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INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

A STUDY OF GAS DESORPTION OF NICKEL POWDERS

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CHAPTER I

INTRODUCTION

The powder metallurgical manufacturing process has been adopted in many special fields because of its unusual capabilities. Bearings, filters, refractory cutting tools, and magnetic materials are typical examples of engineering products produced most economically through the application of powder metallurgical techniques. The most important features of this process include the fabrication of parts at temperatures below their melting points, the control of directional properties, and the control of density.

The sequence of operations in the process normally begins with the compacting of metal powder into the desired shape at room temperature. This is followed by a sintering operation at elevated temperature under a controlled atmosphere or in a vacuum. The sintering operation is conducted at a sufficiently high temperature so that surface tension and diffusional mechanisms will act to coalesce the powder into a dense, continuous mass. The resulting sintered compact retains its original shape, and its properties approach those of metals processed by the usual techniques of casting, working, etc.

Problems which arise during processing include dimensional instability, incomplete welding at the particle interfaces, and uncontrolled porosity. The causes of these problems are not fully understood, but it is believed that gases liberated during sintering are largely responsible for the observed deleterious effects. These gases are usually attributed to one or more of the following sources:

gases dissolved in the metal powder; gases resulting from chemical reactions between the sintering furnace atmosphere and the powder; gases entrapped in the pressed compact; and gases adsorbed on the surface of the powder. When gases from any of these sources are liberated after the interior voids have been closed, they are entrapped in these voids and prevent further densification. In extreme cases this interior pressure may cause the compact to grow.

It was the purpose of this investigation to determine the amounts and compositions of the gases liberated from nickel powders at elevated temperatures, and to determine the mechanism of their evolution. The powders were heated under an inert atmosphere in a loose condition so that chemical reactions with the atmosphere and mechanical entrapment could be eliminated as sources of gas. It was reasonable to expect that powders manufactured by different techniques would exhibit different gas evolution characteristics; consequently a variety of powders produced by several methods were examined. The temperature dependence of the gas evolution from these powders was studied over the range of 70°F to 1800°F. The source of the liberated gases was studied by investigating the influence of surface treatments on the subsequent gas evolution.

The influence of manufacturing method on resulting gas evolution was determined by studying four commercial types of nickel powder: water atomized in air; water atomized in air followed by an annealing treatment in cracked ammonia; water atomized in a nitrogen atmosphere followed by an annealing treatment in hydrogen; and hydrogen reduced

from a nickel-ammonia complex aqueous solution.

The influence of surface area on gas evolution was studied by testing equal weights of powder of three different particle sizes. The temperature dependence of the gas evolution was investigated by collecting gas samples at 600°F, 1000°F, 1400°F, and 1800°F. The influence of surface treatment on the resulting gas evolution was studied by performing various chemical and mechanical treatments on the powder surfaces.

Because the gas volumes desorbed were relatively small, analyses of desorbed gas samples were performed by the use of mass spectroscopy, a technique which has the high sensitivity necessary in a study of this kind. Additional gas analyses of some of the powders were performed by the vacuum fusion technique.

CHAPTER II

REVIEW OF THE LITERATURE

The literature pertaining to the general field of gas-metal systems is voluminous, but very little of it applies directly to the subject of this investigation. The general topic of gas adsorption has been thoroughly covered, but this work is generally conducted at or below room temperature. The reverse mechanism, desorption, which is considered in the present work, has received very little attention, especially at the elevated temperatures such as those used in the powder metal industry.

Sorption Phenomena in General

Adsorption is caused by forces which exist at surfaces of solids. The magnitude and type of forces present are the same as those which are responsible for holding the component atoms together as a solid (58). Two types of adsorption are usually recognized; physical (van der Waals) adsorption and chemisorption (chemical bonding) (20).

Physical adsorption is a fully reversible adsorption of gas caused by the presence of weak bonding forces present on the surface of the solid. This type of adsorption attains equilibrium very quickly, and occurs without dissociation of the adsorbed molecules. It is primarily a low temperature phenomenon and the amount of adsorption increases as the temperature decreases.(5). Chemisorption occurs at higher temperatures than physical adsorption, and reaches equilibrium much more slowly (7). The heat of chemisorption is appreciably greater than that of physical adsorption, and approaches in magnitude that required for chemical

bonding. The resulting surface compound is quite stable, and may consist of stoichiometric proportions of the reactant molecules⁽³⁴⁾.

Among the early contributors to the theory of gas adsorption were Langmuir and Freundlich⁽³¹⁾ (17). The theories put forth by these two investigators still form the basis for the current theoretical approaches to physical adsorption, although their work has undergone considerable modification. Langmuir's concept implied monomolecular layer adsorption, and was applied to both physical adsorption and chemisorption. Basically, the theory stated that the rate of adsorption equaled the rate of desorption. The adsorption effect was accounted for by assuming that the adsorbate molecules remained on the surface for a finite length of time. Thus, in physical adsorption this time would be short, and in chemisorption long.

In the derivation of Langmuir's theory the following assumptions are made: 1. A definite number of adsorption sites per square centimeter exist on the solid due to the regular arrangement of the atoms in the solid lattice. 2. When all adsorption sites are filled, no further adsorption occurs (monolayer adsorption). 3. There is no interaction between adsorbed molecules. 4. The heat of adsorption does not depend on the fraction of the surface covered by an adsorbed layer.

After making these assumptions, the rate of desorption, R_d , is given as:

$$R_d = v\phi \quad (1)$$

ϕ is the fraction of the surface covered by the adsorbed layer, and v is the rate of evaporation. The rate of adsorption, R_a , is given as:

$$R_a = \alpha \mu (1 - \phi) \quad (2)$$

α is a fraction of the striking molecules that condense, and μ is the rate at which molecules strike the surface. At equilibrium, the rate of evaporation is equal to the rate of condensation so:

$$v \phi = \alpha \mu (1 - \phi) \quad (3)$$

and:

$$\phi = \frac{(\alpha/v) \mu}{1 + (\alpha/v) \mu} \quad (4)$$

Since α/v is a constant, and μ is related to the pressure (p) by another constant, then:

$$\phi = \frac{kp}{1 + kp} \quad (5)$$

This equation shows that at low pressures the adsorption is proportional to the pressure, and that at high pressures the surface approaches saturation. This equation is often rewritten in the following form:

$$\frac{\phi}{1 - \phi} = kp \quad (6)$$

In the literature Equation No. 6 is known as the Langmuir Adsorption Isotherm Equation.

The Freundlich equation described adsorption at somewhat higher pressures (17). The equation is empirical and is as follows:

$$v = kp^{1/n} \quad (7)$$

where:

v = volume adsorbed

p = pressure of adsorbate

k = constant

n = constant greater than one

It has been proposed that isotherms (plots of moles adsorbed versus pressure at constant temperature) may be divided into two parts; one of the Langmuir type for adsorption which occurs on a sparsely covered surface at low pressure, and one of the Freundlich type on a highly covered surface at higher pressures (25). The Langmuir and Freundlich equations have generally formed the basis for the more highly complex theories of adsorption that are in use today.

The problem of interaction between adsorbed molecules has introduced a great deal of complexity into adsorption studies. The problem is usually treated by adding a parameter to the adsorption isotherm, and by use of an attraction constant in a two dimensional equation of state (19) (9). These methods fail in general application to the first monolayer

because the effects of coalescence and localization of the adsorbed layer are neglected.

Interaction between two or more molecules adsorbed on adjacent sites may cause these molecules to repel or attract one another. Repulsion is observed when adsorption occurs on sites lying so close together that the adsorbed molecules undergo an interpenetration of atomic radii. Repulsion may also result when similarly charged ions are adsorbed so that their electrostatic repulsion is greater than the van der Waals attraction. However, in most cases observed experimentally, the dominant interaction is one of attraction resulting from van der Waals forces or dipole-dipole interactions⁽¹⁰⁾.

As the pressure is increased, multilayer adsorption occurs. This introduces additional complexities in the theoretical treatments of the problem and the resulting equations are extremely unwieldy^{(36) (37) (38)}. Certain modifications to these rigorous cases are usually made in order to simplify the problem. The most widely used equations are those developed by Brunauer, Emmet, and Teller, commonly known as the BET equations⁽⁸⁾. Their theory of physical adsorption was the first used to explain multilayer adsorption over a wide range of pressures, and is a modification of Langmuir's concept of monomolecular adsorption. Although this theory contains many simplifying assumptions, it is still one of the more useful theories of multilayer adsorption. The following assumptions are made: 1. There are B equivalent sites for localized adsorption in the first layer. 2. Each molecule in the first layer is a possible site for adsorption of a molecule in the second layer, and so on for n layers. 3. Interactions between molecules in the same layer are negligible.

4. The heat of adsorption in each layer, other than the first, is equal to the heat of liquefaction of the bulk adsorbate (i.e. the van der Waals forces of the adsorbent extend to the first layer only). 5. An infinite number of layers may be adsorbed on a free surface. With these assumptions, the BET equation is presented as:

$$\theta = \frac{cx}{(1-x)(1-x+cx)} \quad (8)$$

where:

c = BET constant

$x = p/p_0$

p = measured pressure

p_0 = saturation pressure of adsorbate

θ = fraction of adsorption sites occupied

This relation yields an expression for multilayer adsorption which is in qualitative agreement with experimental data.

Many modifications of the original BET theory have been made, but with each more rigorous treatment the equations become more unwieldy. These modifications usually introduce such factors as the heterogeneity of the surface, the interaction between second and higher layer molecules, and the disturbing effect of horizontal forces.

Using statistical mechanics, Hill has modified the BET model to include mobile and localized adsorption, which involves a consideration of horizontal forces in the monolayer ⁽²⁶⁾. The BET model postulates

only localized adsorption whereas both localized and mobile states are present. An isotherm is derived from Hill's model which is in agreement with some experimental data.

Halsey has modified the BET theory by assuming that adsorbate molecules influence each other during adsorption (22). This theory postulates that the isotherm consists of three parts: the steeply rising low pressure portion of the isotherm where horizontal forces are negligible; the intermediate pressure portion of the isotherm where monolayer adsorption occurs; and the high pressure portion where multilayer adsorption occurs with horizontal interaction. In the second and third portions of the isotherm the adsorption is influenced by the steadily decreasing van der Waals forces (5).

The original BET equation can be rewritten as:

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{(c - 1)p}{v_m c p_o} \quad (9)$$

where:

p = measured pressure of gas

p_o = saturation pressure of gas

v = total volume of gas adsorbed

v_m = volume of gas adsorbed in the monolayer

c = constant

In this form, the BET equation can be used to determine surface areas⁽⁴⁵⁾.

A plot of $p/v (p_0 - p)$ versus p/p_0 may yield a straight line, and from the slope and intercept of this line the only two unknowns, v_m and c , can be determined. Since v_m is the volume of gas required to cover the solid with a monolayer of gas, the effective area covered by each adsorbed molecule must be known in order to compute the surface area of the solid. The usual method of determining this effective surface area is by use of the equation:

$$\sigma = 4(0.866) (M/\sqrt{2} A d)^{2/3} \quad (10)$$

where:

σ = area per adsorbate molecule

M = molecular weight of gas

A = Avogadro's number

d = density of liquefied adsorbate

This equation assumes that the adsorbate molecules are held in close packing on the surface, and that the area occupied by each molecule is the cross section of its structure. These composite areas are of the order of ten square Angstroms⁽¹⁴⁾.

Harkins has indicated some of the experimental difficulties and theoretical shortcomings of the BET method. Experimentally, wide deviations from linearity are observed when p/p_0 exceeds 0.35. The determination of σ , the area per adsorbate molecule, is also subject to error⁽²³⁾.

A simplified BET procedure has been devised by Starkweather and Palumbo wherein one experimental point and the origin are used to construct the isotherm (53). Normally five or six points are required in the standard method. This simplified method yields data that vary less than ten percent from data taken by the standard method. Other adsorption techniques have been devised for the measurement of surface areas with varying degrees of success (5) (24) (28) (39).

Gas Adsorption and Desorption on Nickel at Low Temperatures

A variety of data are available pertaining to the low temperature adsorption of gases on pure nickel. Beeck, Givens, and Ritchie observed a slow "activated" adsorption of hydrogen between -253°C and room temperature, which they interpreted as a solutioning of the adsorbed hydrogen into the interior of the nickel (4). Baker, Jenkins, and Rideal, working in the temperature range -183°C and 20°C , have shown that large amounts of hydrogen are adsorbed at very low equilibrium gas pressures (2). Ledoux presents data which indicate that adsorption of hydrogen is completed almost instantaneously at 183°C , while approximately two hours are required to reach equilibrium at 0°C (32). In studies of the effect of adsorption on magnetization, Selwood showed that the adsorption of hydrogen causes a decrease in the magnetization of the nickel which is attributed to a filling of the "d" electron shells (33) (48).

