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

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FOREWORD

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. Culbertson, 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.

WAYNE H. McCANDLESS
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ABSTRACT

Precipitated silver carbonate was investigated using test tube samples to establish the merits of this approach to an Ag_2O solids system for CO_2 removal. Moisture catalyzes transport of CO_2 or Ag^+ through an Ag_2CO_3 layer protecting the Ag_2O from conversion to Ag_2CO_3. At above $2\frac{1}{2}\%$ CO_2 in the air CO_2 is adsorbed and displaces surface H_2O enough to inhibit conversion. Below 1% CO_2 reduced CO_2 driving force slows conversion. At the optimum 1 to $2\frac{1}{2}\%$ CO_2 over 24 hours are required for good yields, even at 100% humidity. Humidities of 50% result in even slower absorption.

Regeneration to Ag_2O may be accomplished in moist partial vacuum at $125°C$ within 2 hours. H_2O must reach the decomposing Ag_2CO_3 by penetrating a protective Ag_2O layer counterflow to the outflowing CO_2. Moisture is not necessary with Y^{+++} catalyst at $150°C$.

Absorption is speeded 2-3 fold with Y^{+++} catalyst. At $\frac{1}{2}\%$ CO_2 and 50% humidity 75% yield is attained within 16 hours. Y^{+++} dissolved in the cation lattice is believed to induce Ag^+ vacancies in Ag_2CO_3 and increase Ag^+ transport through the Ag_2CO_3 layer. H_2O 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 Ag_2O causing increased absorption rates at between $1-2\frac{1}{2}\%$ CO_2 where diffusion through the Ag_2CO_3 layer is less limiting than the reaction mechanism at the Ag_2O - Ag_2CO_3 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 Ag_2O.

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I. INTRODUCTION

A. REGENERABLE CO_2 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 CO_2.

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 CO_2 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 CO_2 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 10, 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 CO_2 by Ag_2O at room temperature except in Mellor (ref 6) wherein absorption of CO_2 by aqueous suspensions of Ag_2O and by moist Ag_2O 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 CO_2 by Ag_2O, 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 CO_2 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 CO_2. The room temperature absorption has been more extensively studied.

With metallic oxide-carbonate systems as regenerable CO_2 absorbents, the heat of dissociation of the carbonate represents the major heat requirement (15, 000 - 22, 000 cal per gm mol CO_2) and this is relatively unchanging for a variety of metals. For the molecular sieve the heat requirement is about equally split between the heat of desorption of CO_2 (33, 000 cal per gm mol CO_2) 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 Ag_2O contains 19. 0% CO_2, whereas Linde 5A molecular sieve can contain only about 5. 2% CO_2 in equilibrium with 0. 5% CO_2 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 CO_2. 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 H_2O 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

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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 Ag_2CO_3 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 Ag_2O and (2) precipitation of Ag_2O by alkali hydroxide.

B. CYCLICAL SYSTEMS UTILIZING REGENERABLE CO_2 ABSORBENTS

Any practical closed-cycle or even open-cycle life support system probably must contain a device that concentrates the 0.5 to 2% CO_2 maintained in the space capsule air to nearly 100%. With the closed-cycle system any chemical reactor converting CO_2 to C and/or O_2 should probably be fed CO_2 containing as little diluent air as possible in order to increase the reaction rate and to reduce side reactions such as $C + O_2 \rightarrow CO_2$. With the open-cycle system wherein CO_2 is simply concentrated and ejected to space any air diluent obviously would be wasted to space.

When regenerable CO_2 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 CO_2 the ratio of void space to charged bed CO_2 capacity should be a minimum to minimize air trapped in the bed after absorption. Such air would be mixed with the CO_2 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 CO_2 charge (about 5.2 wt % CO_2)

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[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 Ag_2O where the CO_2 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 CO_2. This avoids mixing of air and CO_2 in the regenerating bed. Use of moist purge gas under reduced pressure is possible if higher CO_2 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 CO_2 (not necessarily a disadvantage for a short mission) if the CO_2 is ejected to space. However, such loss of water during regeneration would not be serious if the CO_2 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 Ag_2O-CO_2 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 Ag_2O system, especially in regard to cation catalysis. Practical information on the effect of the main variables in space capsule application of the Ag_2O-CO_2 system has also resulted. Other metal oxide-CO_2 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 $Ag_2O +$ CO_2 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. The 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 H_2O in or on the solid by CO_2 occurs as the CO_2 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^+.

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 CO_2 concentration as the only remaining variable important at a given stage of absorption. (b) The rate of absorption as a function of CO_2 concentration at given stages of absorption (see Figures 25 and 26) has been obtained. A problem of variable H_2O 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 H_2O 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 Ag_2O system and will progress through the study of the influence of catalytic cations on the Ag_2O 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 CO_2 by Ag_2O was obtained by starting with Ag_2CO_3 coprecipitated with alumina

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than with Ag_2O coprecipitated with or precipitated on various materials. They concluded that in preparing Ag_2O by thermal decomposition of Ag_2CO_3 the decomposition perhaps served to develop porosity and perhaps also served to condition the Ag_2O to reabsorption of CO_2. Spencer and Topley (ref 5) previously had reported results on high temperature partial absorption of CO_2 by Ag_2O formed by thermal decomposition of crystalline Ag_2CO_3 and amorphous-like recarbonated Ag_2CO_3. In view of the relative success of preliminary work in the present program with precipitated "amorphous" Ag_2CO_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_2CO_3 (with any coprecipitated $Al_2O_3 \cdot nH_2O$) 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

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the white material to contain mostly metallic silver. Even the bulk of the material which was nominally black Ag_2O contained finely divided metallic silver. (Although black material from the 20% alumina containing preparation and also from a pure silver system was found by X-ray diffraction to possibly contain a small amount of Ag_2O_3, 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 RV 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 carbonate 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

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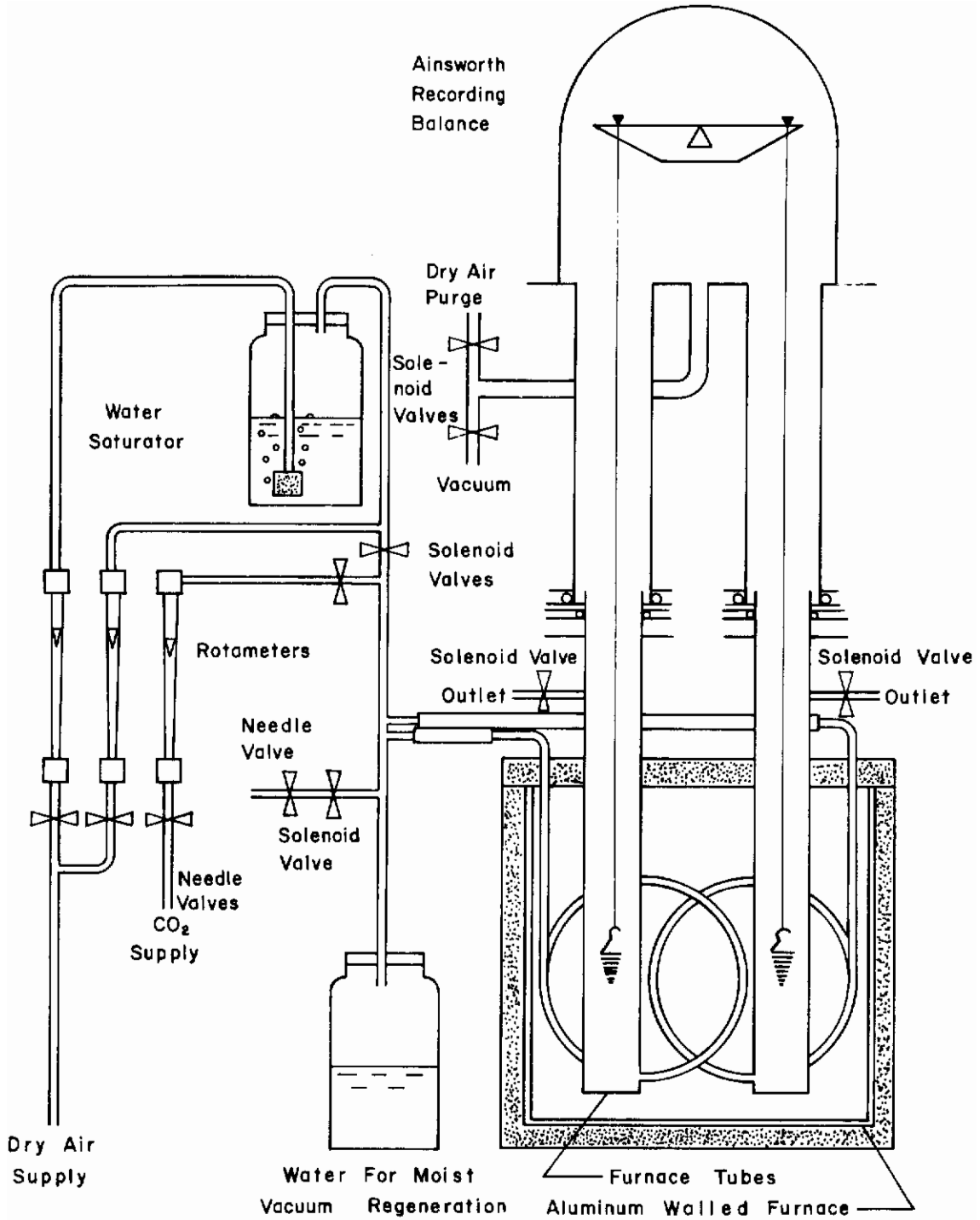
Figure I. Recording Balance Apparatus

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 CO_2 and saturated, partially saturated, or dry. For standardization, during absorption, the CO_2 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 in 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. CO_2 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 Deltatherm 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 Ag_2O SYSTEM

1.   Rate of Regeneration

Study of the regeneration of amorphous or synthetic recarbonated Ag_2CO_3 to Ag_2O is made difficult by two complicating phenomena.   (1) There is a more or less reversible transition in Ag_2CO_3 at 185°C and the resulting high temperature form of the Ag_2CO_3 surprisingly de-composes more slowly than the low temperature form.   (2) The pres-ence of moisture in the gas phase above the solid catalyzes the de-composition of the low temperature form of Ag_2CO_3.

a.   Effect of the 185°C transition in Ag_2CO_3 on its decomposition.

Figure 2 shows a recording balance run consisting of a series of alternate vacuum regenerations and absorptions in which regenera-tion was attempted at too high a temperature.   The 200°C temperature used for the regeneration was higher than the 185°C transition of Ag_2CO_3.   The sluggishness of the regenerations (after a brief spurt at rapid rate before transition had occurred) was the main cause of ap-parent sluggishness of the absorptions.   This resulted because of the lack of sufficient Ag_2O present to adsorb very rapidly the CO_2.   Al-though there was a considerable amount of undecomposed Ag_2CO_3 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 Ag_2CO_3 is shown.

Figure 4 shows a plot of the decomposition rate in vacuum of a 0.863 gm sample of "amorphous" Ag_2CO_3 precipitated in excess K_2CO_3 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 Ag_2CO_3 recarbonated from previously formed Ag_2O.   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.

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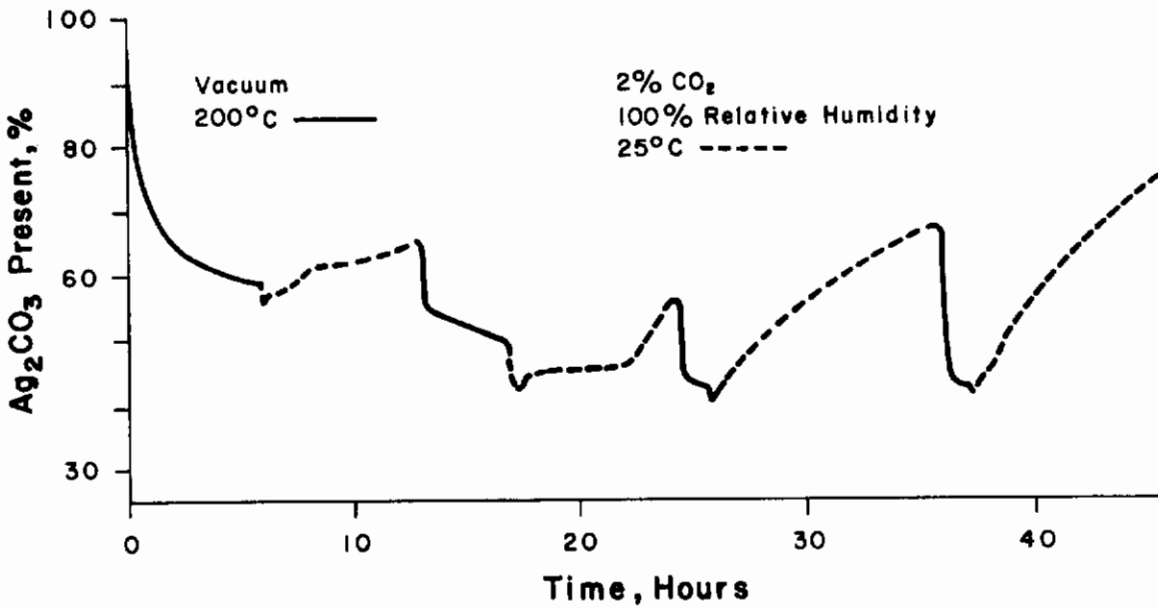
Figure 2. Runs at Too High a Regeneration Temperature
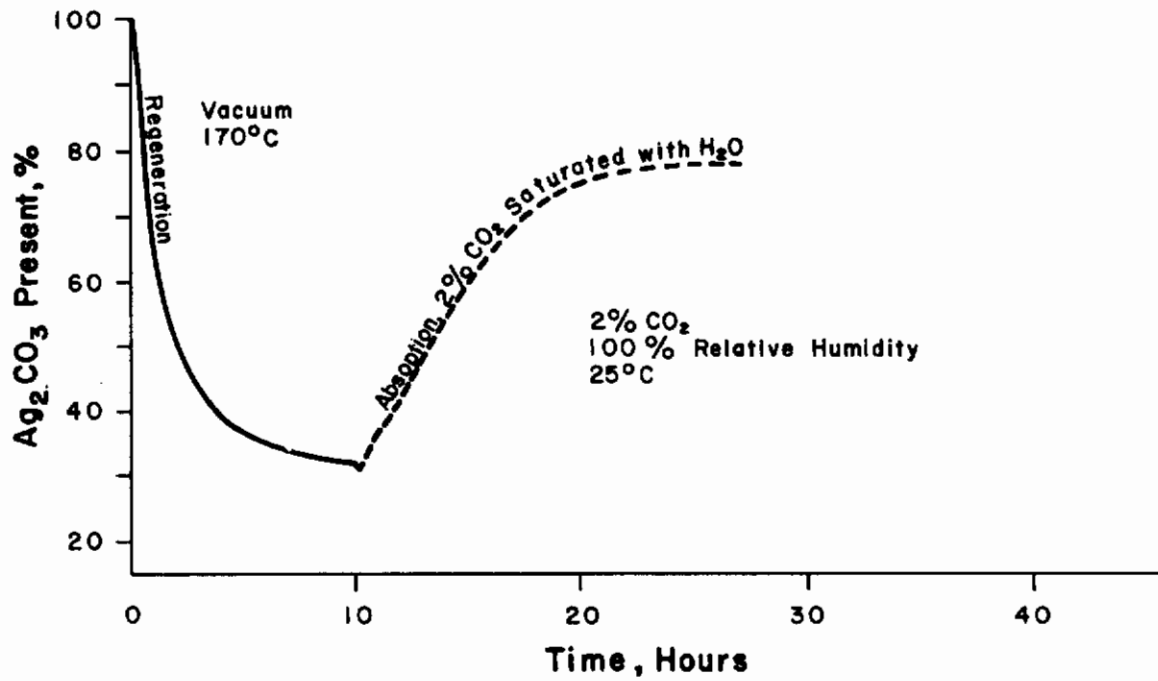
Figure 3. Run with Regeneration Temperature Below Transition Temperature of Ag_2CO_3
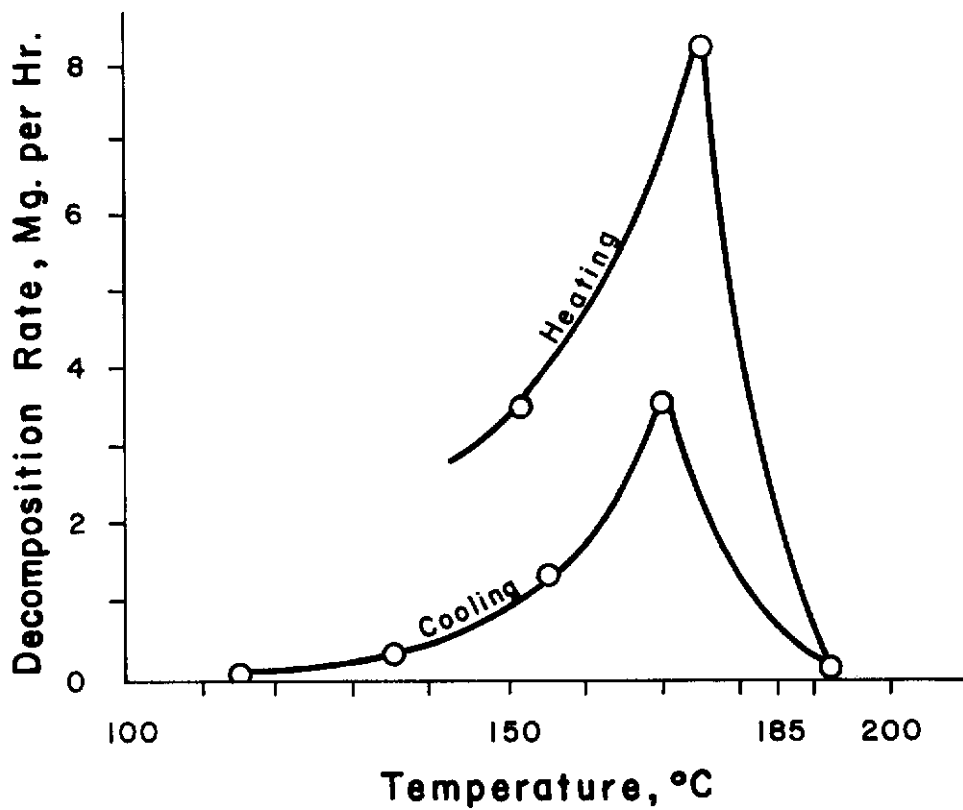
Figure 4. Decomposition of Precipitated Ag_2CO_3
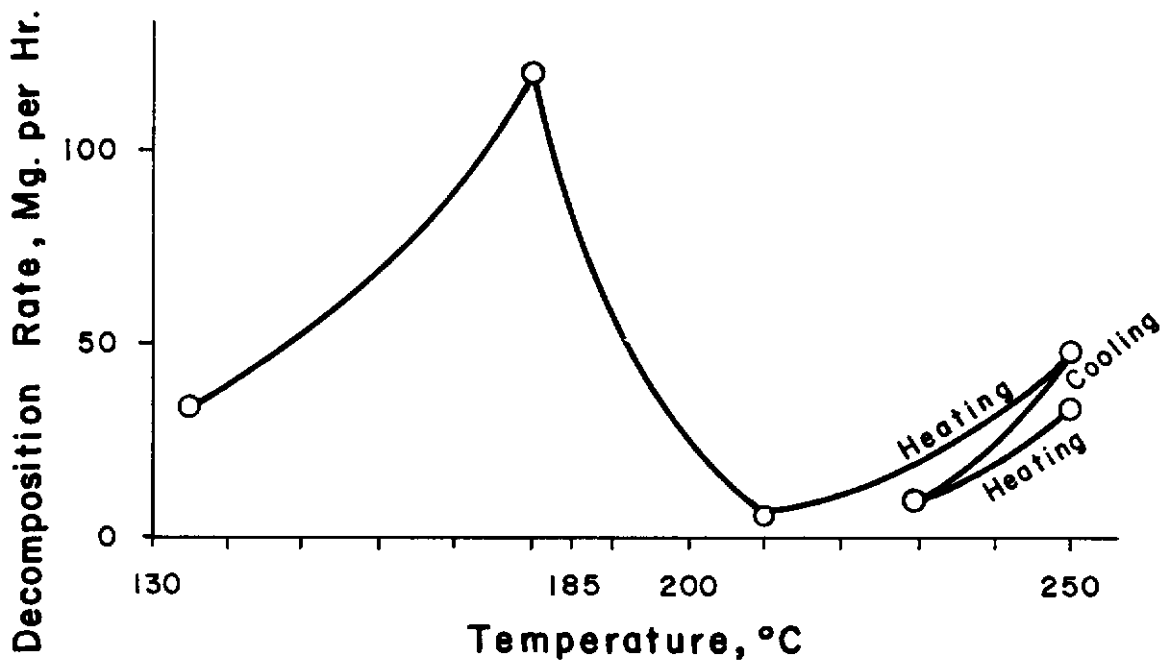
Figure 5. Decomposition of Recarbonated Ag_2CO_3

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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 endotheim; again at 185°C. Furthermore, thermo-gravimetric analysis (TGA) in 1 atm of CO_2 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 $CO_2^=$ anion attains a greater degree of freedom, perhaps because of full rotation. Attempts to obtain infrared absorption of the Ag_2CO_3 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 CO_2 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 Ag_2CO_3 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 Ag_2CO_3 specially precipitated with saturated K_2CO_3 solution the rate effect was especially sharp and could be established within about ±15°C.

