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A STUDY OF GASES ASSOCIATED WITH COPPER POWDERS

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ABSTRACT

This research was concerned with a study of the origin and composition of the gases evolved on heating copper powders. The phenomenon of gas evolution had been noted previously but since the quantities evolved are small, suitable collection and analytical techniques were not available. The possible sources of the gas evolution were believed to be solution in the metal powder, adsorption on the powder surface, interaction between the powder and atmosphere, or mechanical entrapment.

This research program involved the design, construction and operation of suitable gas collection equipment, and the development of a procedure to determine gas compositions using an analytical mass spectrometer. Two of the possible sources of gas evolution were eliminated by the test procedures employed. Loose packed copper powders were tested in an inert atmosphere in order to prevent gas entrapment and atmosphere contamination.

The results of this investigation showed that the gases that were desorbed had their origins on the surface of the powders. The gases were identified as water vapor, carbon dioxide, and sulphur dioxide. The major constituents were water vapor and carbon dioxide. The quantities of gas desorbed were of the order of 0.05 to 1.0 milliliters per gram of powder and were a function of the surface area and temperature of the powder. The results indicate that these gases are chemically

absorbed on the metal surface rather than being physically adsorbed.

Surface alterations produced by different manufacturing methods or by treatment of a given powder type, had pronounced effects on the quantities and compositions of the gases evolved on heating the powders. It has been found that an interaction between the evolved gases and the hot copper powders occurs. The extent of this reaction is believed to be related to the solubilities of the dissociated gas components in the copper and the original purity of the copper powder.

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INTRODUCTION

Powder metallurgy is that section of metallurgy which deals with the fabrication of engineering products from finely divided metal particles. The properties of these products are dependent upon many variables. Some of these are: the mechanical and physical properties of the metal, the compacting conditions used in forming the powders into compacts of the desired shape, and the sintering conditions used to densify the product. In this last operation, sintering, diffusional and coalescent forces act at elevated temperatures to weld the individual metal particles into a single dense metallic mass.

Since the interparticle voids on the surface of a compact tend to close early in the sintering process, it is a natural consequence that gaseous components are trapped within the compact. The resulting pressures may prevent the expected densification from occurring and an inferior product is produced. This investigation is concerned with the determination of the composition, quantity and source of gases that may be liberated on sintering.

Several sources of gas are recognized in powdered metals. These are: chemical reactions between the metal and the sintering atmospheres, gases entrapped during compacting, gases dissolved in the metal, and gases sorbed on the powder surface. The effects of these gases on the powder compact are all similar, varying only in degree. It is thus very difficult to determine, on the basis of mechanical and physical properties of the sintered product, the effective gas source. Very few attempts have been made to identify any of the gases or their sources in the powders, since isolating the very small quantities of gas present make this an extremely difficult problem.

Gases associated with copper powders were studied in this investigation, since it had been observed that the powders evolved gas on heating and the composition and origin of the gas was not known. The powders were tested in the loose packed condition under an inert atmosphere to eliminate the effects of entrapped gases and to prevent possible reactions with the surrounding atmosphere. Because of these restrictions, the gases that are evolved are necessarily dissolved gases or sorbed gases or some combination of these.

It was the purpose of this investigation to determine the nature of the gases and their association with the powders. For this purpose equipment was designed for measuring the volumes of gases evolved during heating of the powders as well as for sampling this gas for analysis. The small quantities of gas subsequently found had to be analyzed with the aid of an analytical mass spectrometer since the sensitivities of other more common methods of analysis were inadequate.

The source of gases was determined by an investigation of the variables affecting the quantity of gas associated with the copper powders. These variables included: method of powder manufacture; surface areas of fractions of the same type of powder; and surface treatments. The kinetics of gas evolution were studied to determine the nature of the association of the gas with the copper powders.

REVIEW OF THE LITERATURE

The importance and significance of the reactions between gases and metals have been recognized for many years and the literature in this field is very extensive. For the most part, however, the work that has been done is concerned with gas solubilities, the effects of atmospheres on properties, the effect of gaseous environment on rates of oxidation or deoxidation and allied subjects dealing with massive metals. Gas adsorption has been used as a means of determining surface areas of powdered metals and elaborate theories have been advanced to explain this phenomenon on clean metal surfaces at temperatures near absolute zero (10)(25)(26)(32). The sorption process has also been studied to some extent on controlled surfaces at normal temperatures.

There are no previous studies reported in the literature dealing with the specific field of this investigation. The studies of room temperature adsorption combined with results of powder metals investigations have lead to speculative discussions on the existence of abnormally high gas contents in powdered metals. The resulting theories do not have as their basis direct experimental evidence. The more important of these dealing with the powder metallurgy are included in this review. No attempt was made to include all the literature relevant to the general topic of gas - metal studies.

Reviews of the existing literature in regard to the effect of gases on powdered metals have been made by Jones (30), Schwartzkopf (43), and Goetzel (19). These authors point out that gases in powdered metals are derived from four sources. These are, chemical reactions during sintering, inclusion during compacting, solution in the metal powder and sorbtion on the powder surface.

Any of the above gas sources, acting separately or simultaneously with others, can have a profound effect on the properties of a sintered powder product. Each of these items must be considered in any study of gas interaction with powdered metals, so that the various effects may be recognized and selectively studied.

Chemical Reactions During Sintering

It is recognized that the type of sintering media used has a pronounced effect on the resulting properties of powder metal compacts. Powders are generally treated in a reducing atmosphere. These atmospheres generally consist of hydrogen, carbon monoxide, or mixtures of hydrogen and nitrogen, or partially combusted hydrocarbons (19). These gases will react with the powder primarily by a reduction of included oxides or dissolved oxygen. The reaction products are water vapor or carbon dioxide (13). These products, as such, are not harmful in the sintering process. It is thought that these reactions are necessary with heavily oxidized powders for proper sintering to occur (27). If, however, these gases are made late in the sintering process they are trapped in the closing pore system of the compact. This produces "water vapor embrittlement" or "carbon dioxide embrittlement" (34)(36).

Water vapor embrittlement, not to be confused with hydrogen embrittlement in ferrous metals, results from hydrogen diffusion into copper and its subsequent reaction with oxide inclusions, or dissolved oxygen. The water vapor produced cannot diffuse through the copper and causes straining or actual bursting of the copper lattice (37). This results in embrittlement of the copper. It is more severe when the copper contains oxides rather than dissolved oxygen.

In powder compacts the oxides are more readily accessible to the hydrogen than in massive copper, since they exist on or relatively near the extended metal surface. Diffusion distances are minimized and water vapor embrittlement can then occur in the sintering compact either by water trapped in the pores of the compact, or by water forming within the powder particles.

Carbon monoxide will not diffuse through the copper lattice, but it will reduce oxygen dissolved in or compounded with the metal surface (36). It therefore does not have an embrittling effect on massive copper, but the resulting carbon dioxide may prevent proper densification of a powder compact if trapped in the pores of the compact.

It has been shown that the surface of a compact has the tendency to sinter before the center (38). Entrapment of gases remaining in the center of the compact is then quite possible. This gas may exist in such quantity that it will develop the pressure necessary to prevent pore diminution in the center of the compact. Frenkel calculated the pressure necessary for such an effect on the basis of a viscous flow theory of sintering (18).

In summary it can be said that gases resulting from chemical reactions during sintering may cause embrittlement of a copper powder compact or may prevent its complete densification. There is, however, no evidence to indicate that surface oxides can cause the frequently observed expansion of the compact during sintering. Reactions between these oxides and reducing gases in the void spaces occur at a constant temperature, the sintering temperature, and the volume of the reactants is just equal to the volume of the products in both reduction reactions discussed.

Some expansion of the compact might occur during sintering if oxides within the powder particles are reduced, since the volume of the water vapor produced is much larger than the volume occupied by the oxide inclusions and the hydrogen diffuses through the lattice as atomic hydrogen (29)(23).

Gases Entrapped During Compacting

Rapid shrinkage occurs early in the sintering process for loose packed copper powders. Densities near ninety-five percent of theoretical may be attained by sintering under various conditions in vacuum (40)(42)(11)(41).

In compacted powders densification does not occur as rapidly. In the initial stages of sintering a marked expansion may even occur. Drapeau measured a two percent increase in the length of a copper compact sintered four hours at 760° C (12). Expansion of this type is frequently attributed to gas entrapped in the powder during compacting.

Balke has reviewed the existing literature on the subject of powder processing. He concludes that an increased porosity is generally associated with higher compacting pressures. This effect is due to the increased difficulty of gas removal in the more thoroughly compacted powder. He suggests that vacuum compacting would prevent this problem from occurring (3). Jones suggests that there is a beneficial effect derived from designing powder metal pressing dies so that the entrapped gases may escape during compacting. He also suggests the use of a vibrating die and powder hopper (30). Hardy found that there was less compact expansion during sintering of powders pressed in fast acting presses and concluded that less gas was entrapped in this method of compacting (24). Schwartzkopf indicates that the exact opposite is true (43).

The methods used to study the effects of entrapped gases, observation of density, porosity and dimensional changes during sintering, after various compacting operations do not give direct evidence as to the quantitative effects of these gases. This is the case since other sources of gas acting simultaneously may have similar effects on the observed properties of sintered compacts.

Gas Dissolved in the Metal Powders

The solubilities of many gases in copper has been investigated. The more important of these are hydrogen and oxygen. These may be introduced at any stage of the powder manufacture or in its treatment.

The solubility of oxygen has been found to increase from .0008 wt. percent at 600°C to .0032 wt. percent at 1040°C (35). Above these limits the compound Cu_2O forms and is present as a second phase. A eutectic reaction occurs at 0.39 wt. percent oxygen in the copper - oxygen system. The characteristic structure of the eutectic makes small quantities of oxygen very obvious when microstructures of cast copper are examined.

Since the equilibrium pressure of oxygen over its solution in liquid copper, is very low, a small percentage of oxygen above a melt will introduce a relatively high oxygen content. This must be removed by the addition of deoxidizers or the powder made from such a melt will show an excess oxide phase since the oxygen is not liberated on solidification (15)(45).

The pressure of oxygen is low over the solid solution and the oxide, consequently normal vacuum treatment, even at temperatures near the melting point will not remove oxygen from copper powder (17)(9).

The solubility of hydrogen in liquid copper is a linear function of the temperature and varies as the square root of the hydrogen pressure at constant temperature (45). At the melting point, the solubility decreases from 54×10^{-5} wt. percent in the liquid to 18×10^{-5} wt. percent in the solid, at one atmosphere of hydrogen pressure (6)(44). This decrease in solubility results in evolution of hydrogen during the solidification process. If powder is made from such a melt, a porous product may result.

The equilibrium pressures of hydrogen over its solutions, liquid and solid, are relatively high. It is therefore possible to remove hydrogen from powders by evacuation at elevated temperatures.

Hydrogen and oxygen may be dissolved in copper simultaneously, however as one component is increased the solubility limit of the other is decreased. A general relationship is shown by Eastwood for this effect (15). Adjustment of the excess is accompanied by the formation of water vapor. As a result of this reaction, copper powder may be high in either oxygen or hydrogen, but is unlikely to be high in both.

Because the solubilities of both hydrogen and oxygen increase with increasing temperature, very little evolution of either gas can be expected during sintering. Some gases may evolve into the pore system until an equilibrium pressure is reached if none of these gases are present in the sintering atmosphere. These pressures are generally quite low and as a result porosity cannot be directly attributed to these dissolved gases (30).

Any gas that is soluble in the copper may be dissipated from the closed pores of the compact by diffusion through the sintering compact, and is unlikely to be the cause of excessive porosity. Exception to this rule exists when reactions occur between two dissolved gases, such as the embrittling reduction of oxygen by diffusing hydrogen. The rate of gas dissipation is made uncertain by the wide variation in diffusion constants, for gases such as hydrogen, published in the literature (47)(7).

Gases may be present in the pore system of a copper compact, because they are not soluble in the copper. The rare gases which are sometimes used for sintering atmospheres are among this group (5). Nitrogen is also insoluble in copper (46). Some of the compound gases are also nonreactive with copper as well as being insoluble in it. Bacho found that carbon dioxide will not react with copper below the melting point and Goetzel suggests that it is a good sintering atmosphere on this basis (2)(19). He also suggests that steam could be used for a sintering atmosphere for copper on the basis of work done by Koehring (31).

Wyman also indicates that no reaction occurs between steam and copper (52). At least he shows that no reducing reaction occurs, however this does not eliminate the steam as a source of dissolved oxygen in the copper.

Gases Sorbed on the Powder Surface

The quantity of gas that may be associated with a metal powder surface is very large. The natures of the various sorbtion mechanisms are such that gas volumes much greater than the pore volume of the compacted powders may be introduced into the sintering process on the powder surface. Furthermore these gases may not be liberated until late in the sintering process after some of the pore spaces have been sealed.

Goetzel has observed a small spherical pore network around copper partial boundaries even after sintering in a vacuum (20). He attributes these to adsorbed films on the powder. Actual swelling of copper powder compacts is frequently attributed to gas desorbtion (19). This is particularly obvious with highly compressed powders. These show a marked decrease in density as the sintering temperature is raised. The effect is due to internal pressure resulting from entrapment of desorbed gases during rapid pore closure at high sintering temperatures. Lower sintering temperatures allow the desorbed gases to be vented through the pore network which is closing at a much slower rate (49).

A reduced copper powder was outgassed at 450°C in a vacuum and then exposed to air by Ruer and Kuschman (39). After seventy hours exposure a weight gain of .01 wt. percent was observed. No identification of the adsorbed material was made. It is, however, apparent that this weight of gas could constitute a relatively large volume at the sintering temperature. Dureau and Franssen have shown that copper powder milled under vacuum will adsorb small amounts of nitrogen, hydrogen and carbon monoxide at room temperature (14). This same powder chemisorbed large quantities of oxygen and carbon dioxide at room temperature.

The binding of gases to a copper surface during chemisorbtion is such that relatively high temperatures and long times are necessary for their removal (46). Consequently these gases may constitute a late source of gas during sintering.

Chemisorbtion has been observed on the surface of massive copper newly formed by electropolishing and by abrading in vacuum (1)(16). In each instance oxygen was found to be rapidly absorbed from air. An electron diffraction study of the films showed that an oxide layer is formed soon after chemisorbtion starts. As the oxide film thickens, the rate of oxygen absorbtion decreases, but is still in evidence.

It is quite possible that compound gases may be absorbed on the surface of copper in the same sequence as oxygen, with compounds resulting in the same manner as a surface film. The limited thickness of such a film would prevent any large quantity of gas being so absorbed on massive copper, but the extended areas present with powders could easily accommodate relatively large volumes of gas. Very little work exists on the nature of such films but a great deal of effort has been expended in preventing their formation.

Powders produced electrolytically from copper sulphate and copper chloride solutions have been stabilized by the deposition of a monolayer of stearate ions on their surface (50). Tarnish resistance has been imparted to flake copper, used as paint pigment, by coating them with a thin layer of partially polymerized urea-formaldehyde resin (8). A 0.5 percent solution of H_3PO_4 has also been found to be effective in preventing oxidation of electrolytic powders (48). A sodium soap layer on the surface of copper powder is also reported as a practical means of preventing atmospheric corrosion of the powder (33).

Indirect evidence for the formation of chemisorbed layers of gases other than oxygen is presented in studies of the corrosion products of copper roofs and statuary. Investigations of copper roofs exposed to the atmosphere for long periods of time have shown that the corrosion product, patina, consists of mixtures of copper sulphate and the basic carbonates of copper (51). The proportion of these compounds varies with existing atmospheric conditions. About three percent carbonate is found in rural areas while this figure increases to twenty-five percent in industrial regions. Artificial patinas have been reported that have the formula $CuO \cdot 3\ H_2O$ (22). This product was claimed to be similar in chemistry to natural patina found on ancient bronze statuary. It is thus evident that chemisorbtion of carbon dioxide, water vapor and sulphur dioxide is possible as a first step in atmospheric corrosion.

Chemisorbed layers of this nature could readily introduce gas into the sintering compact, since all of the above mentioned compounds have relatively high dissociation pressures in the temperature range used for sintering. For example copper sulphate is found to decompose at atmospheric pressure at about 560°C (4). The basic carbonates, azurite $2\ CuCO_3 \cdot Cu(OH)_2$ and malachite $CuCO_3 \cdot Cu(OH)_2$ decompose at 220°C and 200°C respectively. The anhydrous carbonate Cu_2CO_3 is unstable at room temperature (28).

It can be seen that the surface activity of copper and the nature of its corrosion products may constitute a source of gas which far exceeds in volume the amounts present due to the processes previously mentioned.

EXPERIMENTAL PROCEDURES

Materials

In this investigation gas from several types of copper powder was collected and analyzed. The powders varied in several respects. They are classified here, on the basis of method of manufacture, particle size, appearance and microstructure.

The powders were commercial grades of water atomized, air atomized and electrolytic copper. The water atomized powder is made by subjecting a stream of molten copper to a jet of high velocity water. Generally a controlled atmosphere surrounds the liquid copper and atomizing is performed in a closed chamber. Air atomizing is quite similar, except that a jet of air is used to break up the liquid copper stream. Very little control of the reaction between oxygen and the hot copper is possible with this method. The powder resulting from both types of atomizing is generally characterized by a spherical particle shape.

Electrolytic powder is made by depositing metallic copper on an electrode immersed in an electrolyte containing copper salts. Proper control of the current density at the electrode and the electrolyte composition gives a porous and brittle copper deposit that can be broken off the electrode as a fine powder. The particle shape of electrolytic powder is generally quite irregular and is described as being dendritic in shape.

The particle size of the powder was determined microscopically by using transmitted light and measuring the diameters of the particle on a projected image. Averages were taken of at least fifty measurements on each type of powder. Screening was also used for sizing of the water atomized powder, since this was received with mixed particle size.

Visual observation of individual particles or of the loose packed powder furnished information on the powder appearance. The powders ranged from a typical copper red to a black oxidized color.

Powder samples were mounted in bakelite for examination of their microstructures. They were mechanically polished and examined after etching with an ammonia hydroxide hydrogen peroxide etch. (75% NH_4OH and 25% H_2O_2).

The water atomized powder was more thoroughly studied in this investigation than were the other types of powder. The other types were used primarily to verify conclusions reached on the basis of data taken with the water atomized powder. The water atomized powder was relatively coarse as received and had a particle size distribution which varied from about 20 mesh to 200 mesh, with the greater fraction between 20 and 48 mesh. This powder was dark in appearance with some particles showing no tarnish while others were completely black. The smaller mesh fractions of this powder were spherical, while the larger particles were quite irregular in shape. Samples of this powder were tested after separation into various mesh fractions, as well as, in the as-received particle distribution. The microstructure of this powder showed it to have an equiaxed grain structure with very little oxide. Some inclusions of massive oxides were present, but no oxide eutectic was observed. A photomicrograph of this powder is shown in Figure 1. It can be seen that some particles of a second phase do exist in the grain boundaries, but these could not be definitely identified, even at a thousand diameters.

The other powders tested in this investigation were included for the purpose of confirming the general nature of the results from the water atomized powder. Among these other powders were three types of air atomized powder. The microstructures of these powders are shown in Figures 2, 3, and 4. These powders were all spherical, but they varied in average particle size. Powder number one, shown in Figure 2, had an average particle diameter of 15 microns. Powder number two, shown in Figure 3, had an average particle diameter of 17 microns. Powder number three, shown in Figure 4, had an average particle diameter of 230 microns. The microstructures and appearances of these powders varied only in degree. Each of the structures can be seen to contain relatively large amounts of the copper - copper oxide eutectic. The three powders were dark colored. Powder number three differed from the others in appearance, being black while the others were a very dark red.

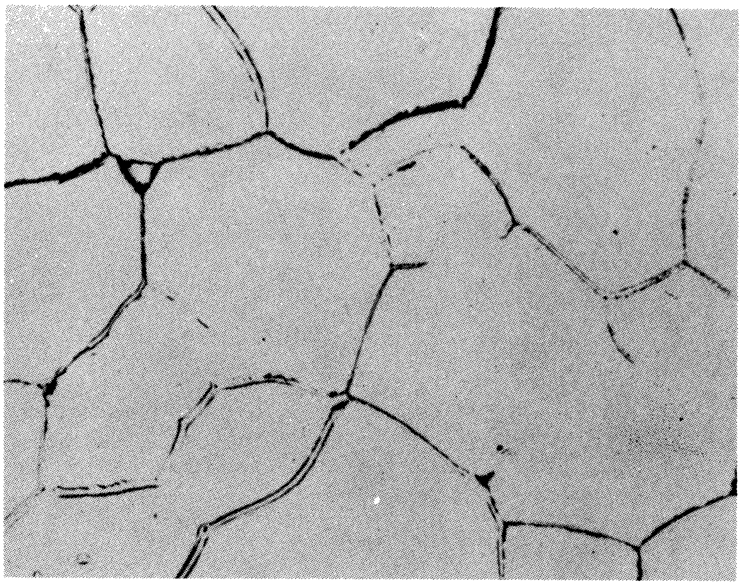

Figure 1 X 1000

Microstructure of Water Atomized Powder

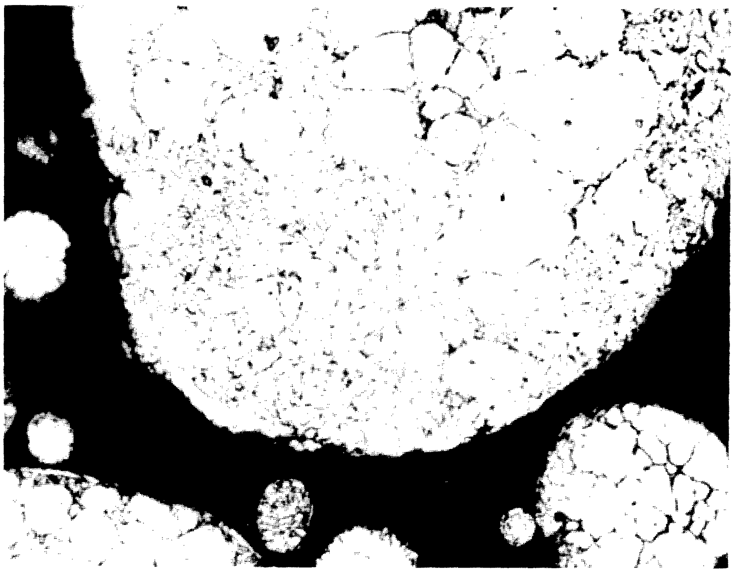

Figure 2 X 1000

Microstructure of Air Atomized Powder No. 1

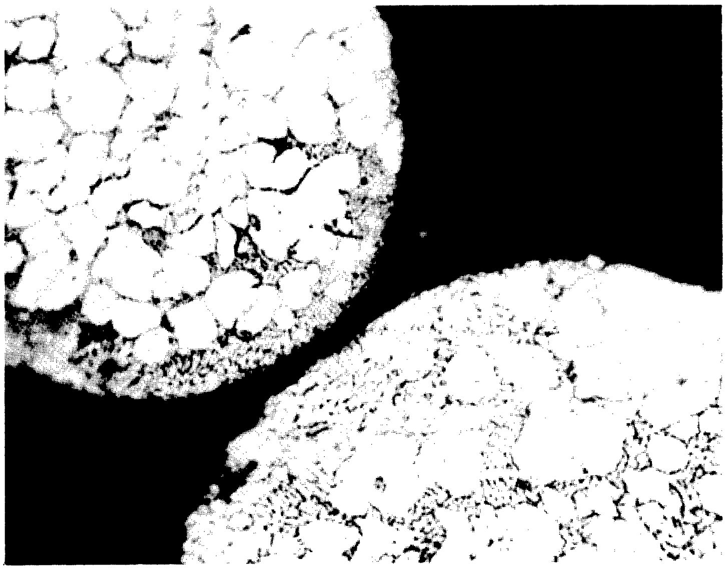

Figure 3 X 1000

Microstructure of Air Atomized Powder No. 2

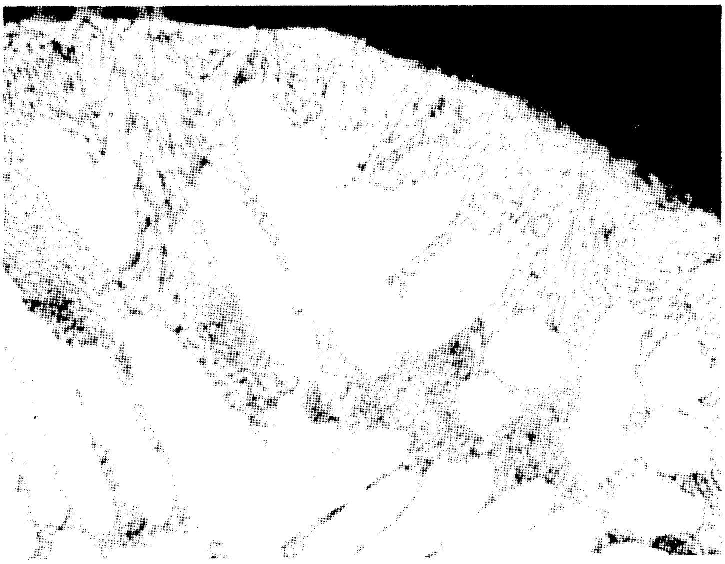

Figure 4 X 1000

Microstructure of Air Atomized Powder No. 3

The finest powder investigated was an electrolytic powder that had an average particle diameter of three microns. This powder was received in a sealed container enclosed with a quantity of desiccant. It was a lusterless red color and it appeared to be relatively free of tarnish. The particles were quite irregular, having a dendritic shape. The structure of this powder, shown in Figure 5, was the typically strained structure to be expected with an electrolytic product. No oxide was apparent.

A powder of unknown type was also tested. On the basis of the microstructure and particle shape shown in Figure 6, which are very similar to those found for the electrolytic powder, it is probable that this powder is an electrolytic powder. The average particle diameter was 5 microns. This powder was somewhat darker than a clean powder normally appears. It was maroon in color rather than the normal red associated with copper. This discoloration may have been due to the relatively long period of storage to which this powder was subjected before testing. It was known to have been stored in the laboratory for somewhat over ten years with no precautions to prevent atmospheric corrosion.