Adsorption of carbon dioxide on nickel has been studied by Kwan and by Dillon and Farnsworth (30) (11). Kwan determined adsorption isotherms at 150°C and 200°C . Dillon and Farnsworth adsorbed radioactive

carbon dioxide on the $\{100\}$, $\{110\}$, and $\{111\}$ faces of nickel single crystals. The heat of adsorption was found to be lowest on the $\{110\}$ and highest on the $\{111\}$. The reason given for this is that the $\{110\}$ face is the least densely packed and hence has the fewest adsorption sites.

The adsorption of carbon monoxide on nickel was studied by Baker and Rideal, and by Wang and Hackerman (1) (60). Baker and Rideal determined the heat of adsorption of CO on nickel between -183°C and 20°C and observed that raising the temperature from 20°C to 150°C resulted in the desorption of carbon monoxide. Wang and Hackerman found that the adsorption of carbon monoxide was irreversible in that it could not be removed by evacuation at room temperature.

The adsorption of water vapor on nickel was studied by Zettlemoyer and Chessick who found that water vapor was only physically adsorbed at 25°C (62). They also confirmed Tingle's observation that water vapor is adsorbed on nickel strongly enough so that it resists removal by room temperature evacuation (55).

The heats of adsorption of these gases on nickel have been determined, and a summation of these data are presented below:

TABLE I
Heats of Adsorption on Nickel

Gas	ΔH , kcal/mol	Reference
H_2	-30	(54) (59)
CO_2	-22	(30)
CO	-15	(1)
O_2	-55	(18)

Gas Evolution at Elevated Temperatures

The gases evolved from nickel wire heated to 750°C were found to consist of carbon dioxide, carbon monoxide and hydrogen in some tests by Smithells and Ransley⁽⁵²⁾. Several hours were required for the completion of the gas evolution which led Jones to postulate that dissolved gases were diffusing to the surface⁽²⁷⁾. This leads to the conclusion that the controlling factor was the rate of diffusion of dissolved oxygen. Warren and Libsch investigated the gases evolved from iron-cobalt compacts at 1400°C and found that compacts heated under helium possessed greater permeability than those heated under hydrogen⁽⁶¹⁾. This effect was explained by assuming that the hydrogen reduced surface oxides fast enough so that the reacted gases could escape before the pores were sealed. In the other case, dissolved carbon reduced the surface oxides, but the diffusion of carbon was too slow to allow the gaseous products of the reaction to escape before the interior voids were closed. In another experiment by the same authors, pure cobalt was heated to 1000°C under vacuum and the evolved gases were collected. About 1.6 milliliters of carbon dioxide per gram of cobalt were liberated. The source of the gas was attributed to chemisorbed carbon dioxide, and reactions between dissolved carbon and surface oxides. Duftschild, Schlecht, and Schubart found that carbon dioxide and carbon monoxide were liberated from carbonyl iron powder⁽¹²⁾. These gases were shown to be the products of reactions between dissolved carbon and iron oxide. Tobin and Sinnott collected and analyzed the gases desorbed from a series of copper powders, and found that water vapor, carbon dioxide and sulfur

dioxide were desorbed on heating to 1400°F⁽⁵⁶⁾. The source of these gases was shown to be surface compounds. Fedorchenko, in experiments with nickel powder compacts, observed growth at elevated temperatures which he attributed to gas evolution and the release of internal stresses⁽¹⁵⁾.

Dissolved Elements in Nickel

Those desorption mechanisms which postulate that dissolved elements are responsible for gas evolution are reasonable in view of the reported solubilities of various elements in nickel. The more important of these dissolved elements are hydrogen, oxygen, carbon, and, to a lesser degree, sulfur.

Hydrogen dissolves in solid nickel by forming an interstitial solid solution. The solubility limit increases from 2.67 milliliters per 100 grams of nickel at 600°F to 14.5 milliliters per 100 grams at 1800°F. These amounts of hydrogen, if liberated within a compact would be sufficient to cause interior voids, and prevent densification of a powder compact⁽¹³⁾⁽⁵¹⁾.

The solid solubility of oxygen in nickel is unusual in that it decreases with increasing temperature. The solubility of oxygen in nickel at 600°C is 0.020 weight percent, while at 1200°C it has decreased to 0.012 weight percent. Oxygen contents present in excess of these amounts cause the formation of nickel oxide. A nickel-nickel oxide eutectic occurs at 0.22 weight percent oxygen⁽⁴⁹⁾.

The solid solubility of carbon in nickel is quite extensive, and reaches a maximum of 0.65 weight percent at 1318°C. The solubility

decreases to 0.25 weight percent at 1000°C, and to about 0.03 weight percent at 500°C. The compound Ni_3C containing 6.42 weight percent carbon has been reported to exist between 1500°C and 2500°C, but is very unstable⁽²⁹⁾.

The solid solubility of sulfur in nickel is quite restricted and reaches a maximum of about 0.005 weight percent at 644°C. The details of the equilibrium diagram at higher sulfur contents are still in question⁽²¹⁾⁽⁴⁰⁾⁽⁴⁶⁾.

These binary system equilibrium solubility data must be modified in their application to commercial nickel powders for two reasons. The first is the non-equilibrium method of powder production, and the second is the simultaneous solutioning of two or more elements in nickel.

The non-equilibrium nature of the powder manufacturing process would probably allow dissolved elements to remain in solid solution in the nickel in amounts exceeding their equilibrium solubility limits. Under these conditions, subsequent heat treatments would result in the precipitation of excess solute atoms.

Normally the presence of one element in solid solution acts to decrease the solubility limit of other dissolved elements in the same system. Thus if the dissolved hydrogen content in solid nickel were high, the dissolved oxygen content would be expected to be low, and vice versa. The same general reasoning would be expected to apply to dissolved carbon and sulfur.

Summary

From this survey of the literature, it can be seen that the published data pertaining to gas evolution at sintering temperatures are quite limited. The present investigation was directed toward an area wherein almost no published data are available; namely, the gas desorption from metal powders at elevated temperatures.

CHAPTER III

EXPERIMENTAL PROCEDURES

Gas Desorption Apparatus

The gas desorption apparatus used in this investigation was a modification of equipment previously used by J. C. Tobin⁽⁵⁷⁾. Quartz was substituted for Vycor in the sampling tubes because of the higher operating temperatures involved in the present program. A schematic diagram of this equipment is shown in Figure 1.

The system was evacuated by means of an oil diffusion pump backed by a duo-seal mechanical pump. A dry ice-methyl alcohol trap was placed in front of the diffusion pump to prevent condensables from collecting in the diffusion pump. This pumping arrangement was capable of reducing the pressure to values between a tenth and a hundredth of a micron. Pressures were measured by a McLeod gauge placed between S_1 and the diffusion pump. The stopcocks were all of the vacuum bulb variety, and air traps were used on all mercury leveling bottles. This arrangement kept the closed system leak rate below one micron per twenty-four hours. The specimen tubes were fabricated from pure quartz, and had an approximate life of fifty hours at 1800°F. They usually failed by distortion and leaking caused by phase changes within the quartz.

The sample tube contained a side arm offset by 180° from five indentations in the lower part of the tube. This arrangement allowed a powder sample to be contained in the sidearm of the sample tube while the system was being evacuated. When the lower part of the sample tube

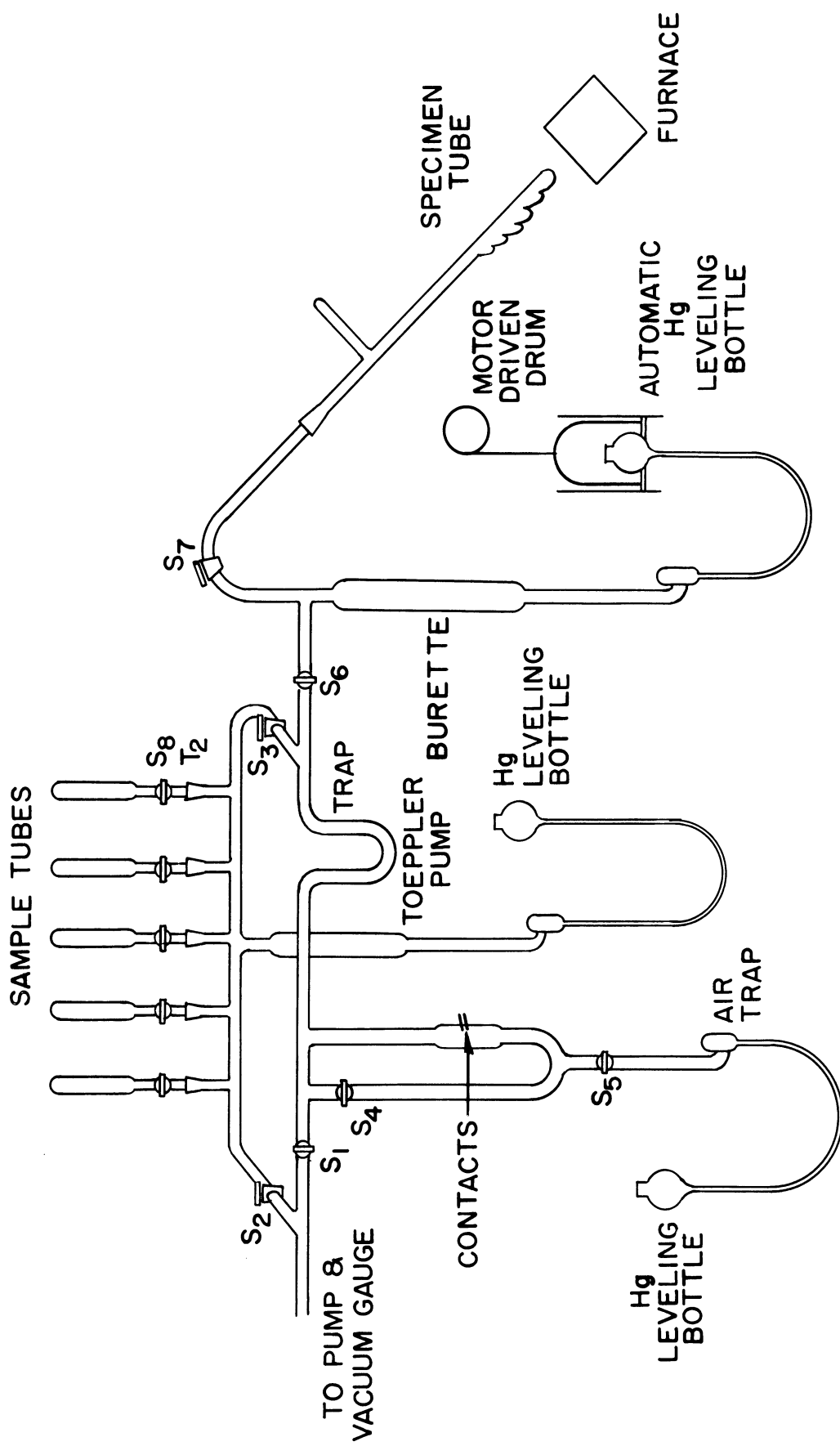


Figure 1. Gas Desorption Apparatus

was at temperature, a 180° rotation of the sample tube about its greased taper would cause the powder to fall into the lower portion of the sample tube and distribute itself among the five indentations. In this fashion packing effects were minimized. Temperatures were maintained by a chromel wound barrel type furnace which could be moved into position after the loaded sample tube was connected to the system. The rest of the system consisted essentially of two interconnected manifolds, constructed of Pyrex glass tubing.

One manifold was used for maintaining constant pressure over the powder and measuring the volumes of the evolved gases, and the other was used for obtaining gas samples which were then analyzed on a mass spectrometer. That part of the manifold used for maintaining pressures and measuring evolved gases was bounded by stopcocks S_7 , S_3 and S_1 , as shown in Figure 1. It consisted of a burette, a cold trap, and a manometer whose total volume represented a calibrated volume. A fixed pressure could be maintained in the system by admitting a given pressure of an inert gas, which was measured in the manometer. The mercury level in the lower leg of the manometer was in contact and level with the upper of two electrical contacts placed in the manometer. As gas was liberated by the powder the manifold pressure tended to rise, thus lowering the mercury level in the leg of the manometer connected to the manifold. As the mercury level dropped, it opened the electrical contact which in turn actuated a motor controlling the mercury leveling bottle on the burette. This automatic leveling device then lowered the mercury in the burette until the manifold pressure was returned to its original value. At this time the

electrical contact in the manometer was closed, thus stopping the motor which controlled the burette leveling bottle.

The volume of gas liberated at the manifold pressure was then read directly from the increase in the burette reading. The burette had a one hundred milliliter calibrated volume which could be read to a tenth of a millimeter. The manometer could be used to control the manifold pressure up to two hundred millimeters, and could be read to a tenth of a millimeter. The cold trap was used to remove gases which might otherwise react with the hot powder. Only those gases which did not liquefy at temperatures of liquid nitrogen and pressures of about twenty millimeters were not removed by this process.