Summarizing, the low temperature form of Ag_2CO_3 decomposes more rapidly than the high temperature form and the effect is reversible
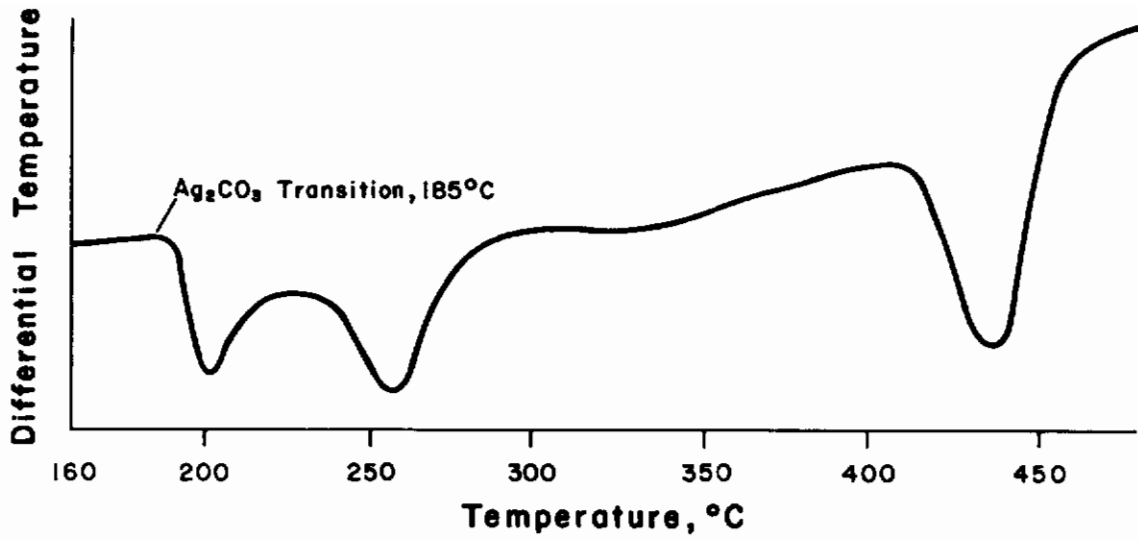
Figure 6. Atmospheric Pressure DTA of Precipitated Ag_2CO_3
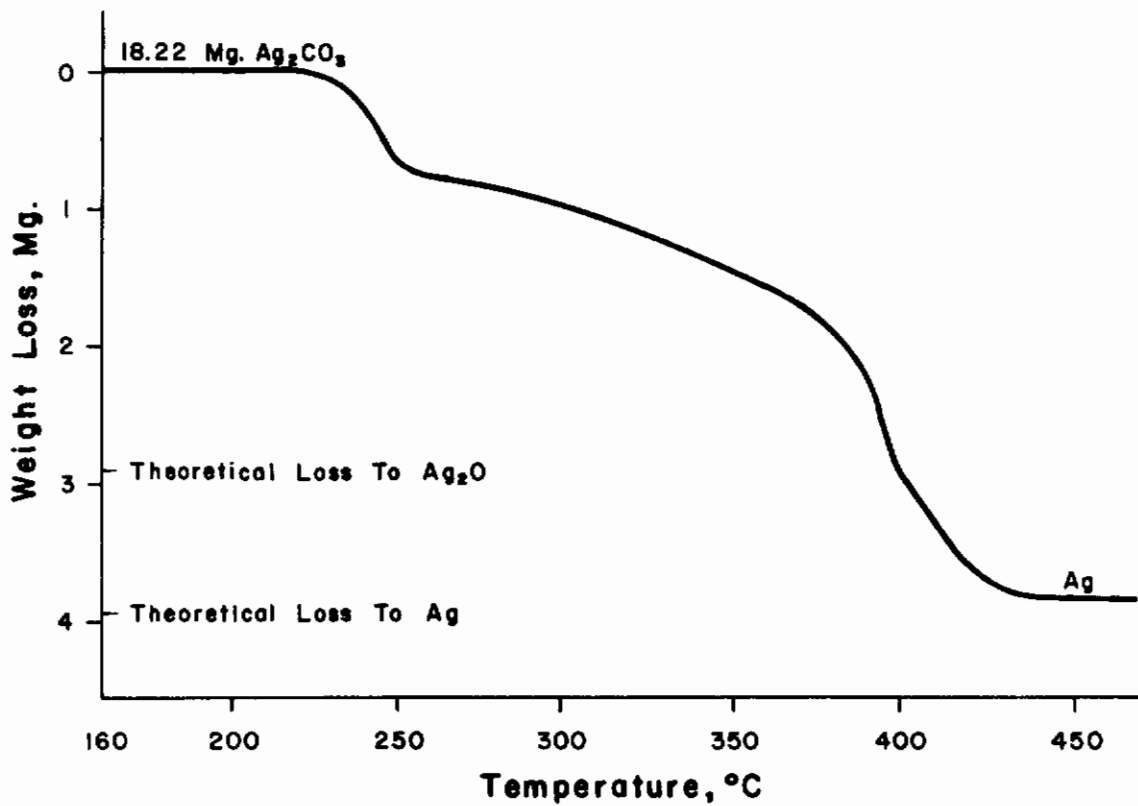
Figure 7. TGA of Precipitated Ag_2CO_3 in CO_2

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- 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 Ag_2CO_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 Ag_2O or Ag_2CO_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 Ag_2CO_3. That regeneration is faster using purge air saturated with moisture than in vacuum for the low temperature form of Ag_2CO_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 Ag_2CO_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 Ag_2CO_3 at 130°C determined by

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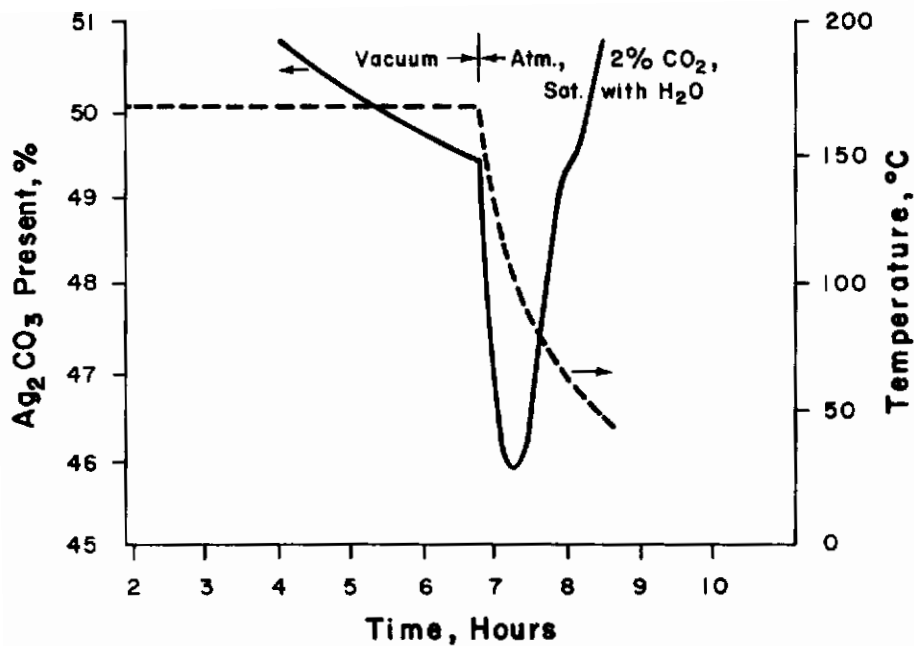
Figure 8. Regeneration to Absorption Switch-Over
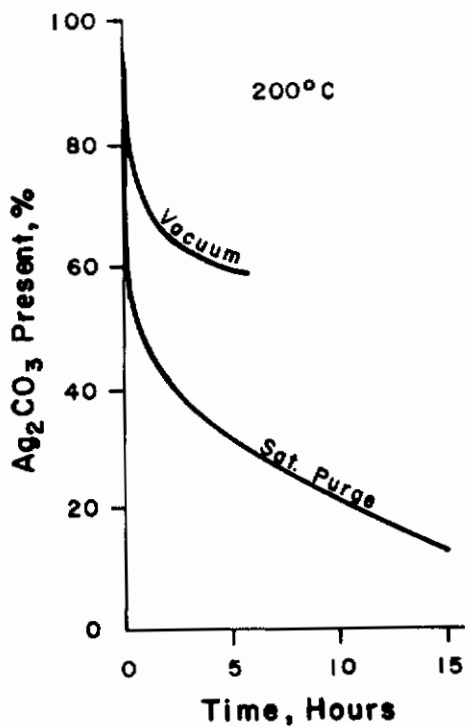
Figure 9. Purge vs Vacuum Regeneration at 200°C

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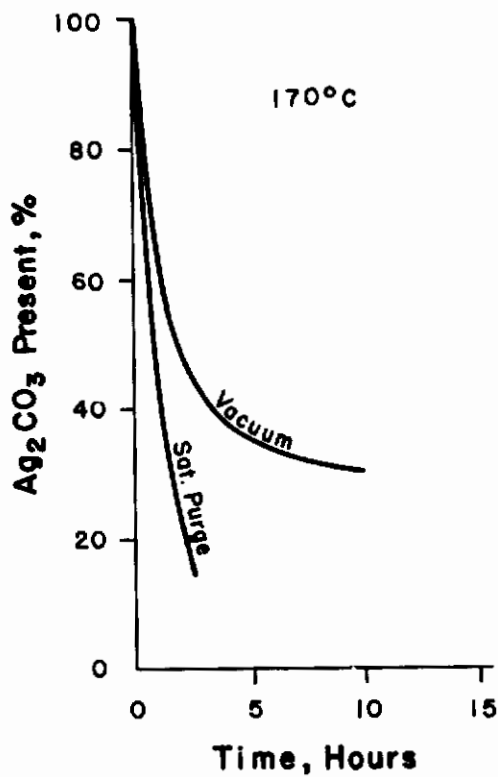
Figure 10.   Purge vs Vacuum Regen-
eration at 170°C
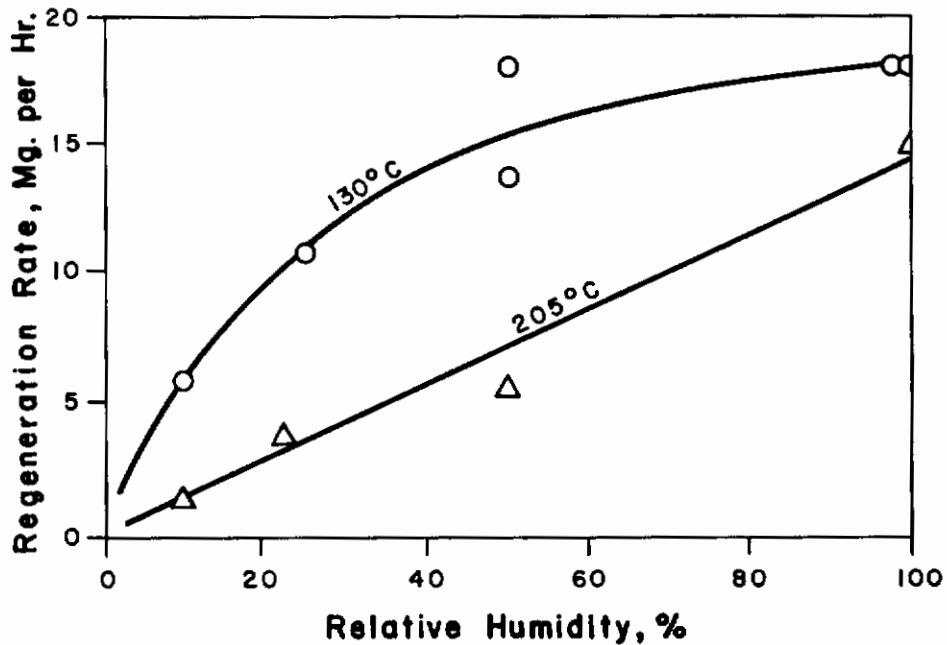
Figure 11.   Effect of Moisture Concentration on Air Purge Regeneration
Above and Below 185°C

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the split-run method. At this temperature the Ag_2CO_3 is in its low temperature form. Also shown in Figure 11 is the effect of moisture on purge regeneration of Ag_2CO_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 Ag_2CO_3 are shown in Figure 12. These are similar to decompositions of precipitated Ag_2CO_3.

d. Activation energy of regeneration of low temperature form of Ag_2CO_3 in vacuum and with purge

In Figure 13 is plotted the log of the rate vs $1/T$ for decomposition of the low temperature form of Ag_2CO_3 in vacuum, 10% relative humidity purge, and 100% relative humidity purge. Dotted lines are for precipitated Ag_2CO_3, solid lines are for reformed Ag_2CO_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, 22.8, and 22.5 K cal per mole in the absence of CO_2.

e. Activation energy of regeneration of high temperature form of Ag_2CO_3 in vacuum and with purge

Regeneration rates of the high temperature form of Ag_2CO_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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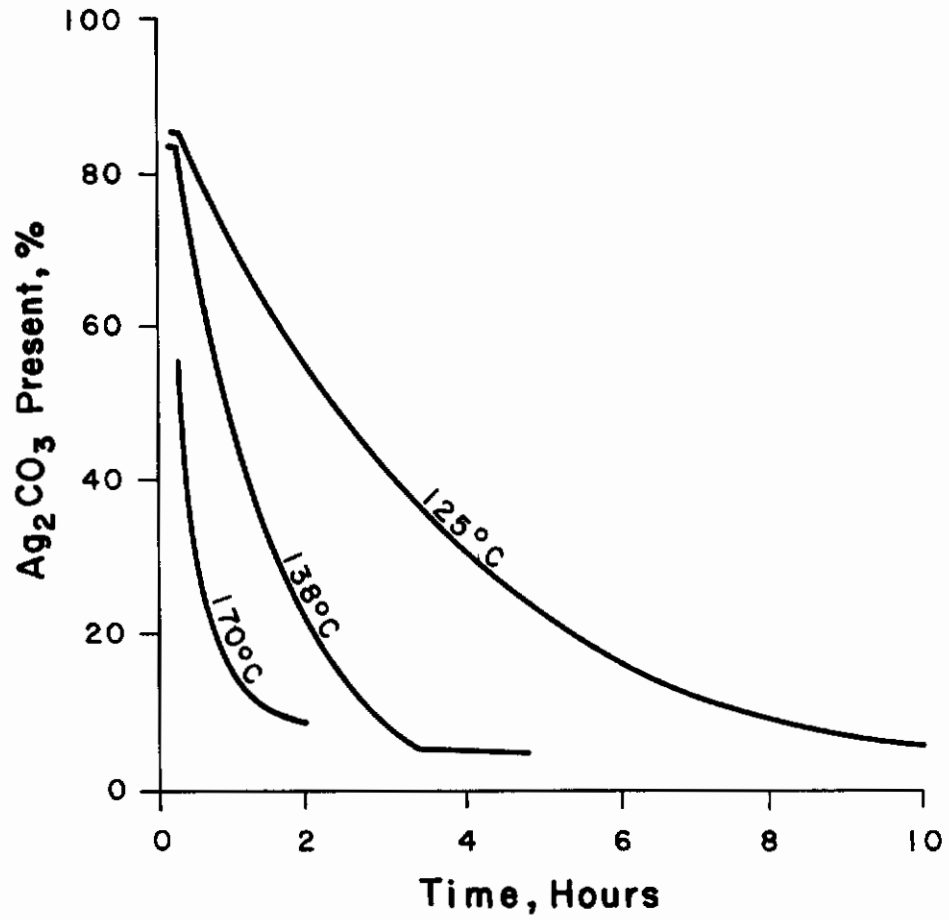
Figure 12.   Saturated Air Purge Regenerations at Various Temperatures

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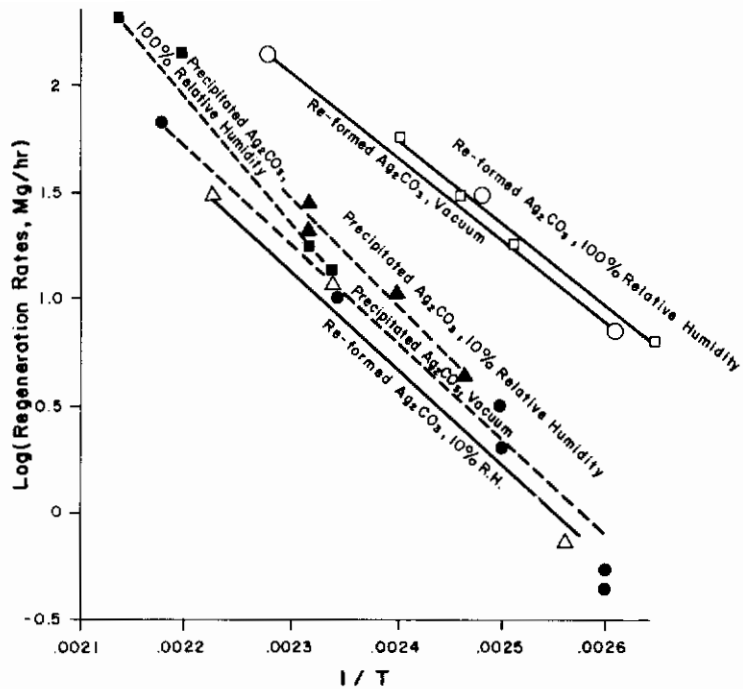
Figure 13.   Log Regeneration Rates vs 1/T
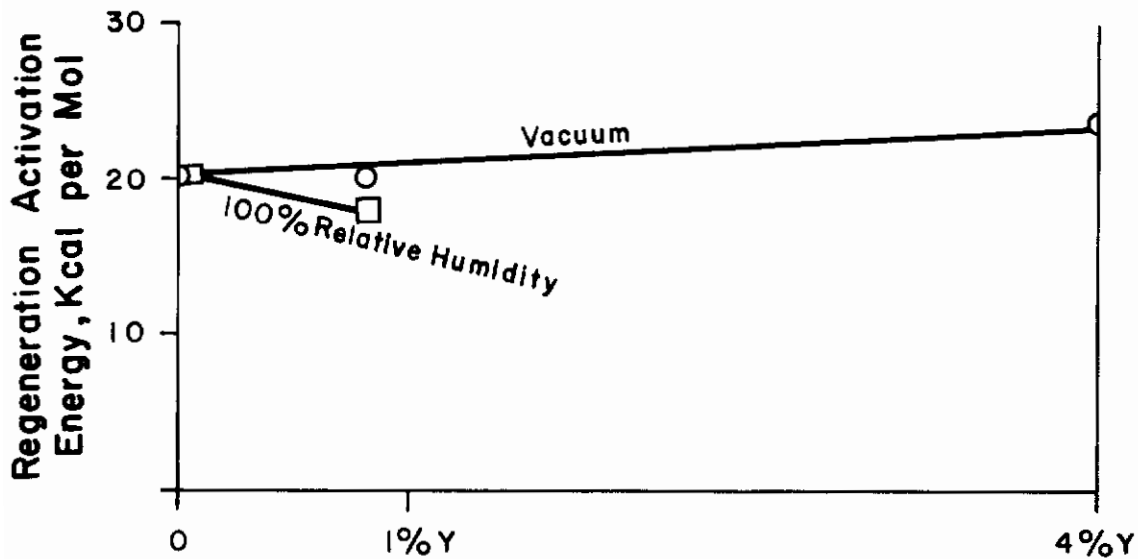
Figure 14.   Regeneration Activation Energies Below 185°C

2.   Equilibrium Dissociation Pressures of Ag_2CO_3 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 H_2O adsorption is negligible and CO_2 driving energy is low enough to not cause hysteresis, the temperature at which this occurs is the dissociation temperature of Ag_2CO_3 at the CO_2 partial pressure existing in the air stream. Figure 15 shows a plot of such temperatures (circles) for the pure Ag_2O - CO_2 system runs as determined by such a "kinetic method." Three equilibrium CO_2 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 Ag_2CO_3 of Spencer and Topley (ref 4), Centnerszwer and Krustinson (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 CO_2 pressures of the kinetic method are those required to force nucleation and growth of Ag_2CO_3 and involve surface energy of the Ag_2O. 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 Ag_2CO_3

