 185°C
transition also show but little high temperature endothermic de-
composition of carbonate also catalyze absorption well. The rare earths
with a half life of 1.22 for La+++ down to 0.99 for Lu+++ nicely cover the
region centering on 1.13 for Ag++. In the rare earth series Dy++,
Y++++, Ho++++, and Er++++ are good catalysts whereas the larger diameter
rare earths than Dy++ are not generally good. An exception discovered
is La++ which seems to catalyze fairly well at a concentration of 1/2%
with one batch and 1/4% with another. Anomalies between batches were
also found with Ca++. In general, concentrations below 1/2% have not
been studied for most catalyst possibilities but it appears they should
be, especially with the larger diameter rare earths.

The best catalyst found may be yttrium. Yttrium has an ap-
parent ionic radius very close to that of silver and is quite ionic with
no directed valencies. Yttrium also has a valence of three and is
reported to be somewhat expandable and compressible.

The regeneration rate was vastly increased with the yttrium
catalyst. The temperature required for rapid vacuum regeneration
was lowered to 150 or 130°C and more of a linear law rather than a
parabolic law was obtained. Although 25°C water saturated air purge
increased regeneration of the pure silver system by perhaps three-fold
the purge reduced the regeneration rate for the yttrium containing
system. Figure 28 shows a comparison of the rates with vacuum and purge regeneration at 150°C.

2. Dissociation Pressure of 1% Y Containing System

Plotted in Figure 29 is the temperature during absorption for which weight gain started for the 1% yttrium runs as a function of the CO₂ partial pressure in the process gas. These temperatures do not differ much from those for the pure silver system (see Figure 15, upper line) thus indicating little or no change in the dissociation pressure by addition of 1% yttrium.

3. Effect of CO₂ Concentration, Humidity, and Temperature on Absorption by Ag₂O Containing 1% Y

In Figure 30 a comparison of the effect of CO₂ concentration on room-temperature absorption after 9 hours at 50% relative humidity is made for Ag₂O containing no Y and that containing 1% Y catalyst. Although the peak rate is at 1 to 1-1/2% CO₂ for both there is much less relative inhibition of the rate by higher CO₂ concentrations for the latter. At lower CO₂ concentrations the rate increases roughly linearly with concentration for both.

Apparently the 1% Y catalyst aids diffusion through the protective Ag₂CO₃ layer in much the same way that 100% humidity does (compare with the 9 hour curve in Figure 25) since the rate inhibition at above 1-1/2% CO₂ attributed previously to CO₂ blocking such diffusion is mitigated by the Y catalyst. The Y catalyst also accelerates absorption at CO₂ concentrations below 1% where CO₂ does not block reaction due to such diffusion but where the rate limiting step may be at the Ag₂CO₃ - Ag₂O interface. Figure 31 shows other absorption times for the 1% Y system.

In Figure 32 the effect of various absorption temperatures for 2 and 4 hour absorptions is shown for 4% Y in Ag₂O at 2% CO₂ and 100% relative humidity at 25°C.

The results of a study of the effect of CO₂ concentration by the split-run method during Stage 3 for 1% Y at 70% relative humidity are presented in Figure 33. The upward concavity of the curve is much greater than for the pure Ag system (Figure 24) perhaps indicating lower initial inhibition by CO₂ even as ultimately, after the equilibrium
Figure 28. Comparison of Vacuum and Saturated Air Purge Regeneration of Ag₂O with 1% Y

Figure 29. Onset of Absorption of CO₂ by Ag₂O with 1% Y
Figure 30. Absorptions After 9 Hours at 50% Relative Humidity by Pure Ag₂O and That With 1% Y

Figure 31. Absorptions After Various Times at 50% Relative Humidity for Ag₂O With 1% Y
Figure 32. Effect of Absorption Temperature With 4% Y at 100% Relative Humidity

Figure 33. Effect of CO₂ Concentration on Absorption Rate With 1% Y at 70% Relative Humidity by Split-Run Method
rate is established, the inhibition by CO₂ as shown in Figure 30 is lower. The almost parabolic nature of the concave curve suggests a second order reaction with CO₂ before inhibition sets in and certainly indicates that gaseous diffusion is not rate limiting.

4. X-Ray, DTA, and Infrared Evidence of Structure Modification of Ag₂CO₃ Catalyzed with 1% Yttrium

Other than the catalytic effects during both absorption and regeneration found with the yttrium-containing silver carbonate there are three lines of evidence that the silver carbonate has been greatly modified. The modification appears to extend beyond simple solid solution or replacement of yttrium for silver and generation of silver vacancies in the original silver carbonate structure.

a. DTA of the 1% yttrium containing carbonate shows but little indication of the endothermic transition at 185°C shown by pure silver carbonate. (This transition is reversible and is not associated with any weight loss at 1 atm although a little loss occurs with vacuum DTA at 1 mm Hg.) Figure 34 shows a comparison of the atmospheric and vacuum DTA runs of pure Ag₂CO₃ and that containing 1% Y. An endothermic dissociation reaction at about 230°C at 1 atm atmospheric pressure is common to both the pure and the yttrium-bearing silver carbonate and results in loss of very close to half of the CO₂ for both materials. At higher temperatures, the pure silver carbonate appears to gradually lose more CO₂ between 230°C and 420°C at 1 atm (or 230°C and 365°C at 5 mm Hg) and metallic silver is formed from the Ag₂O·Ag₂CO₃ remaining. On the other hand, the yttrium-bearing basic carbonate shows a very sharp loss of the rest of its CO₂ and reverts to silver beginning at about 330°C at 1 atm. Summarizing, the main difference between the atmospheric DTA of the pure Ag₂CO₃ and the 1% Y-containing material is that the latter shows little or no transition reaction at 185°C and begins to decompose rapidly to metallic silver at 330°C instead of 420°C.

b. Doping with 1% yttrium may cause formation of vacancies in the Ag⁺ lattice of the Ag₂CO₃ but it also changes the crystal structure of the Ag₂CO₃ from the usual monoclinic to a drastically different pattern which has not yet been identified. This latter effect may be related to the transition point found at 185°C for Ag₂CO₃. High temperature infrared studies perhaps would clarify the conditions for OH⁻ solid solution in the CO₃⁻ lattice of Ag₂CO₃ and the nature of the transition at 185°C.
Figure 34. Atmospheric and Vacuum DTA of Pure Ag₂CO₃ and That With 1% Y
c. Comparison of the infrared absorption of mulls of pure silver carbonate with mulls of the 1% Y-containing material shows that the strong carbonate twin band showing peaks at 1340 cm\(^{-1}\) and 1420 cm\(^{-1}\) becomes less bifurcated with the yttrium. In addition, weak broad bands at 2400 cm\(^{-1}\) and 3400 cm\(^{-1}\) become stronger. A band at 2400 cm\(^{-1}\) is possibly due to hydrogen bonded water.