A Mallinckrodt Chemical Company reagent type copper powder was also tested. This powder was also of a relatively small particle size, having an average particle diameter of 13 microns. Its method of manufacture was not known, but the spherical shape of its particle and the relatively high

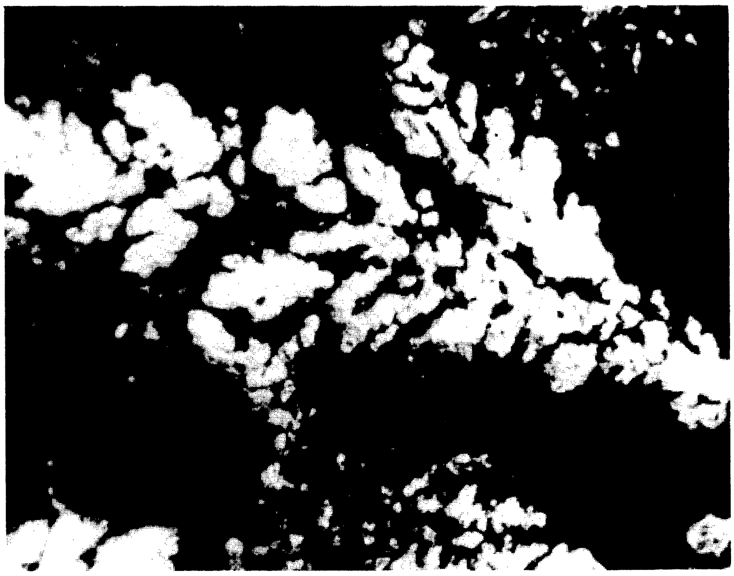

Figure 5 X 1000

Microstructure of Electrolytic Powder

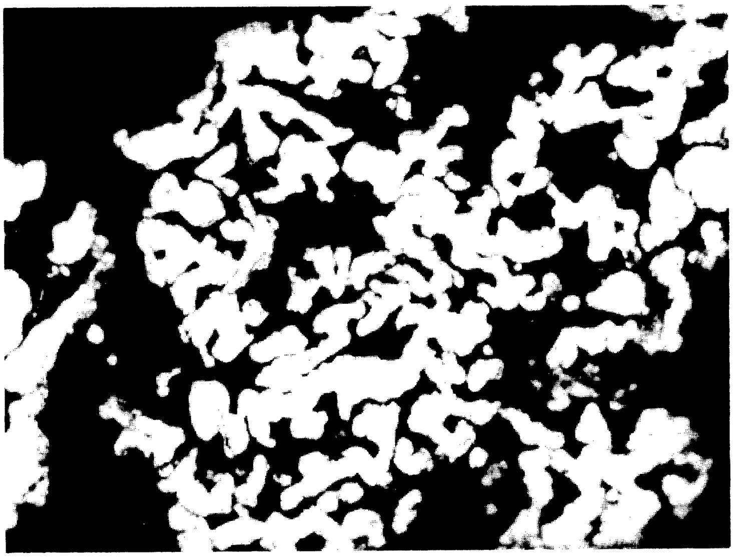

Figure 6 X 1000

Microstructure of Powder of Unknown Type percentage of oxide eutectic in its microstructure indicates that it was probably air atomized. The microstructure of this powder is shown in Figure 7. The powder was dark red in color.

Apparatus

The system that was designed for the removing and collecting of gases from the copper powders is shown in Figure 8. Pyrex glass tubing was used to construct the apparatus except for the specimen tube, which was made of Vycor. The Vycor tube was used to hold the copper powder during outgassing and was necessary because of the relatively high temperature's (1400°F) attained. All stopcocks in the system were the high vacuum type having a hollow plug and an evacuated bulb at their base. These are indicated in the figure by the symbol S_n. No interaction between the system atmosphere and the stopcock grease (Apiezon N) was noted, consequently the greater convenience of stopcocks as compared to mercury cutoffs justified their use in this system. It was found that high vacuums could be maintained for long periods of time in the closed system, if these stopcocks were properly greased.

The system was evacuated by an oil diffusion pump backed by a duo-seal mechanical pump. A liquid nitrogen trap was used in the pumping system between the diffusion pump and the manifold. In operation the pumping system was used to remove gaseous products of previous tests and gases introduced with the copper. Vacuums below 10^{-5}mm of Hg were attainable in the manifold with

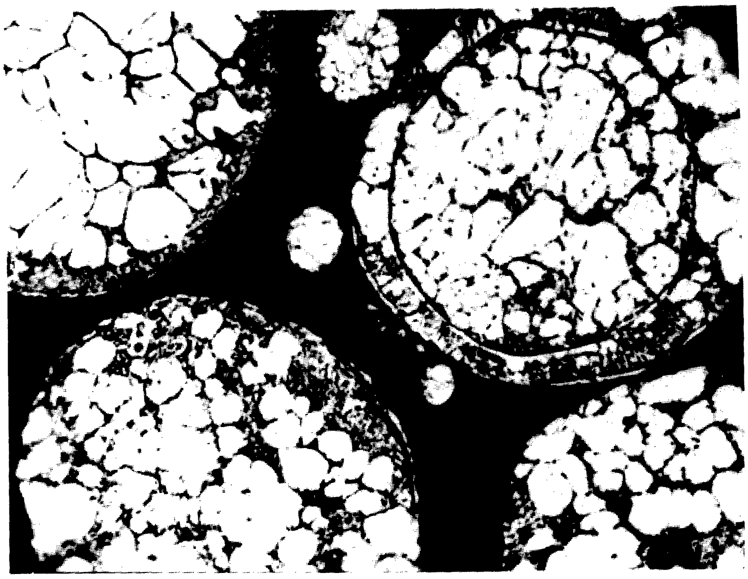

Figure 7 X 1000

Microstructure of Reagent Type Powder

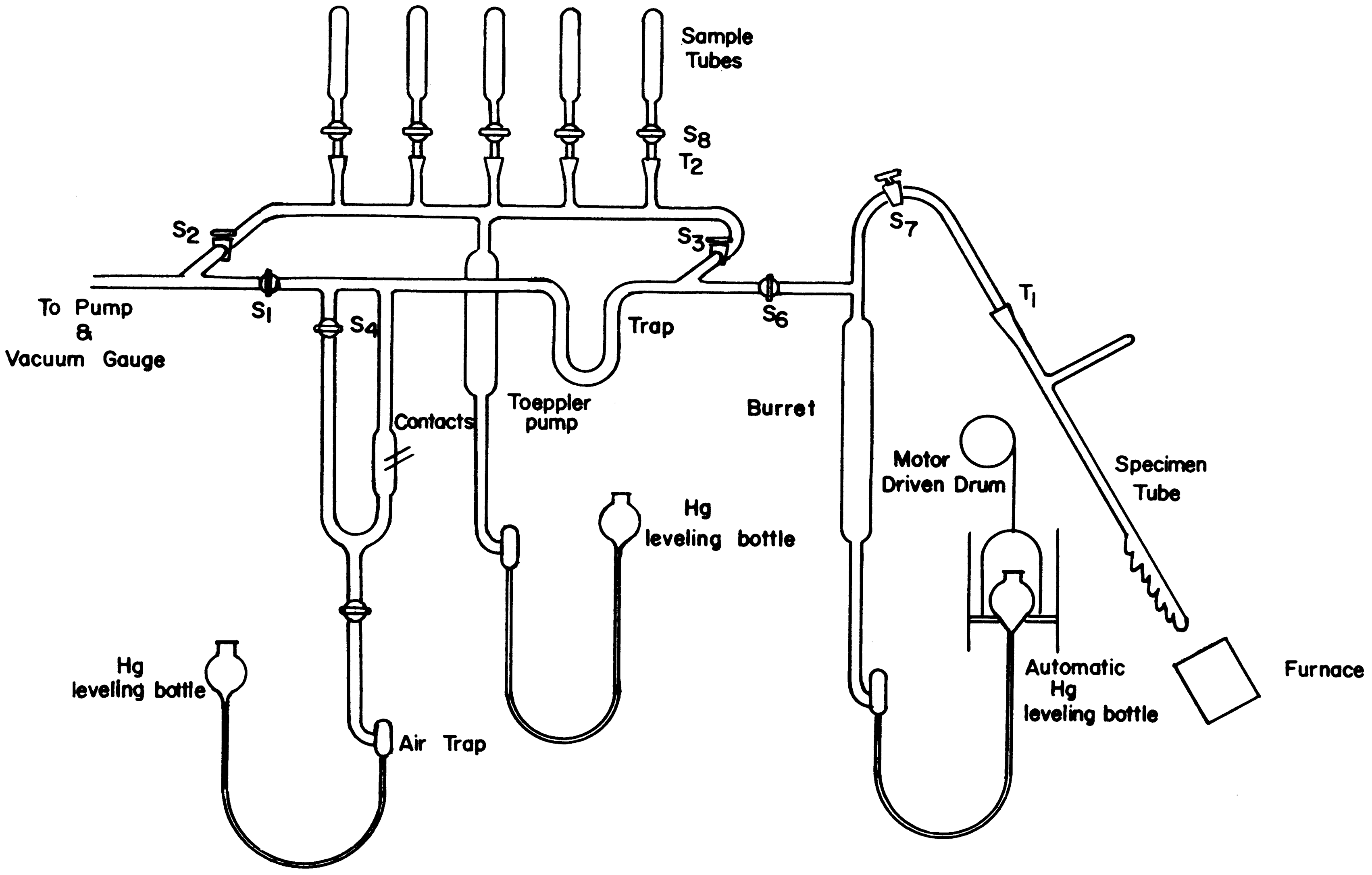

FIGURE 8. APPARATUS FOR MEASURING AND COLLECTING GAS FROM COPPER POWDER.

this system. A McCleod gauge was used as an absolute measuring device for system pressures. This was connected to the system between the liquid nitrogen trap and the manifold.

The apparatus was divided into two manifold systems by the stopcocks S_2 and S_3. The specimen or measuring manifold consisted of the section of 9 millimeter tubing connecting the specimen tube, burette, trap and mercury manometer. The fixed portions of this manifold, constituted a calibrated volume. The second manifold, the sample manifold, consisted of 2 millimeter capillary tubing which connected the Toeppler pump and gas sample tubes to the specimen manifold through stopcock S_3 or to the pumping system through stopcock S_2. This manifold was used to collect samples of the gas in the specimen manifold. For this operation the mercury level in the Toeppler pump was lowered to empty the expansion volume. The stopcock on a sample tube, S_8, was opened as well as stopcock S_3. This operation admitted gas into the expanded volume of the sample manifold. After closing stopcock S_3 the gas pressure in the manifold is increased by raising the mercury level in the Toeppler pump. Closing the sample tube stopcock, S_8, at this point encloses in the tube a gas sample at the higher pressure. When the gas pressure in the specimen manifold was extremely small, this operation was repeated several times.

The gas sample manifold and the sample tubes were evacuated prior to the collection of a gas sample through the stopcock S_2. The sample tubes were connected to the manifold at T_2. Gas samples were transferred directly from these tubes to the Mass Spectrometer for analysis.

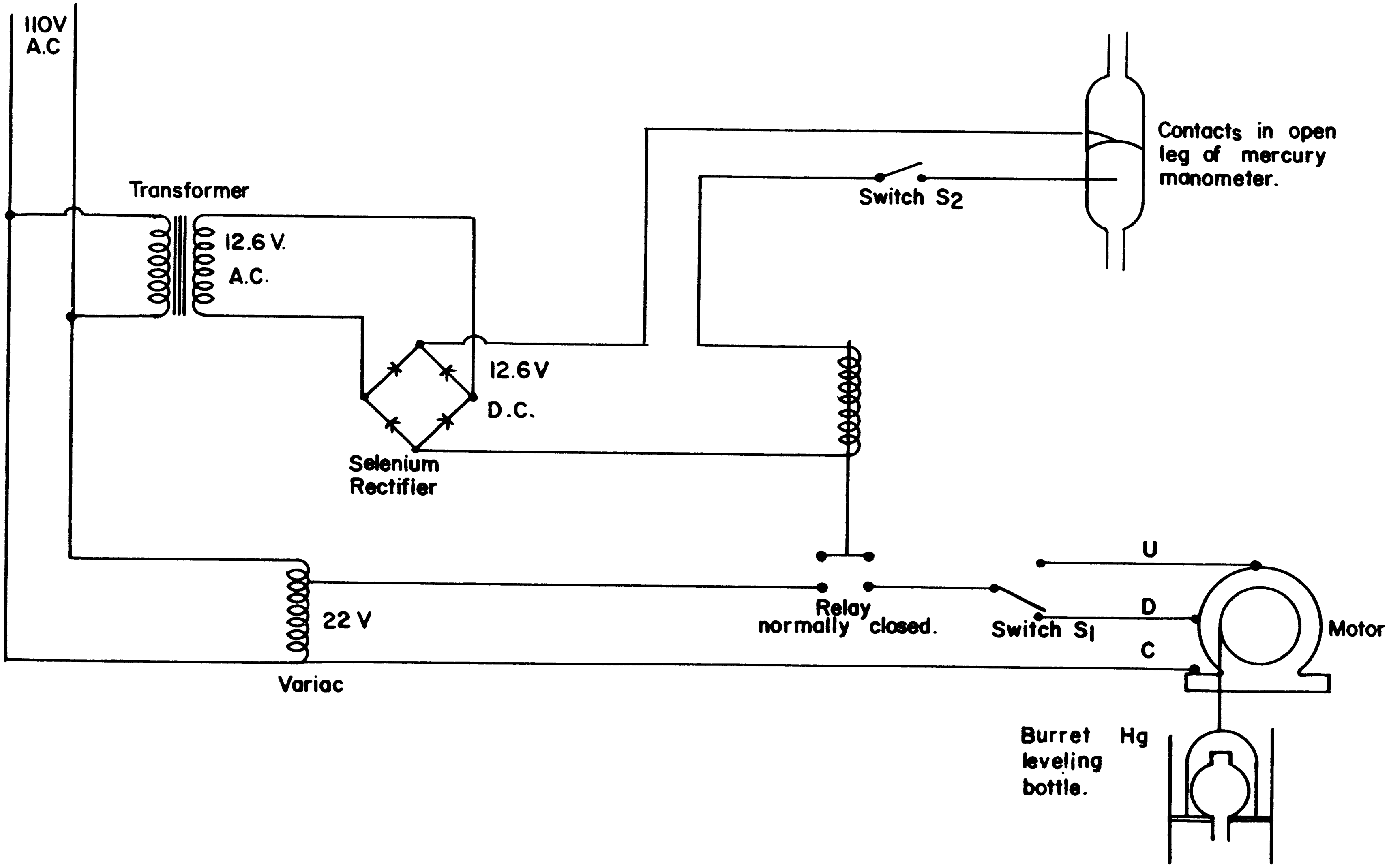

FIGURE 9. WIRING DIAGRAM FOR AUTOMATIC MERCURY LEVELING BOTTLE CONTROL ON BURRET

The volume of the specimen manifold was varied during constant pressure outgassing of the copper powder by lowering the mercury level in the burette. This operation proceeded automatically by means of the motor drive on the mercury leveling bottle connected to the burette. A wiring diagram for the actuating mechanism on this motor drive is shown in Figure 9. During a run switch S_1 is in the down position, since the volume of the system must be increased to maintain a constant pressure during gas evolution. Switch S_2 is closed for automatic operation. The contact at the mercury level in the open leg of the manometer then controls the motor drive. Manual adjustment of the leveling bottle can be made by opening switch S_1.

Copper powder is introduced into the Vycor specimen tube by closing stopcock S_7 and removing the tube from the manifold at the taper T_1. The powder is placed in the perpendicular side arm of this tube. Then the tube is replaced with the side arm down so that the powder remains in it. After outgassing the tube through stopcock S_7, the powder is dropped into the lower portion of the tube by rotating it at the taper T_1 to a position where the side arm is in the raised position. The bulbous projections on the lower portion of the tube usually catch the powder in about an equal distribution. This design for the lower portion of the tube was found necessary, since with close packing of the powder in a straight tube only about fifty percent of the gas was found to evolve.

The burette was calibrated to 0.2 milliliters and had a total volume of 100 milliliters. The mercury level in the burette could be determined to within 0.1 milliliters. Changes in the burette mercury level were used to calculate the amount of evolved gas.

The cold trap was used to condense the evolved gases when their extended contact with the powder resulted in chemical reactions. Liquid nitrogen was used to cool the trap. This lowered the temperature to a point where all of the gases present, except helium, had a very low vapor pressure.

The mercury manometer was adjustable to about 200 millimeters pressure. It was generally used at about twenty millimeters pressure. Adjustment was made by varying the amount of mercury in the manometer through stopcock S_5. The zero point on the open leg of the manometer was always at the point of contact with the upper platinum electrode. Stopcock S_4 on the closed leg of the manometer was generally open during evacuation of the specimen manifold. This kept the pressure in this leg low.

During operation, the pressure in the specimen manifold was determined from the manometer reading. A cathetometer telescope was used to determine the difference in mercury levels in the two legs of the manometer. This difference could be accurately determined to 0.1 millimeter.

Mercury leveling bottles were connected to the burette, Toepler pump and manometer through plastic tubing. Rubber tubing was found to react with the mercury on extended contact. Air traps were found necessary in these lines to keep the small sir bubbles which are occasionally entrained in the moving mercury stream, from entering the manifolds.

It was necessary to know the volume of the measuring manifold as a function of the temperature of the specimen tube in order to determine the total amount of gas evolved from the powder during outgassing. First the volume of the manifold had to be determined at room temperature and then the effect of temperature on the effective volume of the system. This calibration is outlined in Appendix A.

Powder Preparation

The copper powders were all outgassed in the as received condition. Ten gram specimens were generally used. The weighing operation and transfer of the specimens to the outgassing apparatus were the only handling operations to which these powders were subjected.

Some tests were also made on the water atomized powder after washing in a solution of NH_4OH followed by rinsing in distilled water. Ten grams of powder were washed in 100 milliliters of NH_4OH for ten minutes. This operation brightened the powder considerably. 250 milliliters of distilled water was used to remove the traces of NH_4OH and the residue which resulted from the washing operation. This rinse was repeated four times. Finally the powder specimens were vacuum dried at room temperature before outgassing. Tests of this powder were made after various periods of exposure to air at 70°F in a constant humidity room.

Testing Procedures

The powders tested were subjected to two different outgassing procedures. First, the quantity and analysis of evolved gas was determined as a function of powder temperature. The total pressure over the copper powder was maintained at a constant pressure during this testing procedure. This procedure gave information as to the kinetics governing the gas evolution from the powders. A second outgassing procedure was used to determine the total quantity of gas present on the powder. The gas was evolved by rapid heating of the powder to 1400°F in this operation. The pressure was not maintained at a constant value and the gases evolved were condensed in a liquid air trap immediately upon evolution.

Initial steps in both testing procedures were identical. All traces of copper powder from previous tests were removed from the Vycor specimen tube with nitric acid. The tube was then rinsed with distilled water, and dried after washing with acetone. It was then evacuated and heated with a gas torch to remove most of the adsorbed gases. Nitric acid and its derivatives were found to be desorbed in this operation.

The powder specimen was put in the side arm of the specimen tube. After the tube was replaced on the manifold in such a manner as to keep the powder in the side arm, stopcock S_7 was opened slowly to prevent carryover of the powder as the air rushed into the evacuated manifold. All Stopcocks except S_5 were opened at this point and the entire manifold was thoroughly evacuated.

The furnace was placed in position around the lower portion of the specimen tube and the tube temperature was raised to 1400°F. All traces of adsorbed moisture and other gases were removed from the tube in this operation. Heating was continued for about one hour, then the furnace power was turned off. The evacuation of the entire system was continued for twenty four hours after the introduction of the powder specimen. During this time pressures below 10^{-5} millimeters were attained. The system was checked for leaks during this operation.

After the above procedure was carried out, the specimen manifold was filled with helium introduced from a tube on the sample manifold. The pressure in the specimen manifold was adjusted to twenty millimeters. From this point the two outgassing procedures differed from one another. In the first procedure, which was used to determined gas evolution as a function of powder temperature, the temperature of the specimen tube was raised to 400°F. When control of the temperature was established at 400°F, a reading of the burette mercury level was made. At this same time the pressure in the system was accurately determined with the aid of a telescope cathetometer to make readings of the mercury levels in the legs of the manometer. Rotating the specimen tube about the taper T_1 dropped the powder into the heated portion of the tube. The temperature of the powder was held constant for one hour. The leveling bottle on the burette was automatically operated to maintain constant pressure during the resulting gas evolution. The new reading of the burette mercury level was recorded and a gas sample taken in one of the five sample tubes on the sample manifold. Stopcock S_7 was closed during sampling so as not to change the pressure over the powder. A new burette reading was taken after the sampling operation so that the amount of gas in the sample could be used in the calculation of total gas evolved. Then the temperature of the powder was raised to 600 °F and the same operations were repeated. This procedure was repeated at 800°F, and 1100°F and 1400°F.

In the second procedure, which was used to determine the total amount of gas present on the powder, the burette and pressure readings were made with the tube at 1400°F. The trap was then brought to the temperature of liquid nitrogen and the powder was dropped into the heated portion of the tube. During the evolution of gas which followed, the mercury level in the burette was raised and lowered alternately as long as evolution continued. This operation was effective in pumping the evolved gas from the specimen tube to the cold trap where it was condensed. After one hour at 1400°F, a sufficient time for gas evolution to cease, the pressure in the manifold was returned to its original value and the stopcock S_7 was closed. The cold trap was then returned to room temperature and a reading was made on the burette. The difference between original and final readings was the amount of gas evolved during the outgassing. A gas sample was then taken, so that the quantities of the various gases could be determined.

In both procedures the gas samples were immediately introduced from the sample tubes into the mass spectrometer for analysis.

Gas Analysis

An analytical mass spectrometer was used for analyzing the gases evolved from the copper powders since the use of this instrument is the only accurate method of obtaining analyses on the small gas samples collected. A sample generally contained less than thirty milliliters of gas at a pressure of about ten millimeters. The mass spectrometer requires only sufficient gas to develop a pressure of about thirty microns in an expansion chamber with a volume of 3000 milliliters.

A Consolidated Engineering Corporation Model Type 21-103B mass spectrometer was used in this investigation. In this model gas is admitted to the analyzing system through a high vacuum inlet system. This consists of a manifold which connects an expansion volume and an absolute pressure gauge called a micromanometer to the analyzing portion of the instrument through a small leak. The expansion volume, into which the gas sample is first admitted, is large, so that the pressure in the inlet system will not be appreciably changed during the analysis by the small quantity of gas passing through the leak. Gas pressure in the expansion volume is recorded for the purpose of calibrating and checking the material balance in the analysis of a sample of unknown composition.

The small quantity of gas that passes the leak is first subjected to an ionizing voltage of about seventy volts and then to a variable accelerating voltage which has a maximum value of 4000 volts. In the ionizing region a number of molecules are ionized ans others are cracked into lighter fragments. This number is proportional to the total number of molecules of the type in the expansion volume and thus to the pressure, partial or total, of the molecular gas in this volume. The accelerating voltage increases the velocity of the resulting ions due to their positive charge. The ion stream thus accelerated passes through a magnetic field. Reaction between the moving ions and the magnetic field produces a force on the ions perpendicular to their direction of motion in the electric field. As a result of this action the ions travel a circular path. The radius of this path is a function of M/e, mass to charge ratio of the ion, the magnetic field strength, and the electric field strength.

In the spectrometer used, an interceptor slit is located on a five inch radius. The magnetic field is kept constant during a spectrum traverse, but the electric field is varied with time so that ions with various M/e ratios will travel a path of five inch radius during a time interval. In practice the electric field decreased with time so that the M/e values corresponding to a five inch radius increased with increasing time. Only the ions which pass the interceptor slit are detected, these are at any time proportional to the number of ions in the stream with that particular ratio. The M/e spectrum is thus traversed by recording the ion count through the slit as a function of time.

The ion current which passes the interceptor slit is essentially transmitted to a ground potential through a high resistor. The drop across the resistor is amplified and recorded on a photographic chart. The record is produced by a light beam reflecting from a mirror suspended on a galvonometer. The chart moves at a constant rate and the resulting trace is that of M/e against units of deflection. It can be seen from this brief discussion that the galvonometer deflection (intensity) is directly proportional to the pressure of the gas, from which the ions were derived in the expansion volume.

Calibration of the mass spectrometer is complicated by the presence of doubly charged ions and the lighter fragments which result from cracking of heavy molecules in the ionization process. The spectrum, or cracking pattern, must be completely scanned over the range of M/e values where other components may occur when sensitivity measurements are being made for a gas component. In this way interactions between components at any given M/e value may be determined.

The instrument is calibrated for the components that may be present in the gas mixture to be analyzed. A known pressure of each component is admitted to the expansion volume and a traverse of the M/e spectrum is made. The parent peak, which is generally at an M/e value determined by the singly charged uncracked molecule, is found for each component. This peak is the most intense peak in the spectrum. Sensitivities of the instrument are then calculated from the pressure of the gases and the height, intensity, of the parent peaks on the chart. These sensitivities are expressed as units deflection per micron of pressure.

If the mixture to be analyzed contains very few components it is possible that none of the parent peaks will coincide with minor peaks from other components. In this case calculation of the partial pressures of the various components can proceed directly from the peak values on a chart of the spectrum traverse for the mixture to be analyzed. This situation does not generally exist and there are frequent cases of peak coincidence. Corrections must then be made to the observed peak values for the additive effects of the various cracking patterns before the sensitivities can be used to calculate the partial pressures of the components. This calculation is occasionally so complicated that a matrix solution of a number of linear equations must be employed. The matrix consists of a square array of terms, in number equal to the square of the number of components in the gas mixture. Except in simple cases, this matrix is solved by the use of a computer.

A modified gas analysis technique was used in this investigation. The need for modification arose from the adsorbtion of water in the inlet system of the mass spectrometer from the relatively small gas samples. It was found that water content of the evolved gases could best be found by one of two methods, both were used successfully. In the first, the water was frozen in the trap of the measuring manifold before gas sampling, with dry ice and alcohol as a cooling medium. The change in burette reading caused by cooling the trap, corrections being made for gas contraction, gave the quantity of water directly. The trap was returned to room temperature before sampling of the gas in the manifold, so that a wet sample was taken. These samples were run through the mass spectrometer dry, that is, the water was frozen at the time of admission to the instrument, in the sample tube.

When it was determined that water in the samples did not effect the accuracy of the analysis for the balance of the gas sample, the samples were run wet and the water was determined by difference. In this method a total gas balance was made utilizing the known amount of helium that was present in each gas sample. On this basis a dry analysis was calculated from the mass spectrum of the sample and water was obtained from the difference between the calculated amount of dry gas and the total gas sample volume known to be present from data taken on the specimen manifold.

In the initial stages of this work the traces of carbon monoxide, oxygen and nitrogen were thought to be significant, and they were computed as part of the gas analysis. With these gases and the more abundant water vapor, carbon dioxide, sulphur dioxide, hydrogen and helium, an eight component system developed. This system was difficult to analyze since more than one component contributed to a number of the M/e peaks available for calculation. With two peaks included for checks a ten equation system had to be solved for the analysis. This was solved for the various peak values contributed by the gas components by use of a computer. The matrix used in this type of calculation, the cracking patterns from which it was derived, and a description of its use is included in Appendix B.

When it was found that the traces of carbon monoxide, oxygen, and nitrogen were not of practical significance, the gas analysis was considerably reduced in detail. Since none of the remaining components caused any significant coincidence of peak values, a simple computation based on the sensitivities resulted in a complete gas analysis. An example of this method of computation is given in Appendix C.