The second manifold was used for collecting gas samples and was contained between stopcocks S_2 and S_3 , and consisted of five sample tubes and a Toepler pump. In practice, one of the sample bulbs was used as a convenient source of helium, the inert carrier used in the measuring manifold. The remaining four sample tubes were used to contain gas samples collected in the measuring manifold. After a desorption run, stopcock S_3 and a sample bulb stopcock were opened, and a gas sample was taken. In those cases where very little gas had been desorbed, the Toepler pump was used to increase the amount of sample taken by compressing an enclosed amount of gas into a much smaller volume. This operation could be done several times in extreme cases. The calibration of the measuring manifold and sample tube, and the procedure for determining temperature corrections has been outlined in the Appendix.

Testing Methods

The experimental data obtained in this investigation were derived from five procedures: measurements of the total volumes of desorbed gases; measurements of the cumulative volumes of desorbed gases; vacuum fusion analyses; x-ray diffraction; and electron diffraction. The gas desorption studies made use of the previously described desorption apparatus, while the vacuum fusion, x-ray diffraction and electron diffraction analyses were performed on commercially available equipment.

Total and Cumulative Gas Analyses

Both the total and cumulative gas desorption determinations were started by thoroughly cleaning the sample tube with xylene, benzene, acetone, and distilled water. Traces of powder remaining from previous runs were removed by the xylene, while the benzene removed all stopcock grease. After the final rinses in acetone and distilled water, the sample tube was evacuated and heated to remove all final traces of adsorbed gas. After this cleaning procedure the weighed powder sample was placed in the sidearm of the sample tube which in turn was connected to the measuring manifold, with the sidearm in a position such that the powder would remain in the sidearm. The next step was to evacuate the system by opening all stopcocks to the main vacuum line. During this time the furnace was moved into position and the lower part of the sample tube was heated to 1800°F for one hour. This was a precautionary means of insuring that all adsorbed gases in the sample tube were removed. After one hour at 1800°F, the sample tube was cooled to room temperature,

and the system was evacuated for a minimum of six hours, at pressures between a tenth and a hundredth of a micron.

The next step was to fill the measuring manifold and sample tube with about twenty millimeters of helium from a bulb contained on the sample manifold. The inert helium was used in order to facilitate the measurement of the desorbed gases, and to simplify mass spectrographic analyses. Up to this point, the procedures were identical in both the total and cumulative gas desorption runs.

In the total gas desorption runs, it was desired to collect all of the gases liberated from the powder before they could react with the hot powder. This was done by placing a liquid nitrogen cold trap in the system, so that the reactive gases were condensed before they could react. With the specimen tube at 1800°F and the measuring manifold pressure adjusted to about twenty millimeters of helium, a burette reading was made and then the cold trap was brought to the temperature of liquid nitrogen. At this stage, S_1 , S_2 , S_3 , S_4 , and S_5 were closed, and S_6 and S_7 were open. The sample tube was then rotated through 180° about its tapered joint, thus bringing the sidearm into an upright position and causing the powder sample to drop into the heated portion of the sample tube. During the subsequent gas evolution, the system pressure was not held constant, but the burette leveling bottle was alternately raised and lowered manually in order to pump the desorbed gases into the cold trap. Preliminary work had indicated that gas evolution was completed in twenty to thirty minutes, so gas collection was continued for one hour as a margin of safety. After one hour at 1800°F,

the measuring manifold pressure was returned to its original value by adjusting the burette leveling bottle. After S_7 was closed the cold trap was returned to room temperature and the manifold pressure was again returned to its original value. The difference in the initial and final burette readings was the volume of gas desorbed from the sample at the pressure measured on the manometer, and at the temperature measured at the burette. After the desorbed gas volume was measured, a mass spectrometer sample was taken by opening S_3 and one sample bulb. If very small amounts of gas were evolved, the Toeppler pump was used to increase the pressure of the sample by closing S_3 and then raising the Toeppler pump.

In the cumulative gas desorption runs, it was desired to keep the manifold pressure constant, and to allow the desorbed gases to approach equilibrium with the hot metal powder, at a series of temperatures, so that the ensuing gas evolution could be studied as a function of temperature. To accomplish this, the temperature of the sample tube was brought to 600°F, after the helium had been admitted to the measuring manifold. With valves S_1 , S_2 , S_3 , S_4 , and S_5 closed, and S_6 and S_7 open, the pressure was read, and a burette reading was made. After the automatic leveling apparatus was turned on, the powder was dropped into the heated portion of the sampling tube and the system was allowed to approach equilibrium for one hour under a constant pressure.

At the end of this time, a burette reading was made which indicated the amount of gas evolved, and a gas sample was taken. During sampling valve S_7 was closed so that the gas pressure over the powder

remained constant. After the gas sample was taken, the manifold pressure was returned to its original value, and valve S₇ was opened. The temperature was then raised to 1000°F, and the same procedure was used to obtain another gas sample. Other samples were taken at 1400°F and 1800°F.

As a final precautionary step a blank test was performed. The routine total volume gas desorption technique was employed, except that no sample was placed in the sample tube. The burette readings showed that no gas had been evolved, and an analysis of the manifold atmosphere showed it to be pure helium. This test proved that no extraneous gases were present in the system.

Vacuum Fusion

The vacuum fusion analyses were performed on a standard National Research Corporation vacuum fusion gas analysis apparatus. In this method of analysis a previously weighed metal sample was dropped into a graphite crucible maintained under vacuum at several hundred degrees in excess of the melting point of the sample. This high temperature was used to insure rapid melting of the sample, and to cause the decomposition of any nickel oxides and nitrides that might have been present⁽⁵⁰⁾. Thus this method of analysis yielded values which represented the amount of gas present in solid solution and in combined form.

Upon melting, the dissolved and adsorbed gases contained by the sample were immediately liberated in a carbonaceous environment. Nitrogen and hydrogen were evolved in their molecular states, but oxygen was evolved as a mixture of carbon monoxide and carbon dioxide. The liberated gas was collected and measured, and was then passed through an oxidizing

media where all carbon monoxide was converted to carbon dioxide, and hydrogen was converted to water vapor. The analysis of the gas was then made by passing it through a drying tube, where the measured decrease in volume was due to the loss of water vapor. The remaining gas was then passed through a cold trap maintained at the temperature of liquid nitrogen. The measured decrease in volume was due to the condensation of carbon dioxide. The remainder of the gas was assumed to be nitrogen. Simple calculations allowed the amounts of oxygen, nitrogen, and hydrogen contained by the sample to be determined. The only deviation from normal procedures in the testing of the nickel powders was to wrap the powder in a tin foil envelope as a means of containing the sample. Tin was selected because of its low vapor pressure at high temperature and its non-reactivity with the gases contained in or on the sample. Blanks were run on the tin to check its gas content, which was then subtracted from the total.

As a means of checking the vacuum fusion analysis, gas samples were taken immediately after they were liberated, and analyzed on the mass spectrometer in the same manner as the gas desorption samples. Because the carbon monoxide was later converted to carbon dioxide, and the hydrogen was later converted to water in the vacuum fusion unit, the subsequent comparison was made between carbon monoxide plus carbon dioxide as analyzed on the mass spectrometer, and carbon dioxide as analyzed on the vacuum fusion unit, and between hydrogen plus water, as analyzed on the mass spectrometer, and water on the vacuum fusion unit.

X-Ray and Electron Diffraction

X-ray diffraction investigations were made on the ball mill fines resulting from the short-time ball milling of nickel powders. Coarse samples of powder, -70 + 100 mesh, were ball milled in porcelain ball mills for about ten minutes. The powder was then sieved through a -325 mesh screen and the fines were used for x-ray powder pictures using normal Debye-Scherrer techniques. The short times of milling and the coarse fractions of powder insured that only surface layers would be removed and subsequently analyzed. The porcelain mills and balls used prevented contamination of the powder. As an additional safeguard, the mills and balls were boiled in nitric acid for fifteen minutes, washed in distilled water, and dried at 200°C overnight before use.

Electron diffraction investigations were made on both powdered and massive nickel samples. Initial work was done on very fine -325 mesh powder, but polished surfaces of massive nickel were found to yield slightly better results. Both transmission and reflection studies were attempted.

Description of Powders

The materials selected for examination in this program represented a variety of commercially available powders. The chemical analysis of these powders is shown in Table II.

Metals Disintegrating Company Powder

This nickel powder was produced by steam scattering in air. It was produced by the Metals Disintegrating Company and will hereafter

TABLE II
CHEMICAL ANALYSIS OF NICKEL POWDERS

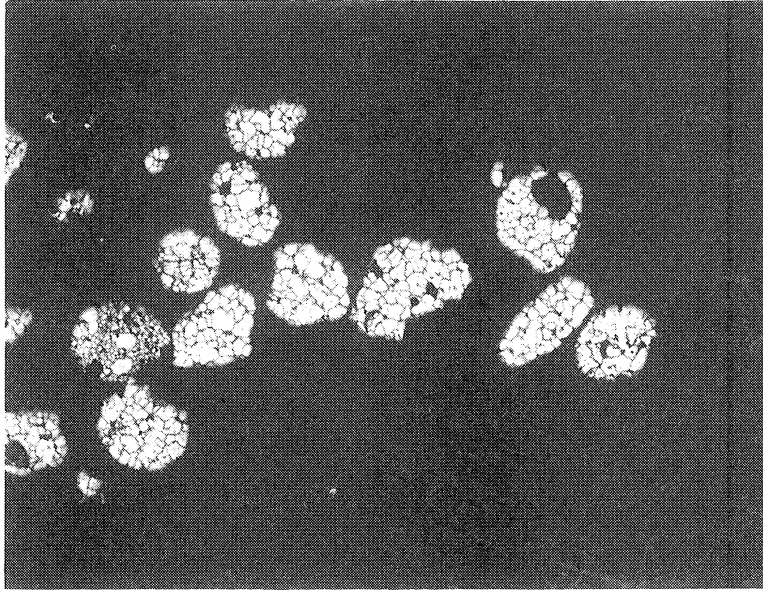
<u>Chemical Analysis</u> <u>Weight %</u>	<u>Metals</u> <u>Disintegrating</u> <u>Company</u> <u>Powder</u>	<u>Plastic</u> <u>Metals</u> <u>Company</u> <u>Powder</u>	<u>Sherritt</u> <u>Gordon</u> <u>Company</u> <u>Powder</u>
Ni + Co	99.3 - 99.5	99.70	99.8
Fe	0.1	0.05	0.071
Acid Insol.	0.1	N.R.	N.R.
S	0.044 - 0.046	0.05	0.019
H ₂ loss	0.25 - 0.45	N.R.	0.16
Cu	N.R.	0.02	N.R.
Si	N.R.	0.06	N.R.
C	N.R.	0.02	N.R.
P	N.R.	0.01	N.R.

N.R.: not reported

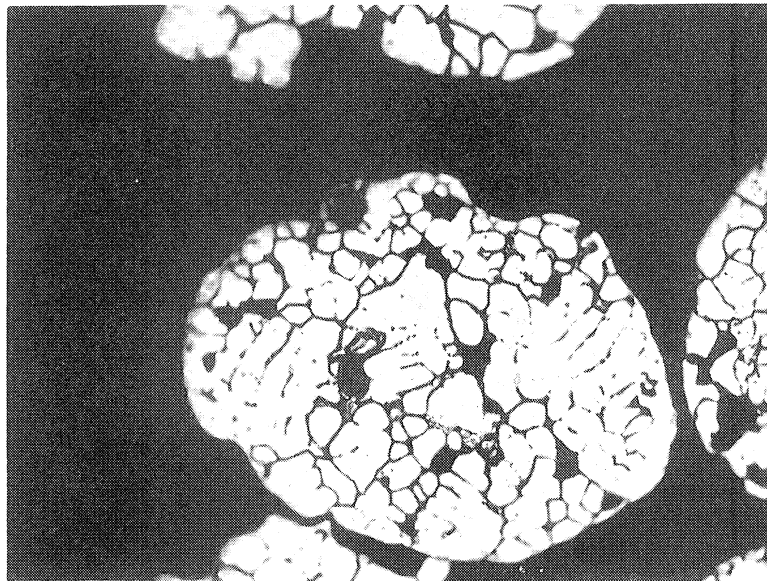
be designated as MD9119 powder. This powder was produced by subjecting a stream of molten electrolytic nickel to a jet of steam which atomized the nickel and gave each powder pellet a roughly spherical shape. This technique resulted in a powder covered with a dull nickel oxide film, containing some nickel-nickel oxide eutectic in the grain boundaries. Photomicrographs of this powder are shown in Figure 2. The microstructure was characterized by a fine, equiaxed grain structure typical of rapidly cooled metals. The sphericity was fairly good, with some interior voids being present. These micrographs were prepared from bakelite mounted samples etched in a solution composed of equal parts of nitric and acetic acid. Some of the impurities noted in the chemical analysis are due to pickup from the melting crucibles, and the atmosphere. The sulfur was added deliberately to facilitate the later grinding operations.