5. Theory of Cation Catalysis of Absorption and its Help in Delineation of Two Modes of \(H_2O\) Catalysis in Series Rate-Limiting Steps

As discussed in the Appendix, Section VII A, two preferred alternate mechanisms of transport through the assumed protective \(Ag_2CO_3\) layer involve diffusion of \(Ag^+\) from the \(Ag_2O\) outward through the \(Ag_2CO_3\) to its surface where the \(Ag^+\) reacts with \(CO_2\) in the air. A possible explanation of water vapor catalysis of absorption is also discussed in the Appendix, Section VII B, Mechanism I. If one of the two preferred mechanisms is valid the water may promote substitution of \(OH^-\) ions for \(CO_2^-\) ions in the carbonate lattice of \(Ag_2CO_3\). In keeping a balance of total charges vacancies in the \(Ag^+\) lattice would be generated. This would increase the diffusivity of \(Ag^+\) in the interior and on the surface of the \(Ag_2CO_3\).

If increase in solid or volume \(Ag^+\) diffusion is the only mode of water catalysis, doping the silver carbonate with suitable multi-valent cations to generate \(Ag^2+\) vacancies could substitute exactly for water catalysis. Actually, such a possibility is approached only for the initial high temperature absorption occurring during Stage 2 where less \(H_2O\) is needed. Stage 3 still is aided by 100% relative humidity; 50% relative humidity reduces the absorption rate much as occurs for the pure \(Ag_2O\). This points either to the fact that not as many \(Ag^2+\) vacancies are generable with cations as with water in the solid, that surfaces or rifts are important which are more abundantly catalyzed by water than with cations, or that some other water catalytic mechanism is important which is poorly or not catalyzed by cations alone. The latter possibility is a different and separate mechanism, involving low temperature \(H_2O\) adsorption, from those involving high temperature \(H_2O\) adsorption which are also able to be catalyzed by solid solution of cations.

That there is a separate low temperature catalysis differing from the high temperature catalysis is further indicated by the fact

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that absorption at a relatively high temperature soon stops, presumably as the protective Ag$_3$CO$_3$ layer becomes thicker and low temperature catalysis is required for diffusion through the layer but is not available because of the high operating temperature. This effect occurs with both pure Ag$_3$O and with the 1% Y and other catalyst containing systems. Figure 31 is an example with 1% Y with 2% CO$_2$ in room temperature saturated air.

There thus appears to be two forms of catalysis by H$_2$O: The one is a high temperature type found is Stage 2 involving, probably, chemisorbed H$_2$O as OH$^-$ in or on the carbonate or oxide lattice, the other is a room temperature type required in Stage 3 occurring coincidentally when the protective Ag$_3$CO$_3$ layer has built up. Fortuitously the temperature normally drops to room temperature by the time much protective Ag$_3$CO$_3$ layer has been formed and the low temperature catalysis effective in promoting transport through the layer is needed.

The data presented earlier in Section III A 5 b, page 32, indicating that there is a high temperature type of CO$_2$ absorption and a room temperature type is in good accord with the conclusion above that there is a high temperature H$_2$O catalysis and a room temperature type. Absorption occurs at a negligibly slow rate in the absence of water catalysis.

Room temperature absorption carried out on the recording balance apparatus thus is dependent of high temperature H$_2$O catalysis during Stage 2 just after regeneration while the sample is still cooling.

1 Spencer and Topley (ref 7), too, implied that there may be two types of H$_2$O catalyses: (1) surface diffusion of CO$_2$ on the Ag$_3$CO$_3$ particles of the protective Ag$_3$CO$_3$ layer required the presence of water vapor and (2) the interface reaction itself, involving the change of one lattice into the other (represented by Ag$_3$O (CO$_2$) adsorbed Ag$_3$CO$_3$) was independent of water vapor, or required much more intensive drying for its inhibition. But we must remember that Spencer and Topley's absorptions were at high temperature and only to about 10-15% yield and it is probably that their first type of catalysis corresponds to the "high temperature catalysis" of the present report (during Stage 2) and their second type, if indeed a water catalysis, has its counterpart, perhaps, in Stage 1.
After cooling to room temperature and during Stages 3 and 4 absorption is dependent on room temperature water catalysis. Stages 3 and 4 the absorption are hypothesized to still be also dependent on the high temperature H₂O catalysis which extends its influence to lower temperatures, although it is not influential during Stage 4 and the latter part of Stage 3.

A physical picture of the relation of high temperature H₂O catalysis and the room temperature H₂O catalysis operating simultaneously is that the former mostly promotes Ag⁺ diffusion through the Ag₂CO₃ particles of the protective layer (and possibly promotes the interface reaction) whereas the latter mostly promotes surface diffusion of Ag⁺ or CO₂ over the Ag₂CO₃ particles of the protective layer. Thus the high temperature H₂O catalysis is essential even for the later stages of room temperature absorption, it being a reaction path in series with the surface diffusion reaction path.

Perhaps a sharp distinction cannot be made between high temperature catalysis and room temperature catalysis - between volume diffusion and surface diffusion, for as suggested under Mechanism 1 discussed in Section VII.1.B, Appendix, Ag⁺ vacancies could be created not only as point defects in the lattice but along rifts or surfaces in or on the Ag₂CO₃ particles. If CO₂ diffusion is important in room temperature catalysis, however, it would be more strictly surface diffusion and a sharper distinction is to be expected.