     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 Ag_2CO_3 is strongly rate determining at above 185°C. The nature of the low temperature form of Ag_2CO_3 is not necessarily rate determining below 185°C, however, and there remains the possibility that there is a protective film of Ag_2O through which the CO_2 must diffuse that limits the rate irrespective of the nature of the low temperature form of Ag_2CO_3. In opposition to the protective Ag_2O film theory is the Pilling-Bedworth relation which states that protective films are unlikely when their molar volumes are less than that of the
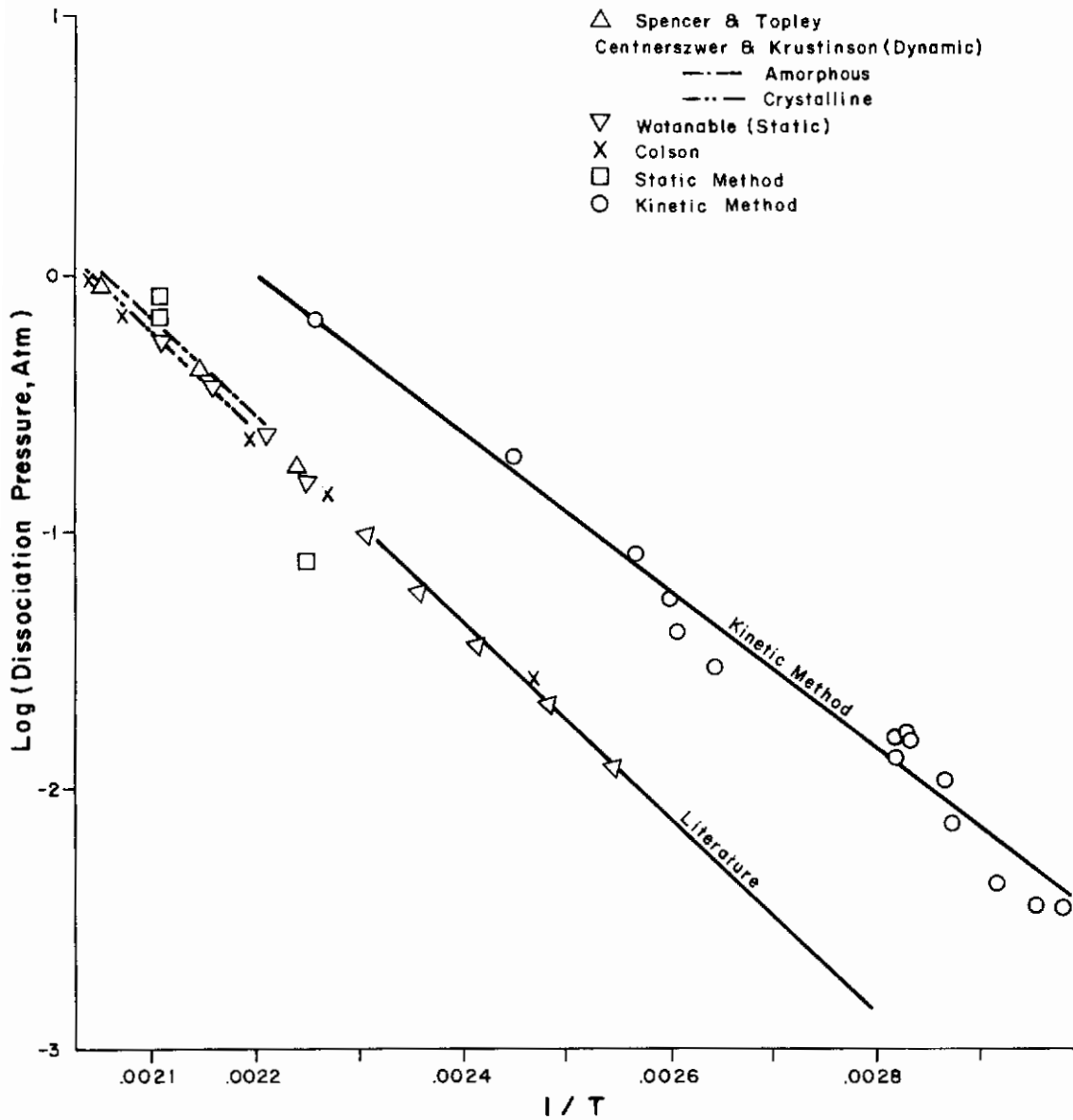
Figure 15. Dissociation Pressures of Ag_2CO_3

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substrate, as in the present case of Ag_2CO_3 - Ag_2O. Nevertheless, a more or less protective powdery layer is possible even if no adherent protective film exists.

a. Argument for a layer of Ag_2O powder obstructing entrance of H_2O catalyst counter to outflowing CO_2.

Rates actually do gradually diminish, as typical with growing protective layers, in vacuum decomposition of both pure Ag_2CO_3 and some catalyst containing samples. Diminishing rates may be caused at least partly by an Ag_2CO_3 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 Ag_2CO_3.

Decomposition in vacuum is choked unusually early with Ag_2CO_3 precipitated with saturated K_2CO_3 solution instead of the usual weak Na_2CO_3 solution. Hardly any choking is observed and a nearly linear law is obtained with Ag_2CO_3 containing 1% Y catalyst, even with temperatures resulting in rates so low that heat transfer limitation could not be a cause of linearity. The contrast of these effects is not believed to be due to a greater size range of the K_2CO_3 precipitated Ag_2CO_3 than of Na_2CO_3 precipitated Ag_2CO_3 or 1% Y^{+++} containing Ag_2CO_3 but is believed to be due to a large particle size with K_2CO_3 precipitated Ag_2CO_3 and to drastic elimination of the effectiveness of the Ag_2O protective layer when Ag_2CO_3 containing 1% Y is used.

Spencer and Topley (ref 4) concluded that in those cases where the decomposition of crystalline Ag_2CO_3 is progressively retarded and virtually comes to an end before all the Ag_2CO_3 has decomposed, such retardation is caused by a surface layer of Ag_2O particles through which CO_2 must diffuse. They suggested that (1) outward CO_2 diffusion from the reaction zone in the center of the particle depends on adsorbed H_2O in the outer layer of Ag_2O around the particle and hence depends on the H_2O vapor concentration and that (2) there is difficulty in H_2O vapor penetrating the increasing thickness of oxide into the reaction zone. These authors hypothesized that removal of CO_2 from the reaction zone is by surface diffusion on the Ag_2O particles surrounding it and that such surface diffusion is catalyzed by the adsorption of H_2O vapor on the

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Ag_2O, possibly as a surface layer of AgOH. The condition necessary for a more linear decomposition uninhibited by the overlying oxide was that CO_2 should diffuse away more rapidly than it is evolved. That, at higher temperatures, a higher concentration of H_2O vapor was required to obtain linear decompositions (indicative that diffusion was not rate-limiting) was in keeping with this latter hypothesis. The adsorption of H_2O 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 CO_2 surface diffusion over Ag_2O is not an important rate limiting step but that some property of Ag_2CO_3 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 Ag_2CO_3 rather than poor CO_2 diffusion out from the Ag_2CO_3 over Ag_2CO_3 surfaces.

The hypothesized Ag_2O protective layer around the unreacted Ag_2CO_3 may simply obstruct entrance of H_2O catalyst to the Ag_2CO_3 interface. The gradually increasing rate limiting action of such an Ag_2O protective layer as reaction proceeds would simply be due to the increased distance H_2O vapor would have to penetrate to the reaction sites at the Ag_2CO_3 interface counterflow to outflowing CO_2. The outflowing CO_2 from the decomposition of Ag_2CO_3 would continually tend to sweep H_2O catalyst away from the reaction interface and a continuing need would exist for entrance of H_2O catalyst.

That lack of H_2O catalyst at the Ag_2CO_3 reaction interface rather than at the surface of Ag_2O 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 H_2O 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 H_2O catalyzed by adsorbing on the surface of Ag_2O thereby allowing more rapid surface CO_2 diffusion the activation energy possibly would be gradually lowered by gradually greater quantities of adsorbed H_2O. It is not certain.

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b. Rate determining step in presence of ample H_2O catalyst.

As proposed above, H_2O 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 Ag_2CO_3 is similar to the 18.6 K cal per mole of the electric conductivity of Ag_2CO_3. This suggests that a volume property of Ag_2CO_3 may have a role in the new limiting step. That the activation energy of electrical conductivity of Ag_2O 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 Ag_2CO_3 and Ag_2O 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 H_2O (which facilitated CO_2 diffusion past the Ag_2O layer as mentioned above in Section III A 3 a) provided a possible explanation of the negative temperature coefficient found by Centnerszwer and Bruzs (ref 9) for the decomposition of amorphous Ag_2CO_3 between 240° and 260°C. At these temperatures the amount of H_2O 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 H_2O 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 Ag_2CO_3, 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 Centnerszwer and Bruzs. 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 Centnerszwer and Bruzs 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.

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4.   Difficulties and Recommendations in Practical Regeneration of
the Pure Ag_2O System

Studies on the regeneration of precipitated "amorphous" and
re-carbonated or "synthetic" Ag_2CO_3 indicate the following disadvan-
tageous characteristics of practical importance.

Vacuum regeneration is slow and difficult to carry to comple-
tion, probably because of lack of moisture at the site of decomposition.
Temperatures above the 185°C transition in Ag_2CO_3 cause reduced re-
generation rates. Temperatures as high as 250°C still give incom-
plete 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 regenera-
tion 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 CO_2
would be recovered diluted with the purge gas. This would require a
CO_2- reduction reactor able to handle the air inerts, or would force
loss of some air to space if the CO_2 is so ejected. The use of CO_2 it-
self as a purge to carry the required moisture, so eliminating inerts,
is inadvisable at atmospheric pressure because to exceed the dissocia-
tion temperature of Ag_2CO_3 at 1 atm requires a temperature above the
185°C transition temperature of Ag_2CO_3. In addition, Spencer and
Topley (ref 4) have shown that CO_2 partial pressures, even though
below the dissociation pressure, reduce greatly the rate of dissocia-
tion of Ag_2CO_3.

A workable compromise method probably would be to regenerate
using pure CO_2 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 CO_2 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 H_2O 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 H_2O 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 CO_2 is to be expelled to space. Complete regeneration of the pure Ag_2O 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 H_2O required to expel a mole of CO_2 has not been determined but it is anticipated that less H_2O 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 CO_2 by Ag_2O left on the recording balance after regeneration was studied by passing air laden with CO_2 and/or H_2O 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, CO_2 concentration, and aging, it is necessary that the resistance to CO_2 mass transfer across the stagnant air film around the gross solid particles of Ag_2O 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 CO_2 concentration at 0.55% and the H_2O concentration saturated at room temperature yielded only a 35% increase

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in rate of absorption by a typical pure Ag_2O sample about half reacted with 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 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 CO_2 from gas saturated with H_2O. The effect of temperature is shown in Figure 16 obtained by the split-run method for pure CO_2 saturated with H_2O at room temperature. Curve A was for 2% CO_2 at nearly full reaction where a thick 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 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 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 minima is obtained at 2% 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 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

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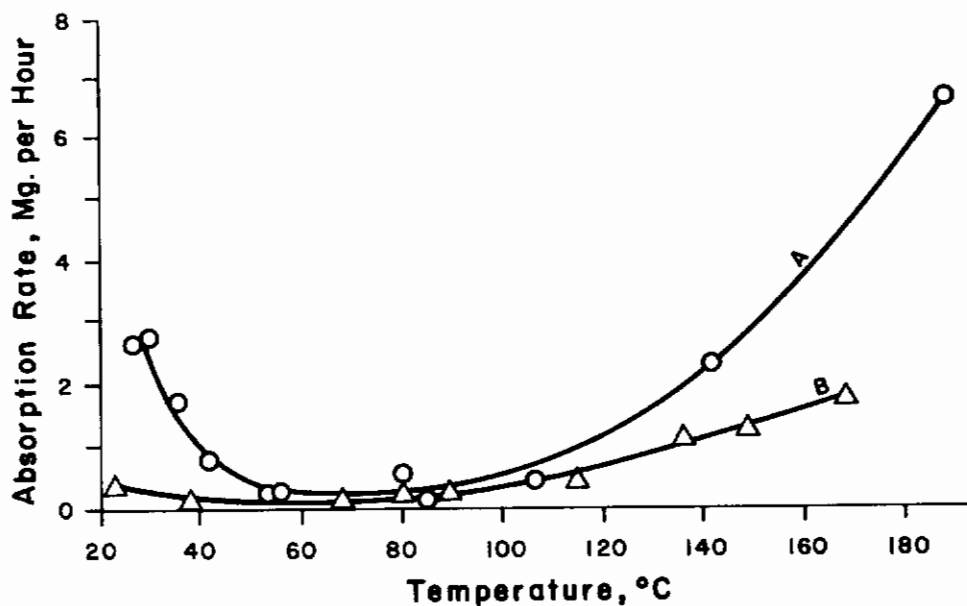
Figure 16.   Effect of Temperature on Absorption Rate of Pure CO_2 Determined by Split-Run Method
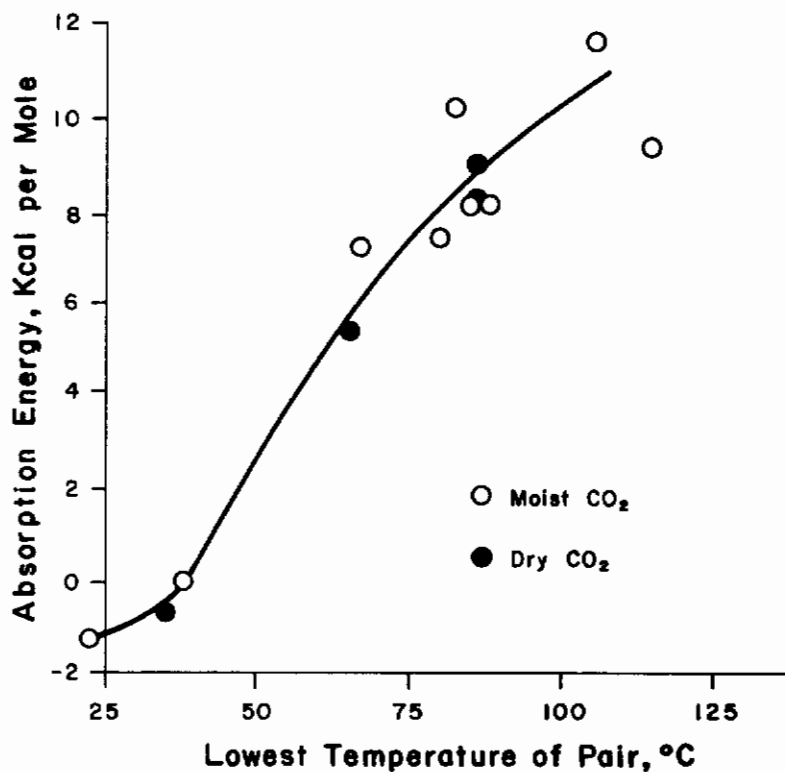
Figure 17.   Activation Energies of Absorption of Pure CO_2 Determined by Split-Run Method

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percentage-wise at the higher temperatures where only more avidly ad-
sorbed 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 CO_2 or Ag^+ diffusion limits the rate,
only by vacancies caused by H_2O 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 Ag_2CO_3. Such
proximity causes abnormally low absorption rates. A pressure attach-
ment 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 Ag_2CO_3 if a film or layer
of such is truly rate-limiting at high temperatures.

c. High temperature absorption - effect of moisture and CO_2
concentration

The high temperature absorption of CO_2 by Ag_2O is of little
practical interest because of the high heating load to preheat the large
amount of diluent air each pass. However, a protective Ag_2CO_3 layer
probably inhibits high temperature absorption similarly as dis-
cussed 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 Ag_2CO_3 is
greater than that of Ag_2O. A protective layer of Ag_2CO_3 had been
hypothesized previously by Spencer and Topley (ref 5) which hindered
inward diffusion of CO_2 to the unreacted Ag_2O core of a particle. Their
absorptions were also at high temperature but involved pure CO_2 at
various pressures with some catalytic water pressure. Alternate
absorption mechanisms other than inward CO_2 diffusion (such as out-
ward Ag^+ diffusion) are considered in the Appendix.

In contrast to room temperature absorption, high temperature
absorption does not give much lag between H_2O 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 uppercurve of Figure 33 only moderate temperatures are workable at 0.5% CO_2. Also space capsule CO_2 absorbents should absorb at near room temperature for lowest power requirements anyway.

In Figure 18 the effect of CO_2 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 CO_2 concentrations may be due to replacement of adsorbed catalytic water by CO_2 or may be due to a reduction of point defects on or in Ag_2CO_3 by which diffusion through an Ag_2CO_3 protective layer occurs (by replacement of OH^- by $CO_3^=$).

d. The stages of room temperature absorption

In Figure 20 the room temperature absorptions of 2% CO_2 from H_2O 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 CO_2. Pure CO_2 appears to give a greater initial gain, about 8 mg; 6% CO_2 about 4 mg; and 1% CO_2 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 H_2O concentration rather than the CO_2 concentration indicating the onset of the catalytic effect of H_2O with Stage 2.

Stage 2. The absorption of CO_2 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 CO_2 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

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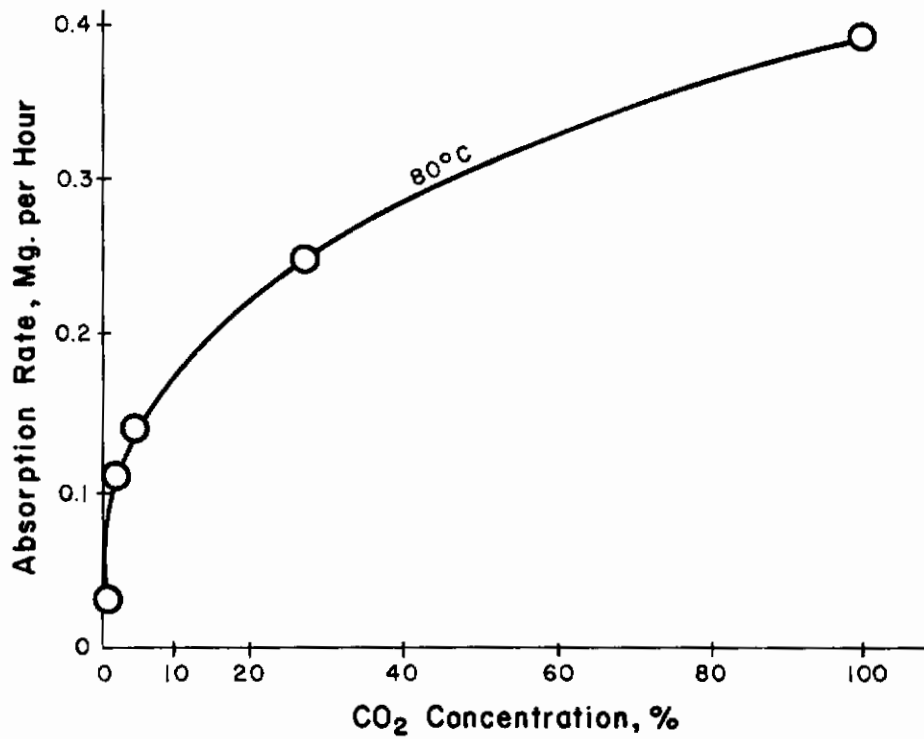
Figure 18. Effect of CO_2 Concentration on High Temperature Absorption by Split-Run Method
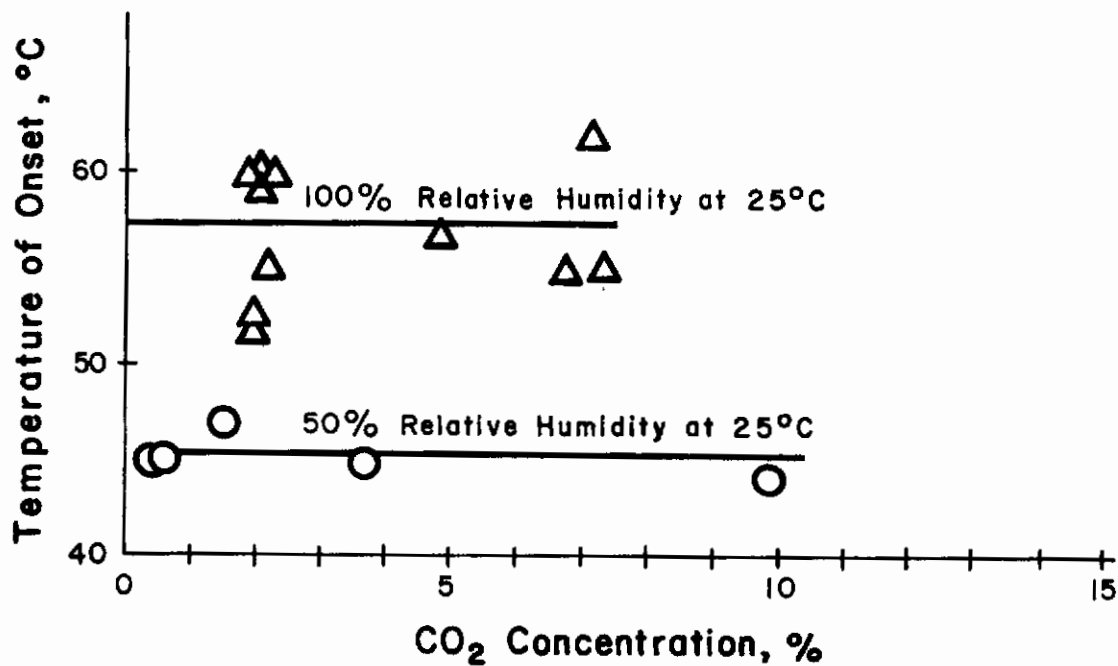
Figure 19. Onset of Stage 2 Due to Adsorption of Catalytic Water