Volume and Partial Pressure Calculations

With the total volume of evolved gas determined from the corrected burette readings in the specimen manifold and the analysis of the various gas samples, a relatively simple procedure was employed to calculate the volume of a gas component accumulated to the various powder temperatures. The partial pressures of the various components were determined directly from the known total pressure and the analysis of the gas samples. Examples of these calculations are given in Appendix D.

The partial pressure data for the carbon dioxide over the various powders can be used to determine the heats of decomposition for the evolution of this component. The simple integrated form of the Van't Hoff equation is used for this calculation. This may be written as:

$$\ln P_2/P_1 = - \Delta H/R \, (1/T_2 - 1/T_1) \qquad \text{Eq. No. 1}$$

Here the pressures P_1 and P_2 are the equilibrium pressures of the gaseous decomposition product at the absolute temperatures T_1 and T_2 respectively. The gas constant is denoted by R and the heat of decomposition by ΔH, both in compatible units. This method of calculation neglects the temperature dependence of ΔH. The precision of the partial pressure measurements did not justify a more complicated method of calculation. The partial pressure data on a log P versus 1/T plot is a straight line over the temperature range for which the calculations were made.

EXPERIMENTAL RESULTS

The experimental part of this program consisted of collecting and analyzing the gases evolved from various copper powders, as a function of temperature, at a reduced pressure in an inert atmosphere. The data presented in the following tables are the volumes of gases evolved as a function of temperature and the partial pressures of these gases over the powders as a function of temperature.

The term "cumulative volume" is used to indicate that the volume of gas given is the sum of the amounts evolved to the temperature indicated. Cumulative volume data are taken at a constant total pressure.

Gas volumes indicated as "total volume" were found by rapid heating of the powder to 1400°F and condensing the evolved gases in a liquid air trap. Indications are that these values represent quite well the total amounts of the various gases on the powder surfaces.

The manner in which gases evolve as a function of time at various temperatures is shown in Figure 10 and the tabulated data are listed in Table I.

The cumulative volumes of H_2O, CO_2 , SO_2 and H_2 collected when ten grams of water atomized powder of mixed particle size were heated are tabulated in Table II and plotted in Figure 11. This powder was outgassed in the as-received condition. The partial pressures of the gases at various temperatures over the

TABLE I

Volume of Gas Evolved at Various Temperatures As A Function of Time

Powder Type: Reagent
Particle Size: .0005 cm

Specimen Weight: 10 grams
Treatment: As Received

Temperature

300°F		500°F		700°F	
Time, Min.	Volume, ml, STP*	Time, Min.	Volume, ml, STP	Time, Min.	Volume, ml, STP
0.0	0.0	0.0	0.0	0.0	0.0
1.4	0.041	0.3	0.021	0.7	0.046
10.9	0.075	1.0	0.070	2.3	0.077
30.0	0.095	1.8	0.111	5.6	0.118
		3.1	0.131	14.4	0.159
		6.0	0.162	26.0	0.200
		12.9	0.214	65.0	0.226
		49.7	0.254		

900°F		1400°F	
Time, Min.	Volume, ml, STP	Time, Min.	Volume, ml, STP
0.0	0.0	0.0	0.0
1.8	0.018	0.6	0.033
2.6	0.069	2.6	0.085
10.5	0.113	6.2	0.141
14.4	0.162	28.3	0.172
26.5	0.183		
58.0	0.218		

* At a temperature of 20°C and a pressure of 760 mmhg

TABLE II

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Water Atomized
Particle Size: Mixed

Specimen Weight: 10 grams
Treatment: As Received

Temp. °F.	Volume, ml at STP				Partial Pressure, mm Hg		
	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
400	0.544	0.057	0.0	0.0	3.43	0.36	0.0
600	0.856	0.088	0.0	0.001	5.13	0.52	0.0
800	0.950	0.118	0.001	0.001	5.63	0.74	0.009
1100	0.807	0.188	0.006	0.109	4.19	1.37	0.054
1400	0.741	0.185	0.004	0.095	3.60	1.39	0.028

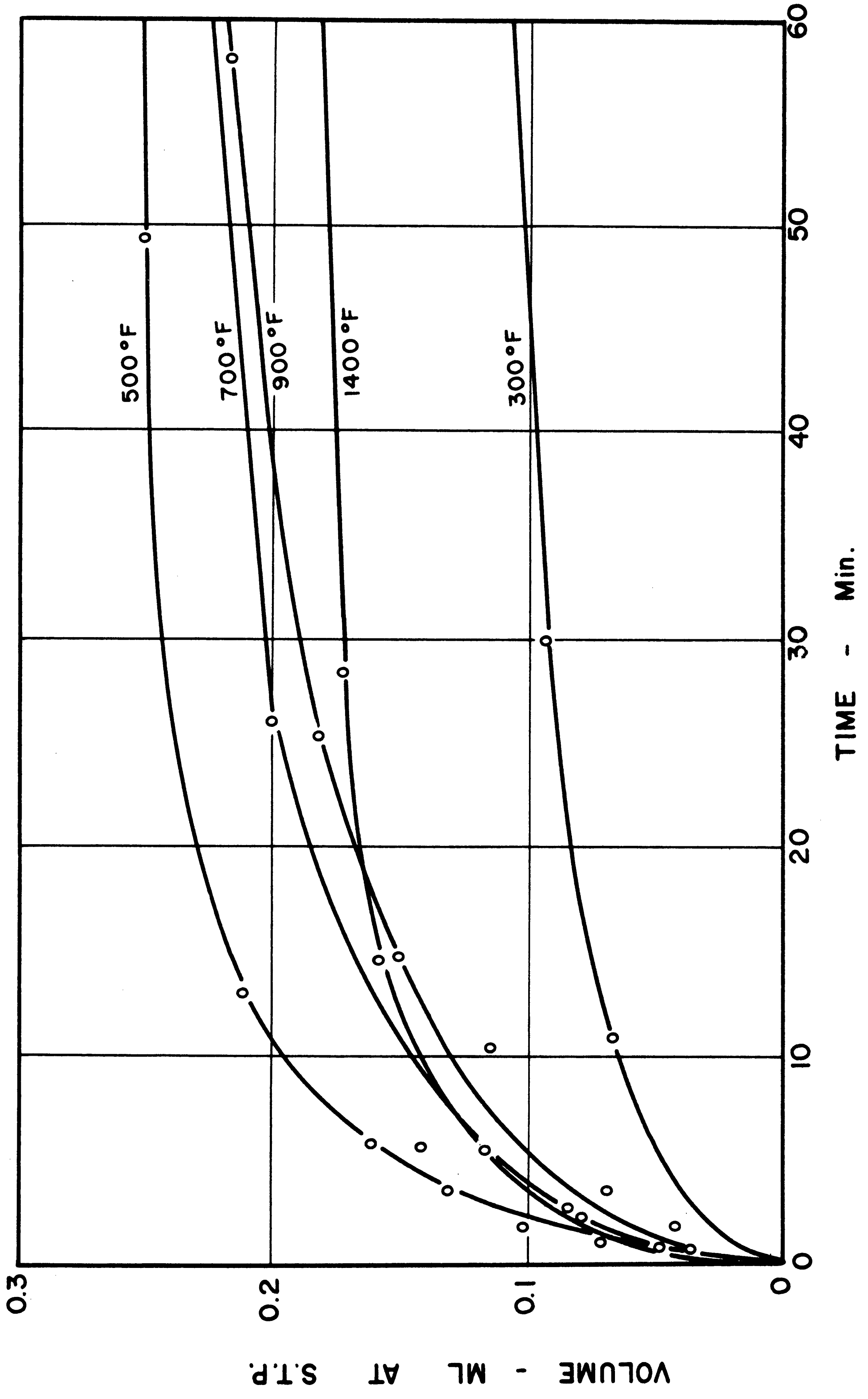

FIGURE 10. GAS EVOLUTION FROM COPPER POWDER AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES.

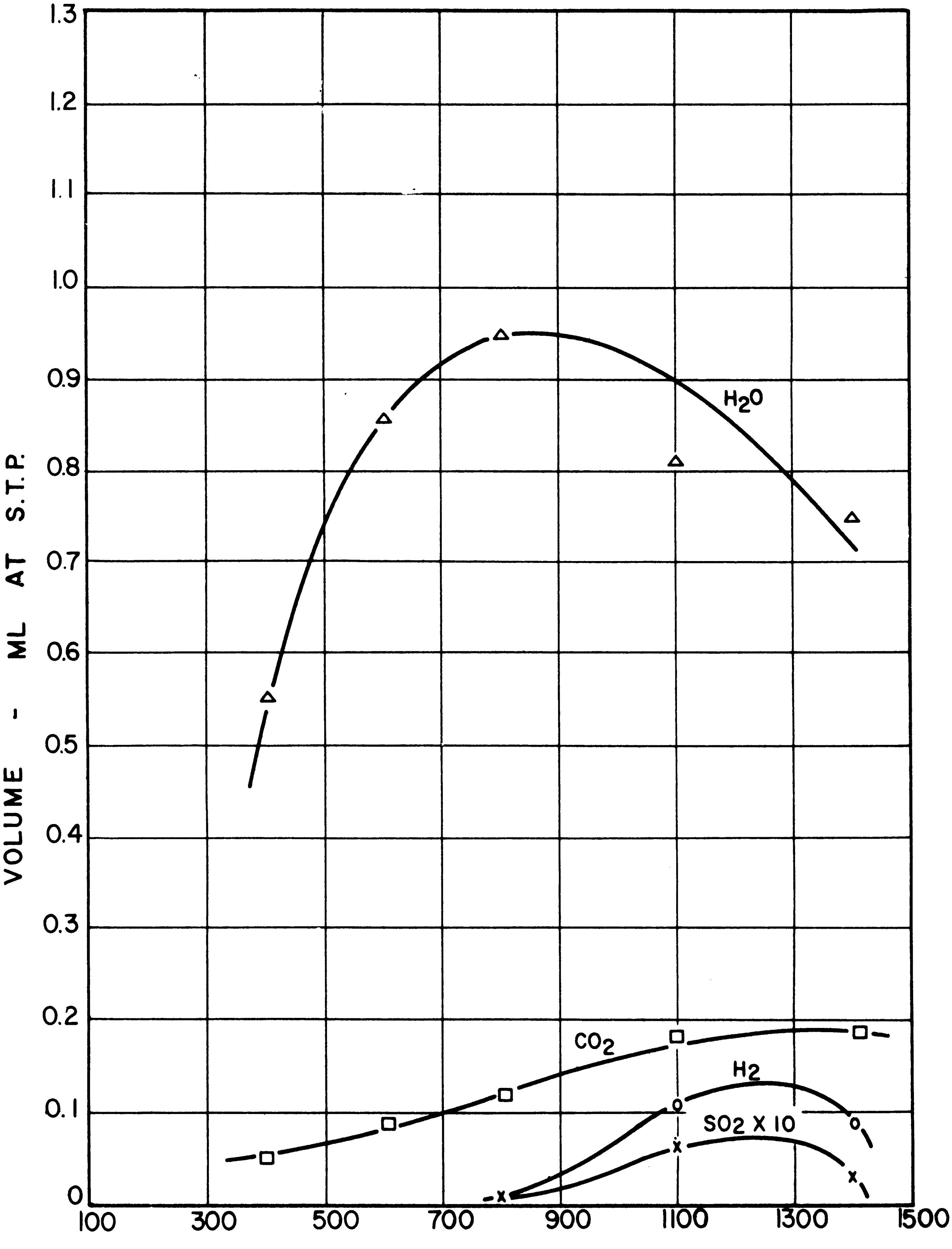

FIGURE 11. GASES COLLECTED FROM COPPER POWDER

Powder type - H_2O Atomized　　Specimen wt - 10 gm.

Particle size - Mixed　　Treatment - As received.

powder are given in Table II. The log of the partial pressures of CO_2 and H_2O versus the reciprocal of the absolute temperature for these tests is shown in Figure 12.

Table III through VI list cumulative volume and partial pressure data for the gases evolved from four mesh fractions of the water atomized powder tested in the as-received condition. These same data are plotted in Figures 13 through 20. The average particle diameters for these mesh fractions are listed in Table VII.

The total volumes of gases evolved from the water atomized mesh fractions on heating to 1400°F are listed in Table VIII. These data are for powders tested in the as-received condition. Similar data are listed in Table IX for these fractions after cleaning in NH_4OH. Plots of the data in both tables are shown in Figures 21 and 22. In these plots the total gas is shown as a function of the specimen areas given in Table VII. The term "corrected area" in this table applies to an area calculated to give a straight line relation between total gas data and specimen area.

The water atomized mesh fraction having an average diameter of 0.068 centimeters was outgassed at various intervals after cleaning in NH_4OH. Tables X through XIII list the cumulative volumes of the gases evolved, along with their partial pressures, as a function of temperature. These data are presented graphically in Figures 23 and 24.

A specimen of water atomized copper powder was outgassed

TABLE III

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Water Atomized
Specimen Weight: 10 grams
Particle Size: .144 cm
Treatment: As Received

Temp., °F	Volume, ml at STP H_2O	CO_2	SO_2	H_2	Partial Pressure, mm Hg H_2O	CO_2	SO_2
400	0.282	0.027	0.0	0.0	1.63	0.16	0.0
600	0.447	0.049	0.0	0.001	2.63	0.29	0.0
800	0.424	0.095	0.001	0.001	2.37	0.62	0.010
1100	0.390	0.139	0.004	0.071	2.04	0.98	0.036
1400	0.309	0.153	0.003	0.066	1.28	1.17	0.021

TABLE IV

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Water Atomized
Specimen Weight: 10 grams
Particle Size: .068 cm
Treatment: As Received

Temp., °F	Volume, ml at STP H_2O	CO_2	SO_2	H_2	Partial Pressure, mm Hg H_2O	CO_2	SO_2
400	0.307	0.060	0.0	0.0	1.85	0.36	0.0
600	0.651	0.082	0.0	0.001	3.78	0.46	0.0
800	0.703	0.112	0.001	0.001	4.03	0.66	0.005
1100	0.617	0.158	0.007	0.083	3.26	1.03	0.062
1400	0.499	0.168	0.003	0.062	2.26	1.23	0.029

TABLE V

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Water Atomized Specimen Weight: 10 grams
Particle Size: .030 cm Treatment: As Received

Temp.,	Volume, ml at STP				Partial Pressure, mm Hg		
°F	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
400	0.437	0.100	0.0	0.0	2.70	0.62	0.0
600	0.928	0.138	0.0	0.001	5.24	0.75	0.0
800	1.054	0.172	0.001	0.001	5.78	0.93	0.004
1100	1.070	0.269	0.014	0.003	5.67	1.65	0.106
1400	0.949	0.271	0.006	0.074	4.75	1.72	0.054

TABLE VI

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Water Atomized Specimen Weight: 10 Grams
Particle Size: .022 cm Treatment: As Received

Temp.,	Volume, ml at STP				Partial Pressure, mm Hg		
°F	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
400	0.586	0.136	0.0	0.0	4.16	0.97	0.0
600	0.996	0.197	0.0	0.0	6.32	1.23	0.0
800	1.044	0.262	0.001	0.0	6.37	1.67	0.007
1100	1.068	0.345	0.017	0.0	6.06	2.21	0.139
1400	0.941	0.418	0.013	0.064	5.07	3.03	0.098

TABLE VII

Particle Size of Water Atomized Powders; Mesh Fractions

Mesh Fraction	Diameter, cm	Area,* cm^2	Corrected Area** cm^2	Roughness Factor
-20	0.144	46.70	302.0	6.45
-20 -48	0.068	98.80	451.0	4.57
-48 -65	0.030	224.00	587.0	2.62
-65 -100	0.022	305.00	634.0	2.08

* Area of ten gram specimen computed on basis of spherical shape.

** Area of ten gram specimen, corrected from total gas evolution data. See Page 84 of text.

TABLE VIII

Total Volume of Gases Evolved From Mesh Fractions on Heating to 1400°F

Powder Type:	Water Atomized	Specimen Weight:	10 grams
Particle Size:	.022 to .144 cm	Treatment:	As Received

Mesh Fraction	Milliliter at STP		
	H_2O	CO_2	SO_2
-20	0.55	0.14	0.007
-20 -48	0.85	0.16	0.017
-48 -65	1.10	0.26	0.024
-65 -100	1.17	0.30	0.030

TABLE IX

Total Volumes of Gases Evolved From Cleaned Mesh Fractions on Heating to 1400°F

Powder Type: Water Atomized
Particle Size: .030 to .194 cm
Specimen Weight: 10 grams
Treatment: NH_4OH Wash

Mesh Fraction	Milliliter at STP		
	H_2O	CO_2	SO_2
-20	0.15	0.036	0.0
-20 -48	0.40	0.054	0.0
-48 -65	0.44	0.068	0.0

TABLE X

Cumulative Volumes and Partial Pressures of Gases Evolved From Cleaned Powder

Powder Type: Water Atomized
Particle Size: .068 cm
Specimen Weight: 10 grams
Treatment: 0 Hours in Air After NH_4OH Wash

Temp., °F	Volume, ml at STP				Partial Pressure, mm Hg		
	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
400	0.120	0.006	0	0.0	0.76	0.04	0
600	0.226	0.018	0	0.0	1.48	0.12	0
800	0.152	0.031	0	0.036	0.86	0.22	0
1100	0.170	0.033	0	0.076	1.02	0.24	0
1400	0.119	0.036	0	0.058	0.45	0.28	0

TABLE XI

Cumulative Volumes and Partial Pressures of Gases Evolved From Cleaned Powder

Powder Type: Water Atomized
Particle Size: .068 cm
Specimen Weight: 10 grams
Treatment: 23 Hours in Air After NH_4OH Wash

Temp., °F	Volume, ml at STP				Partial Pressure, mm Hg		
	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
400	0.049	0.005	0	0.0	0.30	0.03	0
600	0.187	0.020	0	0.0	1.22	0.13	0
800	0.185	0.028	0	0.013	1.19	0.19	0
1100	0.125	0.036	0	0.050	0.63	0.27	0
1400	0.111	0.040	0	0.040	0.49	0.31	0

TABLE XII

Cumulative Volumes and Partial Pressures of Gases Evolved From Cleaned Powder

Powder Type: Water Atomized
Particle Size: .068 cm

Specimen Weight: 10 grams
Treatment: 100 Hours in Air After NH_4OH Wash

Temp., °F	Volume, ml at STP			Partial Pressure, mm Hg		
	H_2O	CO_2	H_2	H_2O	CO_2	SO_2
400	0.009	0.007	0.0	0.06	0.05	0
600	0.205	0.020	0.0	1.33	0.12	0
800	0.147	0.041	0.013	0.86	0.28	0
1100	0.138	0.044	0.021	0.79	0.31	0
1400	0.063	0.046	0.046	0.0	0.34	0

TABLE XIII

Cumulative Volumes and Partial Pressures of Gases Evolved From Cleaned Powder *

Powder Type: Water Atomized
Particle Size: .068 cm

Specimen Weight: 10 grams
Treatment: 198 Hours in Air After NH_4OH Wash

Temp., °F	Volume, ml at STP			Partial Pressure, mm Hg	
	H_2O	CO_2	H_2	H_2O *	CO_2
400	0.013	0.008	0.0	-	0.05
600	0.167	0.016	0.0	-	0.11
800	0.223	0.036	0.0	-	0.27
1100	0.226	0.043	0.0	-	0.33
1400	0.231	0.045	0.0	-	0.35

* Water pressure was kept low during run by maintaining cold trap at the temperature of a dry ice - alcohol mixture.

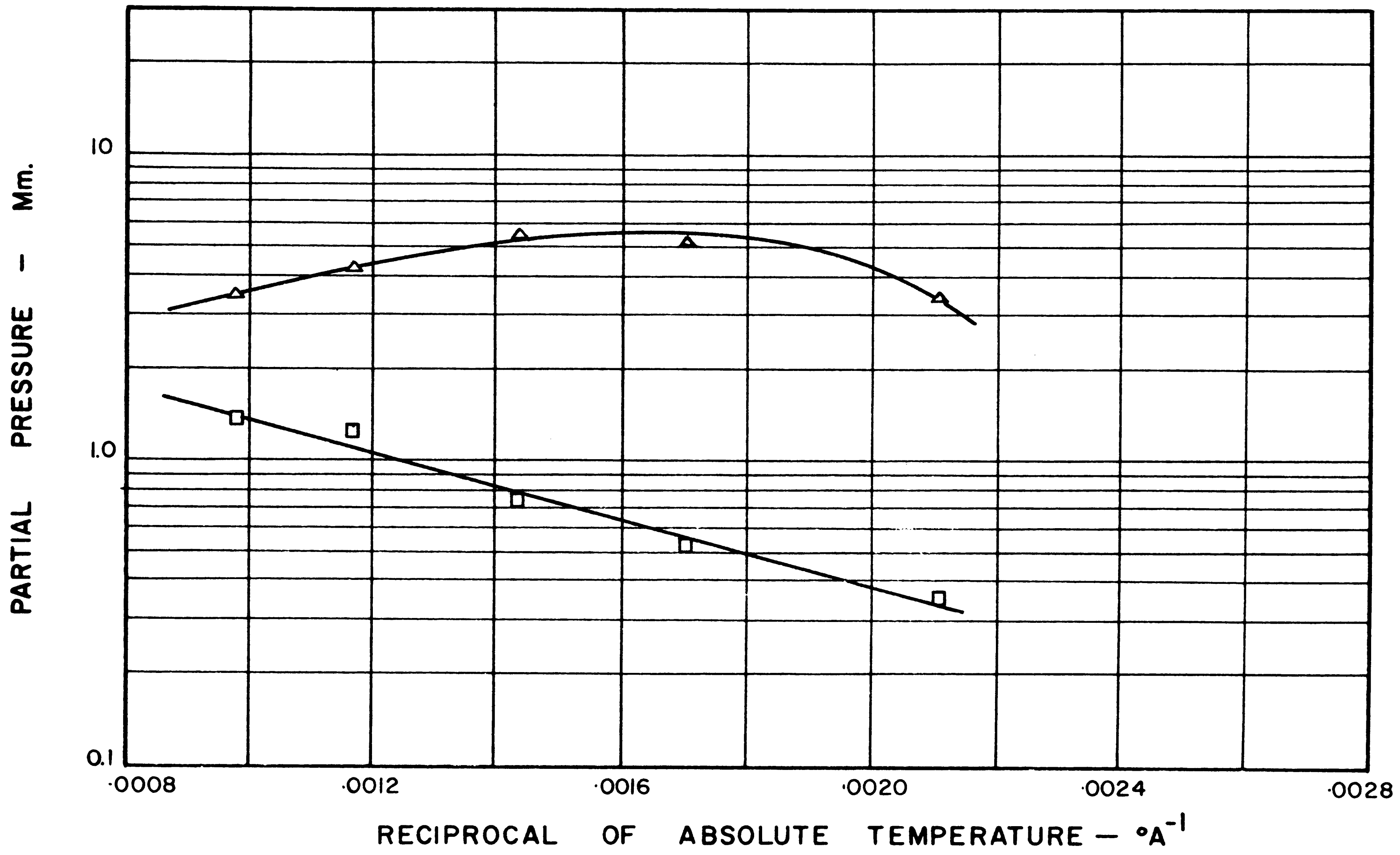

FIGURE 12. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 20.2 Mm. TOTAL PRESSURE

Powder type - H_2O Atomized
Approx. particle size - mixed
Treatment - As received.

H_2O ——— △
CO_2 ——— □

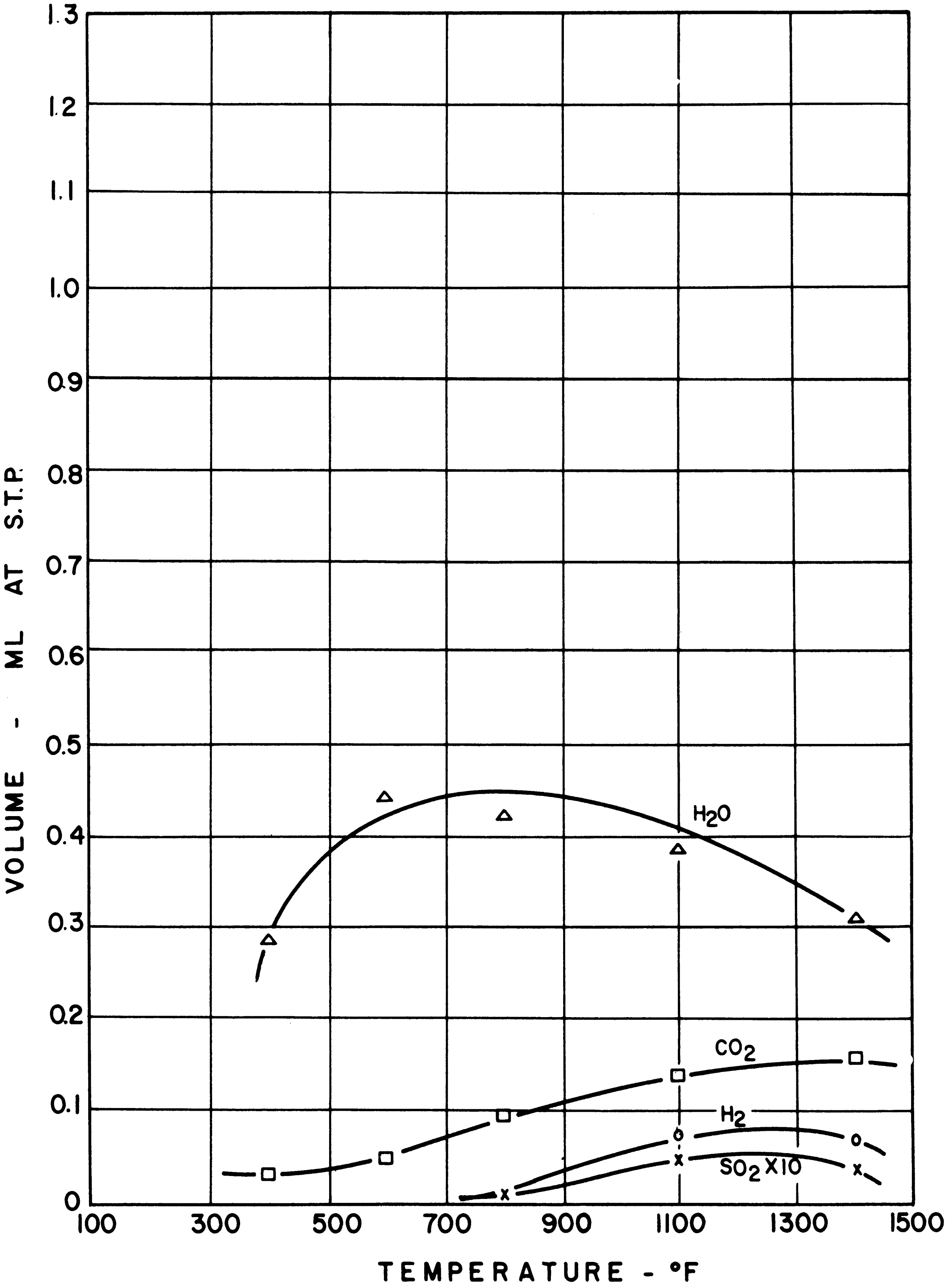

FIGURE 13. GASES COLLECTED FROM COPPER POWDER

Powder type - H_2O Atomized Specimen wt. - 10 gm.