6. Study of Ionic Electrical Conductivity in Relation to Cation Catalysis of Absorption and Regeneration

If diffusion of Ag⁺ through Ag₂CO₃ or Ag₂O is a part of the absorption or regeneration mechanism and such diffusion is promoted by multivalent cations dissolved in the solid it should be possible to obtain correlation between the ionic electrical conductivity and the reaction rate. This is because both ionic electrical conductivity and the diffusion would be dependent on the mobility of the Ag⁺, whether through interstitial, interstitial, or lattice vacancy mechanisms.¹

¹ Because of its simplicity, the vacancy mechanism is assumed throughout this report and this is possibly valid at the cation concentrations studied (1/4-4%) although it is possible that one of the other mechanisms is valid for the intrinsic diffusion and conductivity of the pure compounds or for those with a lower order of magnitude of cation concentrations.
As mentioned in Section III A 3 b there is some doubt that measured conductivities are altogether ionic because of the parallel influence of electronic conduction. However, electrode polarization was noted with the direct current method of measurement used for determining the activation energy of electrical conductivity hence at least some ionic conductivity was present.

Although it was not possible to obtain absolute conductivity values for the above correlation the activation energy of the conductivity (k) has been obtained in some cases from the log k vs 1/T plot obtained for a given specimen at different temperatures. The electrical resistance of a 0.9" x 0.18" x approximately 1/32" pellet pressed at 75,000 lb per sq inch was measured with an ordinary D.C. vacuum tube ohmmeter. Contact was made by alligator clips at each end, the pellets being reinforced on the back by a trimmed microscope slide. One slide could reinforce and hold 4 pellets for simultaneous running. The activation energies calculated for those Ag₂CO₃ compositions giving reasonable straight plots are shown in Table II. Interestingly those showing curved plots, concave upward and flat near room temperature, also seemed to give lower absolute conductivities and also were poor absorbers when tested on the recording balance.

In addition to the absence of curvature in the plots, in some cases low activation energies are a predictor of good absorption, the good absorbers giving lower values than pure Ag₂CO₃. It is felt, however, that absolute conductivity measurements are required since the frequency factor must also be important in rate considerations. These are difficult to measure since accurate measurements of conductor cross-section and length are required and grain-boundary resistances or conductivities are possibly of some influence.

Log k vs 1/T plots were also obtained for Ag₂O containing various catalysts obtained by vacuum regeneration of the carbonates. The activation energies obtained from the lower temperature straight parts of these plots are given in Table III. With the oxide, too, the good absorbers (which are also easily regenerable in vacuum) give lower activation energies of electrical conductivity. This makes it difficult to decide whether increased diffusion in the oxide or in the carbonate is responsible for the catalytic effect.

Typical curved and straight log k vs 1/T plots are given for additives in Ag₂O and Ag₂CO₃ in Appendix III.
TABLE II

<table>
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<th>Cation in Ag₂CO₃</th>
<th>Activation Energy</th>
</tr>
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<tbody>
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<td>18,600</td>
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<tr>
<td>1%Y</td>
<td>11,600</td>
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<tr>
<td>4%Y</td>
<td>10,230</td>
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<tr>
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<td>Curved plot</td>
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<tr>
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<tr>
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<td>Curved plot</td>
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<tr>
<td>1%Dy</td>
<td>Curved plot</td>
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TABLE III

<table>
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<th>Cation in Ag₂O</th>
<th>Activation Energy</th>
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<tr>
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<td>9,780</td>
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<tr>
<td>1%Nd</td>
<td>8,000</td>
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7. Loss of Activity and Possible Corrective Measures

Even with rare earth catalysts there is a loss of both absorbability and regenerability which becomes appreciable after about 10 to 15 complete cycles. This may be related to an observed reduction in gross fragment size by sintering of the 0.08 inch absorbent particles.
used. There is also a tendency for the particles to stick together as a result of the sintering. Crushing such sintered particles to a smaller size, however, only modestly improves the activity or yield in a given time thus indicating a different problem than simple reduction of gas phase CO₂ diffusion rates. Possibly a good part of the activity loss is due to gradual growth of crystal grain size which hinders solid state volume diffusion of Ag⁺ or CO₂. Another possibility is that some sort of separation of the cation catalyst from the lattice occurs. There is no evidence that a change in form of the oxide has slowly occurred as Spencer and Topley suggested as a possibility for the pure silver system, but this should not be discounted.

Experiments should be made on the addition of voluminous inert filler materials to the liquors from which the silver carbonate and catalyst metal carbonates are co-precipitated. Not encouraging is the fact that 50% by weight of diatomaceous earth added to a 2% Sc in Zn system failed to extend its life beyond the previous 10-15 cycles although size reduction of the 1 mm fragments due to sintering was eliminated. A side contribution to activity loss in this case, however, may be formation of zinc silicate. Inert fillers other than co-precipitated Al₂O₃ have not been tried with the silver system.

Blotches of silver formed in the non-yttrium containing system, especially on exposure to light, appeared to not only sinter but to eventually grow and take over the whole particle in which they started. The rare earth containing systems tend to form less metallic silver on surfaces exposed to light during regeneration than does the pure silver system. Also, although there is a certain amount of finely divided silver formed throughout the Y-containing sample during regeneration it disappears during absorption at room temperature in moist air. The pure silver system, by contrast, seems to not form dispersed metallic silver readily, even at higher regeneration temperatures.

Although further study of silver formation during continued cycling is desirable since it represents a serious potential break-down hazard of the whole system if it were to get out of hand, the problem was largely set aside for that of more immediate importance of reducing sintering and/or grain size growth to gain longer life. One method, however, of decisively eliminating the hazard is to regenerate with air purge at oxygen pressures above the dissociation pressure of Ag₂O.
Dissociation pressures from the literature for Ag₂O → Ag + 1/2CO₂ indicate that the presence of oxygen in the air used during purge regeneration should prevent silver formation at temperatures below 135°C. Since regeneration of the yttrium-doped material is possible at a fairly rapid rate at this temperature, purge regeneration appears very feasible within its thermodynamic limitations. Moist air purge only was used in studies to date but study of combined yttrium catalysts and water catalysis of regeneration is desirable.