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ABSORPTION AFTER VACUUM REGENERATION
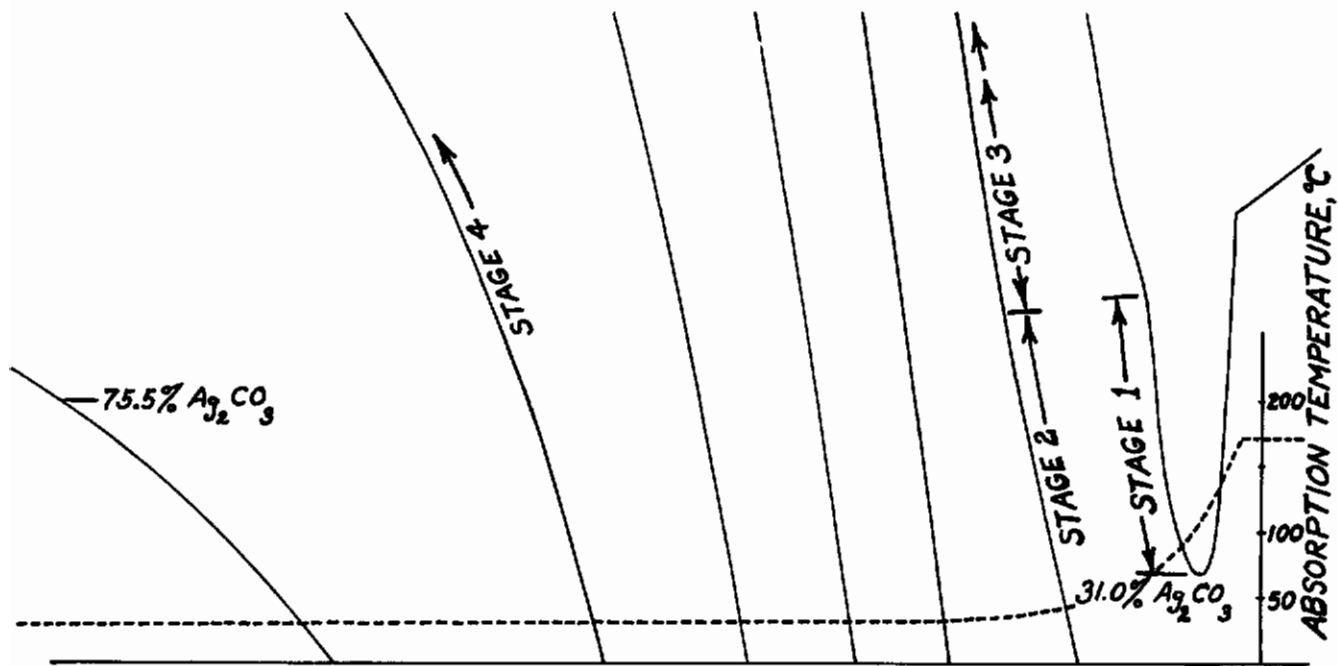
ABSORPTION AFTER PURGE REGENERATION
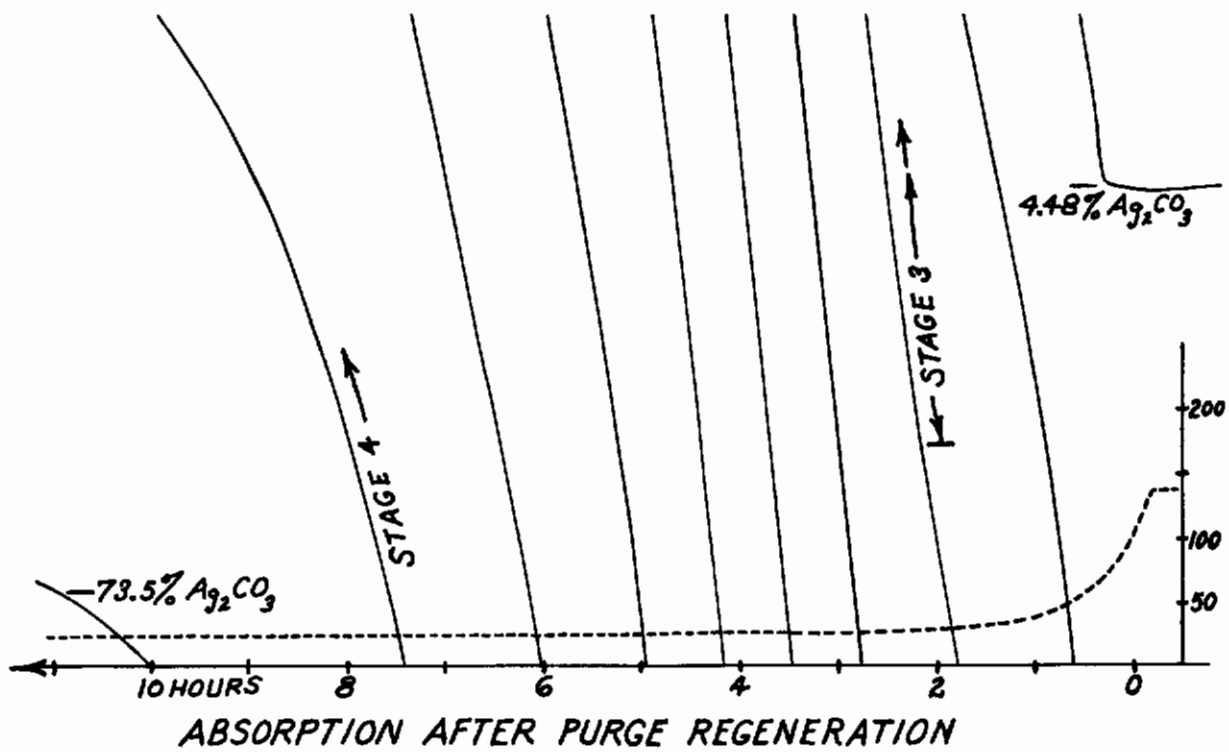
Figure 20.   Comparison of Absorption after Vacuum and Saturated
Air Purge Regeneration

finished and CO_2 pick up is very slow. The spurt may be caused by CO_2 reacting with an Ag_2CO_3 surface or Ag_2O - Ag_2CO_3 interface supply of Ag^+ ions which are soon used up and but slowly replenished, or it may be due to replacement of chemisorbed H_2O or OH^- by heavier CO_2 or $CO_3^=$.

The slow absorption of Stage 2 is greatly accelerated by cation catalysts such as 1% Y^{+++} incorporated in the system during initial precipitation of the Ag_2CO_3. 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 CO_2 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 Ag_2O 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 Ag_2CO_3 layer.

The sensitivity to the amount of moisture in the air of the CO_2 absorption during Stage 3 before its truncation is greatly influenced by the CO_2 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 CO_2 concentration for 100% and 50% relative humidity. At 3 to 7% CO_2 the moisture content of the air has a much greater influence than at below 1-1/2% CO_2. Possibly this is due to catalytic water adsorbed on (or absorbed in) Ag_2CO_3 being replaced by adsorbed CO_2 causing difficult diffusion through the Ag_2CO_3 protective layer. A great H_2O concentration increase is then necessary to maintain sufficient adsorbed water in competition with the CO_2. At below 1-1/2% CO_2 relatively low H_2O concentrations are able to compete with the undesirable CO_2 adsorption and mitigate diffusion resistance through the Ag_2CO_3 layer.

Further illustration of the great sensitivity of the development of Stage 3 to the extent of water adsorption in the 3 to 10% CO_2 region is in its sensitivity to small changes in temperature at a given H_2O concentration.
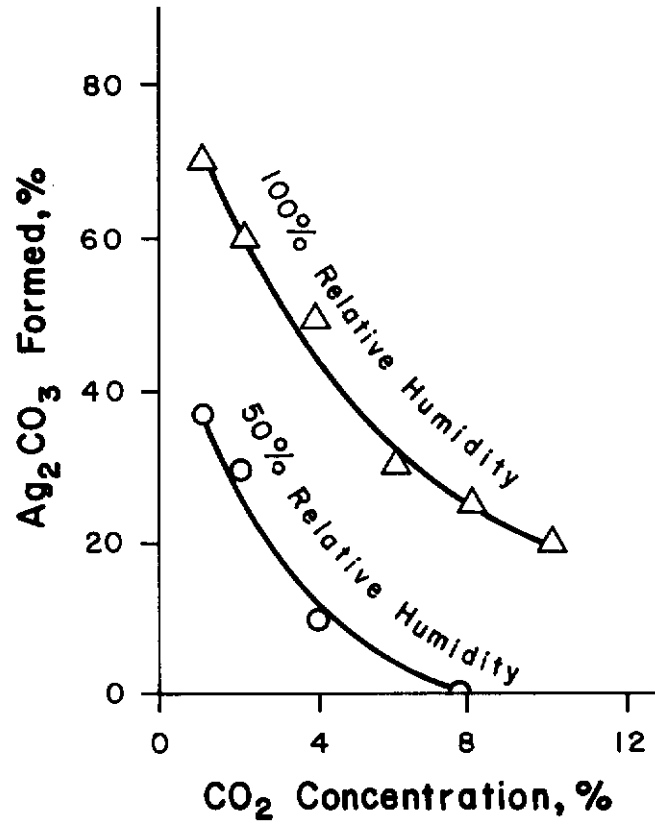
Figure 21. Extent of Absorption before Stage 3 is Finished

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Figure 22 shows the progress of an absorption cycle at about 7% CO_2 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 100% 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 0.54% CO_2.

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 Ag_2CO_3 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 Ag_2CO_3 layer is not the only reaction resistance. The Ag_2O - Ag_2CO_3 interface reaction must also represent appreciable resistance compared to that of the Ag_2CO_3 layer in early stages of absorption when the layer is relatively thin, especially at high relative humidities and at CO_2 concentrations less than 1-1/2% where a given thickness of Ag_2CO_3 layer presents less diffusional resistance due to less inhibition by CO_2.

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 Ag_2CO_3 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 Ag_2CO_3 layer (this is probably fixed for a given extent of absorption) (2) Relative humidity, (3) CO_2 concentration, (4) Temperature.

e. The effect of CO_2 concentration studied by the split-run method

The split-run method was first used in study of the effect of CO_2 concentration. In contrast to split runs of varied H_2O concentration, no short term induction effects were at first apparent. Variations in CO_2 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 CO_2 concentrations, however, it was found that the

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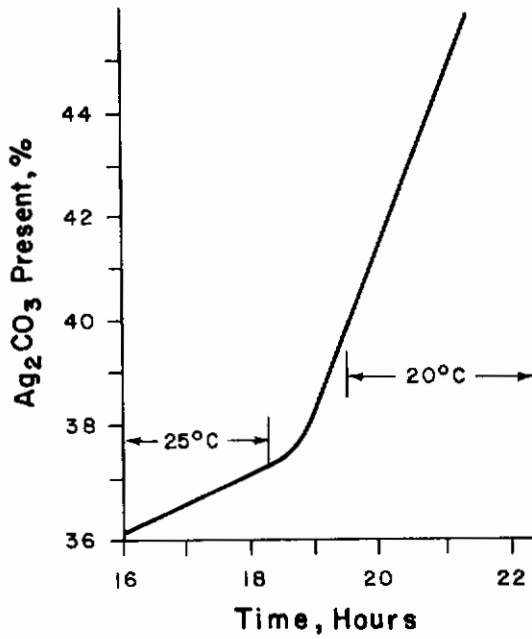
Figure 22. Revival of Stage 3 by Lowered Temperature
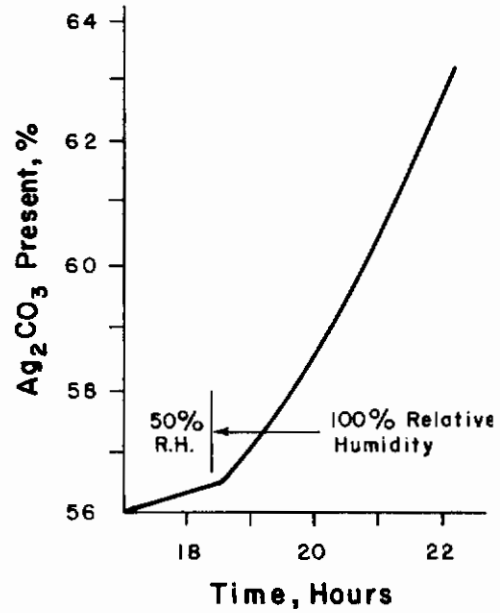
Figure 23. Revival of Stage 3 by Increased Humidity
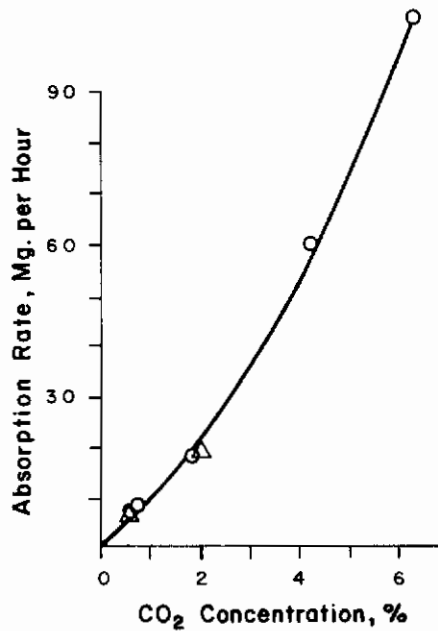
Figure 24. Effect of CO_2 Concentration on Absorption Rate by Split-Run Method

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increased rate due to a CO_2 concentration increase would gradually disappear and the rate would drop markedly. This behavior is believed due to the gradual onset CO_2 inhibition as adsorbed H_2O is gradually replaced by adsorbed CO_2. Thus reduction of H_2O catalysis does not fully occur on short term CO_2 concentration increases although there is an increase in CO_2 diffusion through any protective Ag_2CO_3 layer due simply to the increased CO_2 concentration gradient across the layer.

f. The effect of CO_2 and H_2O 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 CO_2 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 CO_2 concentration.

An inhibition of room temperature absorption by CO_2 itself is evident at CO_2 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% CO_2 at both humidities.

g. Discussion of previous absorption mechanism proposals

Part of the hypothesized mechanism of absorption involving a protective Ag_2CO_3 layer, catalysis by H_2O, and replacement of H_2O catalyst by CO_2 has been suggested already in Section III A 5 d.

Spencer and Topley (ref 5) found some indication of an optimum CO_2 concentration to equilibrium pressure (P_{CO_2}: $P_{equilibrium}$) ratio during high temperature absorption over long-term absorptions. They attributed it to too rapid nucleation of Ag_2CO_3 and to too rapid build-up of a protective Ag_2CO_3 layer thus quickly choking off CO_2 diffusion to the unreacted Ag_2O. They believed that CO_2 diffused more rapidly over Ag_2O surfaces ("wetted" them more easily) than over Ag_2CO_3 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 P_{CO_2}: $P_{equilibrium}$ ratio they

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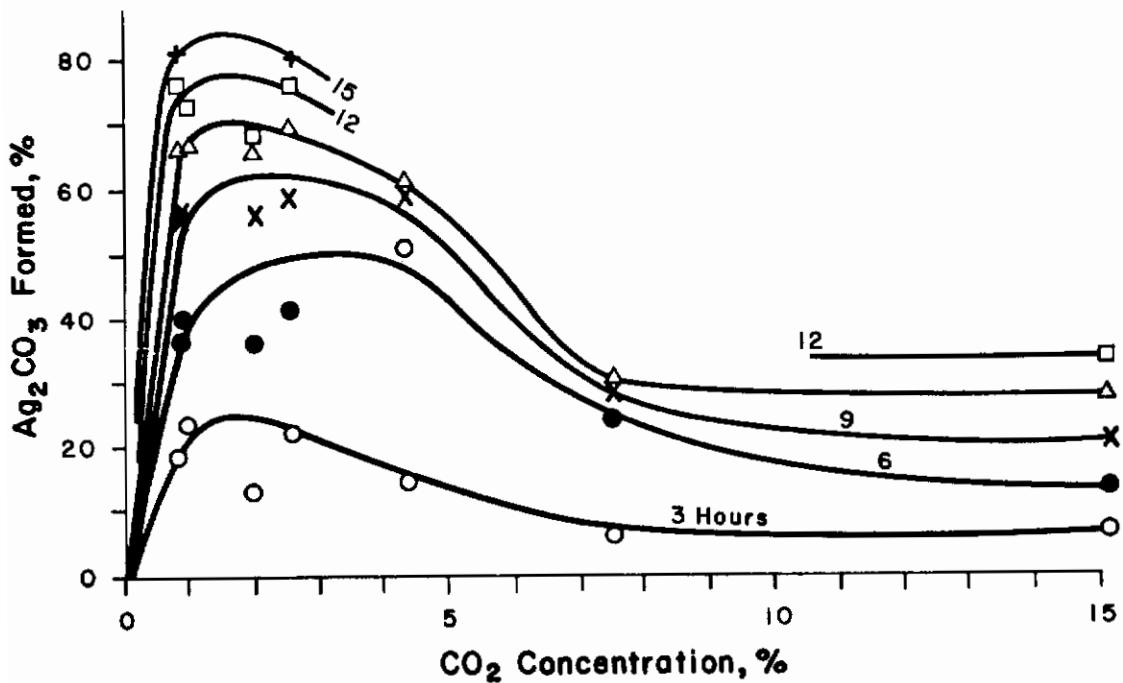
Figure 25.   Extents of Absorption at 100% Relative Humidity
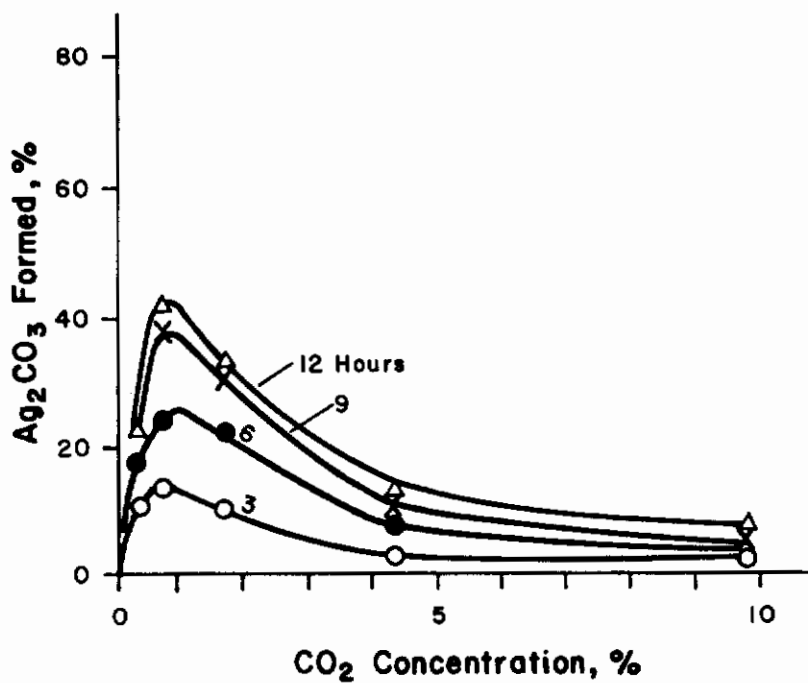
Figure 26.   Extents of Absorption at 50% Relative Humidity

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found may actually be a manifestation of the optimum CO_2 concentration at room temperature demonstrated by the present work.

Spencer and Topley also believed that adsorption of H_2O on small particles of Ag_2CO_3 forming a protective layer aggregate around unreacted Ag_2O may increase the rate of CO_2 diffusion through the layer due to increased surface diffusion over the small Ag_2CO_3 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 H_2O. 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 5 e above), after the CO_2 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 CO_2 inhibition of absorption is caused by CO_2 adsorbing and replacing adsorbed H_2O 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 adsorb 130 mg of CO_2, 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 Ag_2CO_3. The OH^- is replaced by the heavier $CO_3^=$. 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 H_2O by CO_2 to be slower than the thermal expulsion of H_2O which is then replaced by CO_2 as in generation of the above thermal pips.

h. Evidence for two modes of low temperature water catalysis - promotion of diffusion through Ag_2CO_3 layer and catalysis at Ag_2CO_3 - Ag_2O interface
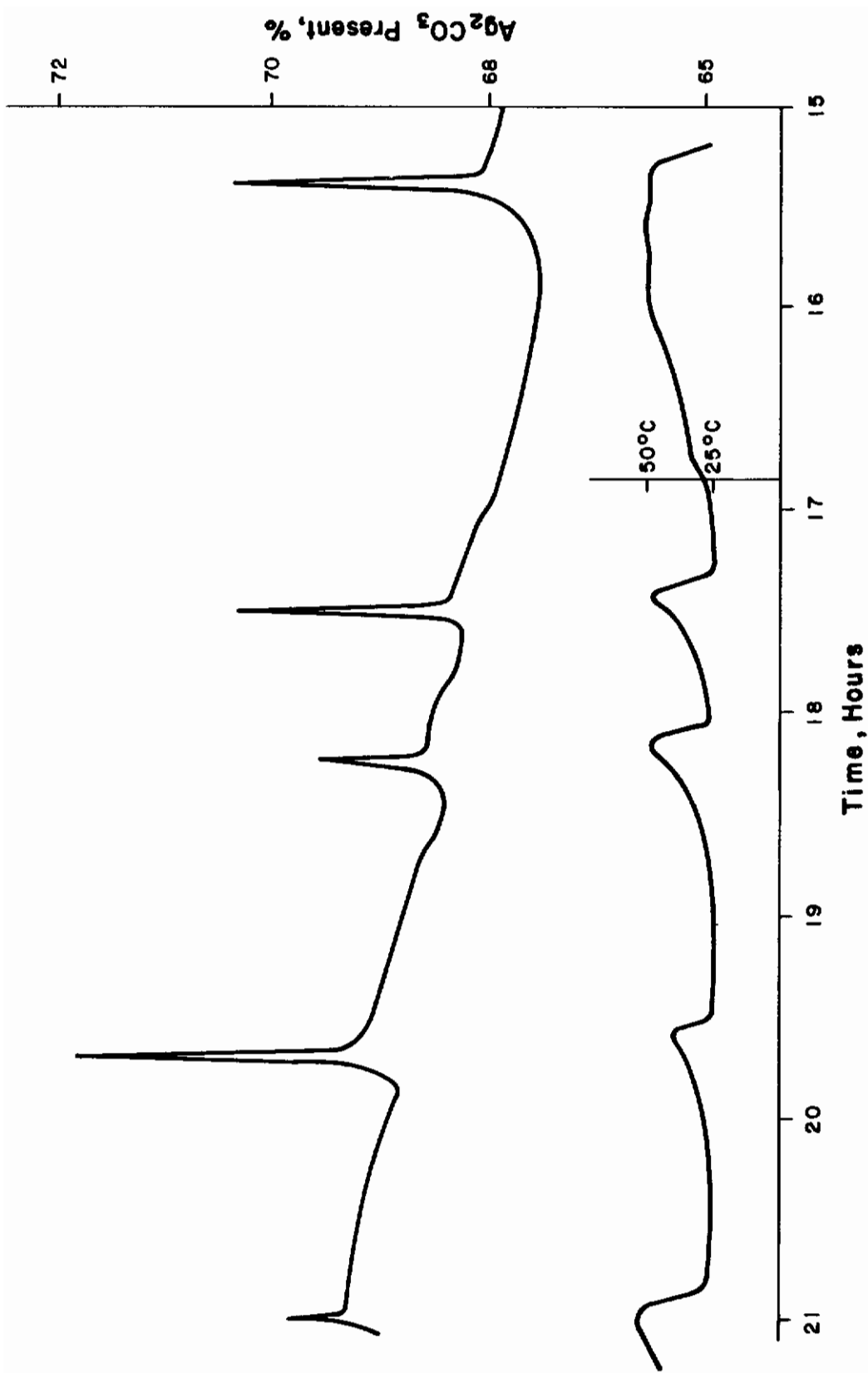
Figure 27. Weight Gain Pips Caused by Small Temperature Increases

Not only did Spencer and Topley hypothesize that adsorbed water catalyzed CO_2 diffusion through the Ag_2CO_3 layer but also that adsorbed CO_2 at the Ag_2CO_3 - Ag_2O 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_2 as well as water catalysis for both diffusion through the Ag_2CO_3 layer and for the Ag_2CO_3 - Ag_2O interface reaction. Perhaps the interface reaction involves chemisorption of CO_2 and H_2O while the diffusion through the Ag_2CO_3 involves physical adsorption of CO_2 and H_2O. Further evidence for this latter view is discussed in the Section III B on cation catalysis.