Particle size - .144 cm. Treatment - As received.

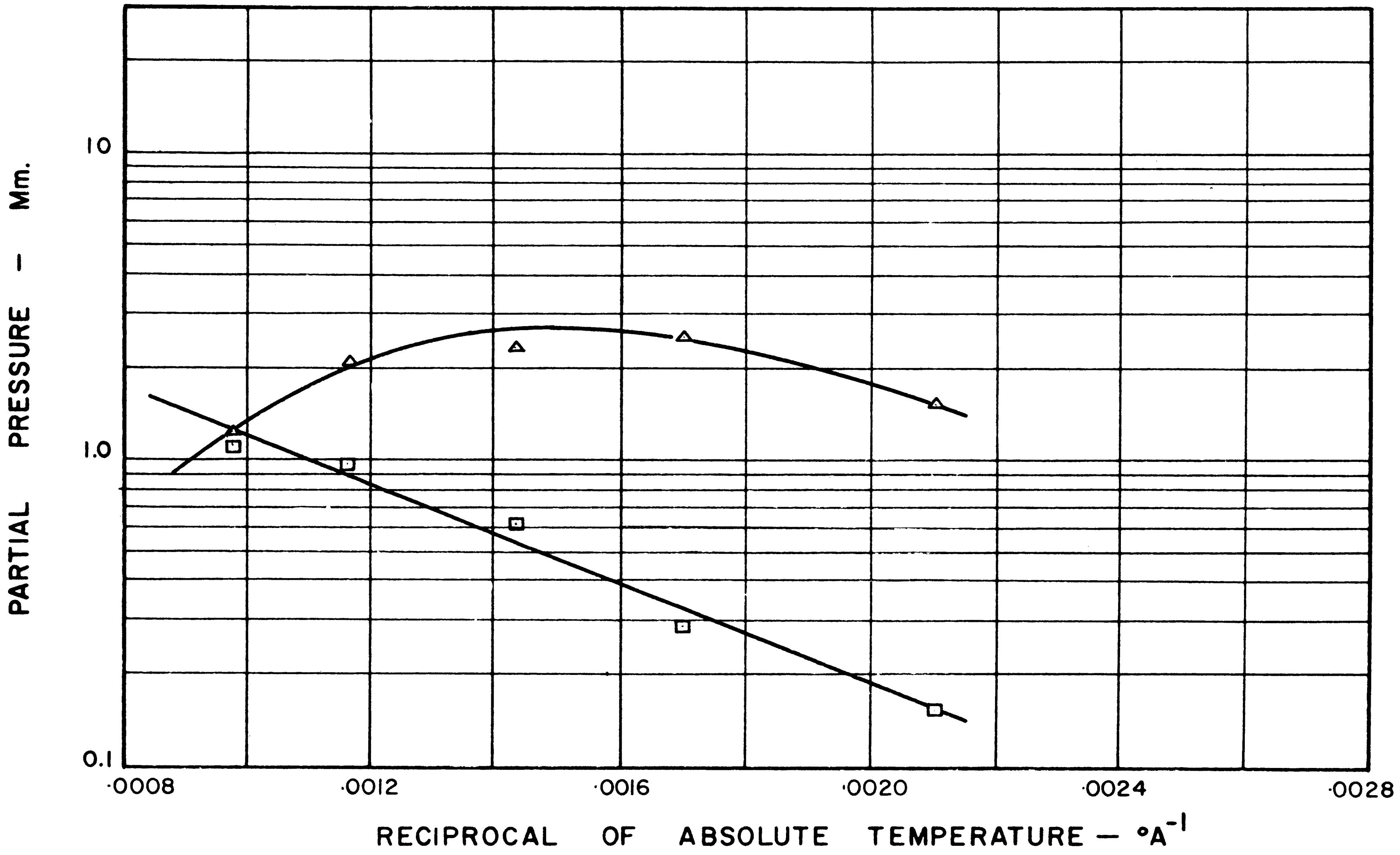

FIGURE 14. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 20.3 Mm. TOTAL PRESSURE

Powder type - H_2O Atomized.
Approx. particle size - .144 cm
Treatment - As received

H_2O ——— △
CO_2 ——— □

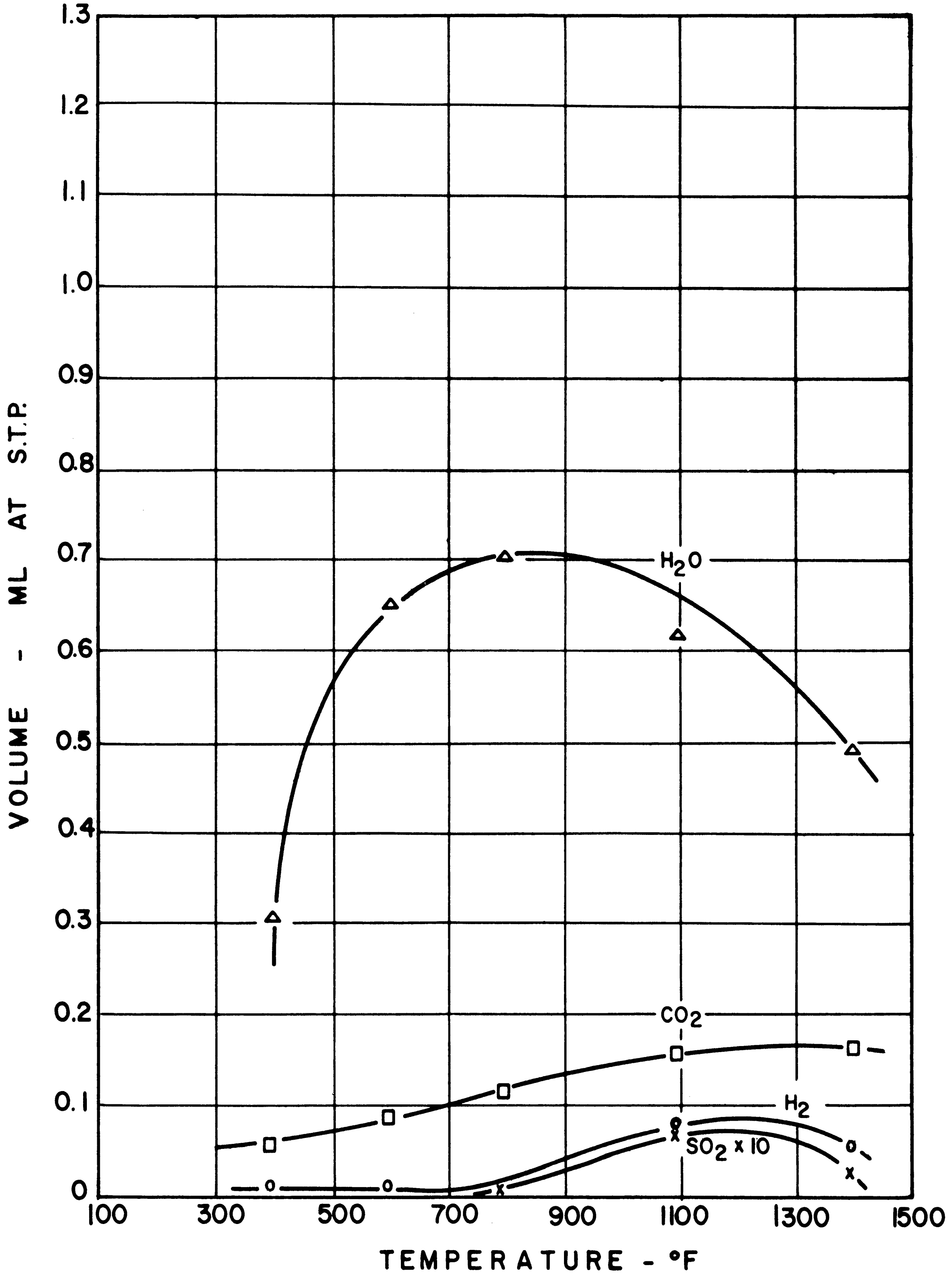

FIGURE 15. GASES COLLECTED FROM COPPER POWDER

Powder type - H_2O Atomized Specimen wt 10 gm.
Particle size - .068 cm Treatment - As received.

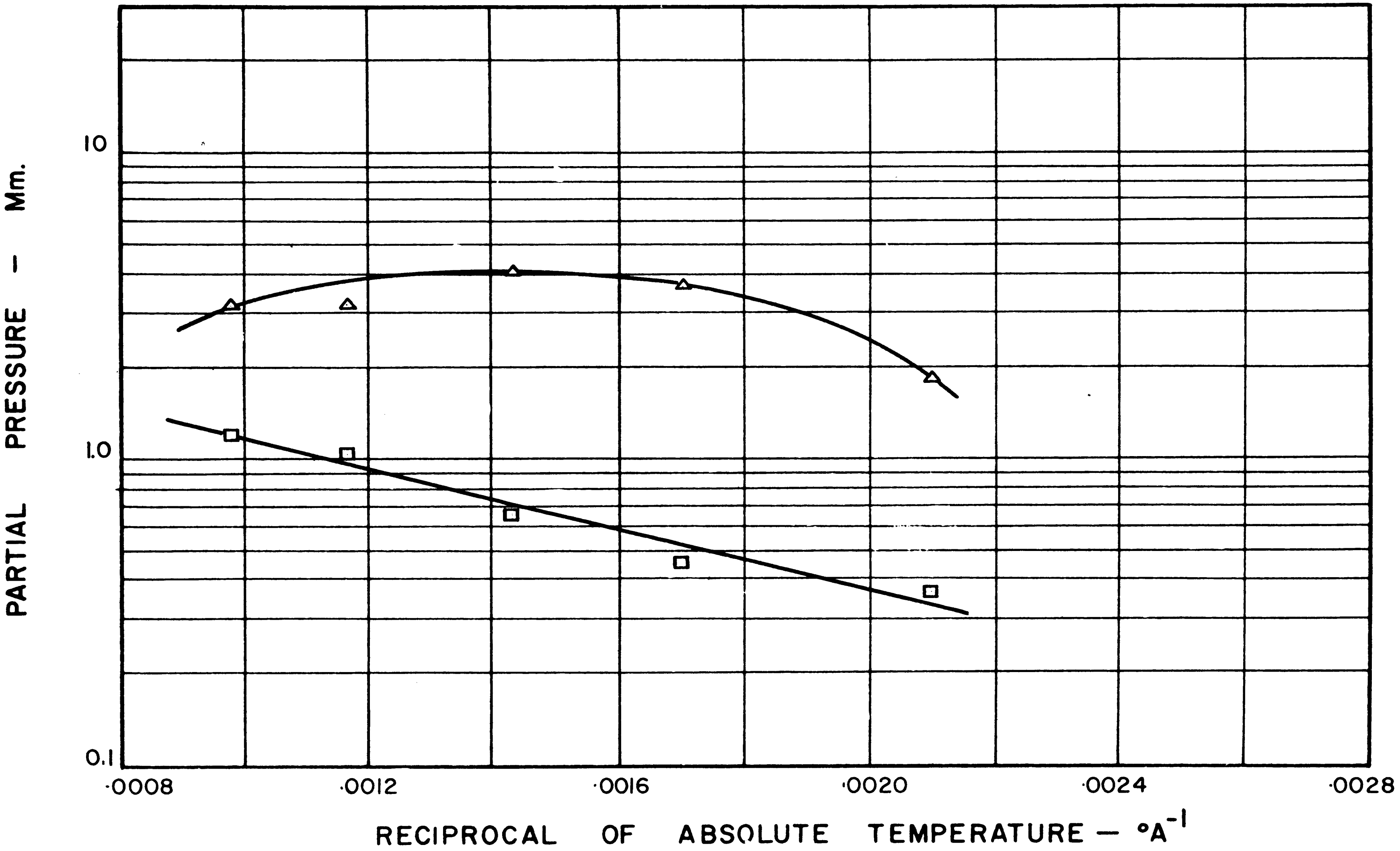

FIGURE 16. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE ● OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 20.1 Mm. TOTAL PRESSURE

Powder type - H_2O Atomized

Approx. particle size - .068 cm

Treatment - As received

H_2O ——— △

CO_2 ——— □

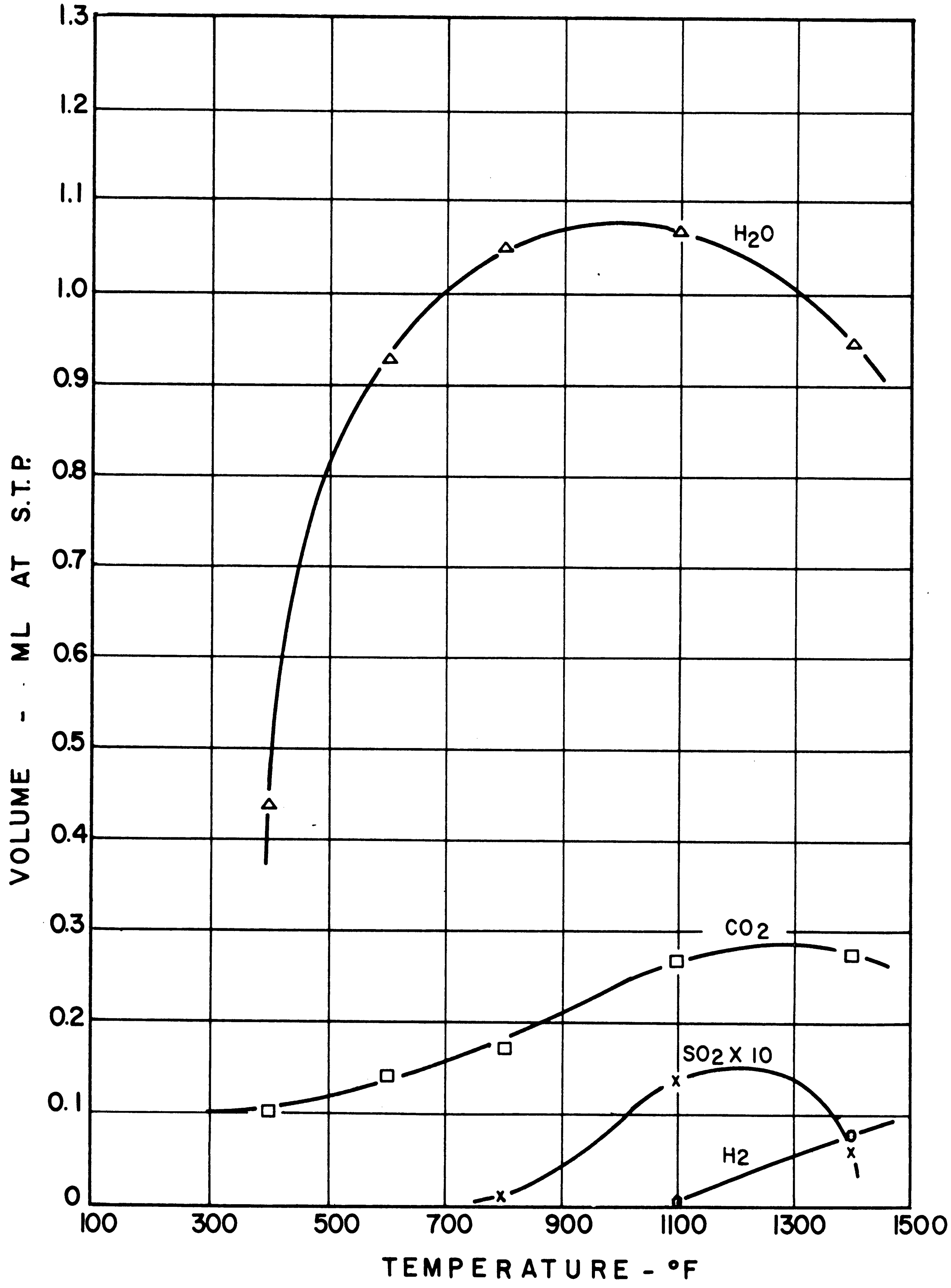

FIGURE 17. GASES COLLECTED FROM COPPER POWDER

Powder type - H_2O Atomized　　Specimen wt. - 10 gm.

Particle size - .030 cm.　　Treatment - As received.

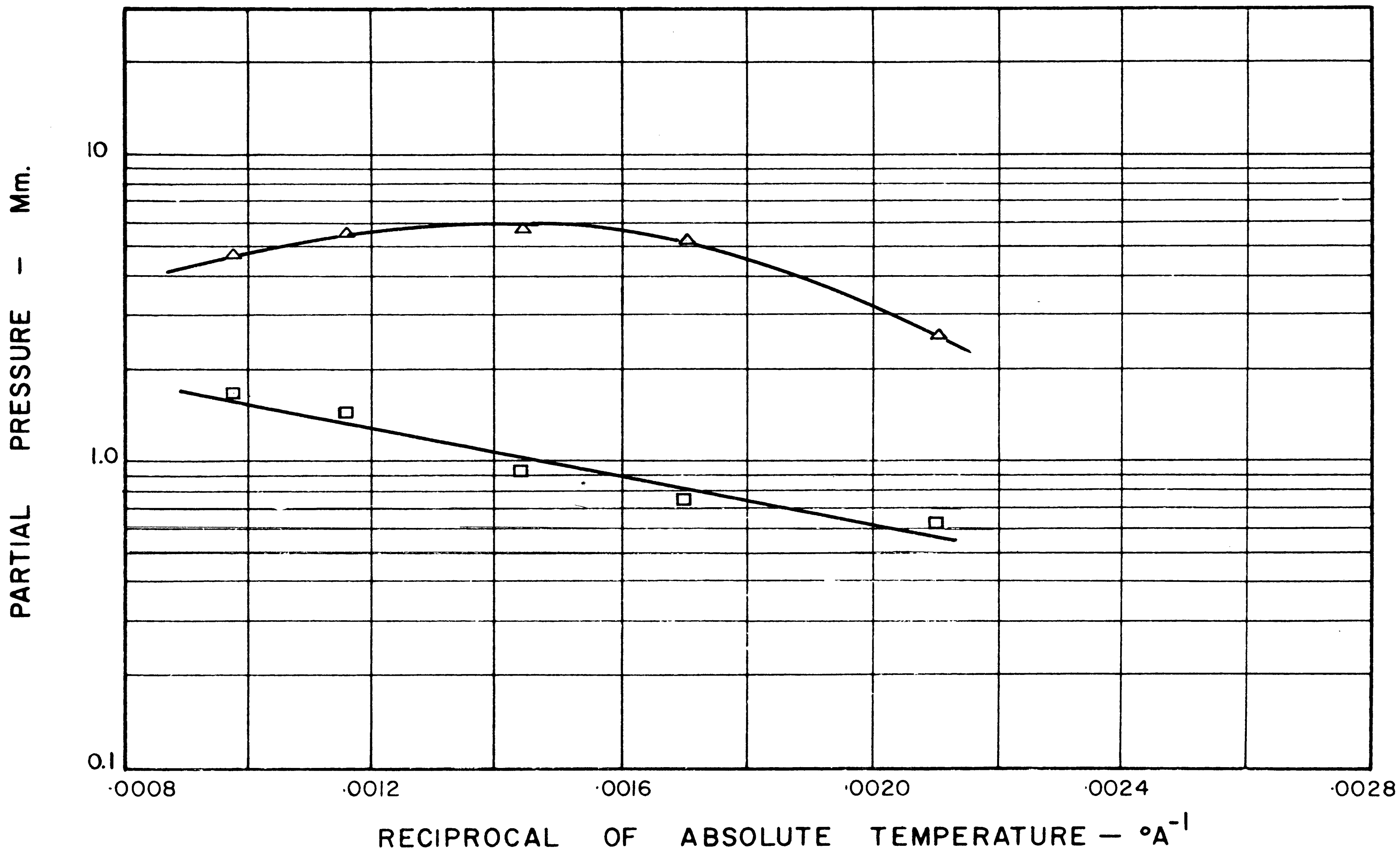

FIGURE 18. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 20.2 Mm. TOTAL PRESSURE

Powder type - H_2O Atomized
Approx. particle size - .030 cm
Treatment - As received

H_2O ______ △
CO_2 ______ □

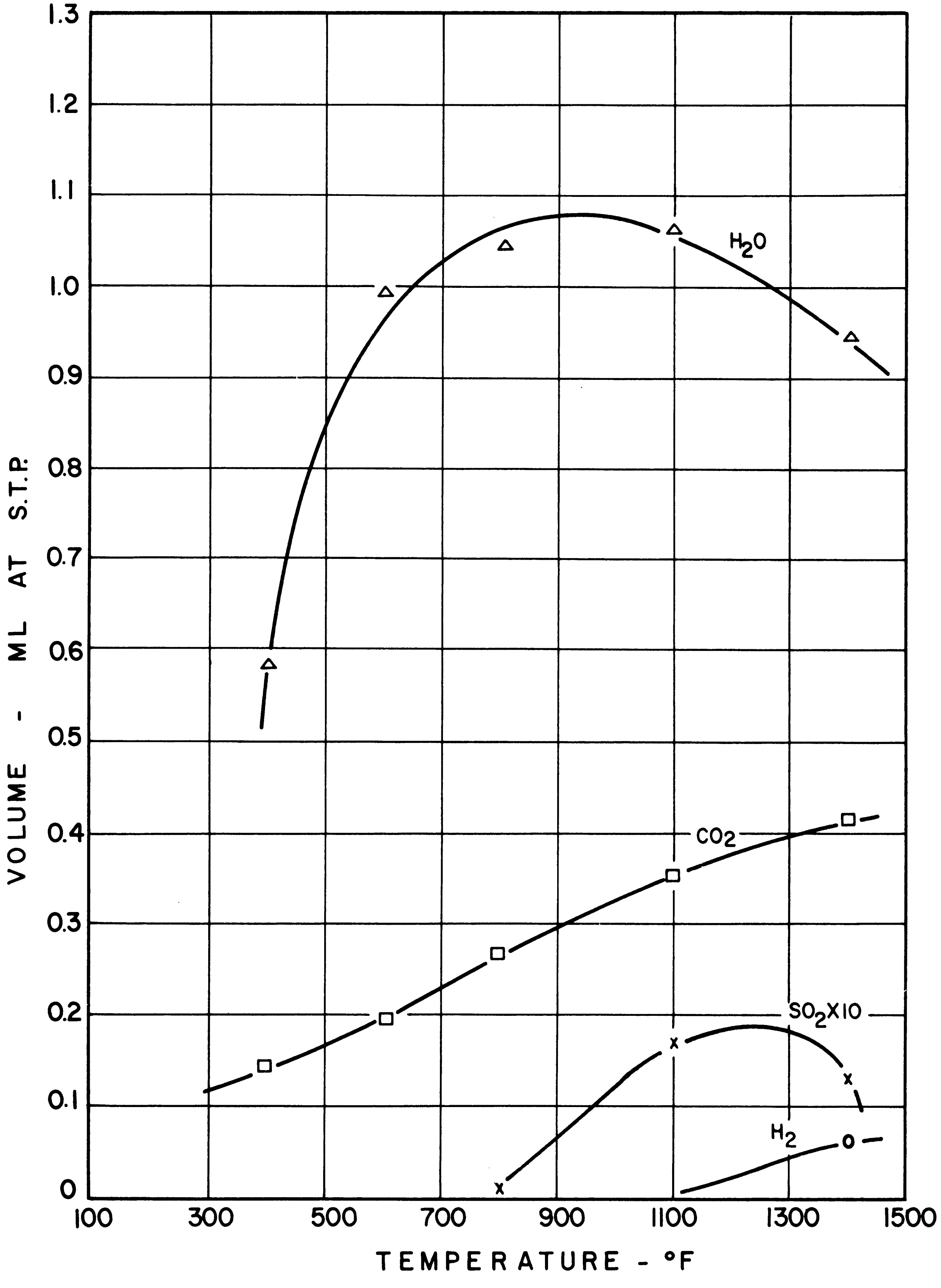

FIGURE 19. GASES COLLECTED FROM COPPER POWDER

Powder type - H_2O Atomized   Specimen wt. - 10 gm.

Particle size - .022 cm.   Treatment - As received.