In order to absolutely remove the possibility of metallic silver formation the following minimum oxygen partial pressures, according to the literature, would be required:

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<th>Pₒ₂ Minimum, Atm</th>
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<tr>
<td>150°C</td>
<td>0.3</td>
</tr>
<tr>
<td>125°C</td>
<td>0.12</td>
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</tbody>
</table>

The maximum CO₂ partial pressures attainable in the purge gas would be:

<table>
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<tr>
<th>Temperature</th>
<th>Pₐₐ₇ CO₂ Maximum, Atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>175°C</td>
<td>0.21</td>
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<tr>
<td>150°C</td>
<td>0.095</td>
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<tr>
<td>125°C</td>
<td>0.020</td>
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</tbody>
</table>

The CO₂ pressures are based on literature values which are somewhat lower than the kinetic results approached from the high side (see Figure 15) by absorption.

Based on the dissociation pressures of Ag₂CO₃ at 135°C the maximum partial pressure of CO₂ obtainable in the effluent gas would be only about 6.066 atm. Thus the purge gas must not be vented to space but to a chemical system that can reduce the CO₂ and leave the O₂ free for recycle. Any apparatus for CO₂ reduction which would be coupled to the silver oxide CO₂ concentrating system would have to operate on a gas rather dilute in CO₂ and containing much oxygen. The presence of oxygen would eliminate from consideration any system using hydrogen as reducing agent. Discovery of an additive to increase the dissociation pressure of Ag₂CO₃ would be very useful for such a
purge regeneration method since it would allow attainment of higher CO₂ concentrations in the effluent gas from the regeneration step.

C. STUDY OF OTHER METAL OXIDE SYSTEMS

In view of the very sparse coverage in the literature on the absorption rate of CO₂ by some of the metal oxides whose carbonates are known to be stable and in view of a lack of information in all cases on the absorption activity of oxides freshly formed by calcination of the carbonate, a brief experimental survey on the recording balance of the action of some of these systems was made. The action of the pure metal systems was thought to possibly bear on the Ag₂O system if such cations incorporated in the Ag₂O system as catalysts would not dissolve. In such a case one might find primary absorption of CO₂ by the metal system which then could transfer CO₂ to the silver system.

Two of the systems, PbO and ZnO, appeared to be good enough as far as tested to show promise as replacements for the silver system itself. This seemed particularly fortunate at the time since early studies on the pure silver oxide system indicated potential trouble with gradual build-up of metallic silver. (Actually, most trouble - with low enough regeneration temperatures - is not with this but with loss of absorption and regeneration speed through gradual sintering.)

Of the uncatalyzed Zn, Cd, Bi, Pb, Y and La carbonate-oxide systems, the Zn, Cd, and Pb systems seemed rather reversible and of these Zn was recommended for further experimental study because of its low atomic weight and valance of 2 which would reduce the weight of a packed bed if good yields were possible. The yttrium and cadmium systems were sluggish in absorption and required a relatively high regeneration temperature but both of these faults could perhaps be eliminated by catalysts.

Because of complications found in study of the Zn system and the untired status and potential light weight of the Y and Cd systems study of the latter two may be relatively more fruitful. Catalysts for Cd possible are rare earths, Na⁺, Cu⁺, and In⁺ and for the Y are Hg⁺⁺⁺, Ca⁺⁺, Cd⁺⁺, Th⁺⁺⁺⁺, Na⁺, Cu⁺, In⁺, Mn⁺⁺, Zn⁺⁺⁺⁺, and Pb⁺⁺⁺⁺.

1. The Yttrium Carbonate-Oxide System. In order to ascertain whether the yttrium carbonate addition to silver carbonate could be catalyzing by acting as a carrier of moisture or carbon dioxide and in

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view of reports that yttrium oxide absorbs carbon dioxide, pure yttrium carbonate was precipitated and studied on the recording balance. It did, in fact, absorb carbon dioxide and moisture in a generally parabolic way and both seem to be required simultaneously for most rapid absorption. Considerable moisture appeared to be absorbed simultaneously with the CO₂ from a saturated test stream.

Regeneration was slow and it, too, was more or less parabolic. Temperatures as high as 300°C with vacuum still could remove some CO₂ and/or water after a useful rate at lower regeneration temperatures had been lost. DTA at 1 atm showed an indefinite endothermic reaction from 150°C clear out to 300°C. Regeneration to a fair extent was possible at about 200°C. The theoretical weight loss from Y₂(CO₃)₃ to Y₂O₃ is 37.0% while the maximum loss obtained at 300°C was 24.4%. The maximum weight gain was about 4.5% in an absorption cycle. A cation catalyst apparently would be necessary to make the pure yttrium system workable and it would probably absorb water along with CO₂. Further work is justified on this system.

2. The Lead Carbonate-Oxide System. Precipitated lead carbonate (probably hydrocerrusite) was found to regenerate briskly at 225°C. Absorption was quite rapid at 2% CO₂ and 100% relative humidity up to a certain extent of where it almost abruptly stopped. It maintained its activity excellently through 30 cycles at which time the sample was removed. If weight were not a consideration due (1) to the high atomic weight of lead and (2) to the slowing of the absorption rate at only partial conversion to PbCO₃, and if the moderately high regenerative temperature would present no problem the lead system would be very attractive.

The atmospheric pressure DTA of precipitated lead carbonate shows a small beginning of decomposition at 220°C followed by three more important endothermic decompositions at 300°C, 355°C, and 420°C. Complete regeneration thus would probably require a rather high temperature. This, with the incomplete absorption to PbCO₃, perhaps due to stable hydroxyl-carbonate formation, tends to prevent good yields.

Addition of 1% Ag⁺ to the lead carbonate did not change its activity. One percent Y³⁺ seemed to lower the absorption rate and extent of absorption in the limited runs made.
3. The Cadmium Carbonate-Oxide System. Cadmium carbonate was slowly regenerated at 200°C, adequately at 250°C and very rapidly at 280°C. Incomplete initial absorption occurred at a rapid rate but it slowed down and proceeded to a lesser extent on further cycling. Except for the high regeneration temperature and high atomic weight of cadmium the system shows promise. Catalysts could perhaps reduce the regeneration temperature and improve the absorption activity life.

4. The Bismuth Carbonate-Oxide System. The bismuth carbonate required a 330°C regeneration temperature and showed little ability to absorb CO₂. DTA showed two decomposition temperatures, the first (probably for moisture) at 220°C and the second at 380°C at 1 atm.