Plastic Metals Company Powder

This nickel powder was prepared by steam scattering in air followed by an annealing treatment in cracked ammonia. It was produced by the Plastic Metals Division of the National-U. S. Radiator Corporation and will hereafter be designated as PM273 powder. This powder was prepared in the same manner as the MD9119 powder, but after atomization was subjected to an annealing treatment at 1400°F for 45 minutes under a cracked ammonia atmosphere. This powder exhibited a much brighter appearance than the MD9119 powder, because the annealing treatment had reduced the surface oxides. Photomicrographs of this powder are shown in Figure 3. The powder was somewhat more irregular in shape than the

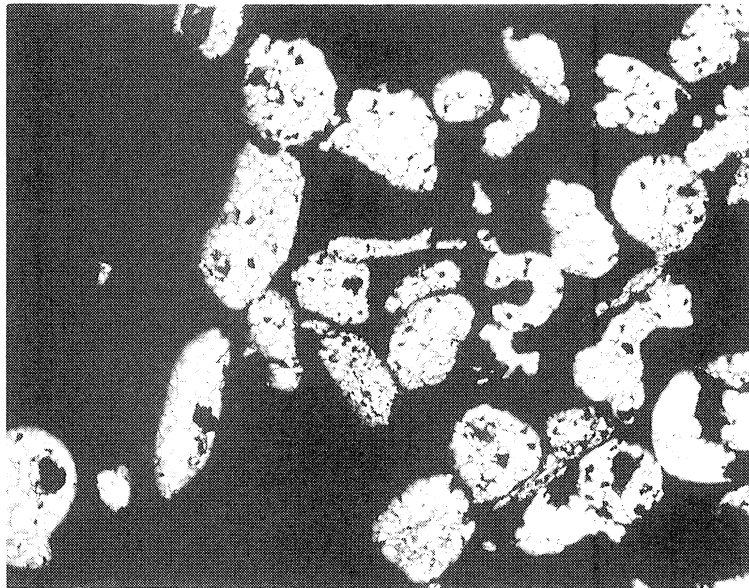


100x 50% nitric acid - 50% acetic acid etch

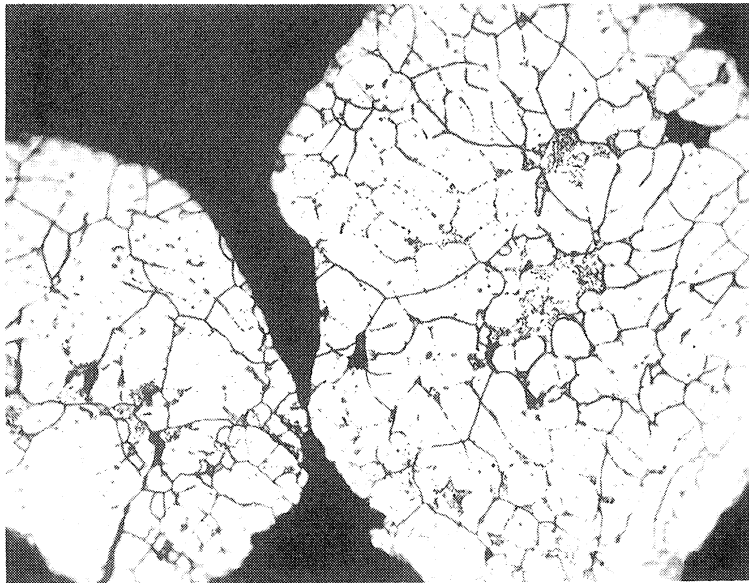


500x 50% nitric acid - 50% acetic acid etch

Figure 2. Microstructure of Metals Disintegrating Company Powder.



100X 50% nitric acid - 50% acetic acid etch



500x 50% nitric acid - 50% acetic acid etch

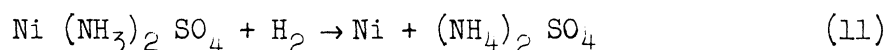
Figure 3. Microstructure of Plastic Metals Company Powder

MD9119 powder, and manifested greater porosity. Some nickel-nickel oxide eutectic was to be seen at the grain boundaries, indicating that the annealing treatment did not reduce the oxides located within the powder.

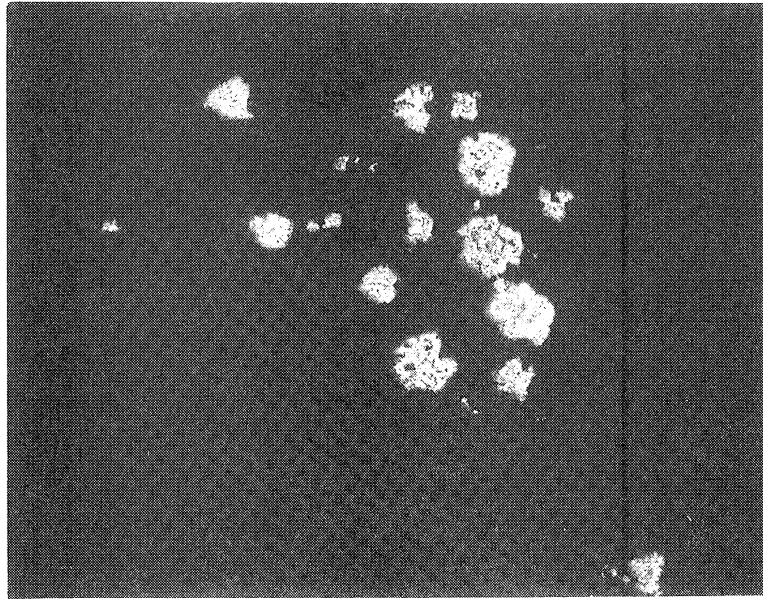
Sherritt Gordon Company Powder

This powder was prepared by hydrogen reduction from a nickel-ammonia complex aqueous solution. It was manufactured by the Sherritt Gordon Mines Ltd., and will hereafter be designated as SG321 powder. The details of this manufacturing process have been described by Forward and by Mackiw, Lin, and Kunda⁽¹⁶⁾⁽³⁵⁾.

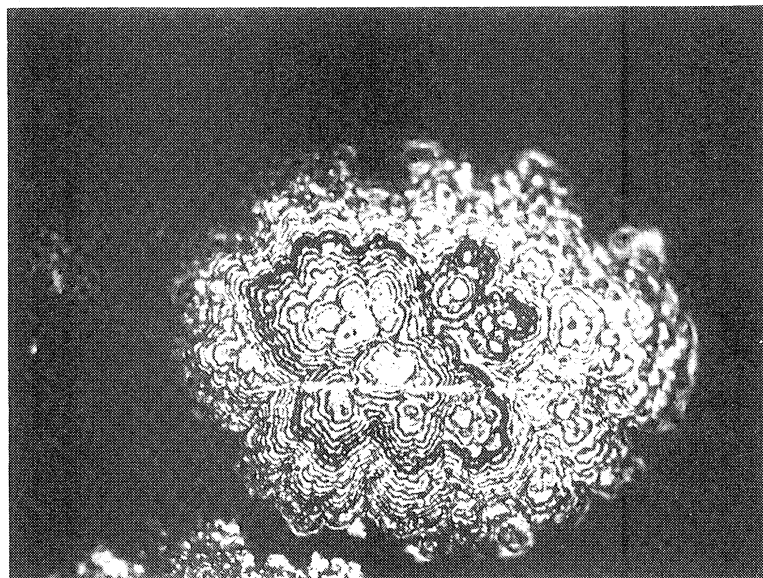
The features of this process included ammonia leaching of a nickel-copper-cobalt sulphide concentrate in which the nickel, cobalt, and copper were recovered as amines. After the copper had been removed as copper sulphide, hydrogen under pressure was bubbled through the purified leach solution precipitating pure nickel by the reaction:



The nickel was precipitated as a very fine powder which was then used as a nucleation agent for further reduction from succeeding charges of the same solution. The precipitation was continued in stepwise fashion, with each subsequent precipitation operation adding another thin layer of pure nickel to the original nickel powder. This procedure was continued until the powder had reached the desired size. Photomicrographs of this powder are shown in Figure 4. The structure appeared to be layer-like, and the grain boundaries were not visible at five hundred magnifications. The manufacturer described the powder configuration as spherical with a corrugated surface.



100x 50% nitric acid - 50% acetic acid etch



500x 50% nitric acid - 50% acetic acid etch

Figure 4. Microstructure of Sherritt Gordon Mines Ltd. Powder.

Federal Mogul Company Powder

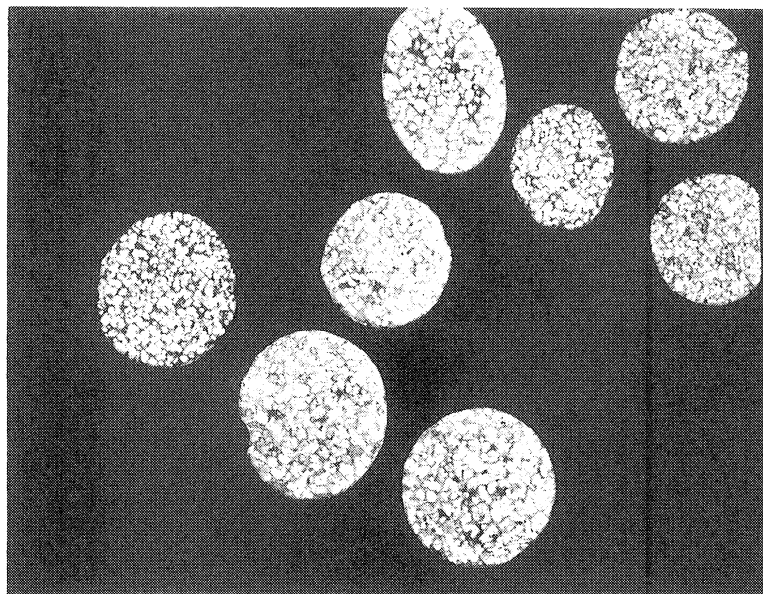
This nickel powder was produced by steam scattering in a nitrogen atmosphere followed by an annealing treatment in hydrogen. It was produced by the Federal Mogul Company, and will hereafter be designated as FM powder. This powder presented a very bright appearance, because the nitrogen atmosphere had minimized surface oxidation, and the hydrogen annealing operation had removed any remaining surface oxides. Photomicrographs of this powder are shown in Figure 5, and reveal excellent particulate sphericity. Some nickel-nickel oxide eutectic is present at the grain boundaries.

Preparation of Powders for Gas Desorption Runs

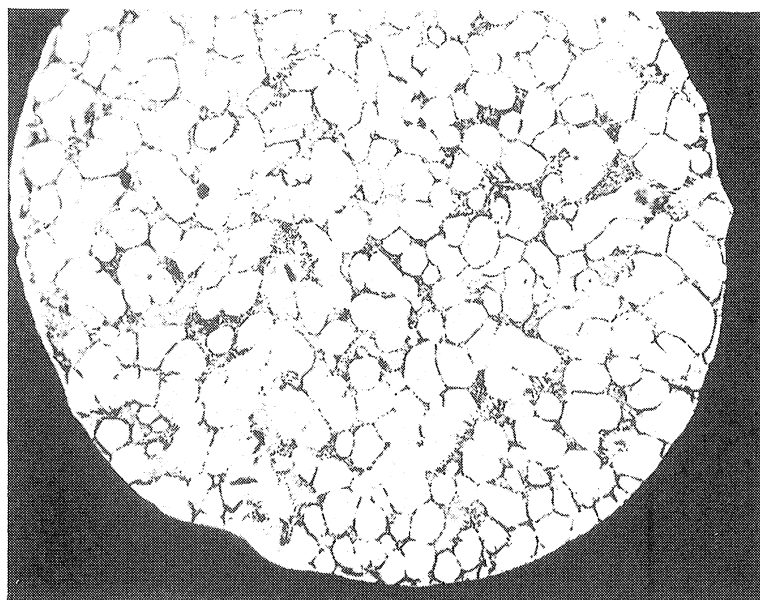
All powders were tested in the as received condition, which simply meant that the powders were kept in tightly covered containers until ready for use. The three mesh fractions selected for study were the -70 +100, -100 +200, and -200 + 325 sizes. These sizes represented typical commercial specifications, and covered a wide range of surface areas. The surface areas were calculated by taking the arithmetic mean of the surface areas of the smallest and largest particles in a given mesh fraction, and then calculating the total surface area represented by ten grams of spherical particles having this mean surface area. The results of these calculations are presented below:

TABLE III

<u>Surface Area of Spherical Nickel Powder</u>		
<u>Mesh Fraction</u>	<u>Weight, grams</u>	<u>Surface Area, mm.²</u>
- 70 + 100	10	28.9
-100 + 200	10	57.3
-200 + 325	10	110.0



100x 50% nitric acid - 50% acetic acid etch



500x 50% nitric acid - 50% acetic acid etch

Figure 5. Microstructure of Federal Mogul Company Powder.