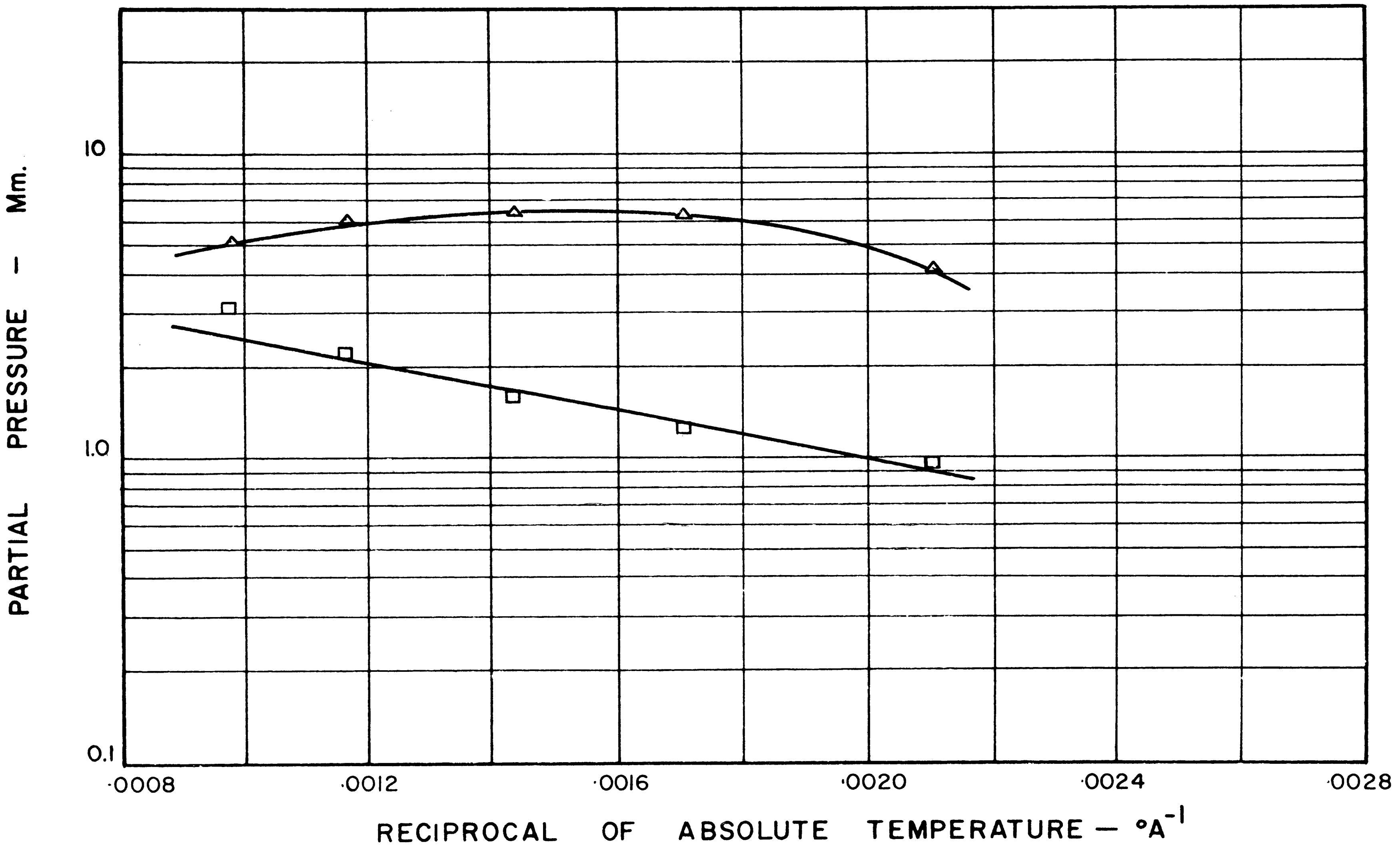

FIGURE 20. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 20.4 Mm. TOTAL PRESSURE

Powder type - H_2O Atomized

Approx. particle size - .022 cm

Treatment — As received

H_2O ——— △

CO_2 ——— □

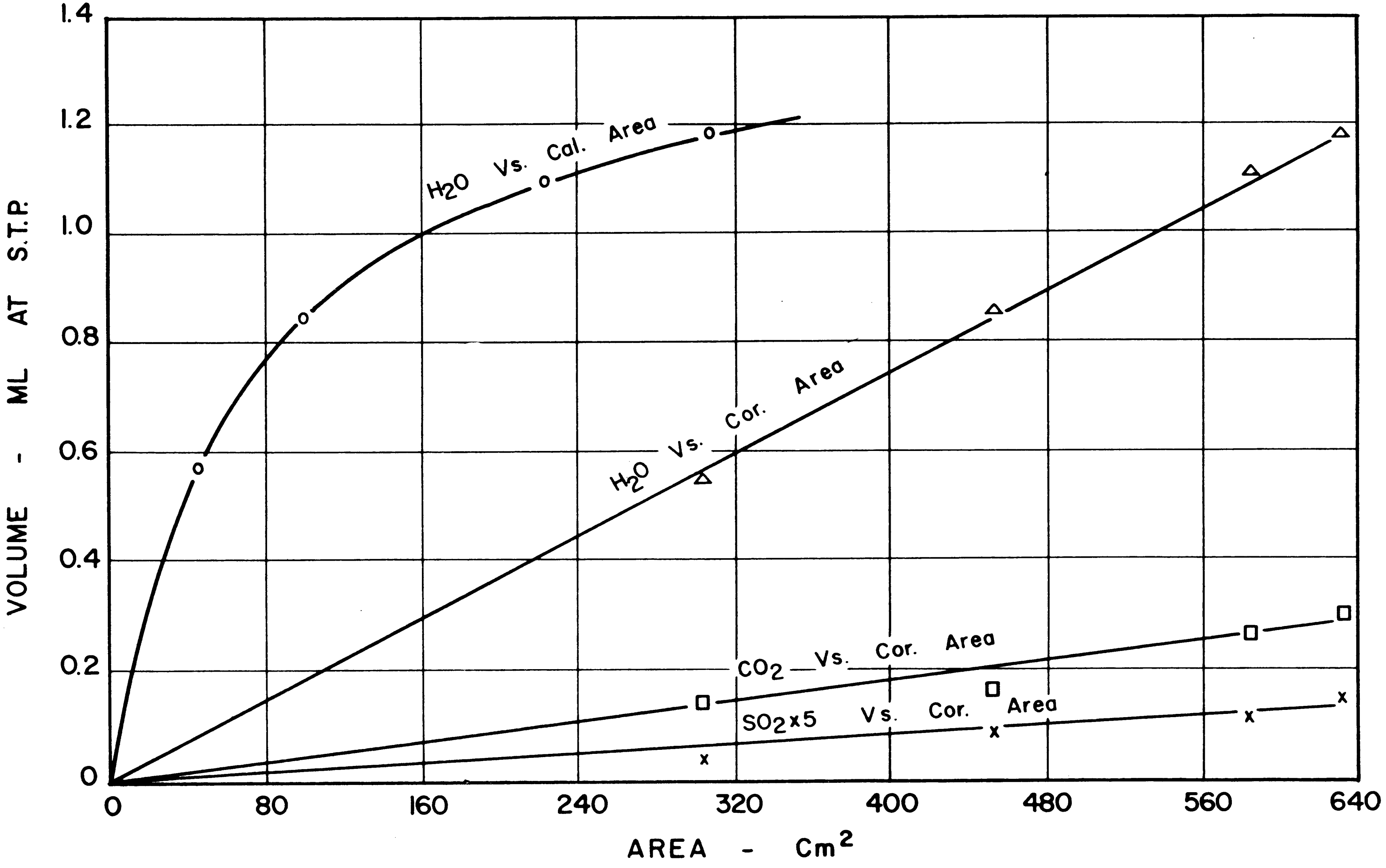

FIGURE 21. EFFECT OF AREA ON THE AMOUNT OF GAS COLLECTED FROM WATER ATOMIZED COPPER POWDER HEATED TO 1400°F

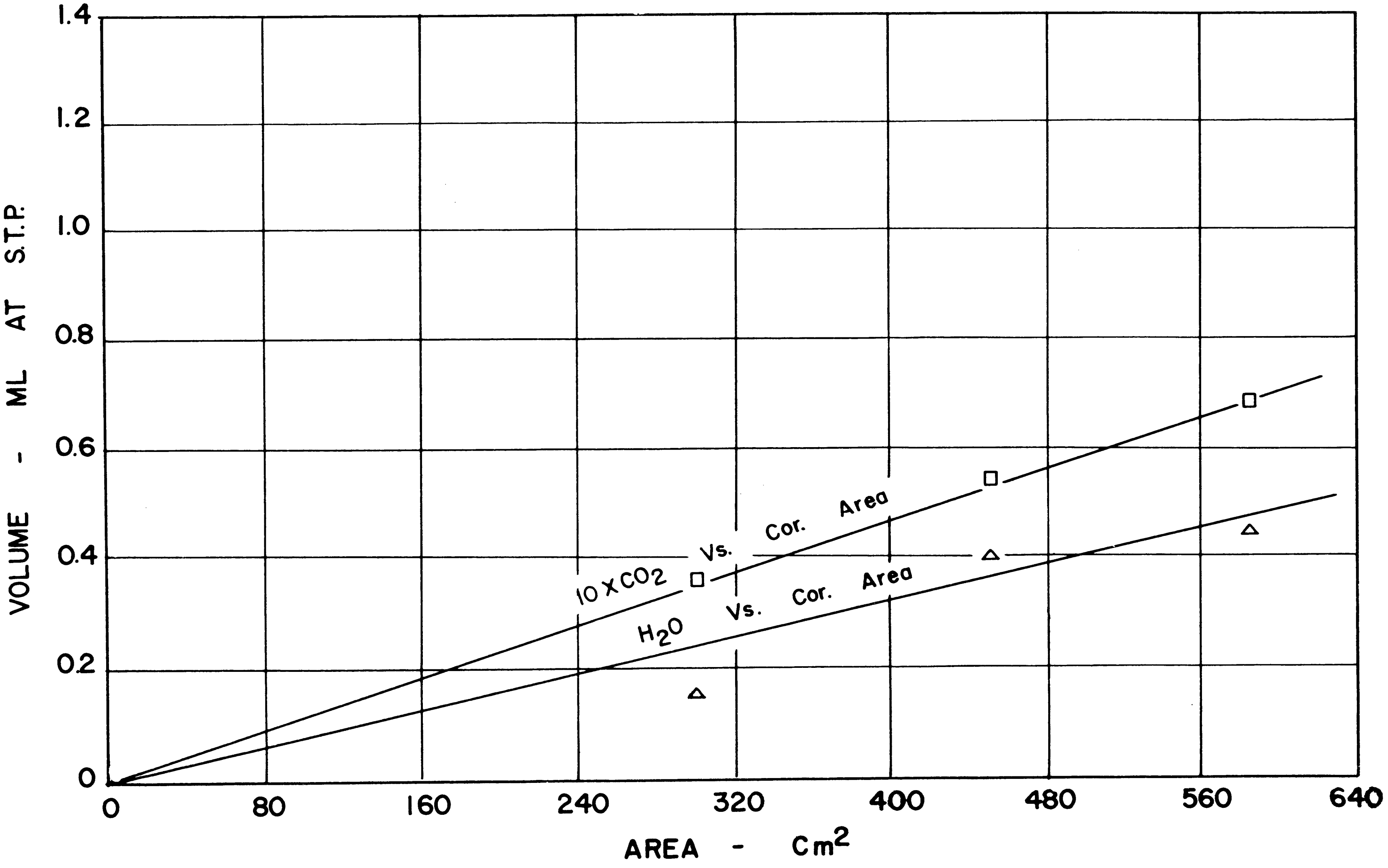

FIGURE 22. EFFECT OF AREA ON THE AMOUNT OF GAS COLLECTED FROM CLEANED WATER ATOMIZED COPPER POWDER HEATED TO 1400°F.

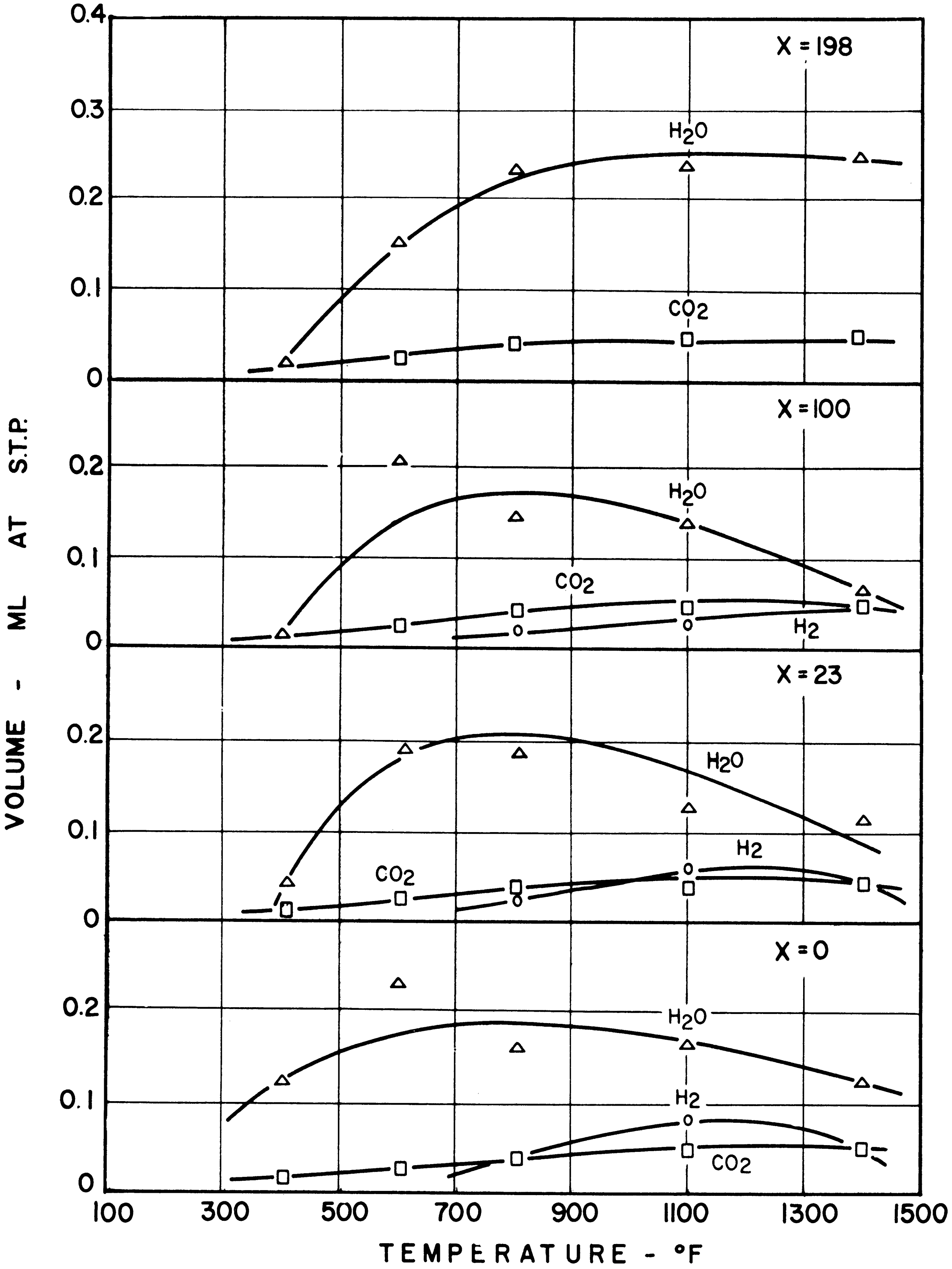

FIGURE 23. GASES COLLECTED FROM COPPER POWDER

Powder type - H_2O Atomized
Particle size - .068 cm.

Specimen wt - 10 gm.
Treatment - X hours in Air after NH_4OH wash

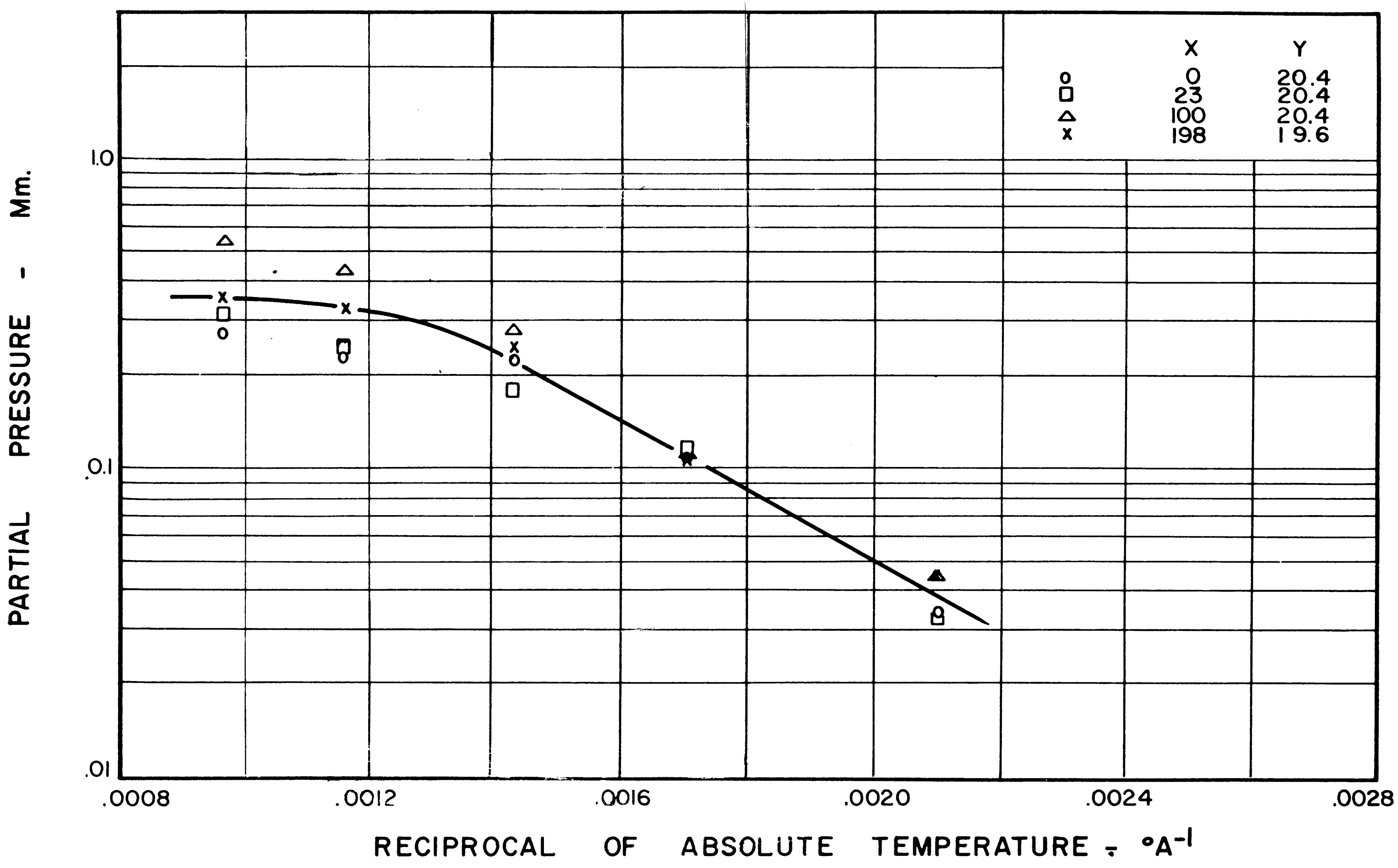

FIGURE 24. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER Y Mm. TOTAL PRESSURE.

Powder type - H_2O Atomized
Approx. particle size - .068 cm.

Treatment - X hours in air after NH_4OH wash.

and then heated in an atmosphere of H_2O and He. The atmosphere was analyzed after one hour at various powder temperatures. Data showing the volumes of water and hydrogen found in this atmosphere are listed in Table XIV. These data are plotted in Figure 25.

The cumulative volumes and partial pressures of gases collected over the air atomized powders are shown in Tables XV through XVII. These data are plotted in Figures 26 through 31.

The cumulative volumes and partial pressures of gases collected over the electrolytic powder are given as a function of temperature in Table XVIII. These data are presented graphically in Figures 32 and 33.

The total gas evolved from the three air atomized powders, the electrolytic powder, the reagent powder and the unknown powder are listed in Table XIX.

Table XX shows the values of heats of decomposition calculated on the basis of carbon dioxide partial pressure data from the various powders.

TABLE XIV

Volumes of Water and Hydrogen Found Over Copper Powder as a Function of Temperature

Powder Type: Water Atomized
Particle Size: .068 cm
Time at Temperature: One Hour

Specimen Weight: 10 grams
Treatment: Previously Outgassed
Initial Atmosphere: He and H_2O

Temp., °F	Milliliters at STP H_2O	Milliliters at STP H_2
77	1.083	0.0
400	1.083	0.0
600	0.977	0.0
800	0.863	0.0
1100	0.837	0.034
1400	0.714	0.115

TABLE XV

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Air Atomized No. 1
Particle Size: .0015 cm

Specimen Weight: 10 grams
Treatment: As Received

Temp., °F.	Volume, ml at STP				Partial Pressure, mm Hg		
	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
400	0.164	0.031	0.002	0.005	1.03	0.196	0.011
600	0.267	0.058	0.003	0.006	1.70	0.370	0.021
800	0.279	0.188	0.011	0.001	2.54	1.982	0.111
1100	0.288	0.337	0.055	0.002	2.44	2.374	0.412
1400	0.187	0.349	0.093	0.001	1.11	2.542	0.762

TABLE XVI

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Air Atomized No. 2
Particle Size: .0017 cm
Specimen Weight: 10 grams
Treatment: As Received

Temp.,	Volume, ml at STP				Partial Pressure, mm Hg		
°F	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
400	0.787	0.203	0.003	0.006	3.97	1.02	0.013
600	1.394	0.444	0.002	0.006	6.33	2.09	0.008
800	1.524	0.576	0.004	0.003	6.64	2.75	0.016
1100	1.519	0.678	0.017	0.003	6.34	3.39	0.111
1400	1.501	0.695	0.086	0.003	6.01	3.43	0.688

TABLE XVII

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Air Atomized No. 3
Particle Size: .023 cm
Specimen Weight: 10 grams
Treatment: As Received

Temp.,	Volume, ml at STP				Partial Pressure, mm Hg		
°F	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
600	0.091	0.044	0.001	0.0	0.59	0.28	0.004
800	0.102	0.096	0.005	0.0	0.64	0.63	0.035
1100	0.098	0.156	0.010	0.0	0.59	1.08	0.071
1400	0.042	0.169	0.037	0.0	0.10	1.21	0.310

TABLE XVIII

Cumulative Volumes and Partial Pressures of Evolved Gases

Powder Type: Electrolytic
Particle Size: .0003 cm
Specimen Weight: 10 grams
Treatment: As Received

Temp.,	Volume, ml at STP				Partial Pressure, mm Hg		
°F	H_2O	CO_2	SO_2	H_2	H_2O	CO_2	SO_2
400	2.943	0.147	0.003	0.010	5.20	0.26	0.003
600	4.023	0.543	0.003	0.007	6.51	0.97	0.004
800	4.690	1.070	0.003	0.010	7.06	1.92	0.004
1100	4.817	1.460	0.003	0.007	6.94	2.67	0.008
1400	4.970	1.327	0.080	0.007	7.25	2.29	0.206

TABLE XIX

Total Volume of Gases Evolved From Various Types of Copper Powder on Heating to 1400°F

Specimen Weight: 10 grams Treatment: As Received

Powder Type	Milliliters at STP		
	H_2O	CO_2	SO_2
Air Atomized No. 1	0.43	0.40	0.182
Air Atomized No. 2	1.57	0.70	0.110
Air Atomized No. 3	0.17	0.20	0.046
Electrolytic	5.24	1.34	0.084
Unknown	4.44	1.85	0.930
Reagent	1.19	0.41	0.073

TABLE XX

Heats of Decomposition as Computed From Carbon Dioxide Partial Pressure Data

Powder Type	Δ H Cal/g mole	Powder Type	Δ H Cal/g mole
Water Atomized		Air Atomized	
Mixed Particle	2600	Number One	6250
.144 cm Diameter	3540	Number Two	2920
.068 cm Diameter	2260	Number Three	5970
.030 cm Diameter	1820		
.022 cm Diameter	1840	Electrolytic	4910
Cleaned	5090 *		

* Average value for the four runs after various times in air.

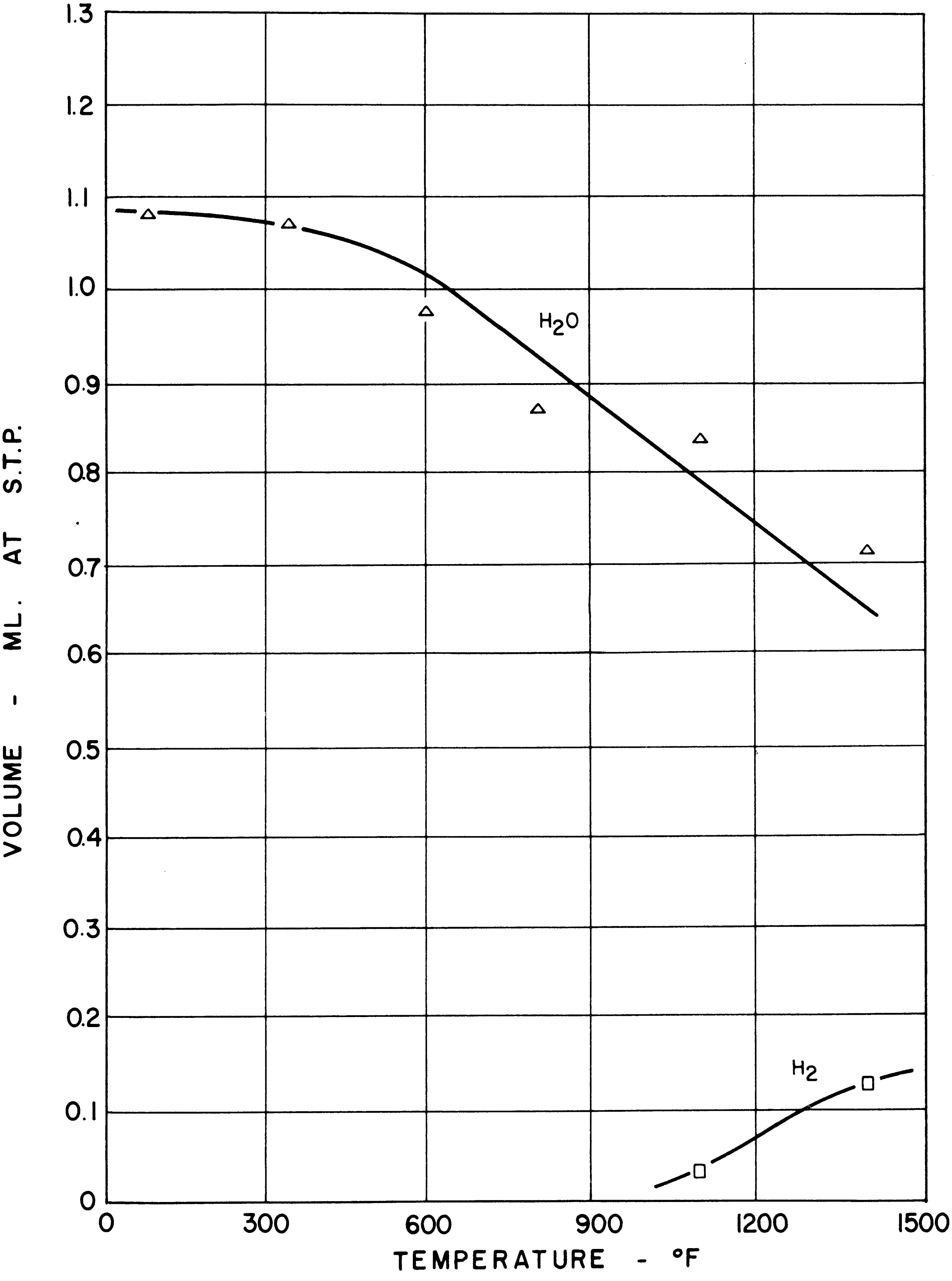

FIGURE 25. EFFECT ON COMPOSITION OF WATER-HELIUM ATMOSPHERE OVER COPPER POWDER AT ELEVATED TEMPERATURE.