5. The Zinc Carbonate-Oxide System. The zinc system has been studied in some detail and found to be as operable in most respects as the silver system. Absorption rates were as rapid during the first half of absorption as with the silver system, weight for weight, but the CO₂ absorbed per unit weight of solid at 100% relative humidity and at room temperature at 100% yield may be twice that of the silver system. (Some uncertainty exists because an undetermined fraction of the weight gain is due to water.) Regeneration periods could therefore be spaced at nearly twice as long intervals and although about 175°C-190°C is required rather than about 150°C as for the cation catalyzed or moist vacuum regenerated silver system there is still a little saving in heat requirements. Life was limited, apparently by sintering, to about 15 cycles but further testing is required.

In contrast to the Ag system, during the absorption of CO₂ by the Zn system, a certain amount of water must also be absorbed, possibly to build up a hydroxidesite (zinc hydroxy-carbonate) phase. Long exposure to CO₂ at 100% relative humidity at room temperature will eventually form a more carbonated material containing twice as much CO₂ as Ag₂O at 100% yield, however. An extended absorption period at 100% relative humidity allows a yield corresponding nearly to ZnCO₃, a material containing more CO₂ than the original hydroxidesite precipitate. Without discovery of a good catalyst, however, it would be impractical to adsorb this far because of diminishing rates beyond a yield of about 50% at only 50% relative humidity. Infrared easily detects the OH⁻ in both of these products but analytical techniques for determining exactly how much weight gain is CO₂ and how much if H₂O have not been utilized.
Differential thermal analysis of precipitated zinc carbonate (which incidentally shows an infrared spectrum corresponding well with hydroxincite) shows a major endothermic reaction starting at 210°C at 1 atm. This apparently represents loss of the greater part of the carbon dioxide at a lower temperature than for silver carbonate (about half decomposition starts at 240°C for the latter). Regeneration on the recording balance under vacuum was found to proceed well at 170°C to 200°C and was about as rapid in stagnant air as in vacuum. Moist vacuum regeneration increased regeneration rates somewhat but not as spectacularly as with the silver system. Three or four hours is sufficient at 185°C in vacuum and two is adequate for moist vacuum regeneration.

Figure 35 shows the effect of CO₂ concentration on the extent of absorption at various CO₂ concentrations and 56% relative humidity by long term runs at room temperature. There appears to be no inhibition of absorption by CO₂ as with the silver oxide system.

Figure 36 shows the effect of inadequately cooling to room temperature on the extent of absorption, even at 100% relative humidity. The zinc oxide system appears to be somewhat less sensitive to absorption temperature than the silver oxide system up to about half absorption yields but much more so if 100% yields are desired. Room temperature at 100% relative humidity decidedly is required for the latter.

Slight slips in the temperature would cause weight gain pipes (due to a momentary loss of water and gain of CO₂) equal to or greater than those noted with the silver system at near 100% absorption. The Pb system gave these also, incidentally, as did the Cd and yttrium systems to some extent. With Zn the specimen would weigh less after than before a weight slip caused by a temperature slip occurred. Of course, slowly the increasing overall absorption base line would over-ride the short-term nature of the pip.

Attempts to dope with 1% Y⁴⁺⁺ or Cu⁺ showed little change in 50% yield absorption rates or in the regeneration temperature required. The 100% yield absorption was improved by 1% Ag⁺ by an increase in the absorption rate in the last slow parabolic stage although it did not aid regeneration much. Regeneration with the 1% Ag was satisfactory in 3 hours at 175°C in vacuum and about half absorption was obtained at 2% CO₂ and 100% relative humidity in 5 hours. Some activity was
Figure 35. Effect of CO₂ Concentration on Absorption by ZnO System at 50% Relative Humidity

Figure 36. Effect of Temperature on Absorption by ZnO System at 100% Relative Humidity and 2% CO₂
lost after about 10 cycles. To date no really good catalyst has been found for the zinc system although Sc^{+++} reduced vacuum regeneration temperatures from 175°C to 150°C for the fresh system and Li^+ seemed to aid absorption somewhat without affecting regeneration.

The zinc system showed three stages of absorption during 100% absorption analogous to the silver system: a relatively slow rate while cooling to room temperature, a faster linear rate attained on reaching room temperature, and finally a slowing rate of parabolic-like law. Early fast rates at room temperature, along with the temperature induced pips (mentioned above) during the room temperature parabolic period indicates, as with the silver system, important low temperature catalytic action by water in aiding diffusion through a protective layer.
The theoretical minimum work to separate one gram mole of 1/2% CO₂ at 25 °C from air and concentrate it to 100% is 3,120 cal. This energy would have to be introduced as high order energy or work, however. If it had to be derived from low order energy through a heat engine, at say 33% efficiency, 10,400 cal of heat from the fuel per mole of CO₂ would be required. As may be seen from Table IV the total heat of vacuum regeneration, which represents the ideal heat input to the separating systems considered, is between 18,510 and 29,480 cal per gm mole for various metal oxide systems, but is 54,000 cal per gm mole for the molecular sieve for which a 175 °C regeneration temperature is used.

The heat requirements shown in Table IV are for systems in which it is assumed that the 50% relative humidity of the space capsule is an adequate catalyst for absorption. If the relative humidity must be raised to, say, 75% during a pass through the absorbing column an additional heat requirement is necessary for regeneration of the silica gel (or other) drying unit required to dry the air returned to the capsule back down from 75% to 50% relative humidity or from 2.34% to 1.56%. The additional heat simply to drive the water out of the silica gel would be at least 10,200 cal per mole of water (neglecting the sensible heat to raise the gel to dehydrating temperature and the adsorption affinity of the gel for the water). If the CO₂ concentration is lowered from 0.75% to 0.25% in a pass through the absorbing column, the extra heat to drive the water out of the silica gel is at least 10,200 cal.