Apparently Ag^+ diffusion could be involved in either the interface reaction step or in diffusion through the Ag_2CO_3 protective layer (rather than CO_2 as previously tentatively assumed, following Spencer and Topley). At the interface Ag^+ diffusion from the interior of Ag_2O to its surface may be involved. In the protective layer Ag^+ would diffuse through Ag_2CO_3 or over its surface. Strong evidence for Ag^+ diffusion is the fact that cation catalysis is possible.

If the reaction sites at the Ag_2O - Ag_2CO_3 interface are Ag^+ ions (or clusters) their concentration will depend on the rate of diffusion of the Ag^+ from the interior of the Ag_2O to its surface. Thus there will be two rate controlling factors in the interface reaction, (1) the presence of H_2O catalyst at the Ag^+ ions and (2) the number Ag^+ ions exposed to CO_2. If both H_2O and CO_2 are necessary at a given Ag^+ ion for reaction, and if they compete for adsorption, there should be an optimum CO_2 concentration at a given H_2O concentration. Such an optimum is found but it is ambiguous in that it may be due to an optimum in diffusion of CO_2 or Ag^+ through a protective Ag_2CO_3 layer as discussed above or to an optimum in the interface reaction rate.

6. Difficulties in Use of the Pure Ag_2O System for Absorption of CO_2

The main difficulty in practical room temperature absorption of CO_2 by the pure Ag_2O 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_2, is also sufficient to greatly reduce the rate and extent of carbonation. The water catalyzes (1) possibly the Ag_2O - Ag_2CO_3 interface reaction if

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such is a rate limiting step, (2) possibly Ag^+ diffusion out from the Ag_2O through the Ag_2CO_3 protective layer, and (3) possibly CO_2 diffusion inward through the protective Ag_2CO_3 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 H_2O concentration to CO_2 concentration. A relative humidity of 50% instead of near 100% is sufficient to appreciably reduce the rate of absorption at all CO_2 concentrations. More work is needed to delineate which of these two conditions is operative in the above three modes of catalysis. Possibly below 1% CO_2 concentration where CO_2 does not inhibit absorption the relative humidity is definitive but above 3% where CO_2 does inhibit the H_2O to CO_2 ratio is important.

The decay of room temperature absorption yields on repeated cycling has been examined wherein the weight of CO_2 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 Ag_2O 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 Ag_2O system.

B.   THE ADDITION OF CATION CATALYSTS TO THE Ag_2O 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]: (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_2CO_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_2CO_3 to the Ag_2O by surface diffusion over and around each component particle making up the aggregate of the Ag_2CO_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^+ outward from the Ag_2O through the Ag_2CO_3 protective layer.

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_2O interface are important. Possibly, also, Ag^+ diffusion through Ag_2O (see Section III A 5 h) 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.

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 CO_2 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 Tl^+ (1.49 Å radius) and Cu^{++} (0.80 Å radius) have been studied (see Table I) 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 decomposition at higher

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TABLE I

Comparison of DTA With Recording Balance Runs

%	Catalyst	Apparent Ionic Radius	Vacuum DTA Results			Extent of Initial Low Temperature Decomp	Vacuum Regeneration		Absorption	
			Position 185°C Transition	Strength 185°C Transition	Area 200°-250°C		150°C	200°C	Above 50°C	Room Temp
1	None		Normal	Normal			Fair	Fair		
1	Tl+	1.49	Normal	Normal				Fair		
1	K+	1.33	Normal	Normal			Fair	Poor		
1	Pb++	1.32								
1	Sr++	1.27						Very Poor	Poor	Poor
1/2	La+++	1.22	Raised		Good		Good	Fair	Excellent	Good
1	La+++	1.22	Raised		Fair		Fair	Poor	Fair	Good
1	Bi+++	1.20								
1	Ce+++	1.18			Fair			Good	None	
1	Pr+++	1.16								
1	Nd+++	1.15	Raised				Poor	Good	Good	Fair
1	Sa+++	1.13								
1	Eu+++	1.13								
1	Hg++	1.12								
1	Gd+++	1.11								
1	Th++++	1.10	Lowered		Excellent	Much	Good		Fair	Fair
1	Tb+++	1.09								
1	Dy+++	1.07		Weak	Good	Some	Good		Excellent	Good
1	Y+++	1.06		None	Excellent	Much	Good		Excellent	Good
1/2	Ca++	1.06			Poor		Fair		Poor	Fair
1	Ca++	1.06			Good		Good		Poor	Good
4	Ca++	1.06								
1	Ho+++	1.05			Fair					
1	U++++	1.05								
1	Er+++	1.04			Good	Some	Good		Excellent	Good
1	Tm+++	1.04								
1	Cd++	1.03		Weak	Excellent	Some	Good	Good	Good	Good
1	Yb+++	1.00								
1	Na+	.98								
1	Lu+++	.99								
1	Mn++	.91		Good	Good	Some		Fair	Fair	Fair
1	Co++	.82	Lowered			Much		Fast to Ag		
1	Cu++	.80			Excellent	Much		Good	Poor	
1	Al+++	.62								

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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 concentration 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 appreciable differences were noted the other concentrations are also presented.

Results of the DTA screening performed to date (see Table I) seem to indicate that it is common for a foreign ion to catalyze regeneration. But only those ions which tend to suppress the 185°C transition and also show but little high temperature endothermic decomposition of carbonate also catalyze absorption well. The rare earths with radii 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 ytrrium. Yttrium has an apparent 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 CO_2 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 CO_2 Concentration, Humidity, and Temperature on Absorption by Ag_2O Containing 1% Y

In Figure 30 a comparison of the effect of CO_2 concentration on room-temperature absorption after 9 hours at 50% relative humidity is made for Ag_2O containing no Y and that containing 1% Y catalyst. Although the peak rate is at 1 to 1-1/2% CO_2 for both there is much less relative inhibition of the rate by higher CO_2 concentrations for the latter. At lower CO_2 concentrations the rate increases roughly linearly with concentration for both.

Apparently the 1% Y catalyst aids diffusion through the protective Ag_2CO_3 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% CO_2 attributed previously to CO_2 blocking such diffusion is mitigated by the Y catalyst. The Y catalyst also accelerates absorption at CO_2 concentrations below 1% where CO_2 does not block reaction due to such diffusion but where the rate limiting step may be at the Ag_2CO_3 - Ag_2O 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 Ag_2O at 2% CO_2 and 100% relative humidity at 25°C.

The results of a study of the effect of CO_2 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 CO_2 even as ultimately, after the equilibrium
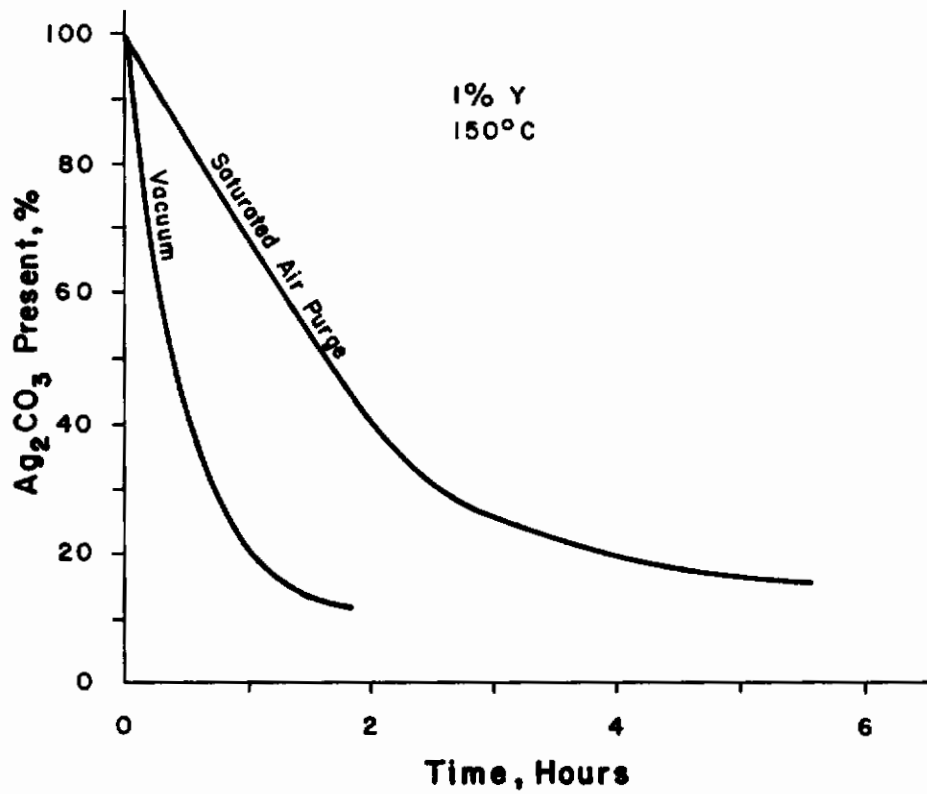
Figure 28.   Comparison of Vacuum and Saturated Air Purge
Regeneration of Ag_2O with 1% Y
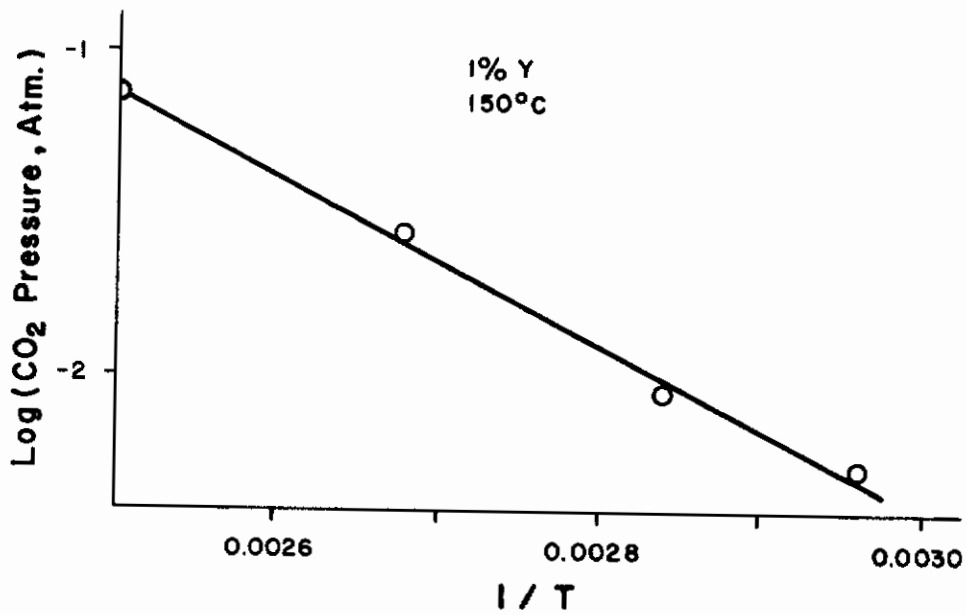
Figure 29.   Onset of Absorption of CO_2 by Ag_2O with 1% Y

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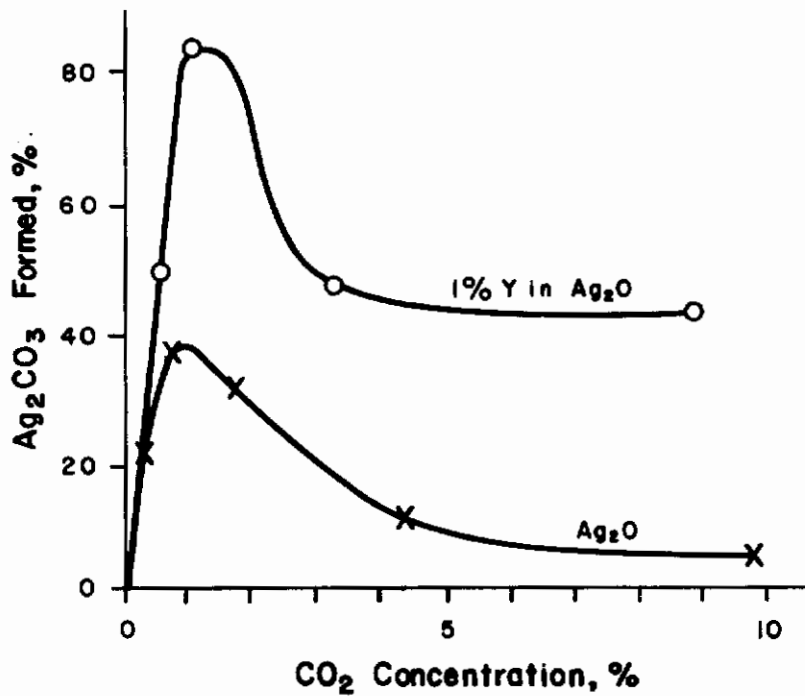
Figure 30.   Absorptions After 9 Hours at 50% Relative Humidity by
Pure Ag_2O and That With 1% Y
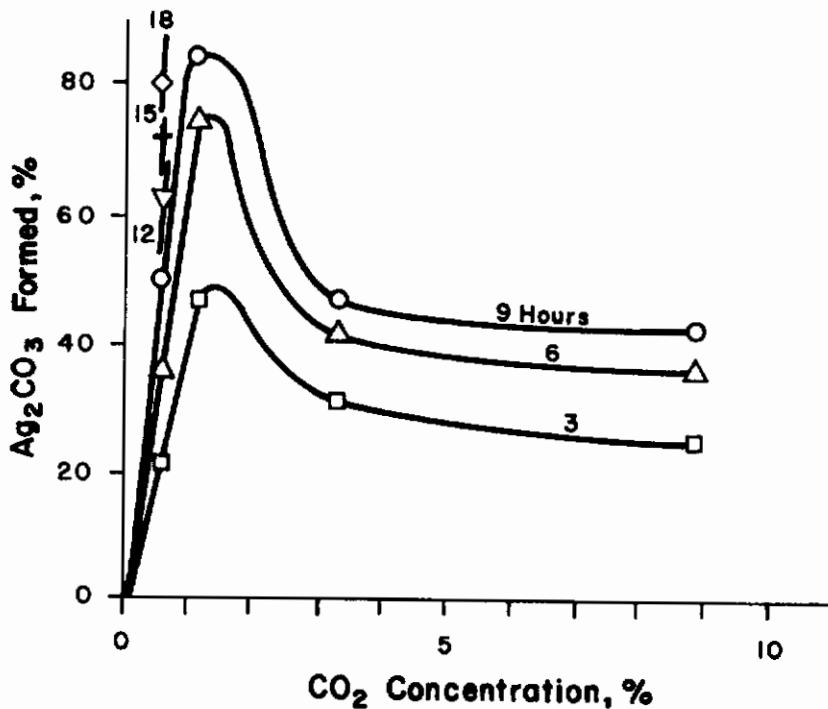
Figure 31.   Absorptions After Various Times at 50% Relative Humidity
for Ag_2O With 1% Y

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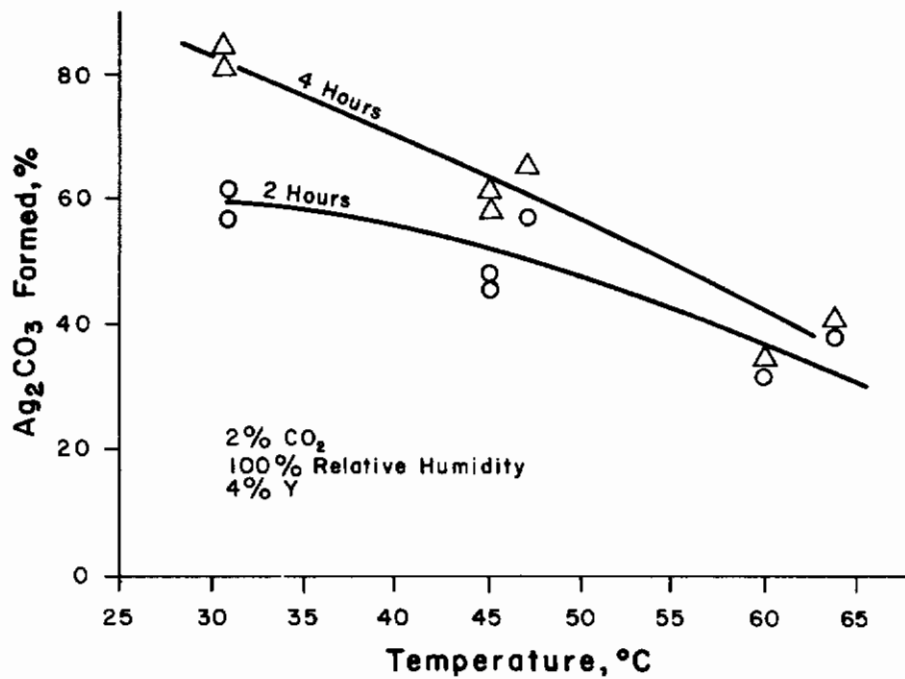
Figure 32. Effect of Absorption Temperature With 4% Y at 100% Relative Humidity
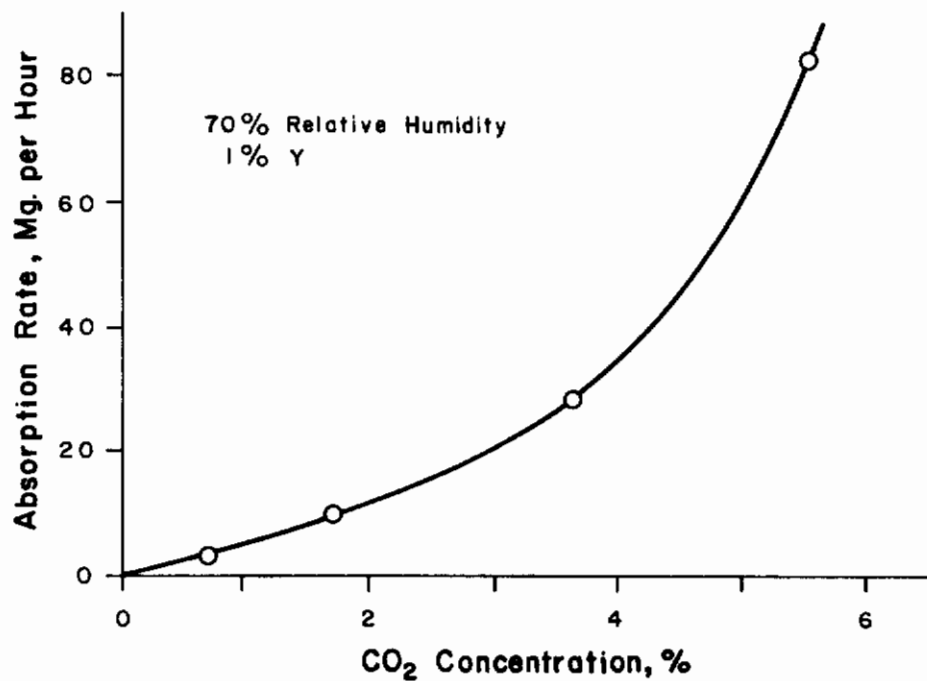
Figure 33. Effect of CO_2 Concentration on Absorption Rate With 1% Y at 70% Relative Humidity by Split-Run Method