The MD9119 and PM273 powders were tested in all three of the previously mentioned mesh sizes. The SG321 powder was tested in the -100 +200, and -200 +325 mesh sizes. The FM powder was tested only in the -70 +100 mesh fraction, because the supply was limited.

Some powders were further investigated to determine the influence of surface preparation on gas evolution. The MD9119 powder was tested immediately after having been rinsed in nitric acid, and also after having been reexposed to air for varying periods of time up to 96 hours after having been rinsed in the same solution. In some tests the rinsed powder was transferred to the sample tube under a nitrogen atmosphere, but when no differences of composition or volume were noticed in the evolved gas, this technique was discarded and the transfer was made in air. The acid rinses brightened the powder appreciably, indicating the removal of surface oxides.

Several samples of MD9119 powder were studied after having been ball milled for short periods of time in order to remove the greater part of the surface oxides. The ball milling also brightened the powder somewhat, again indicating the presence of surface films on the as received powder.

Gas Analysis by Mass Spectroscopy

Mass spectroscopy was selected as the means of determining gas compositions in this investigation, because the small amounts of gas evolved from the powder required a highly sensitive technique of analysis. A Consolidated Engineering Corporation Analytical Mass Spectrometer, model 21-103B, was used throughout this work. In this instrument

gaseous molecules were admitted at low pressure to an analyzing system through a high vacuum inlet system. The molecules were fragmented and ionized by an ionizing voltage of about seventy volts. The ions thus formed were accelerated by an adjustable voltage, and were then passed through a magnetic field where the resultant force of the magnetic field on the moving ions directed the ions in a semicircular path. The radius of this path was dependent on the mass to charge (m/e) ratio of the ion, the accelerating voltage, and the magnetic field.

In this instrument, the magnetic field strength was held constant while the electric field was varied. Under these conditions, ions of continually varying m/e ratios traveled through a constant radius semicircle, and were deposited on a collector located on a five inch radius. The ions striking the collector deposited a charge which was amplified and recorded on a photographic chart. This chart was then a plot of abundance of ions as shown by peaks on the chart, versus the m/e ratios of the ions.

Pure components, when analyzed on the mass spectrometer, gave rise to a variety of peaks which occurred at those m/e values characteristic of the fragments which resulted from the ionization of the pure component. This array of peaks was the mass spectra of the pure component under consideration. The major peak normally occurred at an m/e value corresponding to the molecular weight of the pure, singly charged component. The ratios of the smaller peaks to the major peak were known as the cracking pattern of a compound, and this cracking pattern remained essentially constant over a wide range of inlet pressures for given ionizing conditions.

The procedure for analyzing a mixture of gases began with a calibration of the instrument for the sensitivity of each of the pure components in the mixture. The sensitivity of the instrument for any pure component was the major peak height in divisions divided by the microns of pressure of the pure component in the inlet volume. Thus if a two component mixture, such as helium and nitrogen, were to be analyzed, (neither gas having a minor peak falling on the other's major peak), the instrument would be calibrated by determining the sensitivity of the instrument for each of the pure components. Then the mixture would be analyzed, and the major peak height for one of the pure components divided by the sensitivity for that component, in divisions of peak height per micron, would give the partial pressure of that component in the inlet volume. Since the total pressure in the inlet volume was measured by a micromanometer, the percentage of this pure component in the mixture was determined by the simple ratio of its partial pressure to the total pressure. The percentage of the other pure component could be calculated in the same way, or by difference.

In most cases however, the analysis was not this simple because some gases had major and minor m/e peaks which superimposed themselves on the major and minor peaks of other gases. Thus a certain m/e peak might represent the major peak of one component plus the minor peaks of one or more other components. The problem of analysis then became one of determining the number of divisions contributed to the various major peaks by other minor peaks. In this way the fraction of the major peaks due to the pure component having that major peak could be determined.

In this analysis, typical gas mixtures contained H_2 , He, H_2O , CO, N_2 , CO_2 , and SO_2 . The m/e peaks at values of 2, 4, 44, and 64 were unincomponent peaks in that they represented contributions only from H_2 , He, CO_2 , and SO_2 respectively. Thus the partial pressures of these four gases could be determined directly by dividing these peak heights by their respective sensitivities. The m/e peak at 28 represented contributions from both CO, N_2 , and CO_2 . The first step in the analysis for CO and N_2 was to subtract the contribution of the CO_2 from the 28 peak. This value was simply the height of the 44 peak times the CO_2 cracking pattern fraction determined for the 28 peak. Since the remaining peak height at 28 was due to both CO and N_2 , it was necessary to employ the 14 peak to determine the fraction of the 28 peak due to N_2 . This was possible because of all the gases in this mixture, only nitrogen caused a 14 peak. Knowing the cracking pattern of nitrogen, the 28 peak height due to N_2 was simply the 14 peak height divided by the cracking pattern factor of the 14 peak. The remainder of the 28 peak was due to CO.

The water analysis was obtained by difference, because water vapor tended to be adsorbed on the inlet system tubing, thus yielding erratic data. Freezing of the water vapor prior to analysis was a possible means of analysis, but prior work had indicated that the difference technique yielded comparable accuracy in the analysis for water vapor. This difference technique was adopted in the present study because of its greater simplicity⁽⁵⁷⁾.

If the above procedure left a mixture of gases whose spectra contained only peaks that represented contributions from two or more components, the analysis would have been completed by the solution of

a system of simultaneous equations. These equations would be n in number for n unknowns, and have constant terms that represented the total peak heights, coefficients that were taken from the respective cracking patterns, and unknowns that were the major peak heights of the respective pure components.

In practice, frequent calibration of the mass spectrometer was required, because the sensitivity of the instrument varied from day to day. Cracking patterns were found to remain essentially constant over long periods of time.

This technique of analysis was also found to act as an excellent check on the occurrence of air leaks in the gas desorption apparatus. A peak at an m/e value of 40 was indicative of the presence of argon in the sample, whose only possible source was from an air leak. Thus a routine step in the examination of the mass spectrometer recordings included a check for the presence of an m/e peak at 40, and those samples yielding such a peak were discarded.

CHAPTER IV

EXPERIMENTAL RESULTS

The experimental data presented in this investigation were derived from total volume gas desorption studies, cumulative volume gas desorption studies, vacuum fusion analyses, and x-ray and electron diffraction examinations. The total volume gas desorption studies are presented in tabular form, and show the volumes and analyses of gases liberated from ten gram samples of nickel powder heated to 1800°F. The cumulative volume gas desorption studies are presented in the form of figures and tables, and show the cumulative volumes of the various gases liberated as a function of temperature. The cumulative volumes of the various gases liberated at 1800°F are also presented in tabular form for comparison with the total volume gas desorption runs.

Vacuum fusion and x-ray diffraction data are presented in tabular form. No data from electron diffraction studies are presented, because no positive identifications could be made on the weak diffraction rings obtained.

Metals Disintegrating Company Powder

The total volume gas desorption analyses for duplicate runs on three mesh fractions of this powder in the as received condition are shown in Table IV. Other total volume gas desorption analyses for this powder in the ball milled and rinsed conditions are shown in Table V for the -70 +100 mesh fraction. The data showing the behavior of this powder after being rinsed in nitric acid and then being reexposed to air

TABLE IV

TOTAL AND CUMULATIVE GAS VOLUMES FOR TEN GRAM SAMPLES OF METALS
DISINTEGRATING COMPANY POWDER HEATED TO 1800°F IN THE AS RECEIVED
CONDITION; - 70 + 100, - 100 + 200, AND - 200 + 325 MESH FRACTIONS

	<u>Total Volume</u>					
	Volume, ml. at STP					
<u>Mesh Fraction</u>	<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	<u>Total</u>
- 70 + 100	0.0	0.2	0.1	1.9	0.6	2.8
- 100 + 200	0.0	0.3	0.3	2.5	0.9	4.0
- 200 + 325	0.0	0.2	0.7	4.2	1.5	6.6

	<u>Total Volume, Duplicate Run</u>					
<u>Mesh Fraction</u>	<u>Volume, ml. at STP</u>					<u>Total</u>
	<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	
- 70 + 100	0.0	0.2	0.1	1.9	0.4	2.6
- 100 + 200	0.0	0.3	0.4	2.8	0.6	4.1
- 200 + 325	0.0	0.1	0.9	4.2	1.2	6.4

Mesh Fraction	<u>Cumulative Volume</u>					Total
	<u>Volume, ml. at STP</u>					
	<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	
- 70 + 100	0.0	0.2	0.1	1.5	0.1	1.9
- 100 + 200	0.0	0.5	0.3	2.4	0.1	3.3
- 200 + 325	0.0	0.6	0.6	3.6	0.2	5.0

TABLE V

TOTAL GAS VOLUMES FOR TEN GRAM SAMPLES OF METALS DISINTEGRATING COMPANY POWDER HEATED TO 1800°F IN THE BALL MILLED, RINSED, AND AS RECEIVED CONDITIONS; - 70 + 100 MESH FRACTION

<u>Condition</u>	<u>Volume, ml. at STP</u>						<u>Total</u>
	<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	<u>N₂</u>	
Rinsed in HNO ₃	0.0	0.4	0.0	1.1	0.2	0.2	1.9
Ball Milled	0.0	0.6	0.2	1.1	1.5	0.1	3.5
As Received	0.0	0.2	0.1	1.9	0.6	0.0	2.8

TABLE VI

TOTAL GAS VOLUMES EVOLVED FROM TEN GRAM SAMPLES OF METALS DISINTEGRATING COMPANY POWDER HEATED TO 1800°F AFTER RINSING IN NITRIC ACID AND REEXPOSURE TO AIR; - 70 + 100 MESH FRACTION

<u>Time of Reexposure, Hours</u>	<u>Volume, ml. at STP</u>					<u>Total</u>
	<u>H₂O</u>	<u>CO</u>	<u>N₂</u>	<u>CO₂</u>	<u>SO₂</u>	
0	0.4	0.0	0.2	1.1	0.2	1.9
6	0.6	0.0	0.2	1.4	0.6	2.8
12	1.0	0.0	0.3	1.7	0.4	3.4
24	0.6	0.0	0.2	1.8	0.6	3.2
48	0.4	0.0	0.2	2.0	0.4	3.0
96	0.2	0.0	0.3	1.7	0.6	2.8

as a function of time are presented in Figure 6 and Table VI.

The cumulative volume gas desorption analyses for three mesh fractions of this powder are presented in Figures 7, 8, and 9 and in Table VII. In addition, the cumulative volumes at 1800°F are presented in Table IV for comparison with the total gas desorption volumes at this temperature.

Several plots have been derived from the desorption data and are presented in graphical form. Figure 10 shows the relation between volume desorbed and apparent surface area, and is taken from the total volume analyses presented in Table IV. A plot of $\log P$ vs $1/T$ for CO and CO₂ is presented in Figure 11. These data are taken from the data of Table VIII, and give a means of determining the heat of desorption for CO₂, which exhibits linearity over this temperature range. Figure 12 is a combination of two separate studies. One plot on this graph is a summation of the component gases in the cumulative volume run of Figure 6. The other plot on this graph shows the growth of a powdered nickel compact as a function of temperature, as determined by Fedorchenko (15). These plots are presented on the same graph for later comparison.

The results of X-ray diffraction studies of ball milled fines from the -70+100 fraction of this powder taken before and after cumulative runs are given in Table IX.

Vacuum fusion runs were made on duplicate samples of -70+100 mesh powder after cumulative and total gas desorption studies as well as in the as received condition, and these data are presented in Table X.