Considerations of mass transfer zone length (MTZ), system life, and circulating blower power for forcing the air through the absorbing column against its pressure drop were not considered in preparation of Table IV. The yield of the Ag₂O system was also assumed to be 100% although actually about 80% is the best that can be expected when running to near equilibrium (perhaps due to solid solution formation) and 70% is more reasonable when considering the pure Ag₂O system and its parabolic-like rate law during Stage 4. The cation...
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<th>System</th>
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<th>Gas Solid per mole CO₂ Absorbed</th>
<th>% CO₂ in Order at Given Yield</th>
<th>Heat Cap. of Solid, cal/mole CO₂ at 373 K</th>
<th>Regeneration Temp in Vacuum, °C</th>
<th>ΔT to Heat Solid Up From Room Temp, °C</th>
<th>Thermoch. Heat of Desorption, cal/mole CO₂</th>
<th>Sore Heat to Solid, cal/mole CO₂</th>
<th>Sore Heat to CO₂, cal/mole CO₂</th>
<th>Total Heat of Regeneration, cal/mole CO₂</th>
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<td>Ag₂O</td>
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<tr>
<td>Molecular Steam</td>
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<td>846.4</td>
<td>5.0</td>
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<td>150</td>
<td>25,500</td>
<td>25,400</td>
<td>1,410</td>
<td>26,810</td>
</tr>
</tbody>
</table>

**Notes:**
1. Sore Yield is obtainable in the laboratory.
2. At 0.95% CO₂ in air, T = 1 at 1% CO₂.
4. Perry, ref 15, 100 °C at e = 0,8388 T.
5. Perry, ref 15, 0.0020 T.
6. Perry, 11.4 °C + 0.0145 T. – 187,400
7. 175°C is required for good H₂O removal.
9. Determined from Williams, ref 14, fig 43, ref 31 for 5% CO₂ loading in the molecular sieve. This loading is obtainable by condensation of the equilibrium condition 0.95% CO₂ in air or 5% CO₂ in the molecular sieve at 25°C as shown in Williams' Figure 14, page 43 (Ref 11).
10. Cp = 9.4 cal/mole °C.
catalyzed systems with its more linear law during Stage 4 could allow closer attainment of 80% yields. However, the exact yield is relatively unimportant in determination of the heat requirements because of the great importance of the heat of dissociation compared with the sensible heat required to heat the solid (oxide). The yield is important in determination of the weight of absorbent to be carried aloft, however.
V. RECOMMENDATIONS FOR FURTHER STUDY

Ag₂O System. Although continued cycling of the pure Ag₂O system using saturated air purge regeneration at 150°C coupled with room temperature absorption of 2% or 1/2% CO₂ at 100% relative humidity showed lives of only about 15 cycles, other conditions should also be used in life testing now that more is known about the system. The late-developed moisture injection vacuum regeneration which allows complete regeneration at as low as 125°C should be tested coupled with absorption at 1/2% CO₂ and between 50% and 100% relative humidity. The effect of inert additives on life should be further tested also.

Testing of the moisture injection vacuum regeneration method developed late in the study is desirable in order to determine the amount of H₂O consumption required in a prototype system. To this end an intermediate or full size model containing a large packed bed of Ag₂O is desirable in order to simulate the high CO₂ and low H₂O concentrations in the partial vacuum which would occur in a prototype system. Reduction in regeneration rate at increased CO₂ concentrations has been documented in the literature and such concentrations should be simulated as closely as possible. Practicality of a silica gel bed for moisture supply to the regenerating Ag₂CO₃ bed could also be proved using the bench model.

Some thought and experimentation should be given to deciding between Spencer and Topley’s mechanism involving inward diffusion of CO₂ (to an interfacial Ag₂O - Ag₂CO₃ reaction site) through a protective Ag₂CO₃ layer and the alternate mechanism involving outward diffusion of Ag⁺ in accordance with Wagner’s oxidation mechanism. Perhaps such study would lead to a method for increasing absorption rates and/or extending the life of the absorbent by reducing sintering.

Cation Catalyzed Ag₂O Systems should be life tested with and without inert additives with particular attention to any sintering rate increase induced by the cations.

The ZnO System should be studied in more detail especially in regard to the very critical influence of humidity on the 2nd half of absorption to ZnCO₃. It is also desirable to increase yields to near 100% at only 50% relative humidity, perhaps by use of cation catalysts. It is desirable to devise a good method to determine the extent of H₂O absorption and CO₂ absorption separately.

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The PbO and other systems should also be studied, especially SrO and Y2O3 which may be developed into especially light weight absorbers. In most such systems considerable water absorption, at least in early stages of absorption, is anticipated and it is desirable, as with the ZnO system, to differentiate between weight gain by H2O and that by CO2 absorption if a recording balance or other gravimetric method is used. An alternate approach is to admit some ambiguity in recording balance studies but to rely early on plots of CO2 concentration vs time in effluent gas from bench-scale packed bed mock-ups. These would give "break-through points" such as previous workers have found useful. MTZ lengths could then be directly determined also. 

Use of TGA instead of DTA would be advantageous, especially with the Ag2O system in study of catalysts where it is sometimes difficult to differentiate between the 185°C Ag2CO3 transition endotherm and any early onset of a dissociation endotherm.
VI. REFERENCES


APPENDIX I

A. ALTERNATE MECHANISMS OF TRANSPORT THROUGH THE PROTECTIVE Ag$_2$CO$_3$ LAYER

Four alternate mechanisms of absorption through the assumed protective layer of Ag$_2$CO$_3$ have suggested themselves which were not presented by Spencer and Topley. The first two involve outward diffusion of Ag$^+$ through the solid lattice of the Ag$_2$CO$_3$ protective layer while the last two involve inward diffusion of O$_2^-$ or OH$^-$ through the Ag$_2$CO$_3$ layer. The first two are the more likely and are perhaps simultaneous.

According to the first and second alternate mechanisms it is not CO$_2$ that diffuses through or on the surface of Ag$_2$CO$_3$ inward to the site of the Ag$_2$O as Spencer and Topley (ref 5) suggested but it is Ag$^+$ that diffuses from Ag$_2$O outward through the protective layer of Ag$_2$CO$_3$ to its outer surface where it reacts with gaseous CO$_2$ to give the overall surface reaction:

$$2 \text{Ag}^+ + \text{CO}_2 + \text{O}_2^- \rightarrow \text{Ag}_2\text{CO}_3$$

(It is possible that there are intermediate steps in the surface reaction.) The Ag$_2$CO$_3$ formed on the surface of the existing Ag$_2$CO$_3$ thus increases in depth.

This basis of the first two alternate mechanisms follows closely Wagner’s theory of oxidation of metals for which considerable proof has been found in some systems. The cation diffuses outward by a vacancy or other mechanism to meet oxygen from the air. Simultaneously, to keep charges balanced, an electron must also migrate outward, easily possible if the oxide layer is a semiconductor. In some systems O$_2^-$ has been found to migrate outward in place of two electrons.