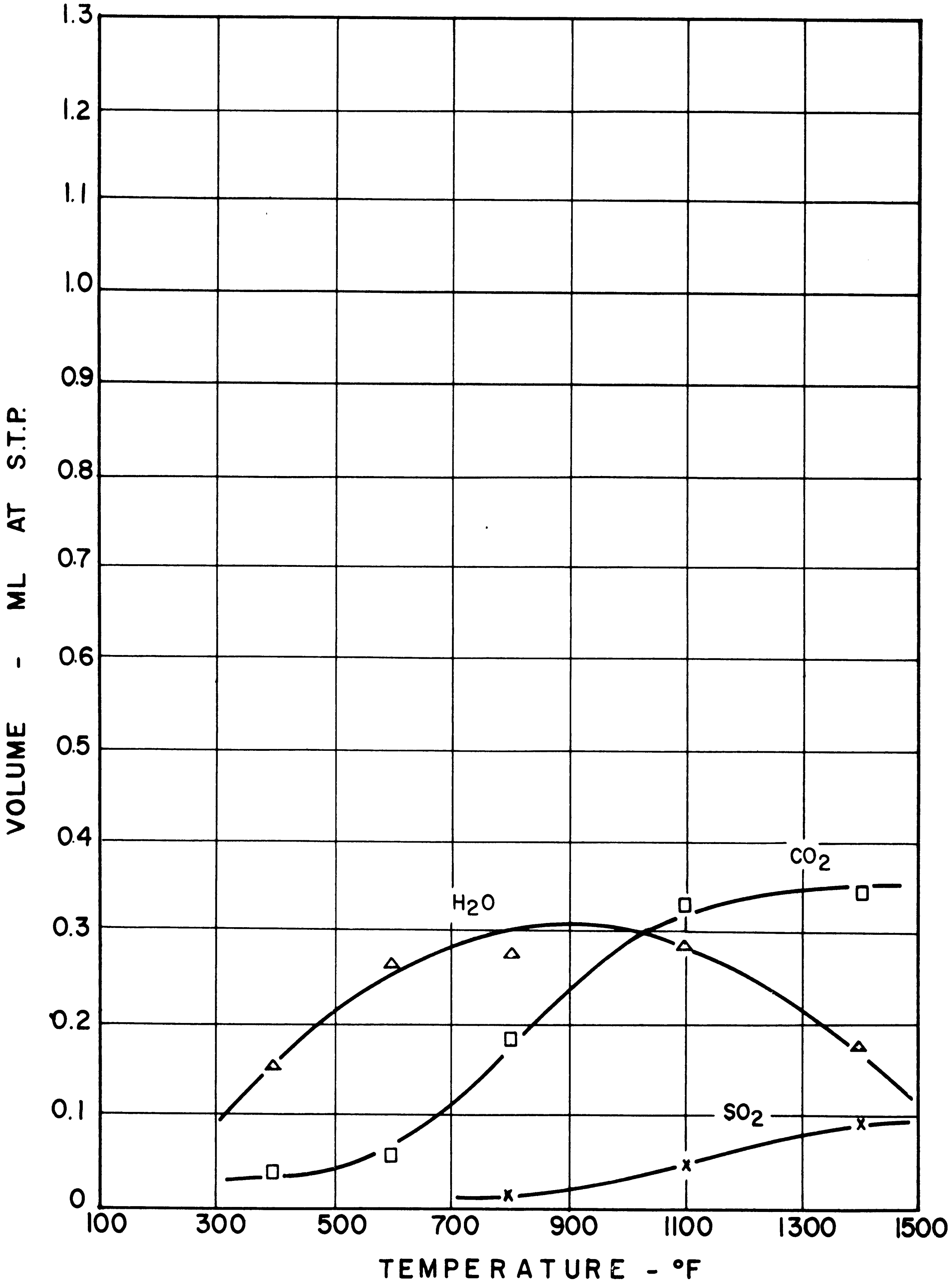

FIGURE 26. GASES COLLECTED FROM COPPER POWDER

Powder type - Air Atomized No. 1 Specimen wt. 10 gm.
Particle size - .0015cm. Treatment - As received.

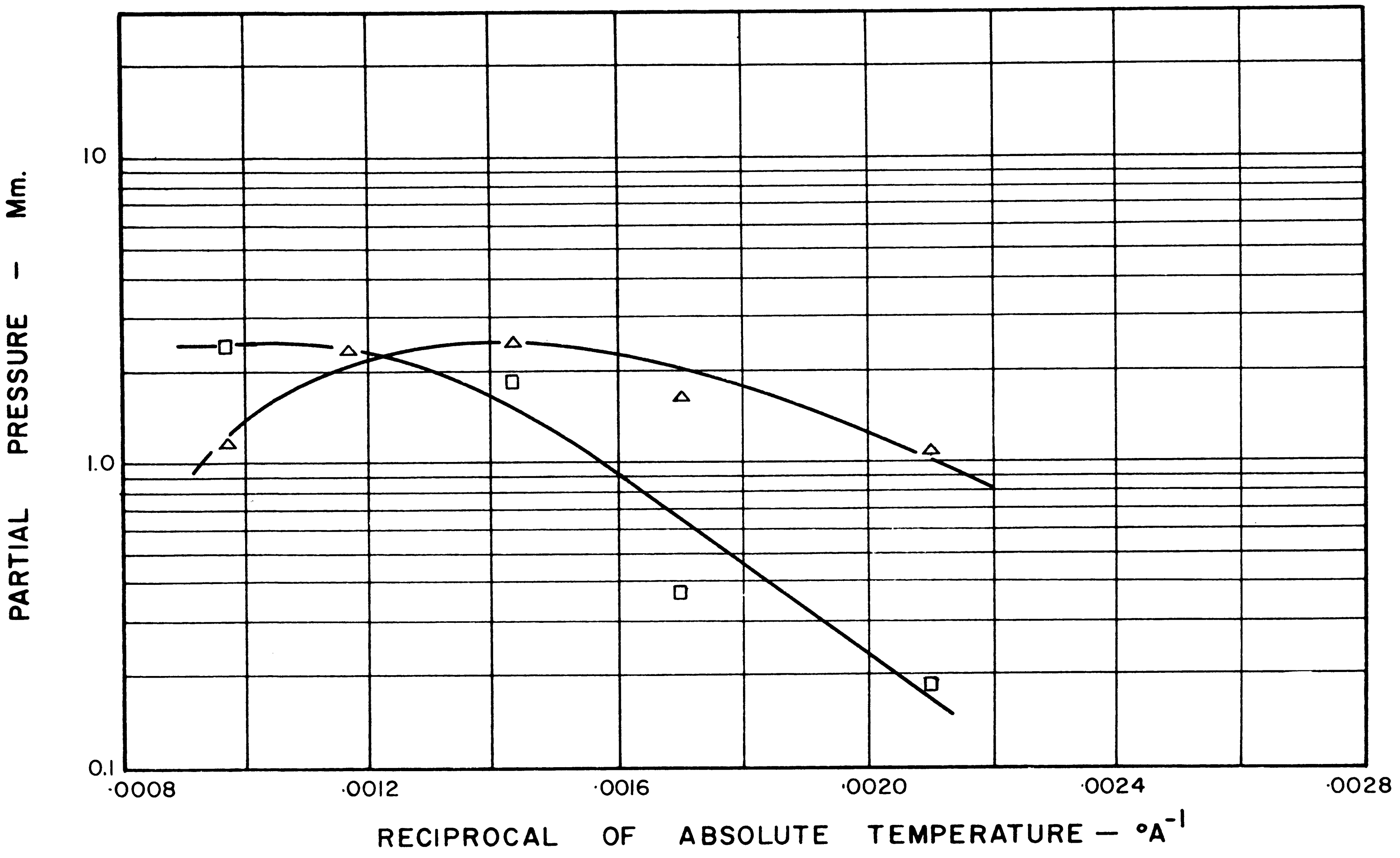

FIGURE 27 THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 20.0 Mm. TOTAL PRESSURE

Powder type - Air Atomized No. 1
Approx. particle size - .0015 cm.
Treatment - As received.

H_2O ——— △
CO_2 ——— □

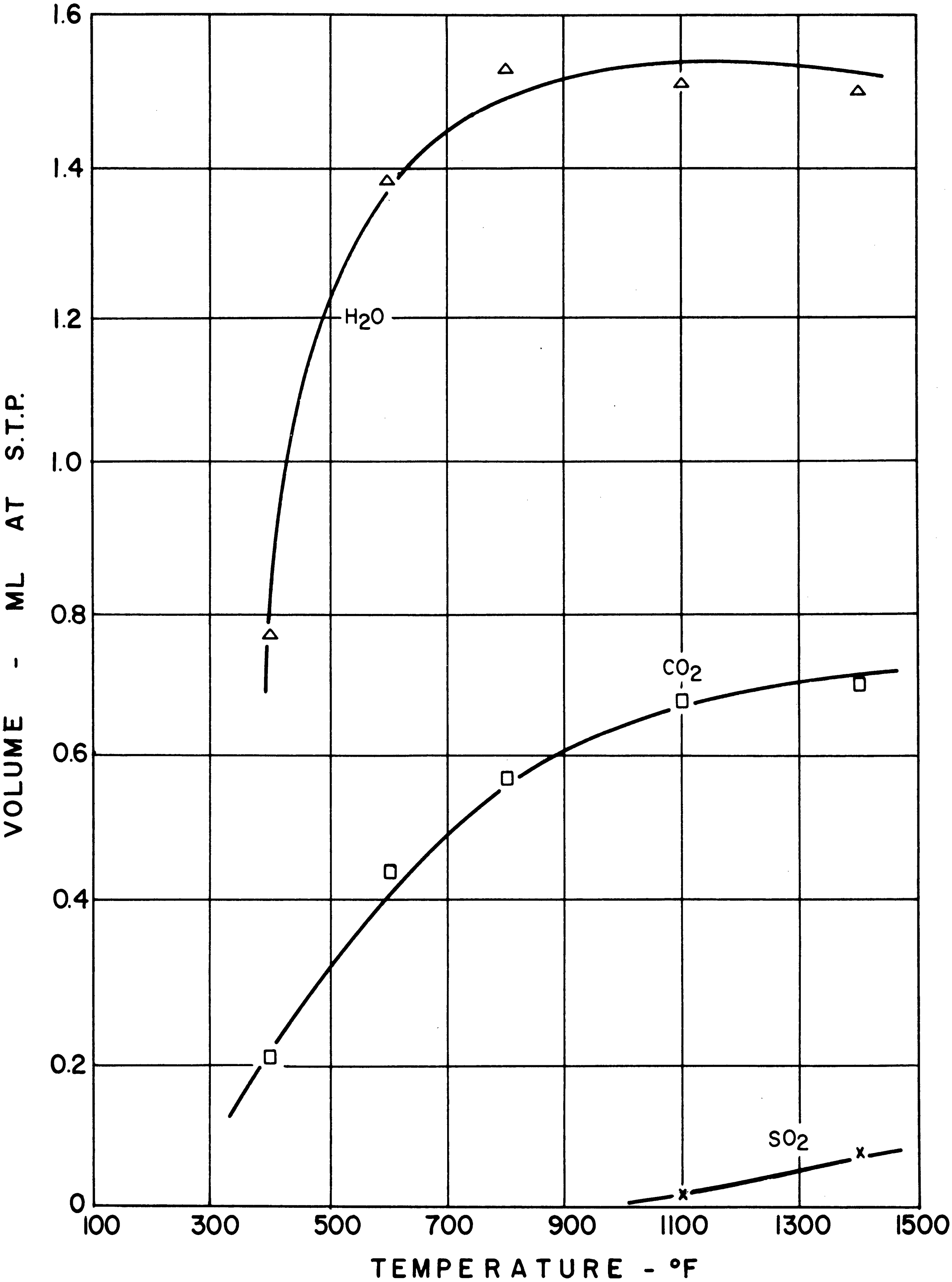

FIGURE 28. GASES COLLECTED FROM COPPER POWDER

Powder type - Air Atomized No. 2 Specimen wt. - 10 gm.

Particle size - .0017 cm. Treatment - As received.

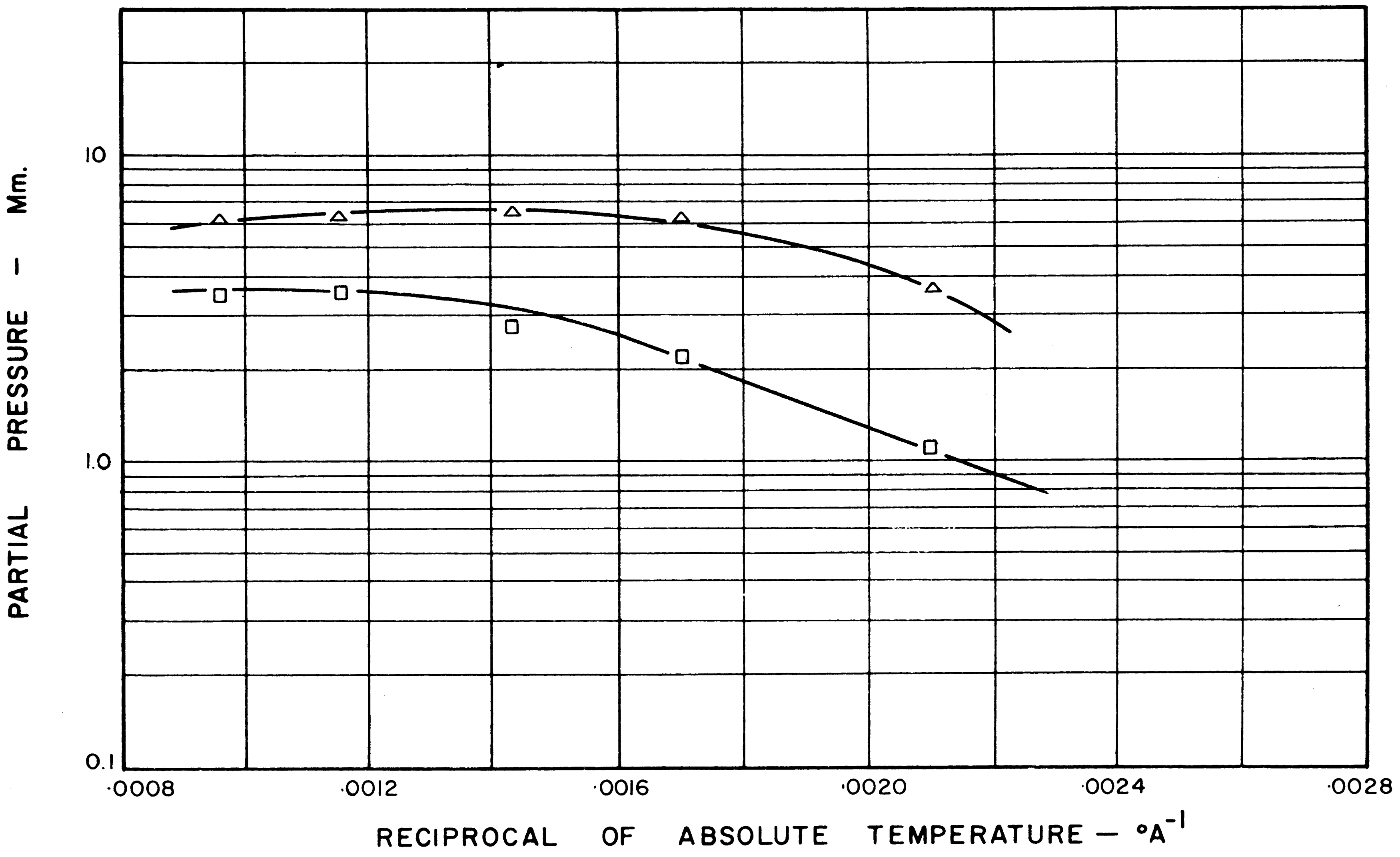

FIGURE 29. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 20.2 Mm. TOTAL PRESSURE

Powder type - Air Atomized No. 2

Approx. particle size - .0017 cm.

Treatment - As received.

H_2O ———— △

CO_2 ———— □

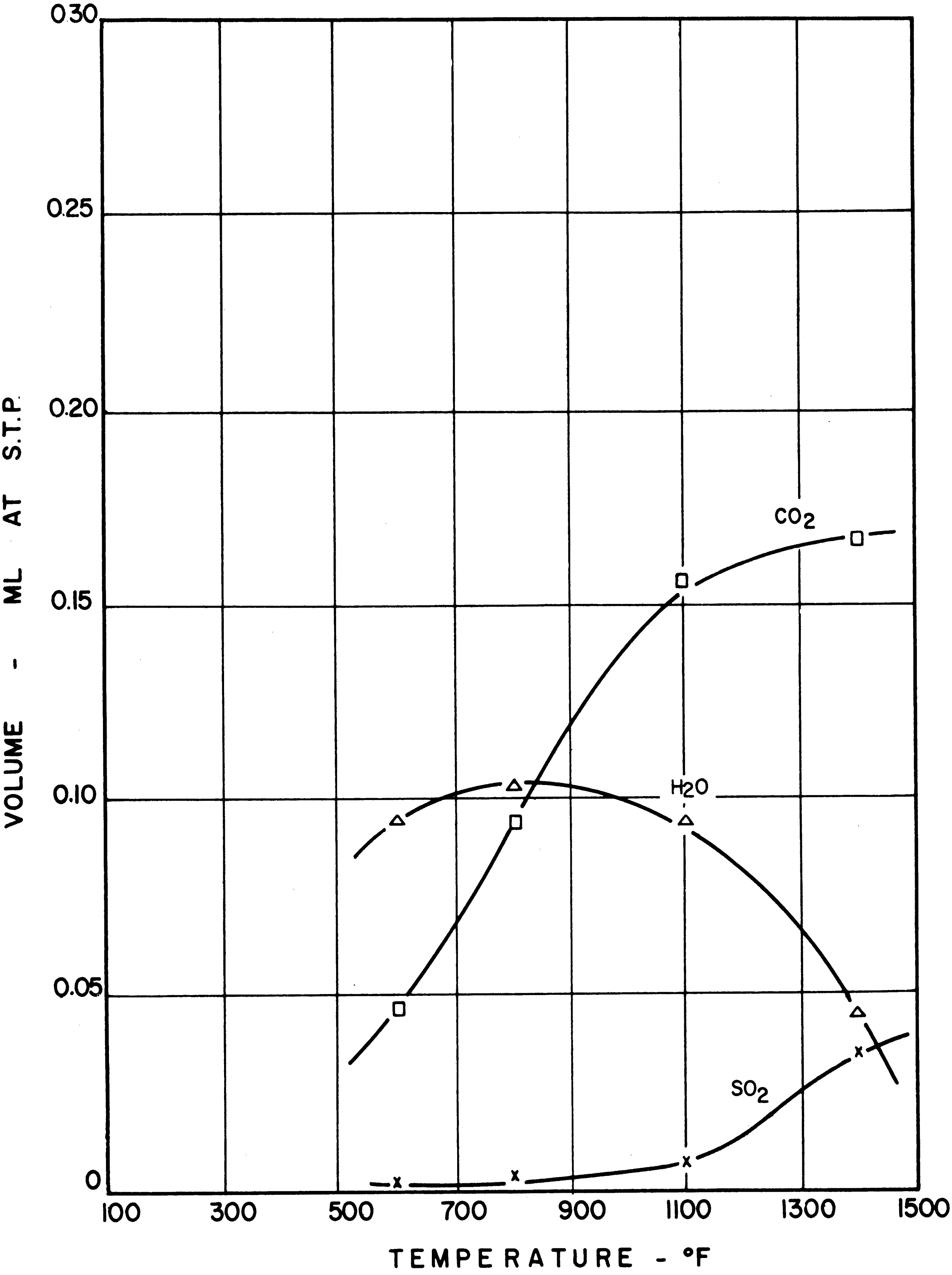

FIGURE 30. GASES COLLECTED FROM COPPER POWDER

Powder type Air Atomized No. 3 Specimen wt. - 10 gm.
Particle size - .023 cm. Treatment As received.

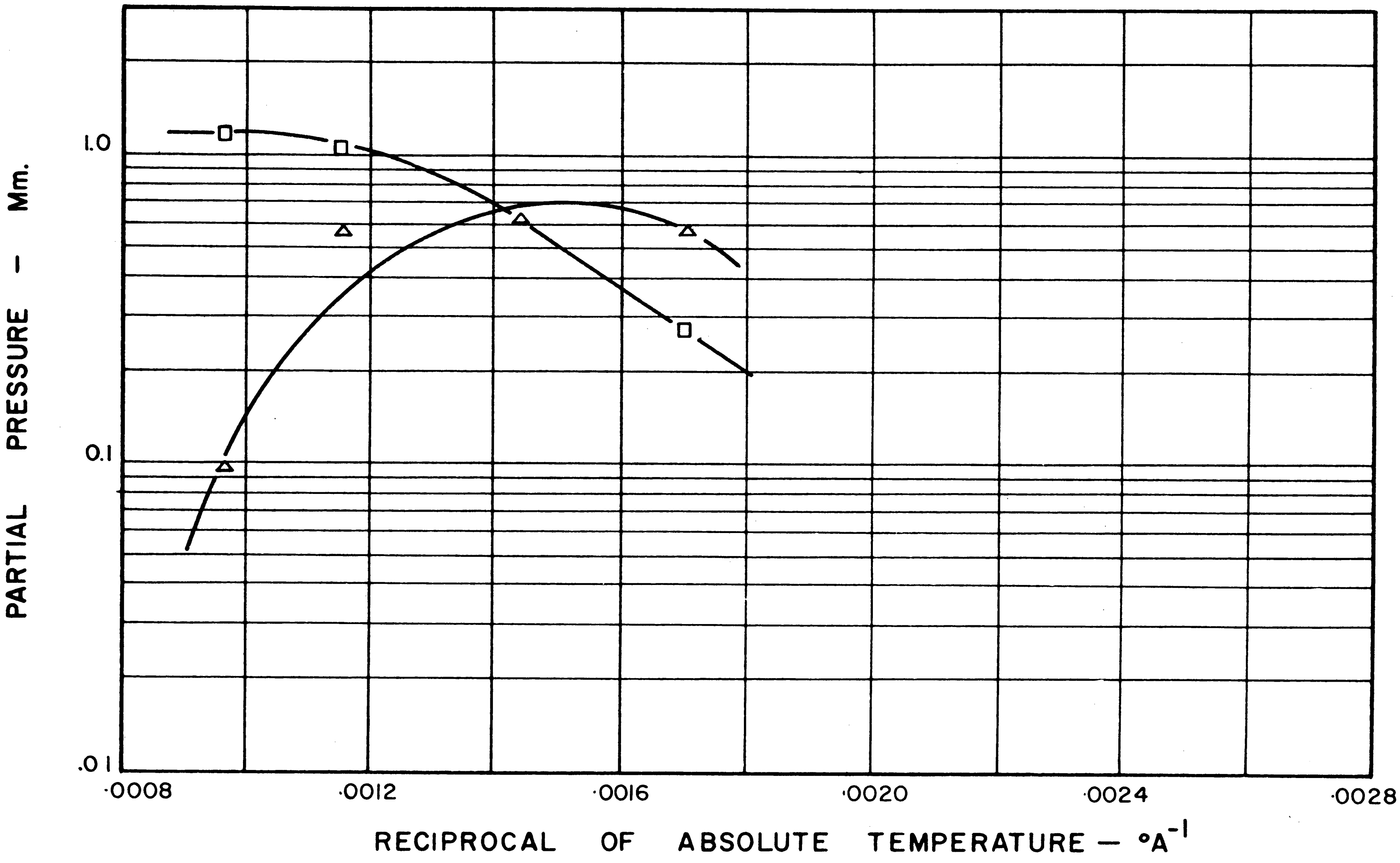

FIGURE 31. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 20.1 Mm. TOTAL PRESSURE

Powder type - Air Atomized No. 3

Approx. particle size - .023 cm.

Treatment - As received.

H_2O ——— △

CO_2 ——— □

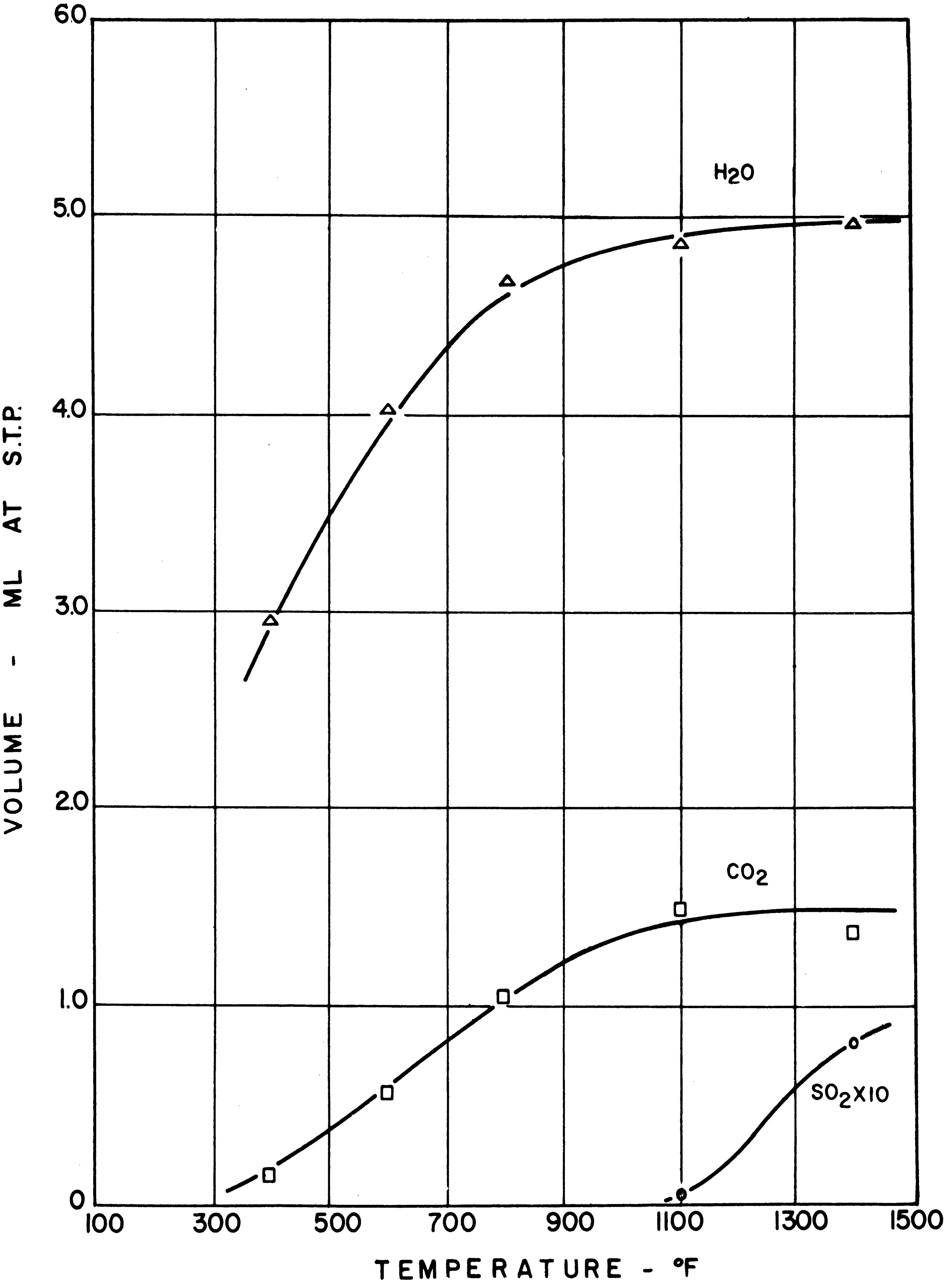

FIGURE 32. GASES COLLECTED FROM COPPER POWDER

Powder type - Electrolytic

Particle size - .0003cm.