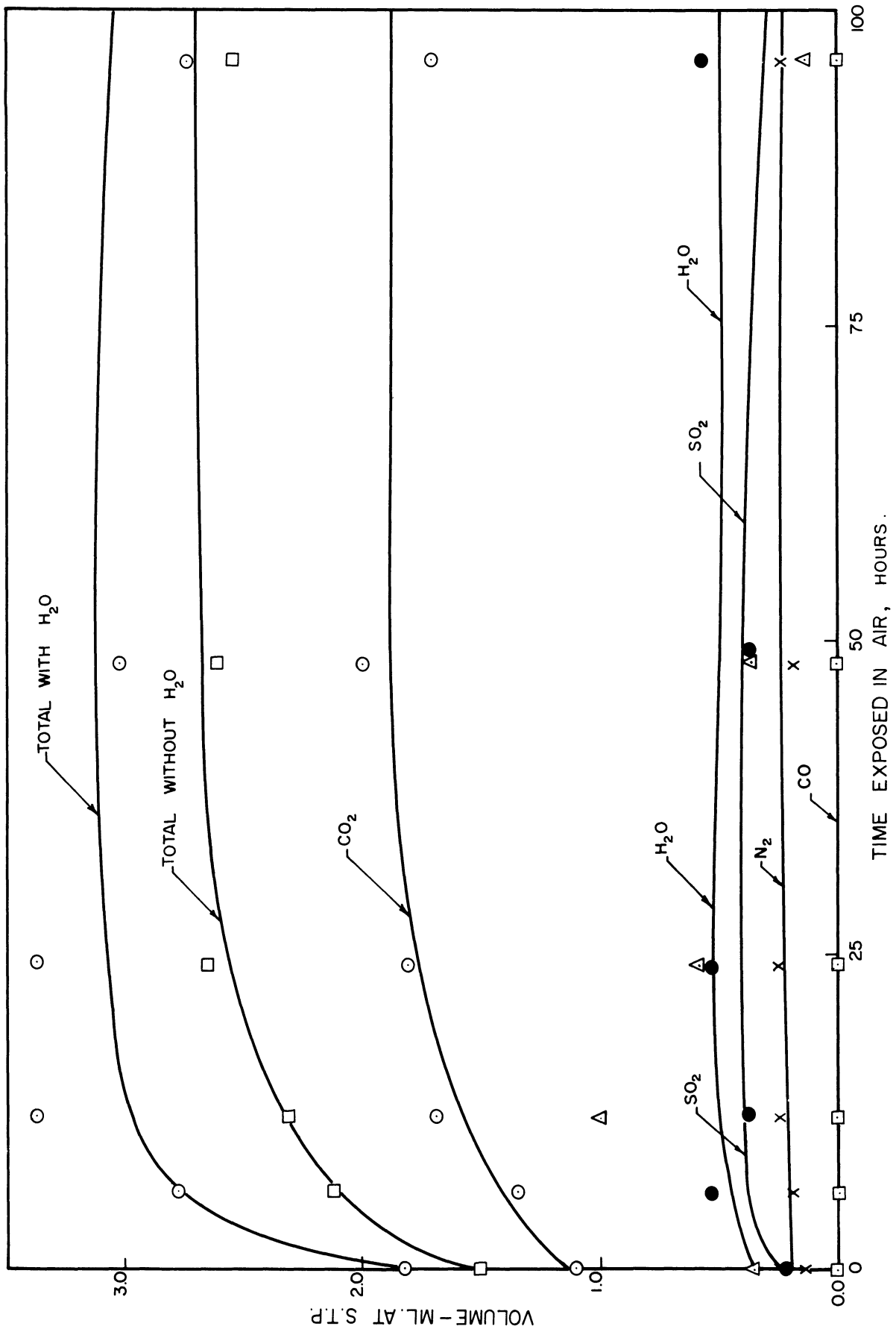


Figure 6. Total Gas Volumes as a Function of Time for Ten Gram Samples of Metals Disintegrating Company Powder Rinsed in Nitric Acid and Reexposed in Air; -70 + 100 Mesh Fraction

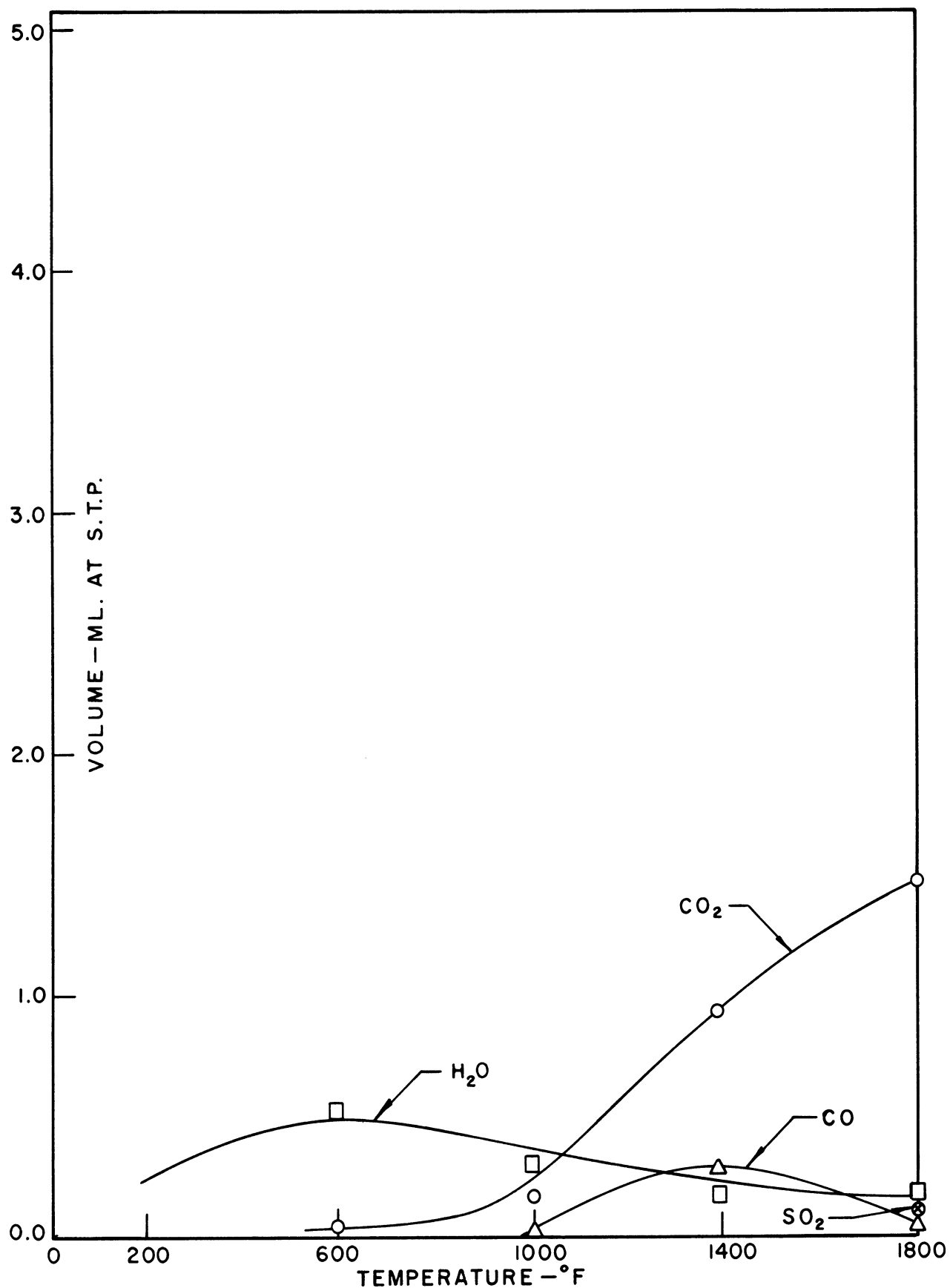


Figure 7. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Metals Disintegrating Company Powder in the As Received Condition; -70 +100 Mesh Fraction.

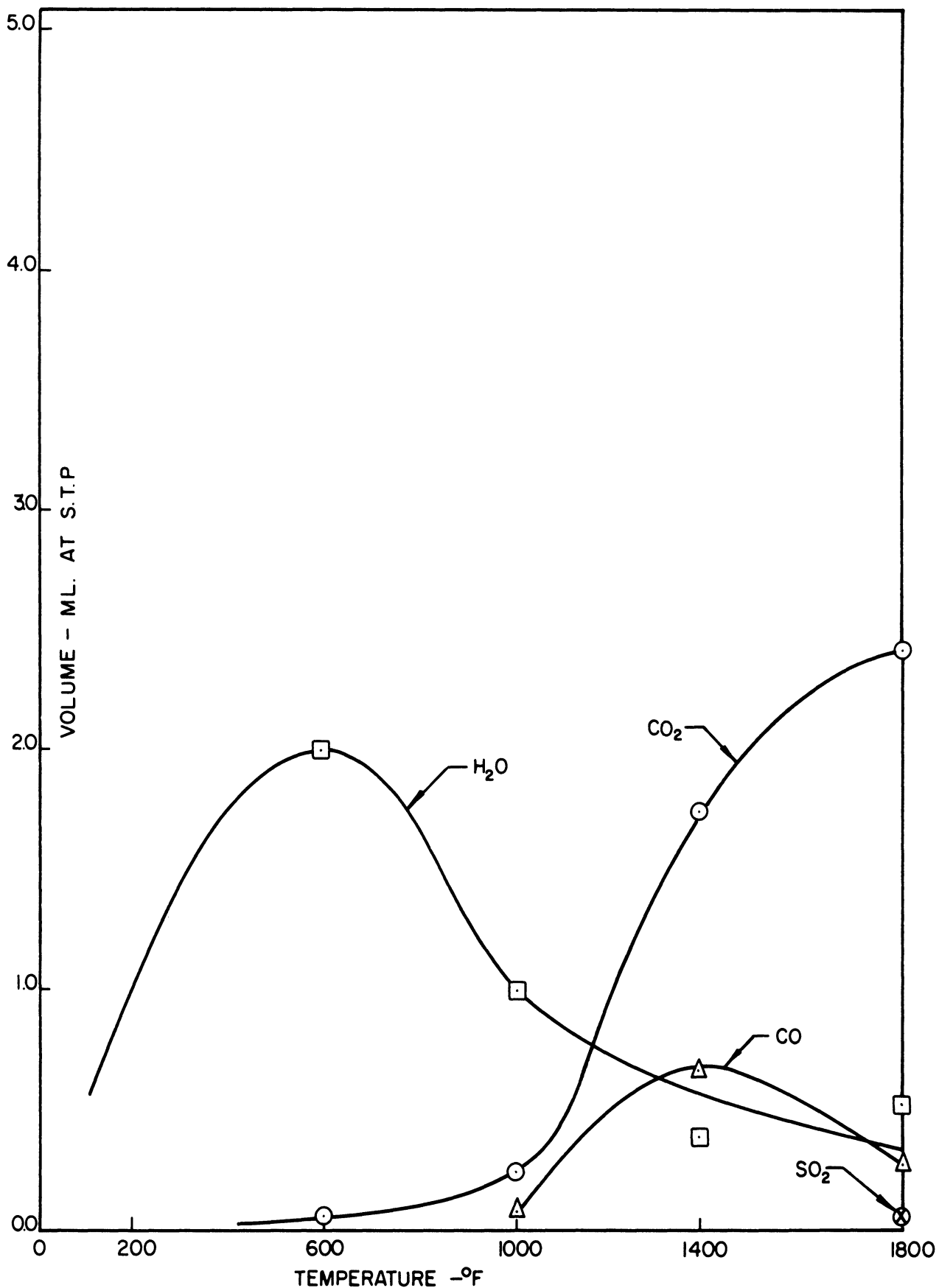


Figure 8. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Metals Disintegrating Company Powder in the As Received Condition; -100 +200 Mesh Fraction.