rate is established, the inhibition by CO_2 as shown in Figure 30 is lower. The almost parabolic nature of the concave curve suggests a second order reaction with CO_2 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 Ag_2CO_3 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 atmosphere 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 Ag_2CO_3 and that containing 1% Y. An endothermic dissociation reaction at about 230°C at 1 atmosphere is common to both the pure and the yttrium-bearing silver carbonate and results in loss of very close to half of the $CO_2$ for both materials. At higher temperatures, the pure silver carbonate appears to gradually lose more CO_2 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 $Ag_2O \cdot Ag_2CO_3$ remaining. On the other hand, the yttrium-bearing basic carbonate shows a very sharp loss of the rest of its CO_2 and reverts to silver beginning at about 330°C at 1 atm. Summarizing, the main difference between the atmospheric DTA of the pure Ag_2CO_3 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 Ag_2CO_3 but it also changes the crystal structure of the Ag_2CO_3 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 Ag_2CO_3. High temperature infrared studies perhaps would clarify the conditions for OH^- solid solution in the $CO_3^=$ lattice of Ag_2CO_3 and the nature of the transition at 185°C.
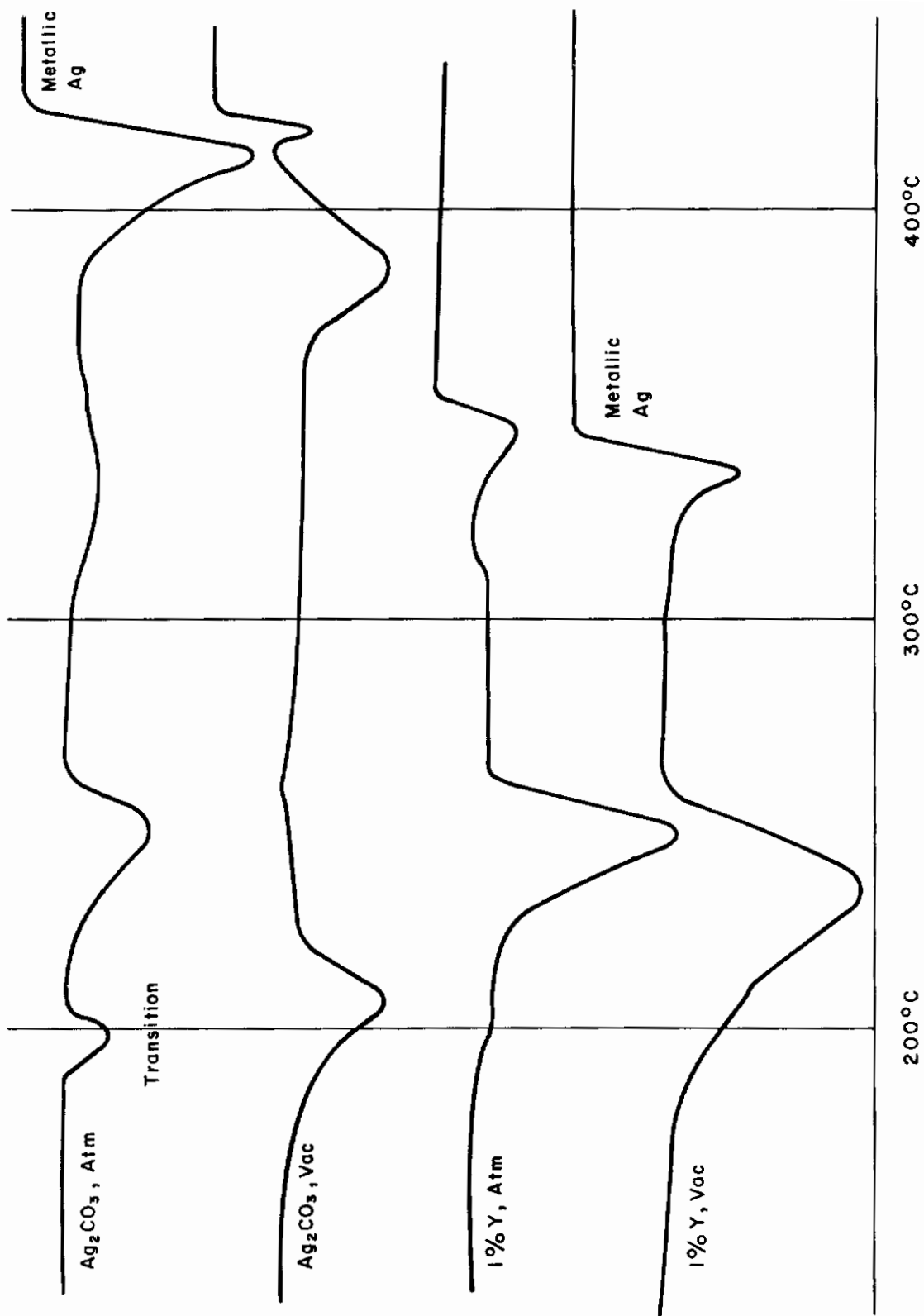
Figure 34. Atmospheric and Vacuum DTA of Pure Ag_2CO_3 and That With 1% Y

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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 1. If one of the two preferred mechanisms is valid the water may promote substitution of OH^- ions for $CO_3^=$ 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^+ 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^+ 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

that absorption at a relatively high temperature soon stops, presumably as the protective Ag_2CO_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_2O 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_2O: The one is a high temperature type found in Stage 2 involving, probably, chemisorbed H_2O 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_2CO_3 layer has built up. Fortuitously the temperature normally drops to room temperature by the time much protective Ag_2CO_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[1] is in good accord with the conclusion above that there is a high temperature H_2O 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_2O catalysis during Stage 2 just after regeneration while the sample is still cooling.

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[1] Spencer and Topley (ref 7), too, implied that there may be two types of H_2O catalyses: (1) surface diffusion of CO_2 on the Ag_2CO_3 particles of the protective Ag_2CO_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_2O (CO_2) adsorbed → Ag_2CO_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 H_2O 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 H_2O catalysis and the room temperature H_2O catalysis operating simultaneously is that the former mostly promotes Ag^+ diffusion through the Ag_2CO_3 particles of the protective layer (and possibly promotes the interface reaction) whereas the latter mostly promotes surface diffusion of Ag^+ or CO_2 over the Ag_2CO_3 particles of the protective layer. Thus the high temperature H_2O 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 Ag_2CO_3 particles. If CO_2 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 Ag_2CO_3 or Ag_2O 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, interstialcy, or lattice vacancy mechanisms.[1]

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[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" × 0. 18" × approximately 1/32" pellet pressed at 75, 000 lb per sq inch was measured with an ordinary D. C. vacuum tube ohmeter. 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 Ag_2CO_3 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 Ag_2CO_3. 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 Ag_2O 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 cation catalytic effect.

Typical curved and straight log k vs 1/T plots are given for additives in Ag_2O and Ag_2CO_3 in Appendix III.

TABLE II

Activation Energy of Electrical Conductivity of Ag$_2$CO$_3$ Containing Various Cation Catalysts

Cation in Ag$_2$CO$_3$	Activation Energy
None	18,600
1% Y	11,600
4% Y	10,230
1% Y, 5% Al	11,330
10% Al	17,000
4% Al	Curved plot
2% Al	Curved plot
1% Al	Curved plot
1/2% Al	Curved plot
4% La	Curved plot
2% La	Curved plot
1% La	Curved plot
1/2% La	Curved plot
1% Dy	Curved plot

TABLE III

Activation Energy of Electrical Conductivity of Ag$_2$O Containing Various Cation Catalysts

Cation in Ag$_2$O	Activation Energy
None	14,500
None	14,500
1% La	8,820
1/2% La	8,410
1% Y	9,780
1% Nd	8,000

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

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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 CO_2 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 CO_2. 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 30% 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 Al_2O_3 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 as 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 Ag_2O.

Dissociation pressures from the literature for $Ag_2O \rightarrow Ag + 1/2O_2$ 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 catalysis 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.

Temperature	Po_2 Minimum, Atm
175°C	0.7
150°C	0.3
125°C	0.12

The maximum CO_2 partial pressures attainable in the purge gas would be:

Temperature	P_{CO_2} Maximum, Atm
175°C	0.21
150°C	0.095
125°C	0.020

The CO_2 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 Ag_2CO_3, at 135°C the maximum partial pressure of CO_2 obtainable in the effluent gas would be only about 0.066 atm. Thus the purge gas must not be vented to space but to a chemical system that can reduce the CO_2 and leave the O_2 free for recycle. Any apparatus for CO_2 reduction which would be coupled to the silver oxide CO_2 concentrating system would have to operate on a gas rather dilute in CO_2 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 Ag_2CO_3 would be very useful for such a

purge regeneration method since it would allow attainment of higher CO_2 concentrations in the effluent gas from the regeneration step.

C.   STUDY OF OTHER METAL OXIDE SYSTEMS

In view of the very sparce coverage in the literature on the absorption rate of CO_2 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 Ag_2O system if such cations incorporated in the Ag_2O system as catalysts would not dissolve. In such a case one might find primary absorption of CO_2 by the metal system which then could transfer CO_2 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 untried 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

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 absorp-
tion. Considerable moisture appeared to be absorbed simultaneously
with the CO_2 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
CO_2 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 $Y_2(CO_3)_3$
to Y_2O_3 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 CO_2.
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% CO_2 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 $PbCO_3$, and if the moderately high re-
generation 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, 350°C, and
420°C. Complete regeneration thus would probably require a rather
high temperature. This, with the incomplete absorption to $PbCO_3$,
perhaps due to stable hydroxy-carbonate formation, tends to prevent
good yields.

Addition of 1% Ag^+ to the lead carbonate did not change its
activity. One percent Y^{+++} 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 CO_2. 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 CO_2 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 CO_2 by the Zn system, a certain amount of water must also be absorbed, possibly to build up a hydrozincite (zinc hydroxy-carbonate) phase. Long exposure to CO_2 at 100% relative humidity at room temperature will eventually form a more carbonated material containing twice as much CO_2 as Ag_2O at 100% yield, however. An extended absorption period at 100% relative humidity allows a yield corresponding nearly to $ZnCO_3$, a material containing more CO_2 than the original hydro-zincite 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 CO_2 and how much if H_2O have not been utilized.

Differential thermal analysis of precipitated zinc carbonate (which incidentally shows an infrared spectrum corresponding well with hydrozincite) 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 will 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 CO_2 concentration on the extent of absorption at various CO_2 concentrations and 50% relative humidity by long term runs at room temperature. There appears to be no inhibition of absorption by CO_2 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 pips in the temperature would cause weight gain pips (due to a momentary loss of water and gain of CO_2) 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 pip caused by a temperature pip 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% Y^{+++} 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% CO_2 and 100% relative humidity in 5 hours. Some activity was
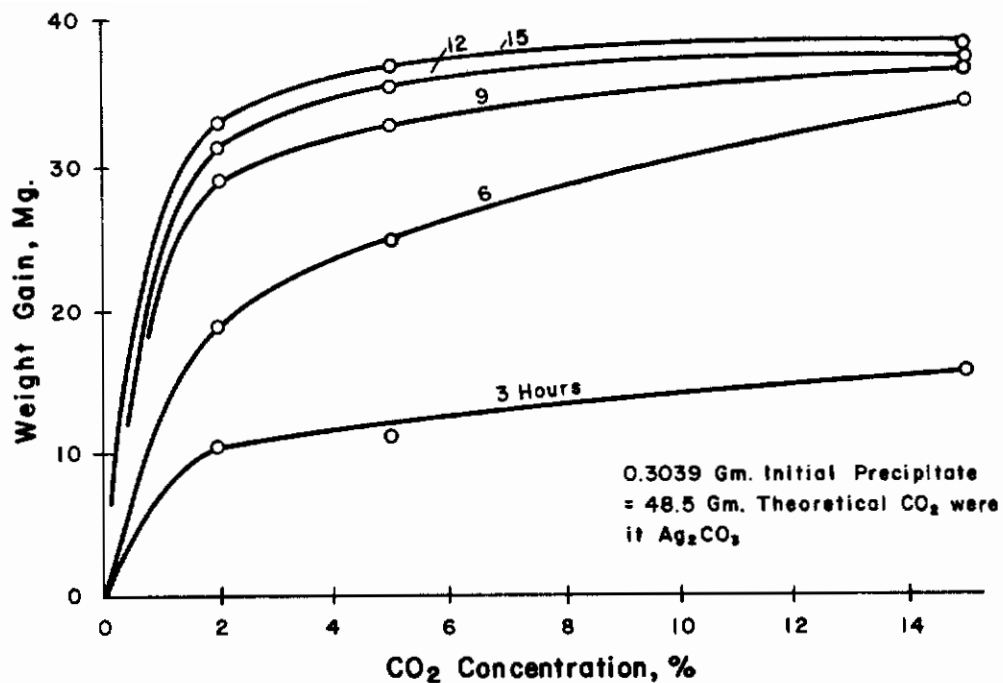
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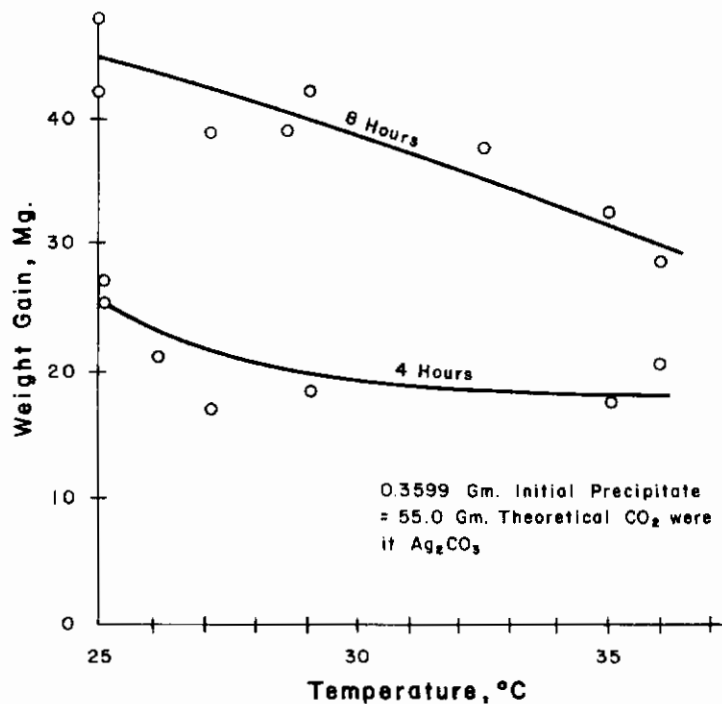Figure 35. Effect of CO_2 Concentration on Absorption by ZnO System at 50% Relative Humidity

Figure 36. Effect of Temperature on Absorption by ZnO System at 100% Relative Humidity and 2% CO_2

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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 analagous 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.

IV. COMPARISON OF MOLECULAR SIEVE, SILVER OXIDE, ZINC OXIDE, AND LEAD OXIDE AS REGENERABLE CO_2 ABSORBENTS

The theoretical minimum work to separate one gram mole of 1/2% CO_2 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 30% efficiency, 10,400 cal of heat from the fuel per mole of CO_2 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 CO_2 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 $10,200 \dfrac{2.35-1.56}{0.75-0.25} = 15,900$ cal per mole of CO_2 absorbed. This is a very appreciable heat requirement and is an incentive to development of a metal oxide system not requiring additional humidity beyond 50%.

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 Ag_2O 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 Ag_2O system and its parabolic-like rate law during Stage 4. The cation

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TABLE IV

Comparison of Weight and Heat Requirement of Various Systems

System	Assumed Yield, %	Gm Solid per mole CO_2 Absorbed	% CO_2 in Oxide at Given Yield	Heat Cap. of Solid, cal/°mol of CO_2 at 373°K	Regeneration Temp in Vacuum, °C	ΔT to Heat Solid Up From Room Temp, °C	Thermochem, Heat of Dissociation[8] cal/mol CO_2	Sens Heat to Solid, cal/mol CO_2	Sens Heat to CO_2 [10], cal/mol CO_2	Total Heat of Regeneration, cal/mol CO_2
Ag_2O	100[1]	231.7	19.0	17.23[3]	150	125	18,520	2,152	1,175	21,847
PbO	100	223.2	19.7	11.52[4]	235	220	21,700	2,540	2,070	26,310
PbO	50	446.4	9.85	23.04	255	240	21,700	5,530	2,250	29,480
CdO	100	128.4	34.2	10.42[5]	265	240	21,820	2,500	2,250	26,590
ZnO	100	81.4	54.0	10.62[6]	175	150	15,510	1,590	1,410	18,510
ZnO	50	162.8	27.0	21.24	175	150	15,510	3,180	1,410	20,100
Molecular Sieve	100	846	5.2[2]	169.1	175[7]	150	27,500[9]	25,400	1,410	54,000

Notes:

1. 85% Yield is obtainable in the laboratory.
2. At 0.5% CO_2 in gas; 7.3 at 1% CO_2.
3. Kobayashi, (ref 14) experimental data.
4. Perry, (ref 15), 10.33 + 0.00318 T.
5. Perry, 9.65 + 0.00208 T.
6. Perry, 11.40 + 0.00145 T - $\dfrac{182,400}{T^2}$
7. 175°C is required for good H_2O removal.
8. Perry.
9. Determined from Willard's Figure 14, page 43 (ref 1) for 6% CO_2 loading in the molecular sieve. This loading is obtained by consideration of the equilibrium condition 0.5% CO_2 in gas ⦻ 6% CO_2 in the molecular sieve at 25°C as shown in Willard's Figure 13, page 41 (ref 1).
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 FURTHUR STUDY

Ag_2O System.   Although continued cycling of the pure Ag_2O system using saturated air purge regeneration at 150°C coupled with room temperature absorption of 2% or 1/2% CO_2 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% CO_2 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 H_2O consumption required in a prototype system.   To this end an intermediate or full size model containing a large packed bed of Ag_2O is desirable in order to simulate the high CO_2 and low H_2O concentrations in the partial vacuum which would occur in a prototype system.   Reduction in regeneration rate at increased CO_2 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 Ag_2CO_3 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 CO_2 (to an interfacial Ag_2O - Ag_2CO_3 reaction site) through a protective Ag_2CO_3 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 Ag_2O 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 $ZnCO_3$.   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 H_2O absorption and CO_2 absorption separately.

The PbO and other Systems should also be studied, especially Sc_2O_3 and Y_2O_3 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 H_2O and that by CO_2 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 CO_2 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 Ag_2O system in study of catalysts where it is sometimes difficult to differentiate between the 185°C Ag_2CO_3 transition endotherm and any early onset of a dissociation endotherm.

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A.   ALTERNATE MECHANISMS OF TRANSPORT THROUGH THE PROTECTIVE Ag_2CO_3 LAYER

Four alternate mechanisms of absorption through the assumed protective layer of Ag_2CO_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_2CO_3 protective layer while the last two involve inward diffusion of $O^=$ or OH^- through the Ag_2CO_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_2CO_3 inward to the site of the Ag_2O as Spencer and Topley (ref 5) suggested but it is Ag^+ that diffuses from Ag_2O outward through the protective layer of Ag_2CO_3 to its outer surface where it reacts with gaseous CO_2 to give the overall surface reaction:

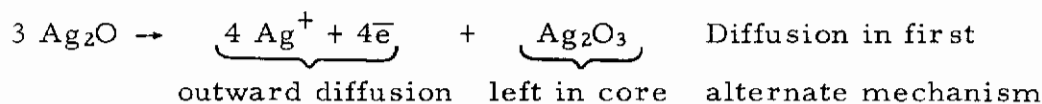$$2 \, Ag^+ + CO_2 + O^= \rightarrow Ag_2CO_3$$
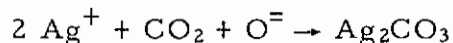
(It is possible that there are intermediate steps in the surface reaction.) The Ag_2CO_3 formed on the surface of the existent Ag_2CO_3 thus increases in depth.

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 $O^=$ 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_2CO_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_2O's remaining silver to give a higher silver oxide, more likely Ag_2O_3 than Ag_2O_2:
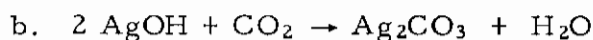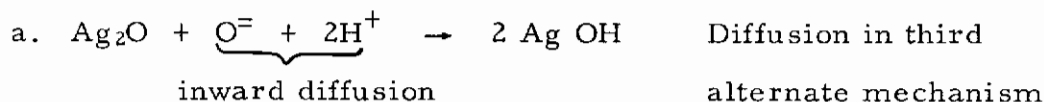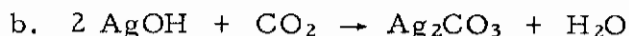
79

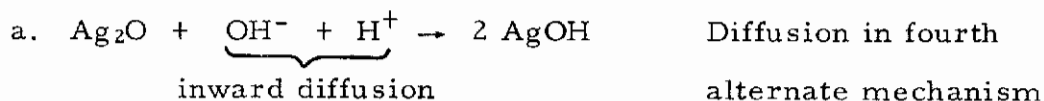$$3 \text{ Ag}_2\text{O} \rightarrow \underbrace{4 \text{ Ag}^+ + 4\overline{\text{e}}}_{\text{outward diffusion}} + \underbrace{\text{Ag}_2\text{O}_3}_{\text{left in core}} \qquad \begin{array}{l}\text{Diffusion in first}\\ \text{alternate mechanism}\end{array}$$

or shrinkage and ultimate disappearance of the Ag_2O, respectively, will occur:

$$\text{Ag}_2\text{O} \rightarrow \underbrace{\text{O}^= + 2 \text{ Ag}^+}_{\text{outward diffusion}} \qquad \begin{array}{l}\text{Diffusion in second}\\ \text{alternate mechanism}\end{array}$$

According to the third and fourth alternate mechanisms it is hypothesized that Ag^+ diffusion does not occur outward through the carbonate layer but that $O^=$ or OH^- (with H^+ as a partner) diffuses inward to the Ag_2O core where the two reactions:
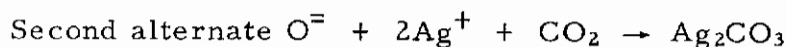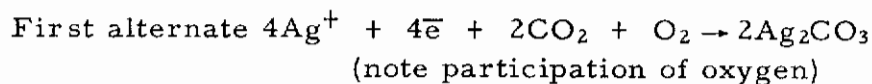
a. $\quad \text{Ag}_2\text{O} + \underbrace{\text{O}^= + 2\text{H}^+}_{\text{inward diffusion}} \rightarrow 2 \text{ Ag OH} \qquad \begin{array}{l}\text{Diffusion in third}\\ \text{alternate mechanism}\end{array}$

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

or the reactions

a. $\quad \text{Ag}_2\text{O} + \underbrace{\text{OH}^- + \text{H}^+}_{\text{inward diffusion}} \rightarrow 2 \text{ AgOH} \qquad \begin{array}{l}\text{Diffusion in fourth}\\ \text{alternate mechanism}\end{array}$

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

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 $4\text{Ag}^+ + 4\overline{\text{e}} + 2\text{CO}_2 + \text{O}_2 \rightarrow 2\text{Ag}_2\text{CO}_3$
(note participation of oxygen)

Second alternate $\text{O}^= + 2\text{Ag}^+ + \text{CO}_2 \rightarrow \text{Ag}_2\text{CO}_3$

Third alternate $H_2O \rightarrow O^= + 2H^+$ (Gaseous CO_2 must eventually react at the AgOH formed at the contact of the Ag_2O and Ag_2CO_3 phases.)