Specimen wt. - 10 gm.

Treatment - As received

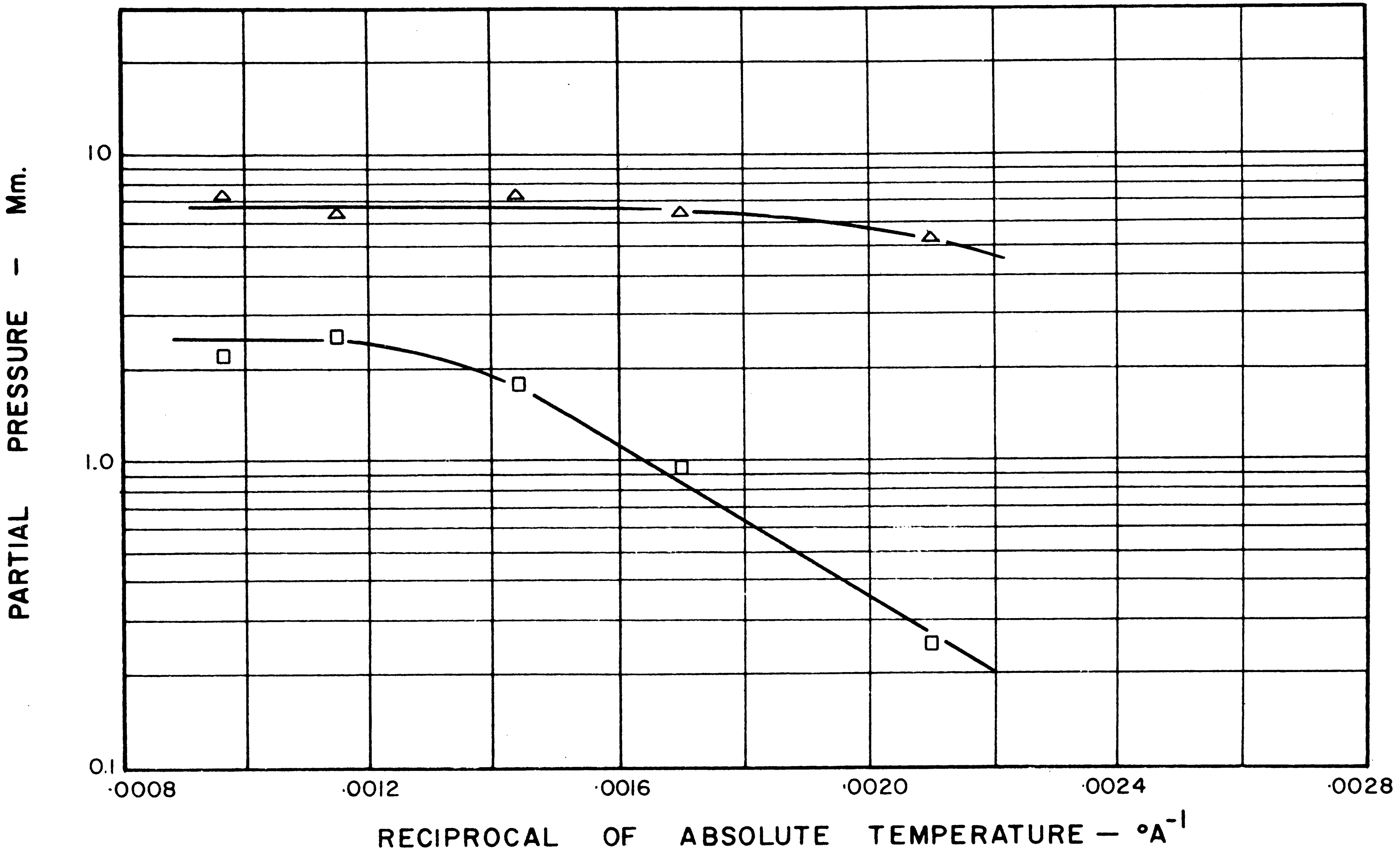

FIGURE 33. THE EFFECT OF TEMPERATURE ON THE PARTIAL PRESSURE OF GASES OVER COPPER POWDER IN A CLOSED SYSTEM UNDER 19.8 Mm. TOTAL PRESSURE

Powder type - Electrolytic.
Approx. particle size - .0003 cm.
Treatment - As received.

H_2O ——— △
CO_2 ——— □

DISCUSSION

All types of copper powder when heated in a helium atmosphere at a total pressure of 20 millimeters of mercury, liberated appreciable quantities of gas. A corresponding quantity of gas was also evolved at other pressures. Twenty millimeters represented a convenient outgassing pressure since the volumes of the evolved gases at this pressure could easily be accommodated in the measuring manifold. The sensitivity of the measurements of changes in gas volumes, which is inversely proportional to total pressure, was also of reasonable value in this pressure range.

The mode of gas evolution as a function of time at a constant powder temperature has been shown in Figure 10. These data are for the reagent type powder, but similar behavior is noted for any of the powders investigated. It can be seen that evolution at any given temperature is essentially complete at the end of one-half hour. For this reason one hour at temperature was considered to be sufficient time for outgassing at a given temperature. In Figure 10 only the isothermal evolution of gas is recorded, however gas was also evolved while the powder specimen was being heated to the temperatures indicated. It was observed that gas evolution occurred continuously whenever a powder specimen was heated. This gas evolution was irreversible in that subsequent cooling did not cause reabsorption nor did reheating to a temperature below the maximum attained previously result in any further gas evolution.

Upon examination of the figures showing the cumulative volumes of gas collected at various temperatures, such as Figure 11, it is apparent that the gases evolved at powder temperatures below 200°F to 300°F are generally negligible in quantity.

Gases were collected to powder temperatures of 1400°F. This represents the maximum attainable temperature with the Vycor tubes operating under reduced pressure for extended periods of time. While no data are presented for evolution above 1400°F, it is believed that the major portion of the gases that would evolve have been removed at this temperature.

From the mass spectrometer analyses of the gases collected from the various powders, it is apparent that in all cases these consisted of water vapor, carbon dioxide, sulphur dioxide and hydrogen. Work to be discussed later showed that hydrogen did not evolve as such from the powders. It was instead found to form from water vapor in contact with the hot copper powder. The amount of water vapor was at least equal in volume to the volumes of any of the other components evolved and in general was considerably greater. The carbon dioxide was the next most abundant component generally found while the sulphur dioxide was usually found to be present only in trace quantities.

It was noted that the appearance of most of the powders investigated changed considerably during outgassing. As a rule all but the very dark powders were appreciably brighter after testing than in the as-received condition. Admittedly, powder color is not a good criterion on which to base conclusions about changes occurring during testing, but extensive X-ray and electron diffraction studies made for this purpose, did not yield any further information about the nature of the surface films causing the observed discoloration. The failure of X-ray diffraction techniques to produce any identifiable patterns was thought to be due to the small quantity of film present. Difficulties arising with the use of electron diffraction techniques on the powder samples were such that the causes of negative results could not be definitely ascertained. Chemical treatments lead to the belief that these surface films are oxides with CO_2, H_2O and SO_2 associated chemically with the film.

Water Atomized Powder

The data resulting from this investigation of water atomized copper powder are presented graphically in Figures 11 through 24. The majority of these are presentations of the cumulative volume data, and partial pressure data as functions of powder temperature. These are the basis for the following observations.

Water vapor starts to come off the powder in appreciable quantities at a temperature of about 300°F and appears to be completely evolved in the temperature range 800° to 900°F. Above 900°F there is a reversal in the quantity of water vapor over the powder. It will be noted that the temperature at which hydrogen is first found in any quantity over the powder corresponds to the temperature of the reversal in the water vapor curve. From this fact, it was deduced that the following chemical reaction must occur.

$$H_2O + Cu \longrightarrow Cu(O) + H_2 \qquad \text{Eq. No. 2}$$

The water vapor in contact with the hot copper dissociates into hydrogen and oxygen. The oxygen is immediately dissolved in the copper and is evidenced by the lack of oxygen in the gas over the powder. Subsequent diffusion of the oxygen into the copper interior accounts for the reaction proceeding as written. This is believed to be a reasonable mechanism for the occurrance of hydrogen over this powder since the powder is originally relatively free of oxygen. This fact is borne out by the small Cu_2O content of the microstructure shown in Figure 1. The apparent decrease in water vapor volume over the water atomized powder of mixed particle size, shown in Figure 11, corresponds to an oxygen pickup of about 10^{-3} weight percent. This amount of oxygen would not result in a noticeable oxide increase of the outgassed powders since it only slightly exceeds the solubility limit of oxygen in copper, even at room temperature (35). Examination of the microstructure after outgassing did not show any increase in oxide content.

An examination of Equation 2 shows that there is no net volume change if the reaction occurs as written. Looking now at the hydrogen volume as a function of temperature it will be noted that it is not sufficient to account for the reversal in the water vapor volume in any of the plots showing these data for the water atomized powder. In some of the cases the quantity of hydrogen reaches a maximum and then decreases at higher powder temperatures. These facts lead to the hypothesis that hydrogen is also being dissolved into the copper powder from the water vapor above it. Calculations based on the net decrease in hydrogen at 1400°F over the water atomized powder of mixed particle size, Figure 11, indicate that about 10^{-4} weight percent of hydrogen is dissolved in the powder specimen. This is probably a reasonable value, but one that cannot be verified, since solubility of hydrogen is a function of its partial pressure, temperature and the oxygen content of the powder.

The occurrence of this reaction was investigated by outgassing a sample of this powder and then enclosing it in the specimen manifold of the outgassing apparatus in contact with an atmosphere consisting of water vapor and helium. The powder was then heated to the various test temperatures for one hour. Results of analyses of the atmosphere over the powder at these temperatures are plotted in Figure 25. A marked decrease in the amount of water vapor in this atmosphere is seen to occur in a manner quite analogous to the decrease occurring in the water over the powder during outgassing. It is also apparent that the amount of hydrogen in these gases is not sufficient to completely account for the decrease in water vapor. A similar test run with no copper powder in the specimen tube showed that the water had no tendency to dissociate in contact with the apparatus alone. Further evidence for the occurrence of the postulated reaction between water vapor and the hot copper powder is given in the results shown in Figure 24. In the test, after 198 hours exposure to air, the water vapor pressure over the hot powder was kept at a minimum value with the aid of a dry ice alcohol mixture around the trap in the specimen manifold. It can be seen that this procedure effectively curtailed the reversal in the amount of water vapor and eliminated hydrogen as a component from the gases found over the powder.

The logarithm of the partial pressure of water vapor over the copper powder versus 1/T plots all show reversals at higher temperatures, indicating that some additional reaction or reactions other than desorption of water is occurring.

Carbon dioxide starts to evolve from these powders below 300°F and continues to the maximum temperature investigated, 1400°F. The logarithm of the partial pressure of the carbon dioxide over the copper powder versus 1/T yields a linear plot indicating that a simple desorption process is the source of this gas. The carbon dioxide is most likely chemisorbed on the copper powder surface, that is, the carbon dioxide is chemically bonded to the copper and not just physically adsorbed on its surface. If the gas were physically adsorbed on the powder, a constant activation energy, heat of decomposition, as indicated by the straight line nature of the plots would not be expected.

Binding forces vary with the amount of adsorbed material in the physical adsorption process and this results in heats of desorption that vary as a function of the amount of adsorbed material left on the surface.

Reference to Table XX shows that the heats of decomposition calculated from the slopes of the partial pressure plots for carbon dioxide vary from 1820 cal/g mole to 3540 cal/g mole for the water atomized powder outgassed in the as-received condition. These values are relatively low for a chemical binding. If, however, it is assumed that an intermediate compound of the type $CuO \cdot CO_2$ is the source of the carbon dioxide, they are reasonable. If the compounds were similar in nature to $CuCO_3$ heats of decomposition of the order of 8000 cal/g mole to 11000 cal/g mole would be expected.

The quantity of sulphur dioxide evolved from the water atomized powder is extremely small, but real. The sulphur dioxide starts to evolve at about 700°F to 800°F and shows a maximum in the cumulative volume plot near 1200°F, after which the quantity decreases. Here again a chemical reaction between the copper powder and the evolution product is thought to occur. A reaction of the following type is postulated.

$$Cu + SO_2 \longrightarrow Cu(O) + Cu(S) \qquad \text{Eq. No. 3}$$

In this reaction both the sulphur and the oxygen are dissolved in the copper powder at the elevated temperature.

From the foregoing it was believed that the evolved gases originated on the powder surface. If this is actually the case then the quantities of gases evolved should be some function of the particle size of the powder being outgassed, since a constant weight of powder, 10 grams, was used for each outgassing operation. From the cumulative volume plots of Figures 13, 15, 17 and 19, which include data from four mesh fractions of the water atomized powder, it can be seen that there is an increase in the maximum gas volumes evolved as the powder size decreases.

Figure 21 shows a plot of the total volume of water vapor evolved as a function of specimen areas for the same four mesh fractions of powder. Measured particle diameters were used to calculate the areas on the basis of spherical particle shapes. This plot does not show the linearity that should exist in the relationship between water vapor volume and area. The nature of the deviation is such as to indicate that it is due to the difference between the assumed particle shape and the actual, which would in turn affect the calculated areas. This condition was not unexpected since the particle shape became more irregular as the size of the particle increased. The larger sizes were actually porous and mossy like. Attempts were made to determine the true surface areas of the mesh fractions by various techniques such as adsorption of stearic acid from a methanol solution, but the results were unsatisfactory due to chemical reactions between the powders and the solutions used. Failing in obtaining an experimental verification of the surface areas, the water vapor data were corrected to yield a linear plot. From this curve, shown in Figure 21 as the water vapor versus the corrected area plot, values of the corrected areas for the mesh fractions were determined. The ratios between the corrected areas and the calculated areas were considered as roughness factors and had values which ranged from 6.5 for the coarse powder to 2.1 for the finest fraction. These factors are tabulated in Table VII.

The total volumes of carbon dioxide and sulphur dioxide evolved from the same mesh fractions considered above showed relationships to the calculated surface areas similar to that for water vapor. On plotting these gas volumes against the corrected areas obtained from the water vapor data, the curves shown in Figure 21 resulted. It can be seen that both of these gases correlate well with the corrected areas. Since the three gas components are present on the water atomized powder fractions in a fairly constant ratio, this result is to be expected, if the corrected area values have any real physical significance. Further verification of the procedure used to correct the area values is presented in Figure 22. This is a plot of the volumes of water vapor and carbon dioxide against the same corrected areas for the mesh fractions of water atomized powder after cleaning in NH_4OH. The resulting plots are seen to be linear even though a marked decrease in total quantity of gas is noted. It would appear on this basis that the surface area with which the gas is associated is a function of the copper powder particle shape rather than the porosity of the surface films, since these films are not present after the cleaning operation.

The powders that were chemically cleaned in NH_4OH and then tested for total gas evolution, Figure 22, showed a marked decrease in the quantities of water vapor and carbon dioxide that were evolved, while the sulphur dioxide was completely absent. The cleaning operation yielded a powder that was completely free of any obvious surface film or coloration. This is still further proof of the surface origin of the evolved gases and indicates that they are associated with the observed darkened powder surfaces.

The cleaning action of the NH_4OH was not due to a solutioning of the surface films, but to the solution of the underlying copper. Turbid solutions containing a fine brown precipitate resulted from the cleaning operation. Subsequent addition of hydrochloric acid to the decanted liquid containing the precipitate resulted in its immediate clearing, leading to the conclusion that the films were hydrated oxides of copper. These are insoluble in NH_4OH, but they are soluble in ammonium chloride solutions.

The carbon dioxide and water vapor remaining on the powder after cleaning were thought to have been picked up during or after the cleaning process. Tests were made on cleaned powders that were allowed to stand under atmospheric conditions for periods up to 198 hours. These data are the bases of the plots shown in Figures 23 and 24. It can be seen that the cumulative volume plots do not show any noticeable increase in the amounts of water vapor and carbon dioxide. The powder remained bright and tarnish free even after six months in the atmosphere. The heats of decomposition, calculated from carbon dioxide partial pressures over these powders, were considerably higher than those obtained for the as-received powder, indicating a stronger chemical binding. It is thus evident that the remaining material on the copper surface was altered by the cleaning operation if not completely replaced by another compound.

Some of the water atomized powder was treated with nitric acid to remove the surface films and then as outgassed. The quantity of gas evolved on immediate testing was somewhat smaller than on the as-received powder, but the analyses was not obtained because of the presence of the oxides of nitrogen in the evolved gases. It is very difficult to obtain analyses of these gases because of their unstable nature. These oxides of nitrogen were present even after extensive cleaning of the powder after the nitric acid treatment. Allowing the powder to stand for a period of a few days produced extensive darkening of its surface and the quantity of gas evolved was considerably greater than with the powder immediately after cleaning.

Air Atomized Powders

The gas evolution data for the air atomized powders are presented graphically in Figures 26 through 31. These data were taken to determine if the same gases were desorbed from these powders as from water atomized powders.

The data show that the same gases are evolved from all three of the air atomized powders tested. The quantities evolved, however, are not comparable to the quantities evolved from the water atomized powder. On the basis of specific surface area as calculated from the particle sizes, it would be expected that greater quantities of gas should be desorbed from these powders, but this was not the result observed on testing. Powder No. 1, the finest of the three powders, actually evolved about the same quantity of gas as the coarsest of the water atomized powder fractions. Powder No. 2 evolved a slighter greater amount of gas than the finest water atomized powder while powder No. 3 evolved less gas than any of the other powders tested. These data indicate that some factor other than specific surface area is controlling the quantities of gases desorbed from these powders.

The appearance of the air atomized powders varied markedly for the three powders tested. Powder No. 1 was bright. Powder No. 2 was reddish brown and Powder No. 3 was very badly oxidized. The third powder evolved the least quantity of gas of the three while the second evolved the greatest quantity, this latter powder was quite similar in appearance to the fine fractions of water atomized powder. These facts give further emphasis to the relationship between the powder surface condition and the subsequent gas evolution.

From the analyses of the total gas evolved into a cold trap, shown in Tables VIII and XIX, it is apparent that the ratios of water vapor to carbon dioxide are considerably different for these powders. This leads to the concept that different surface compounds are formed on the air atomized powders than on the water atomized powders during or subsequent to atomizing. As further evidence of this, the partial pressure data of the carbon dioxide over the air atomized powders indicated that the heats of decomposition, as shown in Table XX for two of the three powders, were considerably greater than those obtained for the water atomized powder. The lowest heat of decomposition found for the air atomized powders, that found for Powder No. 2, corresponds to values obtained with the water atomized powder and the water vapor to carbon dioxide ratio for this powder is also more in line with that found for the water atomized powder. Thus, although the gases evolved are the same as those from the water atomized powder it appears that the association of these gases with the surface is different.

Still further differences between the two types of powders can be noted from the cumulative gas volume data. Very little hydrogen was found in the gases over the air atomized powders at elevated temperatures. With all the powders a drop in the quantity of water vapor found over these powders is noted at elevated temperatures indicating that a reaction did occur between the water vapor and the hot powders. The sulphur dioxide content of the gases over all three powders did not show the reversal at high temperatures found with the water atomized powders. A comparison, however, of total gas volumes with the cumulated gas volumes indicates the same reaction did occur in each case.

The hydrogen present over the water atomized powders would indicate that the powder was relatively high in hydrogen content, and the nature of the water atomization would lead one to expect this high hydrogen content. The air atomized powder, on the other hand, was relatively free of hydrogen and thus could accommodate the hydrogen from the dissociated water vapor at a relatively low hydrogen pressure. It is believed that the sulphur dioxide reversal did not occur as strongly with the air atomized powders as with the water atomized because of the extremely high oxygen content of these powders as shown in Figures 2, 3 and 4.

Electrolytic Powder

The electrolytic copper powder was investigated to determine whether a marked change in manufacturing method affects the composition of the gases evolved from the powder.

The powder tested was extremely fine, of the order of three microns diameter, and was reddish brown in appearance. On the basis of the experience with the air atomized powder it was anticipated that large quantities of gas would be evolved from powder with this appearance. As can be seen from the plot of cumulative gas volumes for this powder, Figure 32, large quantities of gas were evolved when the powder was heated, even larger quantities than had been anticipated. The gases were of the same composition as previously noted with other powders: water vapor, carbon dioxide and sulphur dioxide. The ratio of water vapor to carbon dioxide compared favorably to that ratio found with the air atomized powder. Total gas volumes evolved are shown in Table XIX, these are the data from which the ratios are calculated.

The heat of decomposition as calculated from the carbon dioxide partial pressure data is of the order of 5000 cal per gram mole, a value higher than that obtained for the water atomized powder, but lower than the values obtained on two of the air atomized powders. No reversals are noted in the water vapor and sulphur dioxide in the cumulative plots of these components, however the total gas analyses show some differences from the cumulative data, indicating that reactions were occurring.

Other Powders

A reagent type copper powder marketed by Mallinckrodt Chemical Company, and a powder of unknown origin were tested for total gas evolution and composition as further verification of the evolution of gases from powders stored under somewhat different conditions.

In size and appearance the reagent type powder was similar to the air atomized powder No. 2. This similarity is also noted in the microstructure of the powder shown in Figure 7. The total gas evolution, Table XIX, showed that the similarity between these powders went still further in that the gas compositions were very similar. The greater quantities of the gas components evolved from the reagent type powder are readily explained by the differences in powder size. Air atomized powdwr No. 2 was 17 microns in diameter, while the reagent type was about 13 microns, thus the reagent type powder has the higher specific area.

The unknown powder was similar in structure and appearance to the electrolytic powder as can be seen in Figures 5 and 6. The total gas volumes evolved from this powder were also markedly similar to those found with the electrolytic powder. One exception is to be noted, as shown in Table XIX the quantity of sulphur dioxide evolved from the unknown powder is very much larger than that found with the electrolytic powder. This difference is believed to be the result of absorption of this component on standing in the laboratory for a period of at least ten years. An indication of the origin of these surface gases is thus given by this difference in sulphur dioxide evolution.

Origin of Evolved Gases

This study has shown that the same gases are present on all of the copper powders and that they are associated with the powder surface. The gas evolution results from the decomposition of a surface layer on the powder. The variations in manufacturing methods produce such a wide divergence of the powders' environments that it is hardly likely that similar gas components would be adsorbed on all of the powders. It is much more probable that the surface of the powders are subject to corrosion on contact with the atmosphere. The gases desorbed indicate that the surface layers are similar in composition to patina and verdigris, which contain mixtures of sulphates, basic carbonates, copper oxides and copper hydroxides. These products are frequently found on massive copper after prolonged atmospheric corrosion.

The ratios of the evolved gases do not in all cases correspond to the decomposition of definite chemical compounds such as $CuSO_4 \cdot 5\ H_2O$, $2\ CuCO_3 \cdot Cu(OH)_2$ and $CuCO_3 \cdot Cu(OH)_2$. Further, the heats of decomposition for these compounds are greater than the heats of decomposition obtained for the powders investigated. Values of 8,000 to 11,000 would be expected for decomposition of the carbonates while values of 2,000 to 6,000 were found. On the other hand the linearity of the partial pressure of carbon dioxide versus 1/T plots indicates that it is improbable that the carbon dioxide is physically adsorbed on the powder. This leads then to the conclusion that the surface compounds are intermediate to these two conditions and the source of the gases are compounds such as $CuO \cdot (H_2O)_x$, $CuO \cdot (CO_2)_x \cdot (H_2O)_y$ and $CuO \cdot (SO_2)_x \cdot (H_2O)_y$. The latter two compounds must decompose in a two step process, first losing water and then giving up carbon dioxide. The notation used is meant to imply that these are intermediate compounds only slightly more organized than physically adsorbed materials and not definite chemical carbonates and sulphates. They probably are formed on exposure to the atmosphere and in time in the presents of moisture, transform to the basic carbonates and sulphates found in patina and verdigris.

It is interesting that the powders that contained water and carbon dioxide in the same ratios as those for the basic carbonates had heats of decomposition that more closely approached the values expected with such compounds. It was also noted that with most powders the gases evolved contained an excess of water as compared to either of the basic carbonates. This is believed to indicate that the corrosion process is one in which water vapor must first be absorbed and then subsequent reactions with atmospheric carbon dioxide occur. In all probability the sulphur dioxide pickup occurs in a manner similar to that for the carbon dioxide, but since the same information about this component could not be obtained, the association of this gas with the powder could not be definitely ascertained.

CONCLUSIONS

1. All copper powders desorb water vapor, carbon dioxide and sulphur dioxide on heating to 1400°F.

2. The quantities of gases evolved are dependent on the temperature and the evolution process is irreversible in that cooling does not cause immediate reabsorption of the gases.

3. The source of these gases are surface layers on the copper powders. The gases are not physically adsorbed, but are believed to be compounded with the copper in compounds of the types $CuO \cdot CO_2$, $CuO \cdot (CO_2)_x \cdot (H_2O)_y$ and $CuO \cdot (SO_2)_x \cdot (H_2O)_y$.

4. Cleaning of the surfaces resulted in the complete removal of the sulphur dioxide from the evolved gases and a marked decrease in the amounts of water vapor and carbon dioxide.

5. The quantity of each gas evolved is proportional to surface area, in the case of the water atomized powder, indicating a fixed type and quantity of surface compound for this powder.

6. On continued contact with the hot powders the evolved water and sulphur dioxide have been shown to react with the powders.

7. The extent of the reaction of the water vapor and sulphur dioxide with the hot copper powder appears to be related to the solubilities of the dissociated components in the copper.

8. The heats of decomposition computed from the partial pressure data of the carbon dioxide evolved are lower than for chemical decomposition of known basic carbonates. The fact that they could be determined indicates that physical adsorption is not occurring.

9. The treatment of water atomized powder with NH_4OH stabilized the surface to subsequent adsorption while treatment with HNO_3 accelerated the process.

10. The appearance of powders when compared with gas evolution leads to the conclusion that tarnished powders have greater absorption than bright powders or powders with heavy oxide coatings.

11. The corrosion of copper powder in the atmosphere is a process similar to patina formation found with massive copper.

12. The volume of gas evolved on heating is sufficient to cause extremely high pressures within a sintering powder compact.

13. Vacuum treatment of compacts at intermediate temperatures would remove a large portion of the absorbed gases before sintering began.