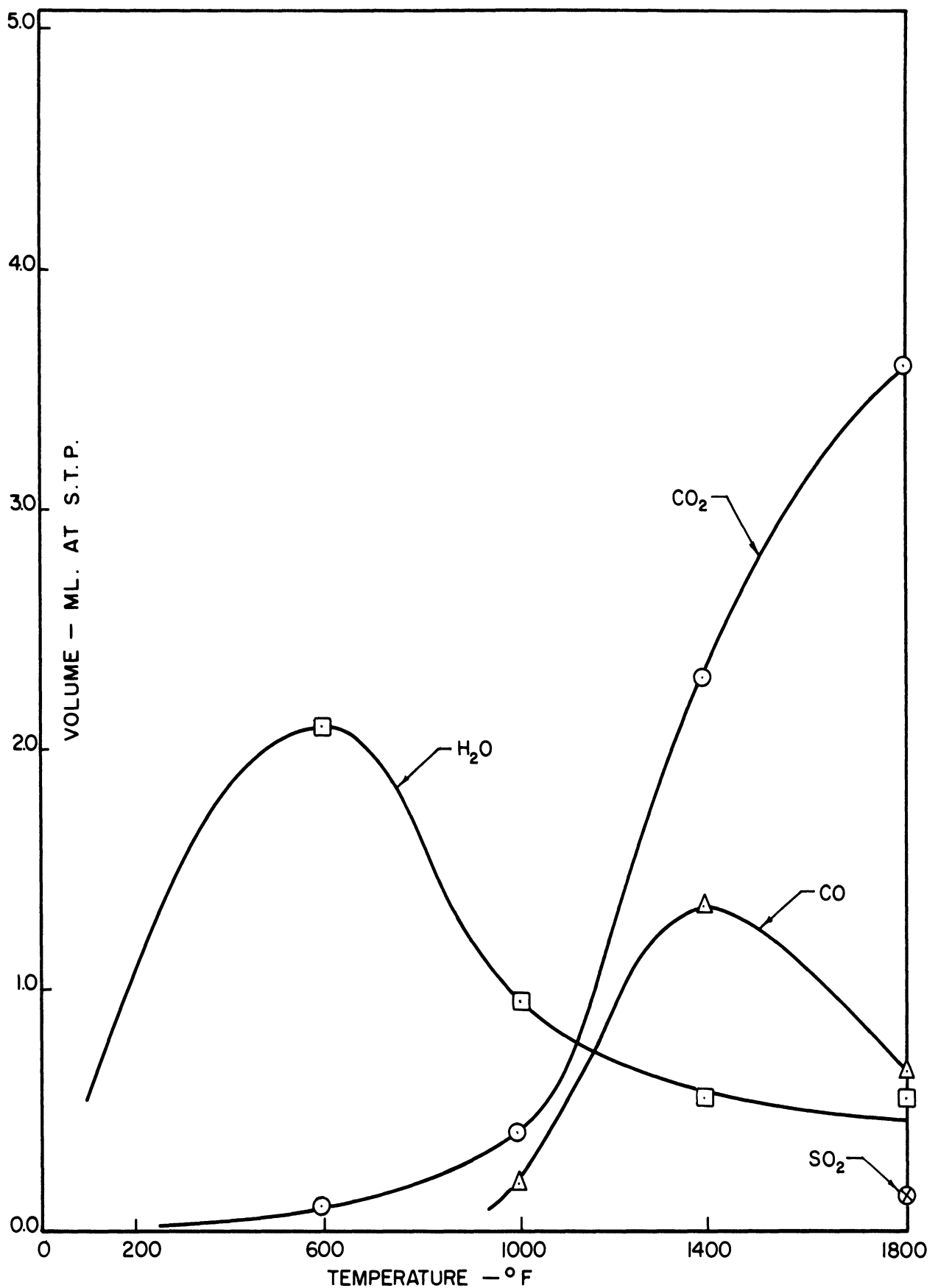


Figure 9. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Metals Disintegrating Company Powder in the As Received Condition; -200 +325 Mesh Fraction.

TABLE VII

CUMULATIVE VOLUMES OF GASES EVOLVED FROM A TEN GRAM SAMPLE OF METALS DISINTEGRATING COMPANY POWDER IN THE AS RECEIVED CONDITION; - 70 + 100, - 100 + 200, AND - 200 + 325 MESH FRACTIONS

<u>Mesh Fraction</u>	<u>Temperature, °F</u>	<u>Volume, ml. at STP</u>				
		<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	<u>Total</u>
- 70 + 100	600	0.5	0.0	0.1	0.0	0.6
	1000	0.3	0.0	0.2	0.0	0.5
	1400	0.2	0.3	0.9	0.0	1.4
	1800	0.2	0.1	1.5	0.1	1.9
- 100 + 200	600	2.0	0.0	0.1	0.0	2.1
	1000	1.0	0.1	0.2	0.0	1.3
	1400	0.4	0.7	1.7	0.0	2.8
	1800	0.5	0.3	2.4	0.1	3.3
- 200 + 325	600	2.1	0.0	0.1	0.0	2.2
	1000	1.0	0.2	0.4	0.0	1.6
	1400	0.6	1.3	2.3	0.0	4.2
	1800	0.6	0.6	3.6	0.2	5.0

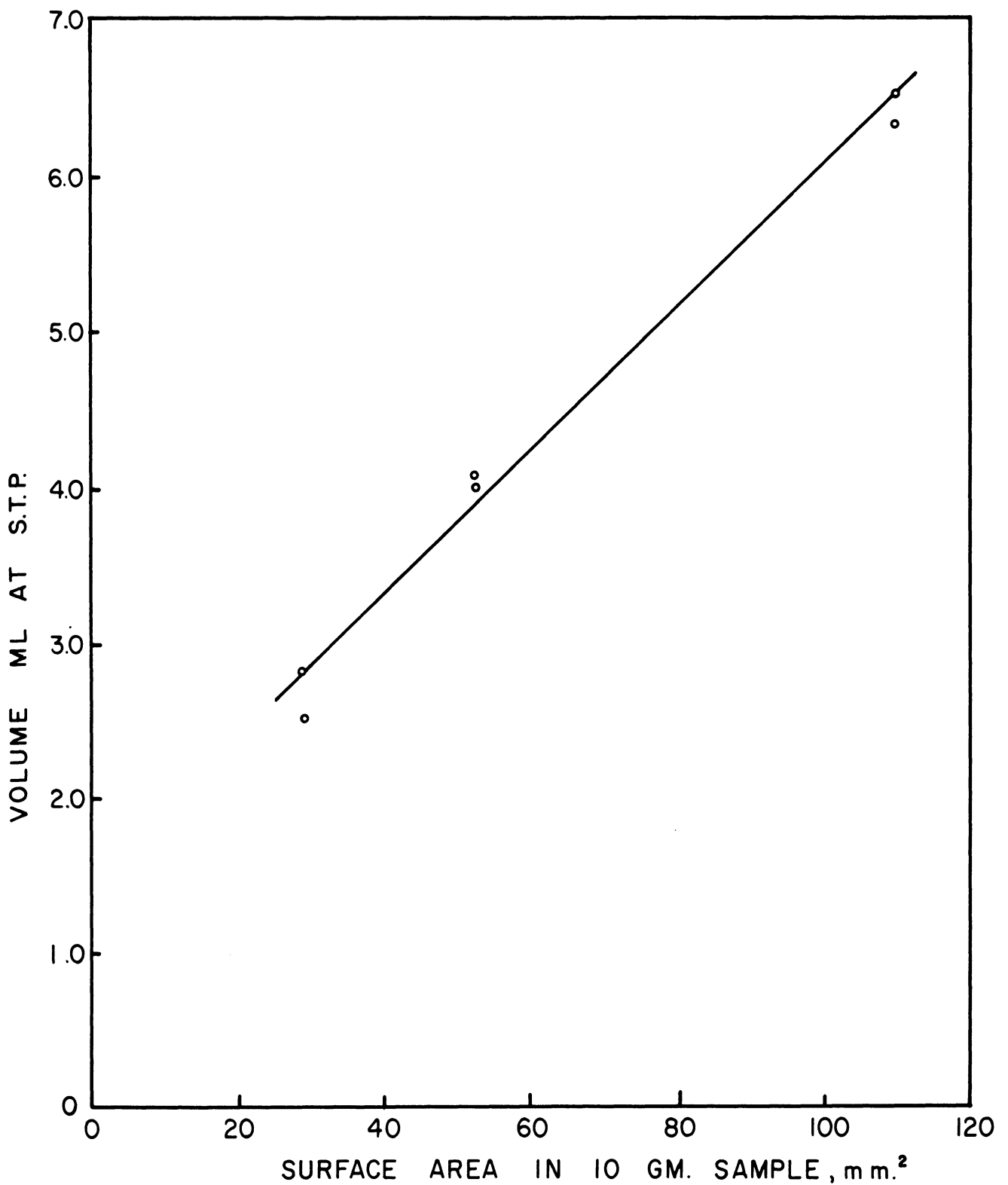


Figure 10. Total Gas Volumes as a Function of Apparent Surface Area for Ten Gram Samples of Metals Disintegrating Company Powder Heated to 1800°F in the As Received Condition.

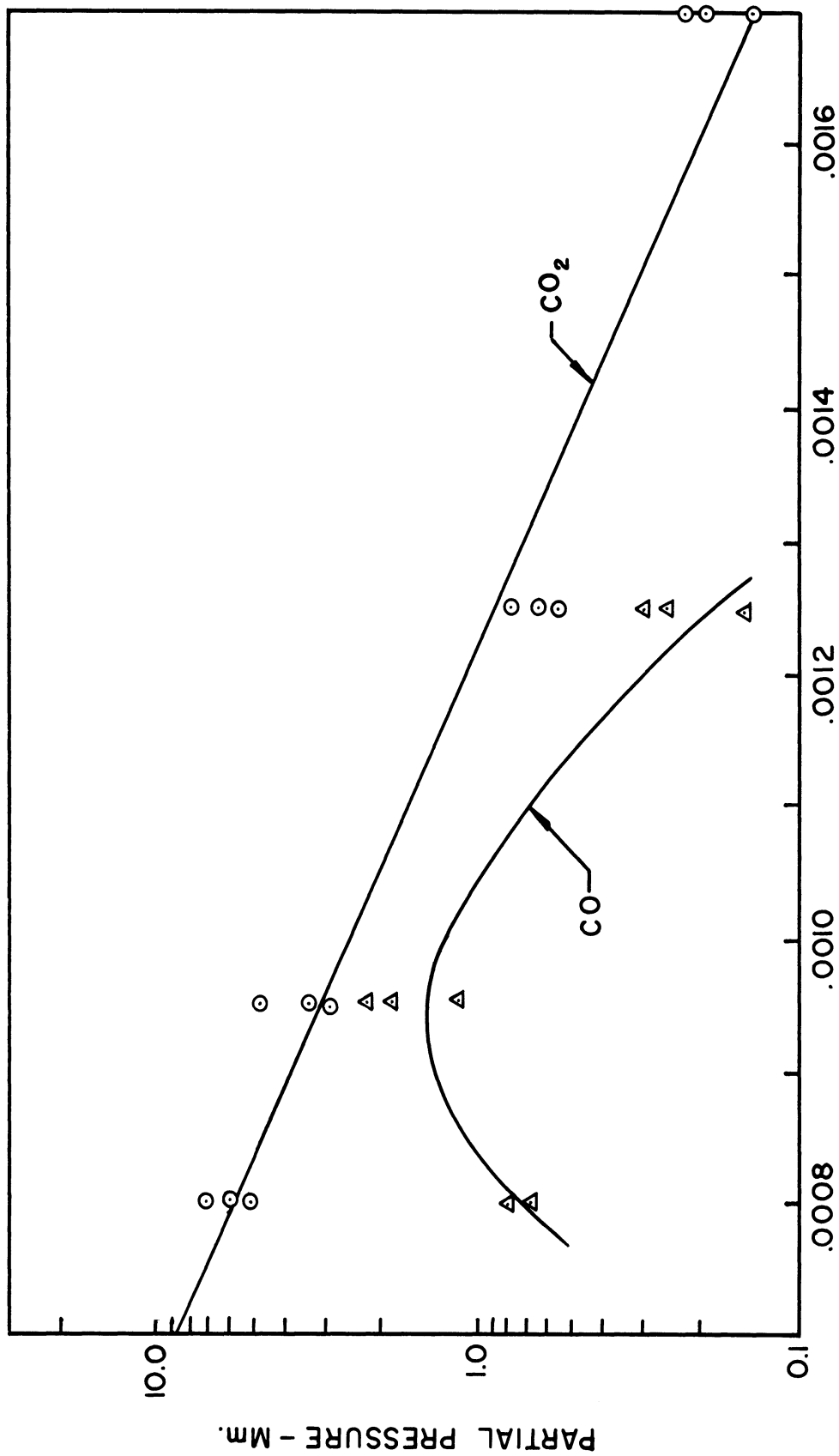


Figure 11. Log Partial Pressure, Carbon Monoxide and Carbon Dioxide, as a Function of the Reciprocal of Absolute Temperature for Metals Disintegrating Company Powder in the As Received Condition; -70 +100, -100 +200, and -200 +325 Mesh Fractions.