Fourth alternate $H_2O \rightarrow OH^- + H^+$ (Here again, the gaseous CO_2 must eventually react at the AgOH formed at the contact of the Ag_2O and Ag_2CO_3 phases.)

In the first and second alternates the gaseous CO_2 reacts at the outside surface of the Ag_2CO_3 layer to build up a thicker Ag_2CO_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_2CO_3 layer where it contacts the Ag_2O. Such a mechanism probably would be helpful since if gaseous CO_2 were at the interface it would probably react directly with the Ag_2O there in the first place, or if the CO_2 were transported there by surface diffusion or solid diffusion we have essentially Spencer and Topley's hypothesis of inward CO_2 transport but with the addition of inward water (as $O^= + 2H^+$ or $OH^- + H^+$) transport. The simultaneous transport of CO_2 and water through the carbonate layer to the Ag_2O core where the water first reacts with Ag_2O to form AgOH and the CO_2 then reacts with the AgOH to form Ag_2CO_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_2O 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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Direct Source of Oxygen - 18

Mechanism of Ag_2CO_3 Formation	Gaseous $^{18}O_2$	Gaseous $C^{18}O_2$	Moisture, $H_2^{18}O$	$Ag_2^{18}O$
Spencer and Topley's	Ag_2COOO	$Ag_2CO^{18}O^{18}O$	Ag_2COOO	$Ag_2COO^{18}O$
First Alternate	$Ag_2CO^{18}O^{18}O$ and/or $Ag_2COO^{18}O$	$Ag_2CO^{18}O^{18}O$ and/or $Ag_2COO^{18}O$	Ag_2COOO	Ag_2COOO
Second Alternate	Ag_2COOO	$Ag_2CO^{18}O^{18}O$	Ag_2COOO	$Ag_2COO^{18}O$

It would be necessary to detect the ^{18}O in the Ag_2CO_3 by decomposing the Ag_2CO_3 by heat and leading the CO_2 so formed into a mass spectrograph. 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 CO_2 by silver oxide.

1.   The water may promote substitution of OH^- ions for $CO_3^=$ ions in the carbonate lattice of Ag_2CO_3 thereby, in keeping a balance of total charges, causing vacancies in the Ag^+ lattice. This would probably increase the diffusivity of Ag^+ in the Ag_2CO_3, 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 Ag_2CO_3 particles or film comprising the protective layer. If this mechanism of water catalysis is valid the catalysis by doping 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 saturated air reduces the absorption rate of 1% 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_2CO_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_2O - Ag_2CO_3 interface such as silver bicarbonate which catalyze absorption of CO_2:

$$Ag_2O + H_2O + CO_2 \rightarrow 2AgHCO_3$$

$$2AgHCO_3 \rightarrow Ag_2CO_3 + H_2O + CO_2$$
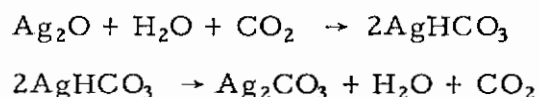
Silver hydroxide is another possible intermediate of more probability:

$$Ag_2O + H_2O \rightarrow 2AgOH$$

$$2 AgOH + CO_2 \rightarrow Ag_2CO_3 + H_2O.$$
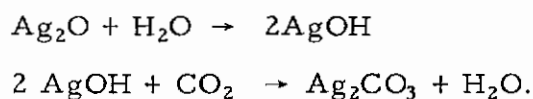
The intermediate $AgHCO_3$ or $AgOH$ may be formed on the surface of the particles of the Ag_2CO_3 layer to increase mobility of CO_2 diffusing inward (or Ag^+ diffusing outward) but such a mechanism is more properly classified under Mechanism 2 (or Mechanism 1 for the Ag^+).

4. Water may be physically adsorbed and dissolve some AgOH to form a liquid or glassy coating around the Ag_2CO_3 particles of a protective layer or in rifts in the Ag_2CO_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 Ag^+ diffusion or 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 Ag^+ or 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 Ag_2O SYSTEMS

ILLUSTRATIONS IN APPENDIX II

Figure II-1. Vacuum DTA Curves of Pure Ag_2CO_3 and That Containing Various Catalysts

87
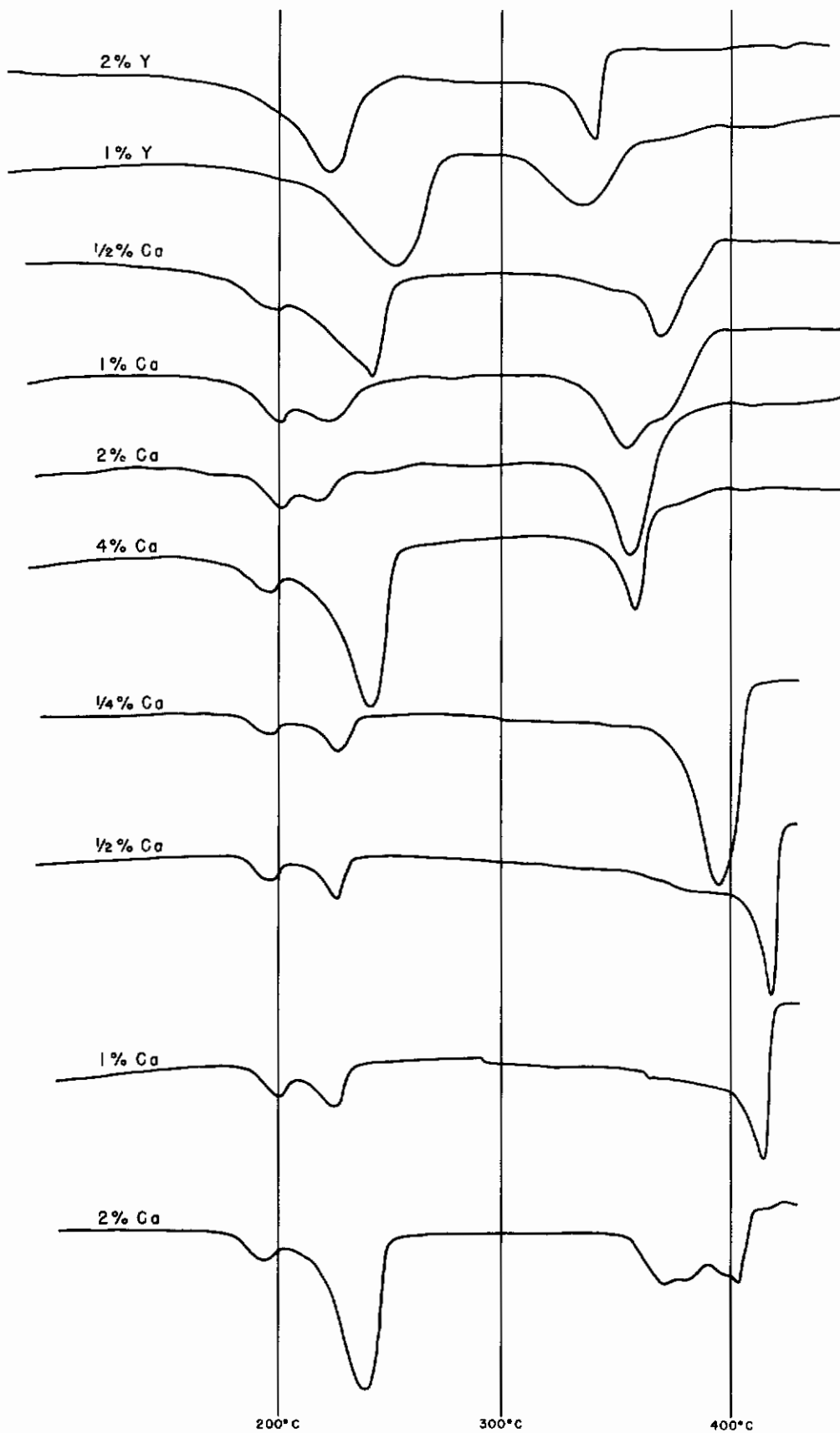
Figure II-2. Vacuum DTA Curves of Ag_2CO_3 Containing Various Catalysts

88

1% Tl
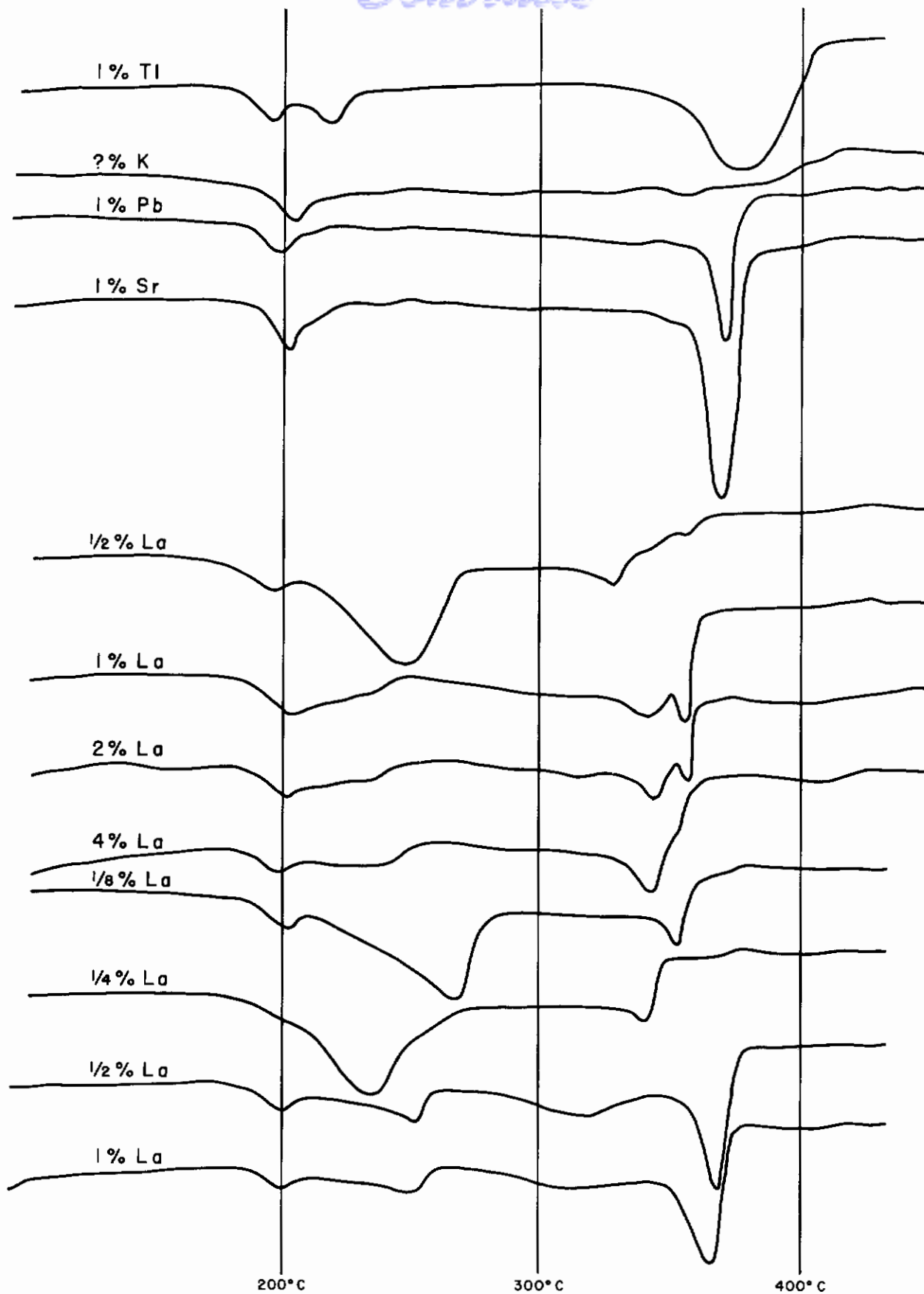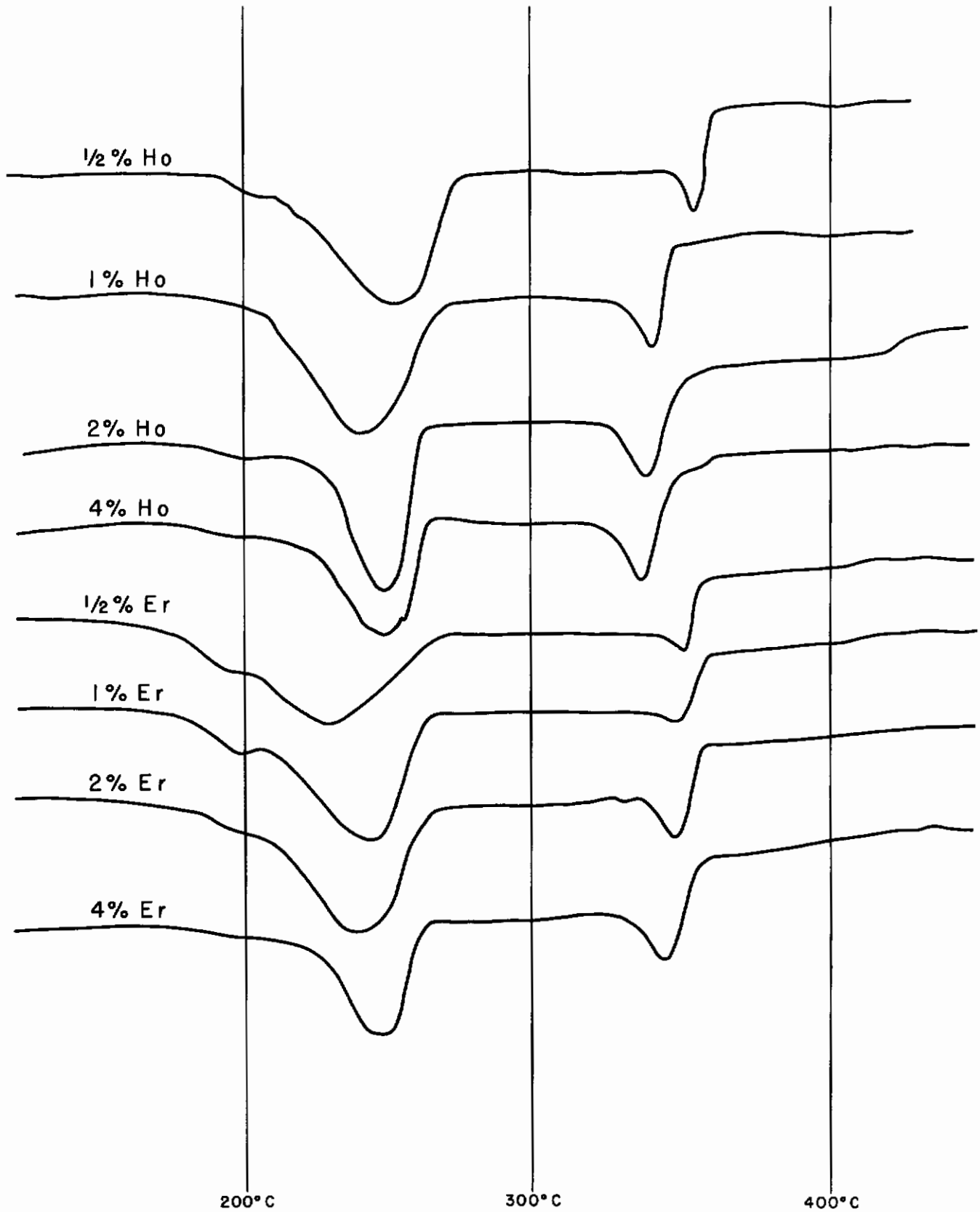
?% K