Thus in the carbonation of silver oxide it may be that Ag$^+$ diffuses outward through Ag$_2$CO$_3$ accompanied either by an electron or by 1/2O$_2^-$. Depending on whether an electron or the O$_2^-$ migrates with the Ag$^+$ we have either the first alternate or the second alternate mechanism, respectively. These two negatively charged diffusion partners for Ag$^+$ will cause either of two different reactions at the interior oxide core: either oxidation of the Ag$_2$O’s remaining silver to give a higher silver oxide, more likely Ag$_2$O than Ag$_2$O$_2$.
3 Ag₂O → 4 Ag⁺ + 4 e⁻ + Ag₂O³⁻ Diffusion in first
 outward diffusion left in core alternate mechanism

or shrinkage and ultimate disappearance of the Ag₂O, respectively, will occur:

Ag₂O → O²⁻ + 2 Ag⁺ Diffusion in second
 outward diffusion alternate mechanism

According to the third and fourth alternate mechanisms it is hypothesized that Ag⁺ diffusion does not occur outward through the carbonate layer but that O²⁻ or OH⁻ (with H⁺ as a partner) diffuses inward to the Ag₂O core where the two reactions:

a. Ag₂O + O²⁻ + 2H⁺ → 2 Ag OH Diffusion in third
   inward diffusion alternate mechanism

b. 2 AgOH + CO₂ → Ag₂CO₃ + H₂O or the reactions

a. Ag₂O + OH⁻ + H⁺ → 2 AgOH Diffusion in fourth
   inward diffusion alternate mechanism

b. 2 AgOH + CO₂ → Ag₂CO₃ + H₂O

occur. In both of these variations involving H⁺ diffusion the core does not disappear but grows and turns into AgOH which gives, at least temporarily, a third phase contacting the oxide and carbonate phases between them.

The reactions with the gaseous phase at the outside surface of the carbonate layer for the four alternates are:

First alternate 4Ag⁺ + 4e⁻ + 2CO₂ + O₂ → 2Ag₂CO₃
(note participation of oxygen)

Second alternate O²⁻ + 2Ag⁺ + CO₂ → Ag₂CO₃
Third alternate \( \text{H}_2\text{O} \rightarrow \text{O}^\cdot + 2\text{H}^+ \) (Gaseous CO\(_2\) must eventually react at the AgOH formed at the contact of the Ag\(_\text{O}\) and Ag\(_2\text{CO}_3\) phases.)

Fourth alternate \( \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^\cdot \) (Here again, the gaseous CO\(_2\) must eventually react at the AgOH formed at the contact of the Ag\(_\text{O}\) and Ag\(_2\text{CO}_3\) phases.)

In the first and second alternates the gaseous CO\(_2\) reacts at the outside surface of the Ag\(_2\text{CO}_3\) layer to build up a thicker Ag\(_2\text{CO}_3\) layer. (The first requires participation of gaseous oxygen as well as CO\(_2\).)

In the third and fourth alternates, however, the gaseous CO\(_2\) must react at the inside interface of the Ag\(_2\text{CO}_3\) layer where it contacts the Ag\(_\text{O}\). Such a mechanism probably would be helpful since if gaseous CO\(_2\) were at the interface it would probably react directly with the Ag\(_\text{O}\) there in the first place, or if the CO\(_2\) were transported there by surface diffusion or solid diffusion we would have essentially Spencer and Topley's hypothesis of inward CO\(_2\) transport but with the addition of inward water (as \( \text{O}^\cdot + 2\text{H}^+ \) or \( \text{OH}^- + \text{H}^\cdot \)) transport. The simultaneous transport of CO\(_2\) and water through the carbonate layer to the Ag\(_\text{O}\) core where the water first reacts with Ag\(_\text{O}\) to form AgOH and the CO\(_2\) then reacts with the AgOH to form Ag\(_2\text{CO}_3\) seems very complicated and unlikely compared to the simplicity of the first or second alternates or to Spencer and Topley's hypothesis of inward CO\(_2\) transport alone. Moreover, the inward diffusion of so large an ion as H\(^+\) seems unlikely.

It may be possible to use the isotope oxygen-18 in tagging experiments in which oxygen in O\(_2\) in the gas phase, in CO\(_2\) in the gas phase, in moisture in the gas phase, or in the Ag\(_\text{O}\) is tagged. The following table gives the results to be expected with Spencer and Topley's hypothesis or the first two most reasonable of above presented four alternate mechanisms:

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Mechanism of Ag₂CO₃ Formation | Moisture, Gaseous C³⁻¹⁸O₂ | Gaseous Ag⁺ | H₂¹⁸O | Ag₂¹⁸O
--- | --- | --- | --- | ---
Spencer and Topley's | Ag₂COOO | Ag₂CO¹⁸O⁻¹⁸O | Ag₂COOO | Ag₂COO¹⁸O
First Alternate | Ag₂CO⁻¹⁸O | Ag₂CO¹⁸O⁻¹⁸O | Ag₂COOO | Ag₂COO
and/or | and/or | Ag₂CO⁻¹⁸O | Ag₂CO⁴⁻¹⁸O
Second Alternate | Ag₂COOO | Ag₂CO⁻¹⁸O | Ag₂COOO | Ag₂COO¹⁸O

It would be necessary to detect the H²O in the Ag₂CO₃ by decomposing the Ag₂CO₃ by heat and leading the CO₂ so formed into a mass spectrophotograph. Although differences should be obtained between the Spencer and Topley mechanism and the first alternate mechanism, this would not be true between the former and the second alternate mechanism. Thus ambiguity in interpretation is possible but not necessary.

B. THE WATER VAPOR CATALYSIS OF ROOM TEMPERATURE ABSORPTION

There are at least four possible mechanisms by which water could catalyze absorption of CO₂ by silver oxide.