14. Since the total quantity of gas present is a function of the surface area, a spherical powder shape should result in a minimum amount of difficulty from absorbed gases at a given particle size.

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APPENDIX A

CALIBRATION OF SPECIMEN MANIFOLD

The effective volume of the specimen manifold, shown in Figure 8, had to be determined in order to calculate the volume of evolved gas. Changes in the burette mercury level necessary to maintain constant pressure in the manifold resulted from the temperature change of the Vycor specimen tube as well as gas evolution. Therefore it was necessary to find the apparent volume of this system as a function of the specimen tube temperature.

The fixed volume of the manifold, designated as $\underline{V}_s$, was defined as that volume enclosed between stopcocks S_1, S_2, S_3, S_4, and S_7 exclusive of the burette, which was calibrated before installation. This volume was determined by enclosing dry helium in the manifold at a pressure near 150 millimeters of mercury, with the burette reading near zero. The pressure, $\underline{P}$, was then measured with the mercury manometer as a function of the burette reading r. The ideal gas law was assumed to be applicable at these low pressures. The functional relationship between pressure, volume and the burette reading is,

$$K/P = V_s + r \qquad \text{Eq. No. A-1}$$

K is a constant. A plot of 1/P versus r yields a straight line as shown in Figure A-1. The intercept of this line on the r axis is equal to $\underline{V}_s$.

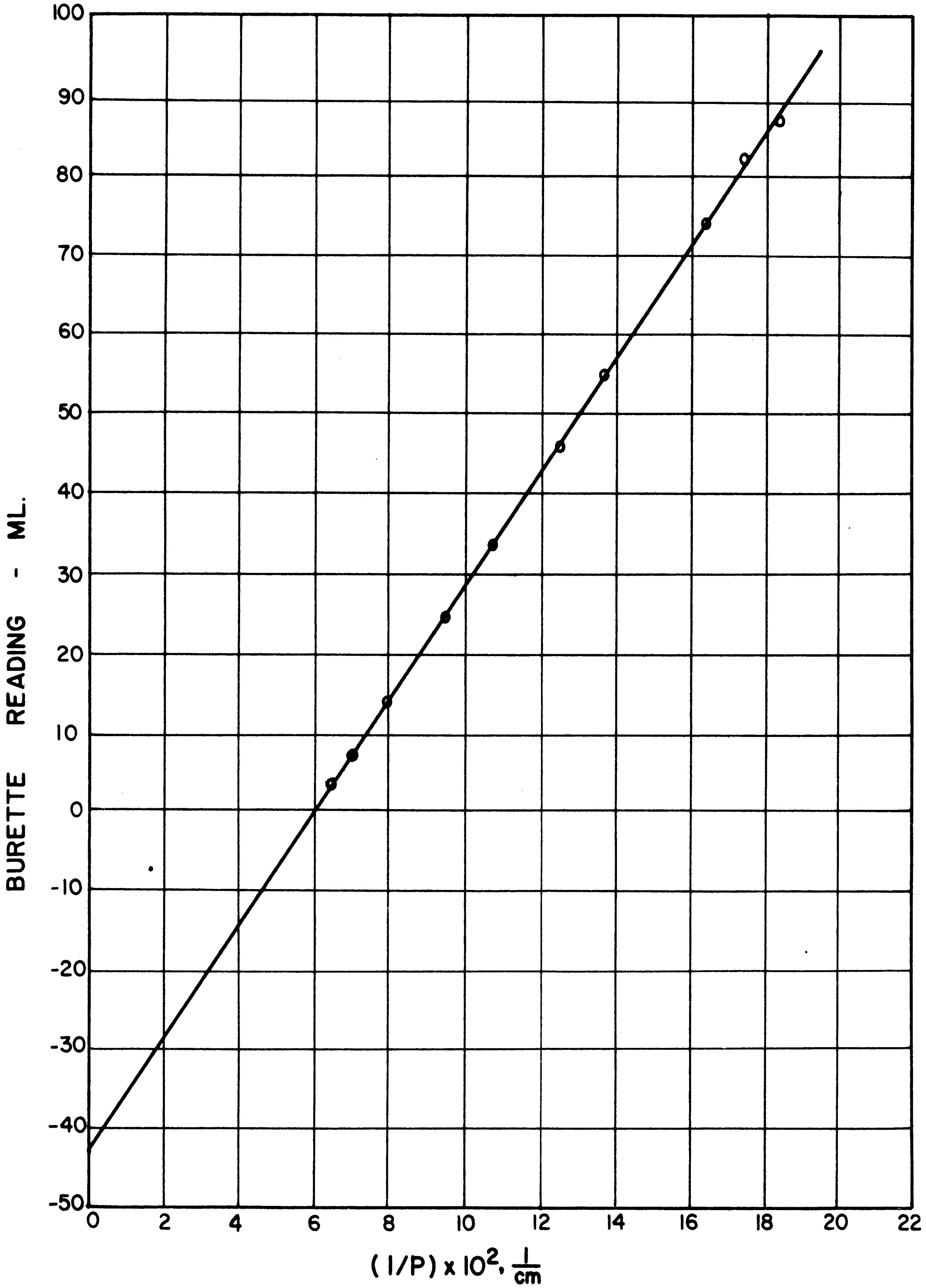

FIGURE A-1. CALIBRATION OF FIXED VOLUME OF SPECIMEN MANIFOLD.

The volume $\underline{V}_s$ can also be calculated from any two points on the line (P_1, r_1) and $P_2, r_2)$ as

$$V_s = (P_2r_2 - P_1r_1)/(P_1 - P_2) \qquad \text{Eq. No. A-2}$$

The results of typical calibrations gave values of 42.1, 42.3 and 41.6 milliliters for an average of 42.0 milliters for the volume $\underline{V}_s$. The deviation from the average value represents an error of less than one per cent.

The volume of the specimen tubes $\underline{V}_t$ were determined separately since several tubes were used during the course of the investigation. A separate determination made repetition of the calibration procedure for the fixed system unnecessary at each change of specimen tube. The specimen tube volume was determined by enclosing an amount of helium in the fixed system at a given pressure and burette reading $\underline{r}_1$ and the opening stopcock $\underline{S}_7$ connecting the previously evacuated specimen tube to the manifold. The pressure was then returned to its original value and a new burette reading was recorded $\underline{r}_2$. The volume of the specimen tube was then equal to the difference in burette readings.

$$V_t = r_1 - r_2 \qquad \text{Eq. No. A-3}$$

Several determinations were made for each tube. A typical group of readings gave values of 26.3, 26.5 and 26.7 milliliters as the volume of a specimen tube for an average value of 26.5 milliliters. The close agreement of the three determinations represents a deviation of less than one per cent from the average value of the tube volume.

The effective volume $\underline{V}_e$ of the manifold varied with the temperature $\underline{T}_2$ of the heated portion of the specimen tube. A relation between this temperature and the effective volume was developed as follows,

Letting $\underline{V}_1$ and $\underline{V}_2$ represent the volumes of the two sections of the manifold at the two temperatures $\underline{T}_1$ and $\underline{T}_2$ respectively, where $\underline{T}_1$ is room temperature, $\underline{n}_1$ and $\underline{n}_2$ are the amounts of gas in the manifold at these same temperatures. We can write the ideal gas law in terms of the effective volume as,

$$PV_e = (n_1 + n_2) R\,T_1 \qquad \text{Eq. No. A-4}$$

Substituting into Equation A-4 the expressions of the amounts of gas in each section of the manifold in terms of the pressure which is constant, the volumes, and the temperatures of these sections gives an expression for $\underline{V}_e$.

$$V_e = V_1 + V_2\,(T_1/T_2) \qquad \text{Eq. No. A-5}$$

From Equation A-5 it can be seen that a plot of $\underline{V}_e$ versus T_1/T_2 gives a straight line. $\underline{V}_e$ is determined by noting the change in burette readings as the temperature of the specimen tube is raised with a constant pressure of helium enclosed in the manifold. The plot, an example of which is shown in Figure A-2, is useful since it is applicable for all conditions of ambient temperature. Corrections were taken from this curve

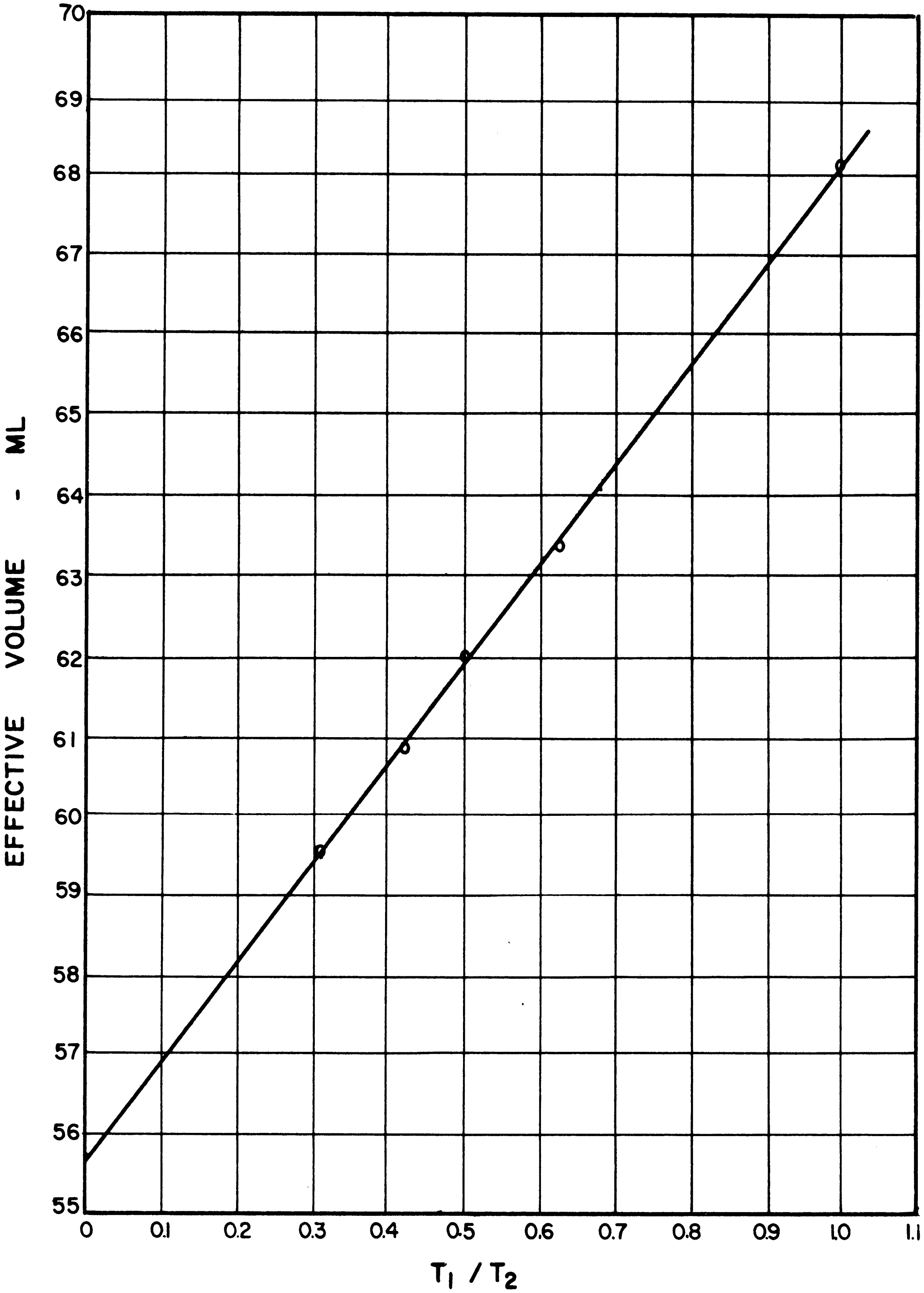

FIGURE A-2. EFFECTIVE VOLUME OF SPECIMEN MANIFOLD AS A FUNCTION OF SPECIMEN TUBE TEMPERATURE (T_2).

and subtracted from the burette changes in calculating the volume of evolved gas when a temperature change occurred between the two burette readings from which the volume was being calculated.

Several determinations of this calibration gave values of $\underline{V}_e$ at a given temperature which varied by less than 0.5 milliliters. This represents an error of less than one per cent in the volume, which varied from a value of 68 milliliters to 59 milliliters over the range of 70°F to 1400°F. On the basis of this reproducibility and the linear nature of the plot, calibration can be made with only two data points, one of which can be taken at room temperature where the effective volume is known.

APPENDIX B

MATRIX AND SENSITIVITY CALCULATIONS FOR THE MASS SPECTROMETER

In a gas mixture of several components the parent peaks, those on which the mass spectrometer sensitivities are calculated, frequently coincide with those of cracked fragments from other components. It is therefore necessary to distinguish between the parent peak and the additive effects of other components. Since the various coincident peaks add linearly, an expression from which the parent peak can be found is easily developed as the sum of the various intensities. Considering the peak height as the intensity $\underline{I}$, we can write the following sum.

$$I_1 = A_{11}I_{p1} + A_{12}I_{p2} + \dots\dots A_{1n}I_{pn} \qquad \text{Eq. No. B-1}$$

Where I_{pn} is the intensity of the parent peak of the nth component in the inlet system. Its value is related to the partial pressure of the component as follows,

$$P_n = I_{pn}/S_n \qquad \text{Eq. No. B-2}$$

$\underline{S}_n$ is the sensitivity of the mass spectrometer for the nth component.

In Equation B-1 the constants A_{1n} are the ratios of the peak contribution at the M/e value to the parent peak intensity for the component n. The constants so determined for all of the peaks in the spectrum of a given component are called the cracking pattern.

A system of n components will give n equations of the type shown in Equation B-1. A spectrum for the mixture will give values for I_1 through I_n which can be expressed as shown below.

$$
\begin{aligned}
I_1 &= A_{11}I_{p1} + A_{12}I_{p2} + \cdots\cdots \quad A_{1n}I_{pn} \qquad \text{Eq. No. B-3}\\
I_2 &= A_{21}I_{p1} + A_{22}I_{p2} + \cdots\cdots \quad A_{2n}I_{pn}\\
&\cdot\\
&\cdot\\
I_n &= A_{n1}I_{p1} + A_{n2}I_{p2} + \cdots\cdots \quad A_{nn}I_{pn}
\end{aligned}
$$

To determine the amount of each component present the equations in B-3 must be solved for I_{p1} through I_{pn}. In a simple case, where most of the A values are zero, the solution may be made directly. When many of the A values are finite and n is greater than 3 or 4, the solution may be more readily obtained by computer techniques. The solution involves an n by n matrix made up of the coefficients of the equations in B-3.

The computer uses a method of successive approximations in this solution. In order that the approximations converge to a solution in a minimum of operations, the matrix must be properly arranged. The highest coefficients, which are unity by definition, are arranged along the diagonal of the matrix from upper left to right. The zero valued coefficients are best handled in the upper right hand portion of the matrix.

A matrix of this type was derived for a system containing helium, water vapor, carbon dioxide, carbon monoxide, nitrogen, oxygen, sulphur dioxide and hydrogen. The derivation was made by running the pure components through the mass spectrometer. The resulting derived matrix is shown in Table B-I.

In the matrix of Table B-I the columns are the cracking patterns of the pure standards and the rows correspond to the coefficients in Equation B-3. Since the parent peaks of both carbon monoxide and nitrogen occur at an M/e ratio of twenty-eight, this peak was used to calculate the sensitivities for both of these components. Because of the lack of spectral resolution this peak was not included in the matrix. As a result the coefficients for the twelve and fourteen peaks that were used are necessarily calculated as a fractional relation of these to the twenty-eight peak. This results in the diagonal terms being less than unity. In practice the twenty-eight peak and the sixteen peak were frequently used to check the matrix calculation by determining a balance around these two peaks. This operation was quite sensitive to errors in peak determination or to shifts in cracking patterns, since the two peaks occurred in the cracking patterns of several of the components.

The same standard runs were used to calculate the sensitivities of the instrument for the various components. The

TABLE B-I

DERIVED MATRIX

COMPONENT		He	H_2O	CO_2	H_2	CO	N_2	O_2	SO_2
M/e	n	1	2	3	4	5	6	7	8
4	1	1.0000	0	0	0	0	0	0	0
18	2	0	1.0000	0	0	0	0	0	0
44	3	0	0	1.0000	0	0	0	0	0
2	4	0	.0019	0	1.0000	0	0	0	0
12	5	0	0	.1010	0	.0811	0	.0067	0
14	6	0	0	.0007	0	.0097	.1411	0	0
32	7	0	0	.0007	0	0	0	1.0000	.1461
64	8	0	0	0	0	0	0	0	1.0000

\- - - - -

operation was quite simple, consisting of a division of the parent peak height by the pressure of the pure gas in the inlet system. An example of the values found for various gas sensitivities is given in Table B-II. These are in units of divisions (peak height) per micron (pressure). Cracking patterns vary with the conditions of the instrument, as do the sensitivities, consequently frequent calibrations must be made.

TABLE B-II

MASS SPECTROMETER GAS SENSITIVITY

Component	Sensitivity Divisions Per Micron
Helium	11.15
Water	38.84
Carbon Dioxide	68.13
Hydrogen	30.53
Carbon Monoxide	64.10
Nitrogen	61.29
Oxygen	48.41
Sulphur Dioxide	52.22

APPENDIX C

GAS ANALYSES

The two techniques used for determining the gas analyses differed in the following respects. In the detailed method initially used, the matrix determination of the parent peak intensities was necessary and the water content of the gases was determined by freezing it in the collection manifold. In the second method the minor components are ignored and the water is determined by difference, using a material balance. An example of treating the same data by both methods is shown below and the results of the analyses are compared.

Data taken on the specimen manifold for this test are shown in Table C-I.

The mass spectra of the five gas samples taken during the outgassing operation are listed in Table C-II along with the sample analyses found by the two methods used.

TABLE C-I

SPECIMEN MANIFOLD GAS DATA

Powder type Water Atomized
Particle Size 0.030 cm.
Pressure 20.2 millimeters
V_s 42.00 milliliters

Treatment As Received
Specimen Weight 10 grams
Room Temperature 82.4°F
F (H_2O) 1.6 milliliters

	Temp.	X	r	V_e	H_2O	$V_s + r$	% H_2O	Sample
400°F	82.4	1.000	36.6	68.5				
Gas Sample	400.0	0.630	62.7	63.7	14.0	104.7	13.37	19.6
600°F	400.0	0.630	43.1	63.7				
Gas Sample	600.0	0.512	66.0	62.2	28.0	108.0	25.93	19.5
800°F	600.0	0.512	46.5	62.2				
Gas Sample	800.0	0.430	54.4	61.1	27.6	96.4	28.63	18.1
1100°F	800.0	0.430	36.3	61.1				
Gas Sample	1100.0	0.347	41.4	60.1	23.4	83.4	28.06	16.6
1400°F	1100.0	0.347	24.8	60.1				
Gas Sample	1400.0	0.291	22.2	59.3	15.1	64.2	23.52	-

The symbols and notation used in Table C-I have the following definitions:

X - The ratio of the absolute room temperature to the absolute temperature of the specimen tube. It is used to determine the change in effective volume of the manifold due to changes in specimen tube temperature.

r - Reading of the mercury level in the burette.

V_e - The effective volume of the entire specimen manifold in milliliters with the specimen tube at the temperature, °F, indicated in the column headed Temp.

H_2O - The amount of water found in the fixed portion of the specimen manifold by freezing with a dry ice alcohol mixture.

F(H_2O) - The change in effective volume due to cooling the gases enclosed in the manifold by surrounding the trap with dry ice and alcohol. Its value was 1.6 milliliters.

$V_s + r$ - The volume of the specimen manifold exclusive of the specimen tube, used to calculate the percent water.

Sample - The amount of gas taken in the sample tube at the indicated powder temperature, shown in milliliters.

TABLE C-II

GAS ANALYSES

400°F Sample

n	Component	M/e	I_n Div.	I_{pn} Div.	p_n Microns	Volume Percent 1st method	Volume Percent 2nd method
1	He	4	620.0	620.0	55.61	83.36	83.15
2	H_2O	18	12.4	12.4	0.32	13.37	13.77
3	CO_2	44	139.5	139.5	2.05	3.07	3.06
4	H_2	2	0.5	0.5	0.02	0.02	0.02
5	CO	12	14.1	0.3	0.01	0.01	-
6	N_2	14	1.0	5.8	0.10	0.14	-
7	O_2	32	1.0	0.8	0.02	0.03	-
8	SO_2	64	0.0	0.0	0.00	0.00	0.00
					600°F Sample		
1	He	4	639.0	639.0	57.32	70.18	69.27
2	H_2O	18	10.9	10.9	0.28	25.93	27.05
3	CO_2	44	205.8	205.8	3.02	3.70	3.65
4	H_2	2	0.8	0.8	0.03	0.03	0.03
5	CO	12	20.6	0.3	0.01	0.01	-
6	N_2	14	1.2	7.0	0.11	0.14	-
7	O_2	32	0.9	0.8	0.02	0.02	-
8	SO_2	64	0.0	0.0	0.00	0.00	0.00
					800°F Sample		
1	He	4	568.0	568.0	50.95	66.51	65.19
2	H_2O	18	9.4	9.4	0.24	28.63	30.27
3	CO_2	44	240.0	240.0	3.52	4.60	4.51
4	H_2	2	0.4	0.4	0.01	0.02	0.02
5	CO	12	24.5	3.0	0.05	0.06	-
6	N_2	14	1.2	7.0	0.11	0.15	-
7	O_2	32	1.0	0.6	0.01	0.02	-
8	SO_2	64	0.8	0.8	0.02	0.02	0.02

TABLE C-II (Cont'd)

GAS ANALYSES

1100°F Sample

n	Component	M/e	I_n Div.	I_{pn} Div.	p_n Microns	Volume Percent 1st method	Volume Percent 2nd method
1	He	4	519.0	519.0	46.55	62.94	62.56
2	H_2O	18	8.1	8.1	0.21	28.06	28.73
3	CO_2	44	410.0	410.0	6.02	8.14	8.09
4	H_2	2	2.3	2.3	0.08	0.10	0.10
5	CO	12	41.3	3.0	0.05	0.06	-
6	N_2	14	1.4	7.0	0.11	0.15	-
7	O_2	32	4.0	0.6	0.01	0.02	-
8	SO_2	64	20.3	20.3	0.39	0.53	0.52

1400°F Sample

n	Component	M/e	I_n Div.	I_{pn} Div.	p_n Microns	Volume Percent 1st method	Volume Percent 2nd method
1	He	4	500.0	500.0	44.85	63.89	63.94
2	H_2O	18	13.0	13.0	0.34	23.52	23.79
3	CO_2	44	408.0	408.0	5.99	8.53	8.54
4	H_2	2	74.3	74.3	2.43	3.47	3.47
5	CO	12	40.8	4.7	0.07	0.10	-
6	N_2	14	1.6	8.9	0.15	0.21	-
7	O_2	32	2.4	0.6	0.01	0.02	-
8	SO_2	64	9.7	9.7	0.19	0.27	0.27

Water was frozen out of these gas samples before they were introduced into the mass spectrometer. This accounts for the low 18 peak intensity. In the first method the dry analysis was corrected by the amount of water determined in the specimen manifold for the gas sample in question. In the second method the ratio of the dry gas components as determined from the mass spectrometer analysis and the known amount of helium in the gas sample were used to calculate the amount of water in the sample on a difference basis.

It can be seen that very close agreement between the results of the two methods of analysis is obtained. On the basis of this good agreement and the simplicity of the second method it was generally used in calculating the gas analyses.

APPENDIX D

CUMULATIVE VOLUME AND PARTIAL PRESSURE CALCULATIONS

Partial pressures of the various gas components at the temperature at which the gas sample was taken were calculated directly from the sample gas analysis since the total pressure in the specimen manifold was known. The relationship used was,

$$P_n = f_n \cdot P_t \qquad \text{Eq. No. D-1}$$

Where

P_n - is the partial pressure of the nth component over the powder in the manifold.

f_n - is the fraction of this component present in the gas sample.

P_t - is the total pressure in the manifold over the powder.

Cumulative volumes of the various gases were calculated on the basis of the amount of gas present in the manifold at the temperature in question and the amount already removed in previous gas samples. The relationship used in making this calculation is as follows,

$$V_{nm} = f_{nm}(V_e + r) + G_{n1} + G_{n2} + \ldots G_{n(m-1)} \qquad \text{Eq. No. D-2}$$

Where

V_{nm} - is the total volume of the nth component evolved to and including the mth temperature point.

f_{nm} - is the fraction of the nth component in the gas sample taken at the mth temperature point.

$(V_e + r)$ - is the total volume of the specimen manifold at the temperature in question

G_{nm} - is the volume of the nth component in the gas sample taken at the mth temperature point. It is equal to

$$f_{nm}V_{bm}$$

V_{bm} - is the volume of the gas sample taken at the mth temperature point.

The gas volumes calculated with Equation D-2 were converted to equivalent volumes at standard temperature and pressure (20°C and 760 millimeters of mercury pressure).

Table D-I lists the stepwise calculations used to determine the cumulative volumes of the various gases for the samples treated in Appendix C.

TABLE D-I

GAS VOLUME CALCULATIONS

400°F Sample

Component	f	G ml	$f(V_e + r)$ ml	Cumulative Volume	
				ml at 20.2 mm	ml at STP
He	0.8315	16.30	105.10	105.10	-
H_2O	0.1377	2.70	17.40	17.40	0.45
CO_2	0.0306	0.60	3.87	3.87	0.10
H_2	0.0002	0.00	0.03	0.03	0.001
SO_2	0.0000	0.00	0.00	0.00	0.00
600°F Sample					
He	0.6927	13.51	88.80	105.10	-
H_2O	0.2705	5.28	34.68	37.38	0.97
CO_2	0.0365	0.71	4.68	5.28	0.14
H_2	0.0003	0.01	0.04	0.05	0.001
SO_2	0.0000	0.00	0.00	0.00	0.00
800°F Sample					
He	0.6519	11.80	75.30	105.10	-
H_2O	0.3027	5.48	34.96	42.93	1.11
CO_2	0.0451	0.82	5.21	6.52	0.17
H_2	0.0002	0.00	0.02	0.03	0.001
SO_2	0.0002	0.00	0.02	0.02	0.001
1100°F Sample					
He	0.6256	10.39	63.50	105.10	-
H_2O	0.2873	4.77	29.16	42.61	1.10
CO_2	0.0809	1.34	8.21	10.34	0.27
H_2	0.0010	0.02	0.10	0.12	0.003
SO_2	0.0052	0.09	0.53	0.53	0.014
1400°F Sample					
He	0.6394	-	53.11	105.10	-
H_2O	0.2379	-	19.39	37.61	0.97
CO_2	0.0854	-	6.96	10.43	0.27
H_2	0.0347	-	2.83	2.86	0.074
SO_2	0.0027	-	0.22	0.31	0.008