1% Pb

1% Sr

½% La

1% La

2% La

4% La

⅛% La
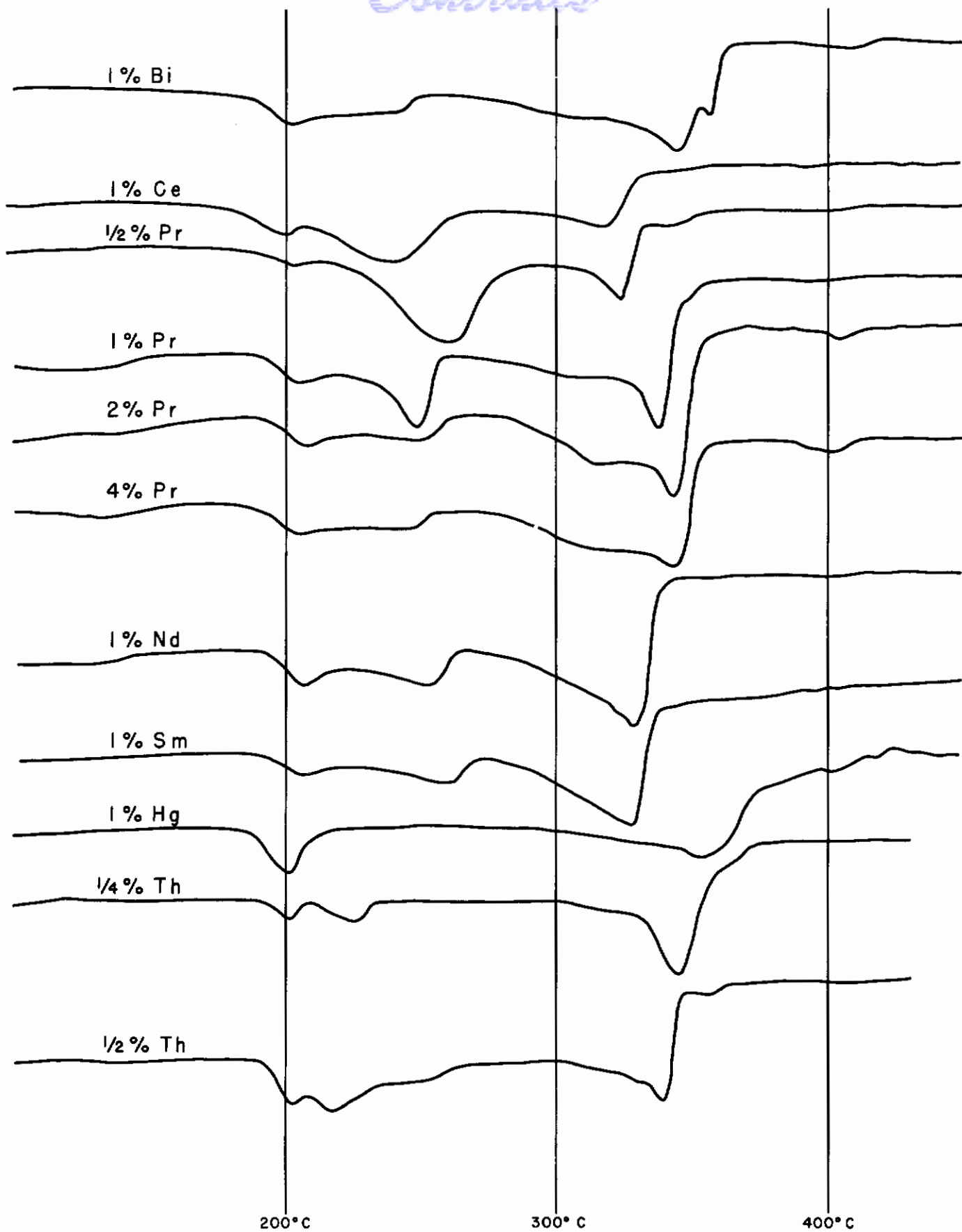
¼% La

½% La

1% La

200°C   300°C   400°C
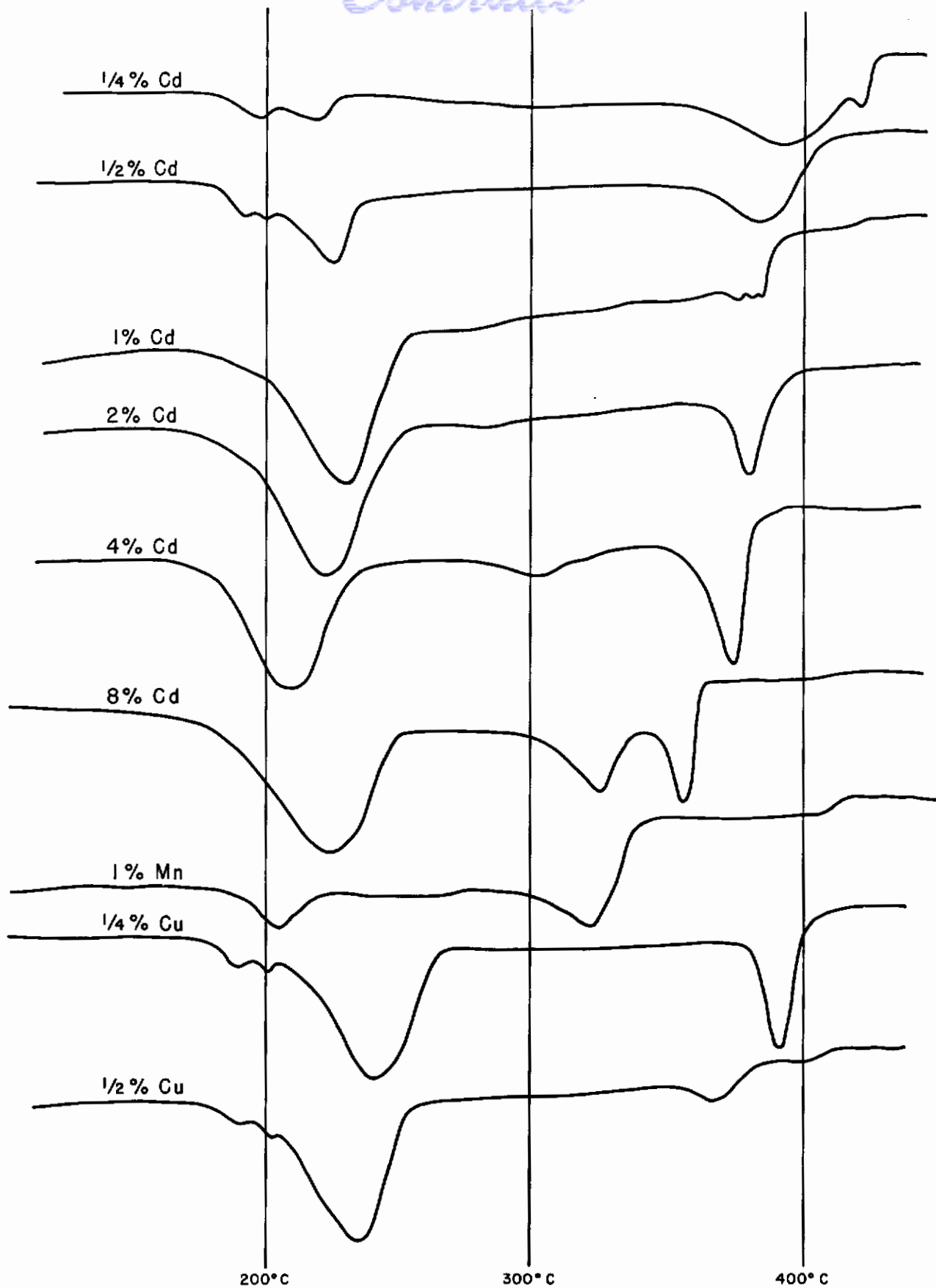
Figure II-3.   Vacuum DTA Curves of Ag_2CO_3 Containing Various Catalysts

Figure II-4. Vacuum DTA Curves of Ag_2CO_3 Containing Various Catalysts

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Figure II-5. Vacuum DTA Curves of Ag_2CO_3 Containing Various Catalysts

1% Bi

1% Ce

½% Pr

1% Pr

2% Pr

4% Pr

1% Nd

1% Sm

1% Hg

¼% Th

½% Th

200°C   300°C   400°C

91

1/4 % Cd

1/2 % Cd

1% Cd

2% Cd

4% Cd

8% Cd

1% Mn

1/4 % Cu

1/2 % Cu

200°C   300°C   400°C

Figure II-6.   Vacuum DTA Curves of Ag_2CO_3 Containing Various Catalysts
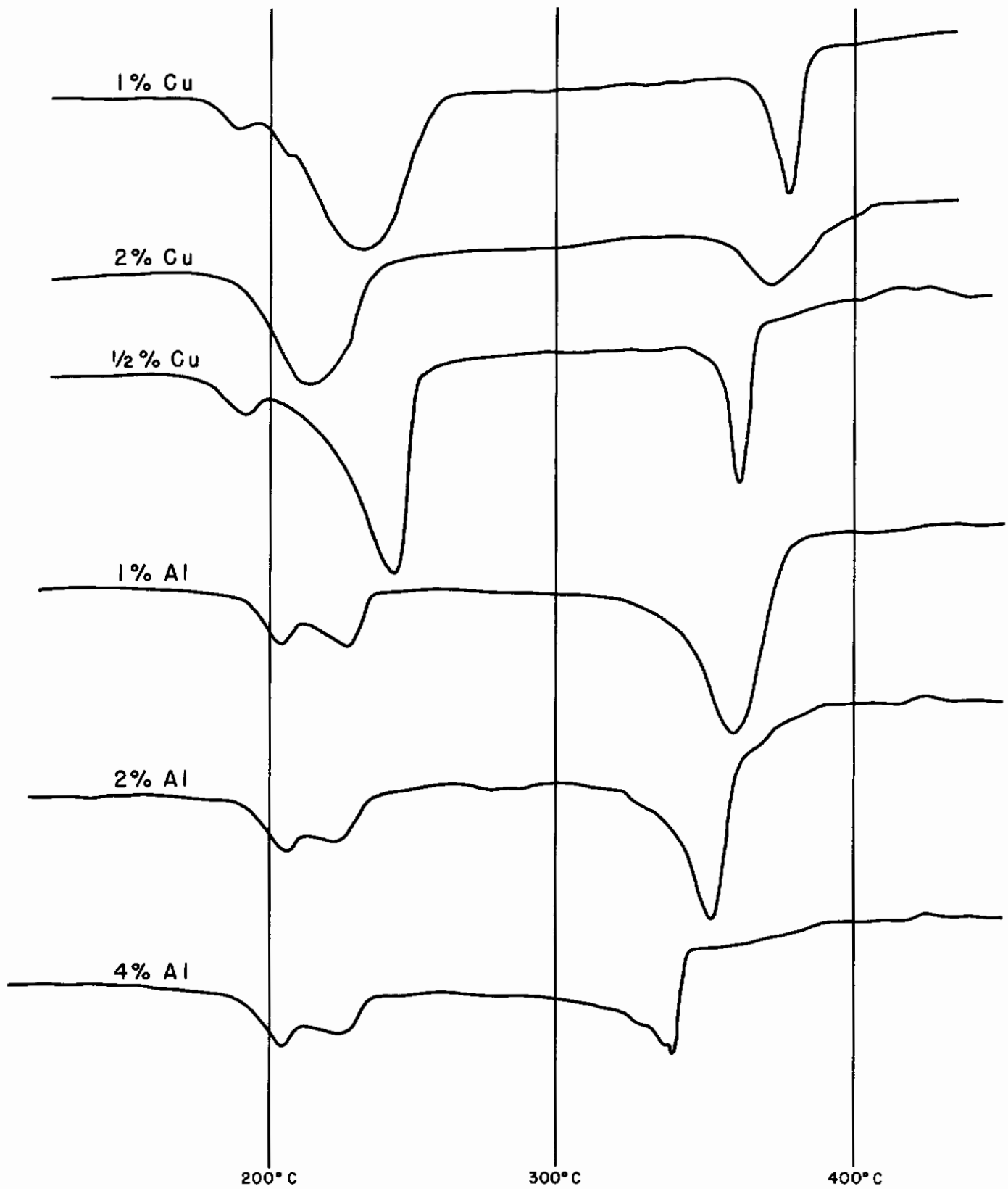
92

Figure II-7. Vacuum DTA Curves of Ag_2CO_3 Containing Various Catalysts

93

APPENDIX III

LOG (ELECTRICAL CONDUCTIVITY)
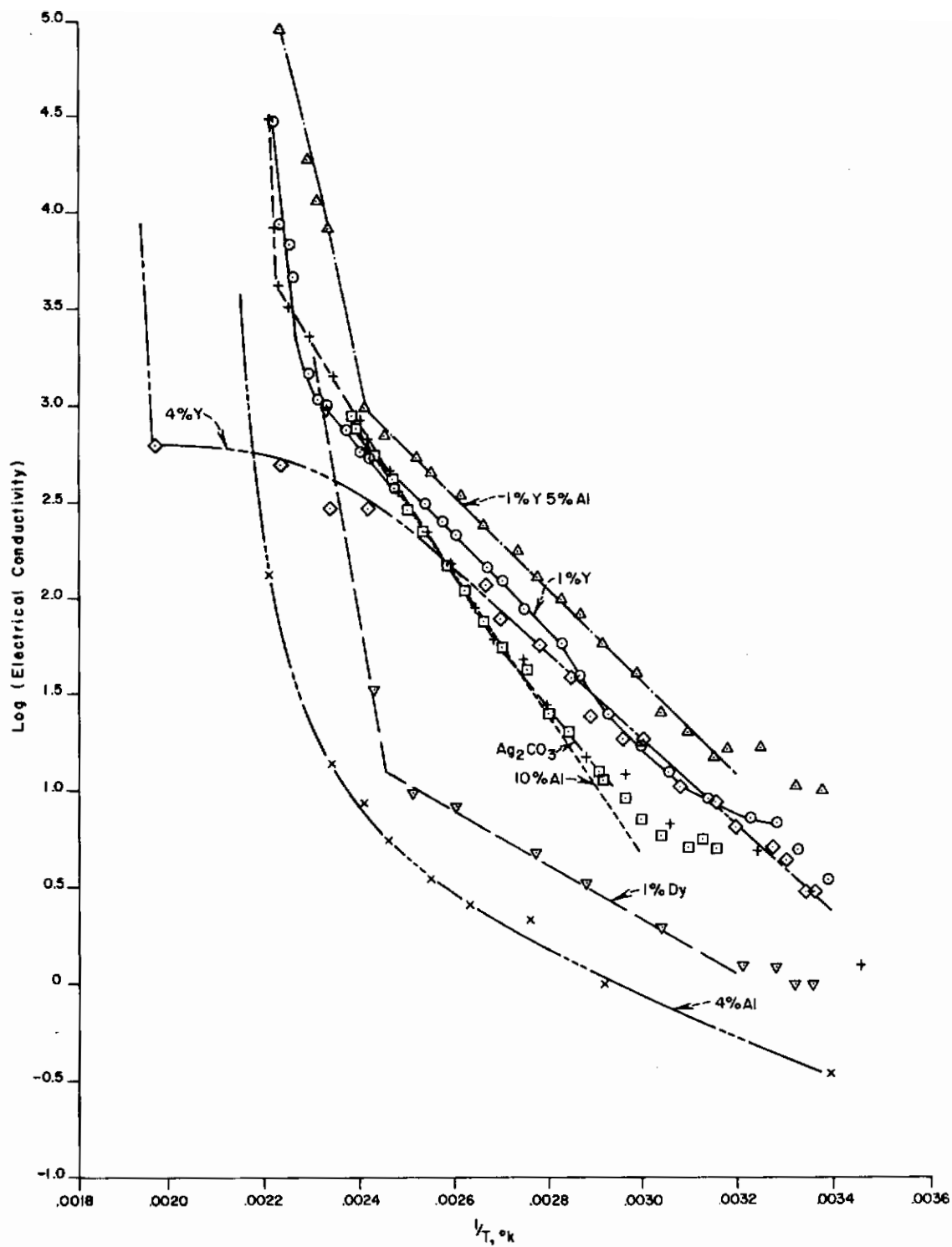VS 1/T PLOTS

95

ILLUSTRATIONS IN APPENDIX III

Figure III-1.   Log (Electrical Conductivity) vs 1/T for Pure Ag$_2$CO$_3$ and
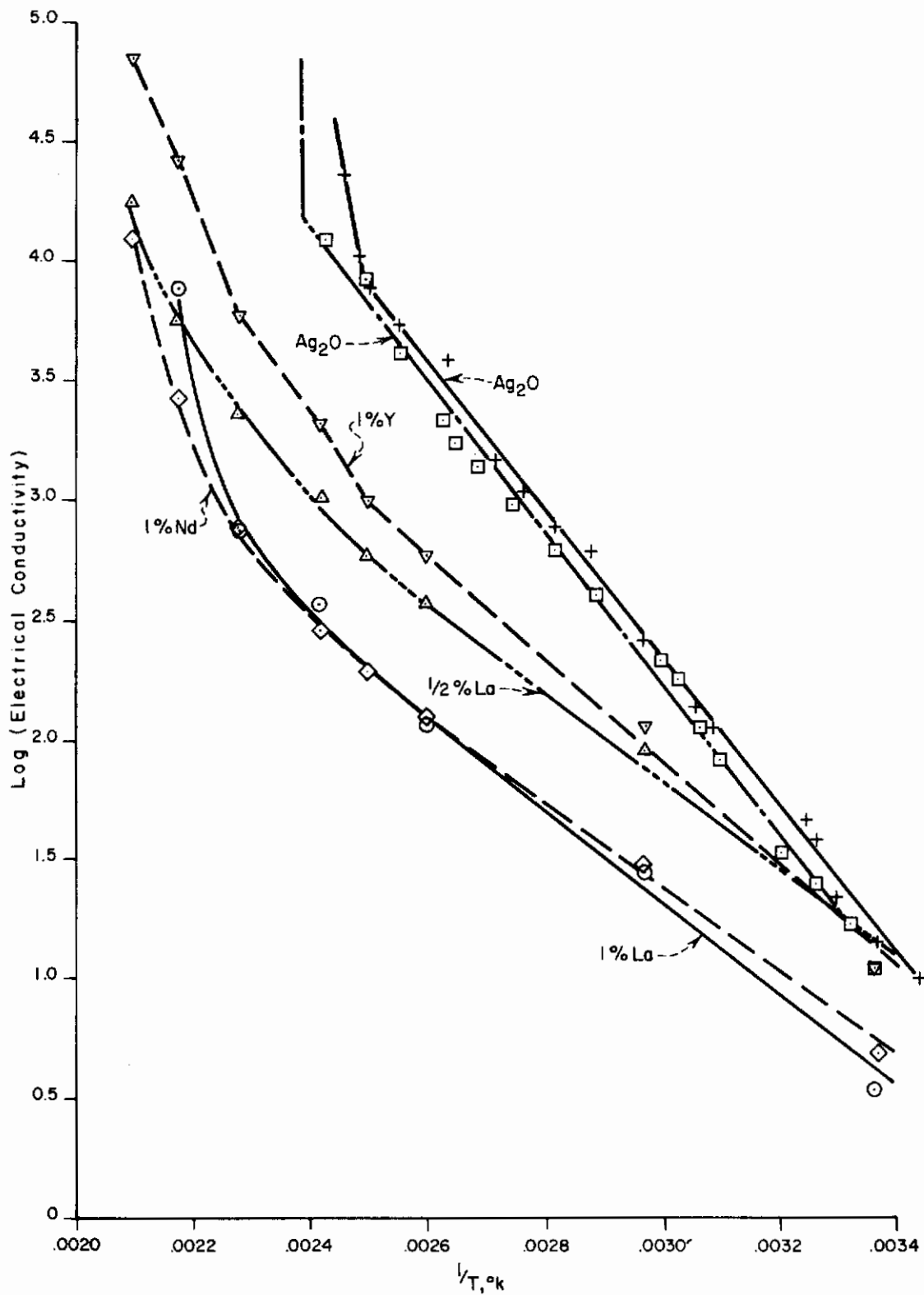That With Various Catalysts

97

Figure III-2. Log (Electrical Conductivity) vs 1/T for Ag_2CO_3 Containing Various Catalysts
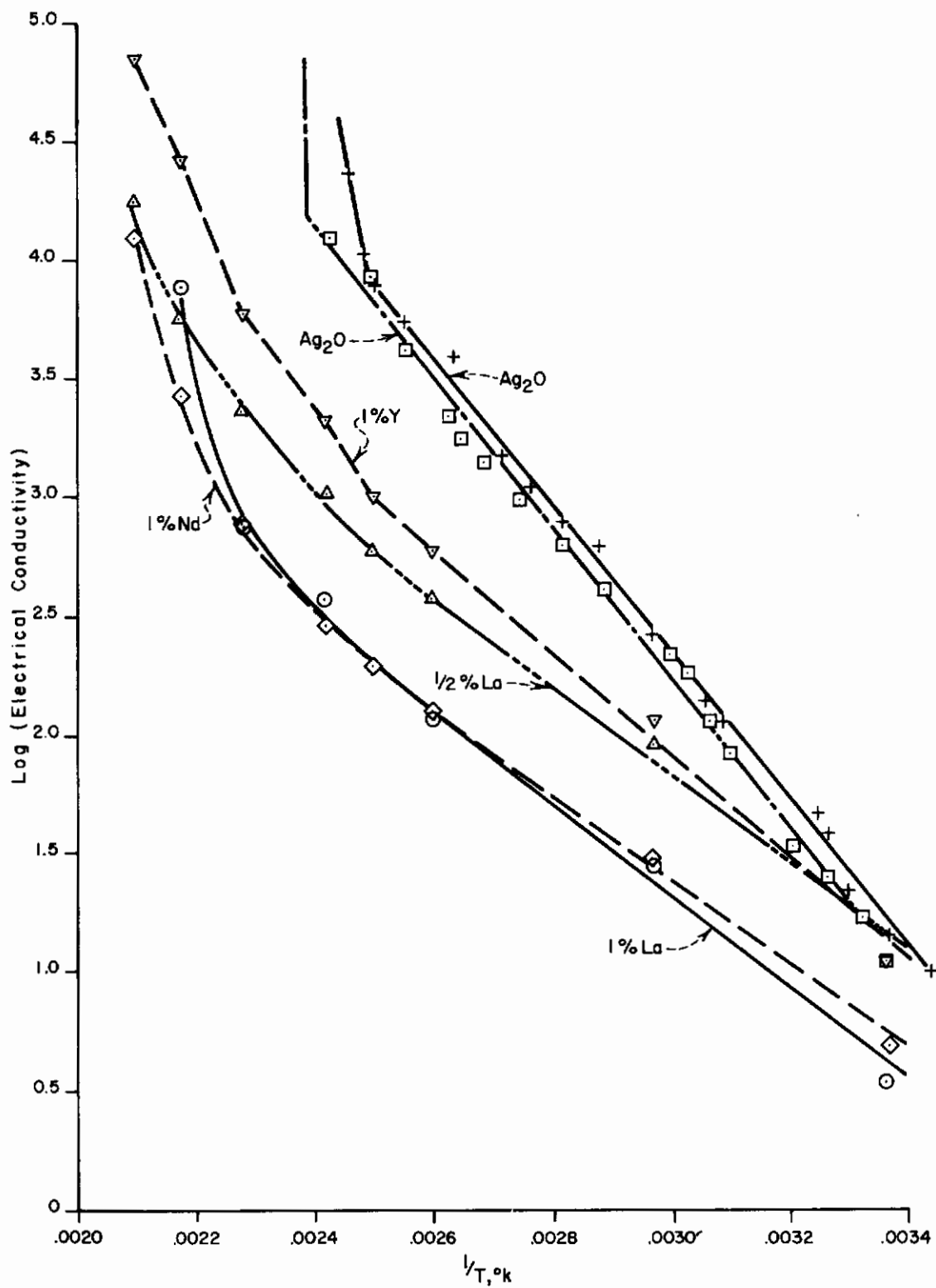
98

Figure III-3. Log (Electrical Conductivity) vs 1/T for Pure Ag_2O and That Containing Various Catalysts

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13. ABSTRACT Precipitated silver carbonate was investigated using test tube samples to establish the merits of this approach to an Ag_2O solids system for CO_2 removal. Moisture catalyzes transport of CO_2 or Ag through an Ag_2CO_3 layer protecting the Ag_2O from conversion to Ag_2CO_3. At above $2\frac{1}{2}\%$ CO_2 in the air, CO_2 is adsorbed and displaces surface H_2O enough to inhibit conversion. Below 1% CO_2 reduced CO_2 driving force slows conversion. At the optimum 1 to $2\frac{1}{2}\%$ CO_2 over 24 hours are required for good yields, even at 100% humidity. Humidities of 50% result in even slower absorption. Regeneration to Ag_2O may be accomplished in moist partial vacuum at 125°C within 2 hours. H_2O must reach the decomposing Ag_2CO_3 by penetrating a protective Ag_2O layer counterflow to the outflowing CO_2. Moisture is not necessary with Y^{+++} catalyst at 150°C. Absorption is speeded 2-3 fold with Y^{+++} catalyst. At $\frac{1}{2}\%$ CO_2 and 50% humidity 75% yield is attained within 16 hours. Y^{+++} dissolved in the cation lattice is believed to induce Ag^+ vacancies in Ag_2CO_3 and increase Ag^+ transport through the Ag_2CO_3 layer. H_2O 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 Ag_2O causing increased absorption rates at between $1-2\frac{1}{2}\%$ CO_2 where diffusion through the Ag_2CO_3 layer is less limiting than the reaction mechanism at the $Ag_2O - Ag_2CO_3$ 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 Ag_2O.

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