1. The water may promote substitution of OH⁻ ions for CO₃²⁻ ions in the carbonate lattice of Ag₂CO₃ thereby, in keeping a balance of total charges, causing vacancies in the Ag⁺ lattice. This would probably increase the diffusivity of Ag⁺ in the Ag₂CO₃, a very helpful thing if the first or second alternate mechanisms of absorption are important (see Section A). Possibly Ag⁺ vacancies are created not only as point defects in the lattice but along rifts or surfaces in or on the Ag₂CO₃ particles or film comprising the protective layer. If this mechanism of water catalysis is valid the catalysis by topping silver carbonate with multi-valent cations may, to some extent, during high temperature absorption substitute for water catalysis but it does not do so during room temperature absorption as is evidenced by the fact that 1/2 satu-rated air reduces the absorption rate of 1½ Y containing material much as it does for the pure silver system.
2. The water may, by adsorption on the surface of the carbonate, increase the mobility of adsorbed CO$_2$ over the surface of each particle comprising the protective Ag$_2$CO$_3$ layer. This was suggested by Spencer and Topley and assumes CO$_2$ diffusion is rate limiting.

3. Water may allow the formation of intermediate compounds at the Ag$_2$O - Ag$_2$CO$_3$ interface such as silver bicarbonate which catalyse absorption of CO$_2$:

$$\text{Ag}_2\text{O} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{AgHCO}_3$$

$$2\text{AgHCO}_3 \rightarrow \text{Ag}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

Silver hydroxide is another possible intermediate of more probability:

$$\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{AgOH}$$

$$2\text{AgOH} + \text{CO}_2 \rightarrow \text{Ag}_2\text{CO}_3 + \text{H}_2\text{O}.$$ 

The intermediate AgHCO$_3$ or AgOH may be formed on the surface of the particles of the Ag$_2$CO$_3$ layer to increase mobility of CO$_2$ diffusing inward (or Ag$^+$ diffusing outward) but such a mechanism is more properly classified under Mechanism 2 (or Mechanism 1 for the Ag$^{2+}$).

4. Water may be physically adsorbed and dissolve some AgOH to form a liquid or glassy coating around the Ag$_2$CO$_3$ particles of a protective layer or in insets in the Ag$_2$CO$_3$ of a protective film. The molecular disorganization of such a liquid or glass could allow rapid diffusion through it of CO$_2$ or Ag$^+$. This would be more likely with room temperature absorption. It is possible, also, that such a gross layer could inhibit absorption. Evidence for an AgOH layer has appeared in that after long room temperature absorption periods at temperatures perhaps a little lower than the saturation temperature of the air some absorbed weight is slowly lost (up to 5%). Slightly raising the temperature allows the weight to be slowly regained. This is attributed to re-carbonation of the AgOH. Infrared absorption shows on some occasions an absorption band at 3600 cm$^{-1}$ corresponding to OH$^-$ but this could also be due to OH$^-$ substituted in the lattice, supporting Mechanism 1.

Here, as with intermediate formation of Mechanism 3, the result is either promotion of Ag$^+$ diffusion outward or CO$_2$ diffusion inward.
In conclusion if it can be decided whether or under what conditions \( \text{Ag}^{+} \) diffusion or \( \text{CO}_2 \) diffusion limits reaction one can attain much help in deciding between Mechanism 1 or 2 as possibilities (which are clear-cut for the former or latter diffusion mode, respectively). Mechanisms 3 and 4 are not clear-cut for \( \text{Ag}^{+} \) or \( \text{CO}_2 \) diffusion as stated but can be reclassified so the opposite poles of each can be absorbed in the appropriate Mechanism 1 or 2.
APPENDIX II

VACUUM DTA CURVES OF CATION CATALYZED Ag₂O SYSTEMS
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<th>Illustration Description</th>
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<td>II-2</td>
<td>Vacuum DTA Curves of Ag₂₃CO₄ Containing Various Catalysts</td>
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Figure II-4. Vacuum DTA Curves of Ag₂CO₃ Containing Various Catalysts

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Figure II-5. Vacuum DTA Curves of Ag₂CO₃ Containing Various Catalysts
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APPENDIX III

LOG (ELECTRICAL CONDUCTIVITY) VS 1/T PLOTS
## ILLUSTRATIONS IN APPENDIX III

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Figure III-3. Log (Electrical Conductivity) vs 1/T for Pure Ag₃O and That Containing Various Catalysts
INVESTIGATION AND DESIGN OF A REGENERABLE SILVER OXIDE SYSTEM FOR CARBON DIOXIDE CONTROL

Cubberston, W. J., Jr.

December 1964

Available, for sale to the public, from the Clearinghouse for Federal Scientific and Technical Information, CFSTI (formerly OTS), Stills Bldg, Springfield, Virginia 22151.

Precipitated silver carbonate was investigated using test tube samples to establish the merits of this approach to an Ag₂O solid system for CO₂ removal. Moisture catalyzes transport of CO₂ or Ag through an Ag₂O layer protecting the Ag₂O from conversion to Ag₂CO₃. Above 2½% CO₂ in the air, CO₂ is adsorbed and displaces surface H₂O enough to inhibit conversion. Below 1% CO₂ reduced CO₂ driving force slows conversion. At the optimum 1 to 2½% CO₂ over 24 hours are required for good yields, even at 100% humidity. humidities of 50% result in even slower absorption. Regeneration to Ag₂O may be accomplished in moist partial vacuum at 125°C within 2 hours. H₂O must reach the decomposing Ag₂CO₃ by penetrating a protective Ag₂O layer countercflow to the outflowing CO₂. Moisture is not necessary with Y⁺⁺⁺ catalyst at 150°C. Absorption is speeded 2-3 fold with Y⁺⁺⁺ catalyst. At 3% CO₂ and 50% humidity 75% yield is attained within 16 hours. Y⁺⁺⁺ dissolved in the cation lattice is believed to induce Ag⁺ vacancies in Ag₂CO₃ and increase Ag⁺ transport through the Ag₂OCO₃ layer. H₂O may catalyze by supplying OH⁻ which dissolves in the anion lattice inducing Ag⁰ vacancies. Y⁺⁺⁺ may also induce Ag⁰ vacancies and/or strain in the Ag₂O causing increased absorption rates at between 1-2½% CO₂ where diffusion through the Ag₂OCO₃ layer is less limiting than the reaction mechanism at the Ag₂O - Ag₂O CO₃ interface. Preliminary work on several other metal oxides showed Zn and Pb to be most promising of these as a substitute for the short-lived Ag₂O.
Life support
Inorganic chemistry
Carbon dioxide, removal (chemistry)
Space craft, respiration
Silver oxide