TABLE VIII

PARTIAL PRESSURES OF GASES EVOLVED FROM METALS DISINTEGRATING COMPANY POWDER IN THE AS RECEIVED CONDITION; - 70 + 100, - 100 + 200, AND - 200 + 325 MESH FRACTIONS

Mesh Fraction	Temperature °F	Pressure, mm. of Hg			
		H ₂ O	CO	CO ₂	SO ₂
- 70 + 100	600	0.17	0.00	0.20	0.00
	1000	0.95	0.13	0.59	0.00
	1400	0.50	1.08	3.28	0.00
	1800	0.41	0.04	5.26	0.00
- 100 + 200	600	6.35	0.02	0.21	0.00
	1000	2.80	0.22	0.83	0.00
	1400	0.00	2.08	5.40	0.00
	1800	2.44	0.62	7.10	0.02
- 200 + 325	600	2.77	0.21	0.15	0.00
	1000	0.74	0.32	0.60	0.00
	1400	0.00	1.85	3.20	0.00
	1800	0.00	0.64	5.25	0.00

Heat of Desorption for CO₂:

$$\log \frac{P_2}{P_1} = \frac{\Delta H_d}{2.3R} \left(\frac{T_2 - T_1}{T_2 \times T_1} \right)$$

$$\log \frac{6.0}{0.15} = \frac{\Delta H_d}{(2.3)(1.987)} \left(\frac{1255 - 589}{1255 \times 589} \right)$$

$$\Delta H_d = 8150 \text{ cal/mol}$$

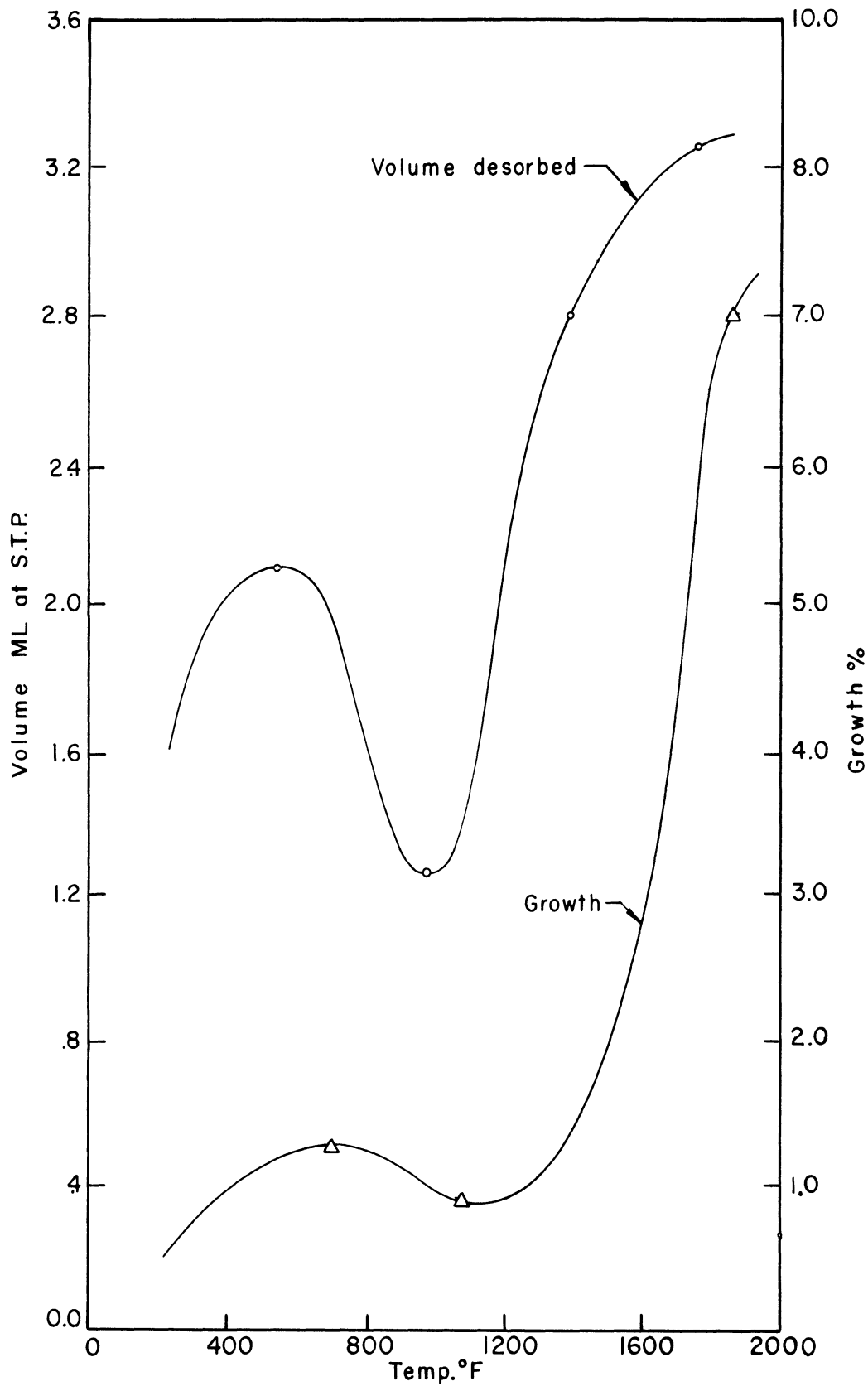


Figure 12. Summation of Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Metals Disintegrating Company Powder; -70 + 100 Mesh Fraction, and Growth of a Powdered Nickel Compact as a Function of Temperature

TABLE IX

X-RAY DIFFRACTION ANALYSES OF BALL MILL FINES FROM METALS
DISINTEGRATING COMPANY AND PLASTIC METALS COMPANY POWDER,
BEFORE AND AFTER CUMULATIVE GAS DESORPTION TESTS

<u>"d"</u>	<u>Identification</u>	<u>Metals Disintegrating Company Powder</u>		<u>Plastic Metals Company Powder</u>	
		<u>before</u>	<u>after</u>	<u>before</u>	<u>after</u>
0.788	Ni	P	P	P	P
0.808	Ni	P	P	P	P
0.881	Ni	P	P	P	P
1.017	Ni	P	P	P	P
1.062	Ni	P	P	P	P
1.246	Ni	P	P	P	P
1.476	NiO	P	NP	NP	NP
1.762	Ni	P	P	P	P
2.034	Ni	P	P	P	P
2.088	NiO	P	NP	NP	NP
2.410	NiO	P	NP	NP	NP

P = Present

NP = Not Present after
One Hour Exposure

TABLE X

VACUUM FUSION ANALYSIS OF METALS DISINTEGRATING COMPANY POWDER
IN THE AS RECEIVED CONDITION, AND AFTER BOTH TOTAL VOLUME
GAS DESORPTION TESTING AND CUMULATIVE GAS DESORPTION TESTING

<u>Condition</u>	<u>Gas Content</u>					
	<u>Wt. %</u>			<u>ml. per 10gm.(S.T.P.)</u>		
	<u>N₂</u>	<u>O₂</u>	<u>H₂</u>	<u>N₂</u>	<u>O₂</u>	<u>H₂</u>
As Received	0.00163	0.296	0.00040	0.1	20.7	0.5
As Received	0.00061	0.214	0.00058	0.1	15.0	0.7
After Cumulative Run	0.00098	0.255	0.00075	0.1	17.9	0.8
After Cumulative Run	0.00194	0.299	0.00099	0.2	20.9	1.1
After Total Run	0.00177	0.258	0.00068	0.1	18.0	0.8
After Total Run	0.00150	0.218	0.00268	0.1	15.3	3.0

TABLE XI

GASES EVOLVED FROM A TEN GRAM SAMPLE OF METALS DISINTEGRATING
COMPANY POWDER DEGASSED AND REEXPOSED TO A CO ATMOSPHERE;
- 70 + 100 MESH FRACTION

<u>Temperature, °F</u>	<u>Volume, ml. at STP</u>	
	<u>CO</u>	<u>H₂O</u>
1800	0.1	0.0

The results of a test made to determine the readsorption characteristics of carbon monoxide on this powder are presented in Table XI.

Plastic Metals Company Powder

The total volume gas desorption analyses for three mesh fractions of this powder are shown in Table XII. The cumulative volume gas desorption analyses for the same three mesh fractions are shown in Figures 13, 14, and 15 and Table XIII. The cumulative gas desorption volumes at 1800°F are also presented in Table XII for comparison with the total volume runs.

The results of X-ray diffraction studies of ball milled fines from the -70+100 fraction of this powder taken before and after cumulative gas desorption studies are given in Table IX.

Sherritt Gordon Company Powder

The total volume gas desorption analyses for two mesh fractions of this powder are presented in Table XIV. The cumulative volume gas desorption analyses for these same two mesh fractions are shown in Figures 16 and 17 and in Table XV. In addition the cumulative volumes at 1800°F are presented in Table XIV for purposes of comparison.

Federal Mogul Company Powder

The cumulative volume gas desorption analyses of a -70+100 mesh sample of this powder is given in Figure 18 and Table XVI. The results of vacuum fusion work on this powder in the as received condition are presented in Table XVII.

TABLE XII

TOTAL AND CUMULATIVE GAS VOLUMES FOR TEN GRAM SAMPLES OF PLASTIC METALS COMPANY POWDER HEATED TO 1800°F IN THE AS RECEIVED CONDITION;
- 70 + 100, - 100 + 200, and - 200 + 325 MESH FRACTIONS

	<u>Total Volume</u>					
	<u>Volume, ml. at STP</u>					
<u>Mesh Fraction</u>	<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	<u>Total</u>
- 70 + 100	0.1	0.4	5.2	0.6	0.0	6.3
- 100 + 200	0.0	0.3	4.0	1.1	0.0	5.4
- 200 + 325	0.4	0.4	4.5	0.8	0.0	6.1

<u>Mesh Fraction</u>	<u>Cumulative Volume</u>					
	<u>Volume, ml. at STP</u>					
	<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	<u>Total</u>
- 70 + 100	0.6	0.2	5.0	0.4	0.0	6.2
- 100 + 200	0.3	0.5	3.4	1.3	0.0	5.5
- 200 + 325	0.9	0.4	4.8	1.0	0.0	7.1

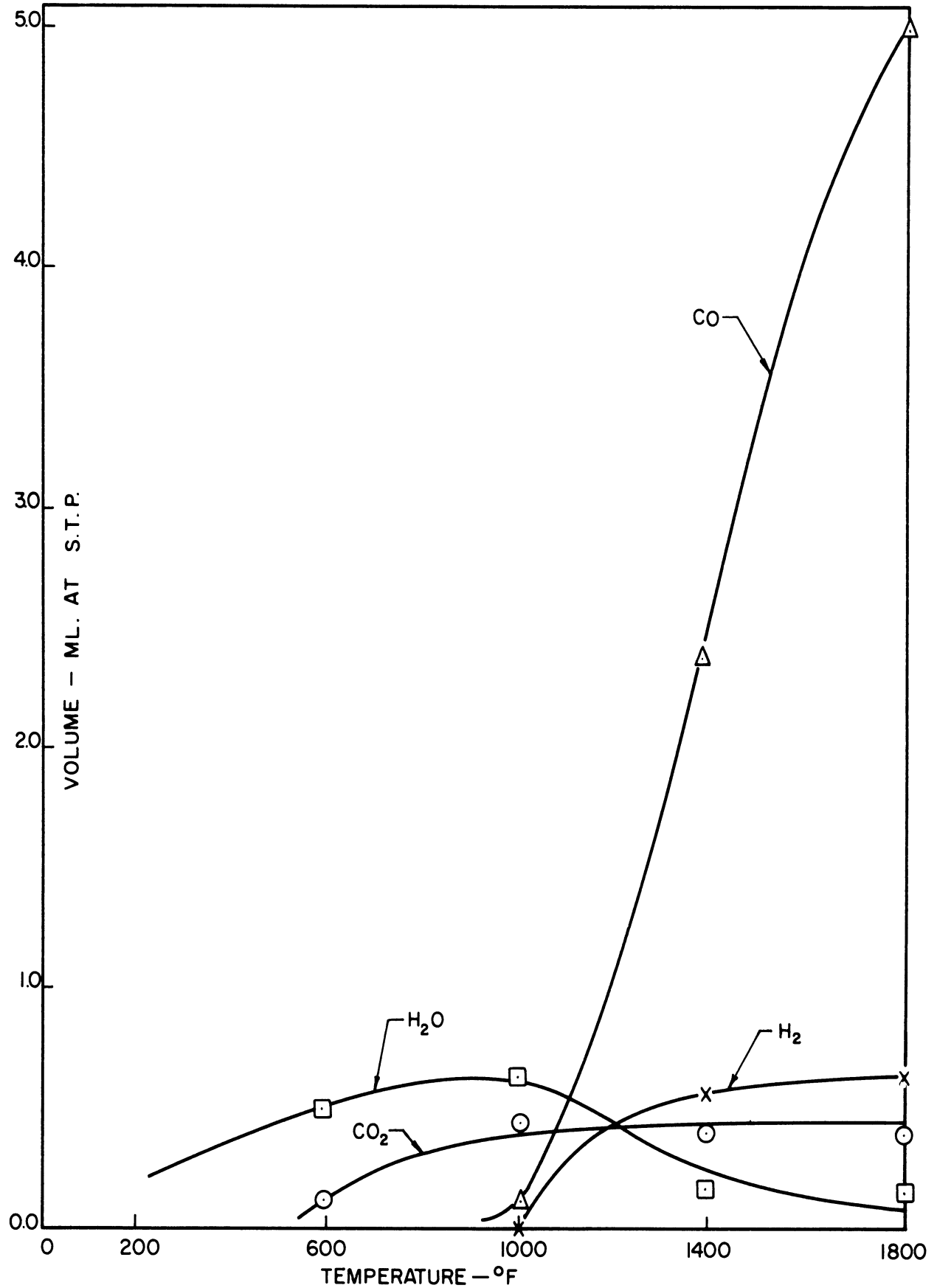


Figure 13. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Plastic Metals Company Powder in the As Received Condition; -70 +100 Mesh Fraction.

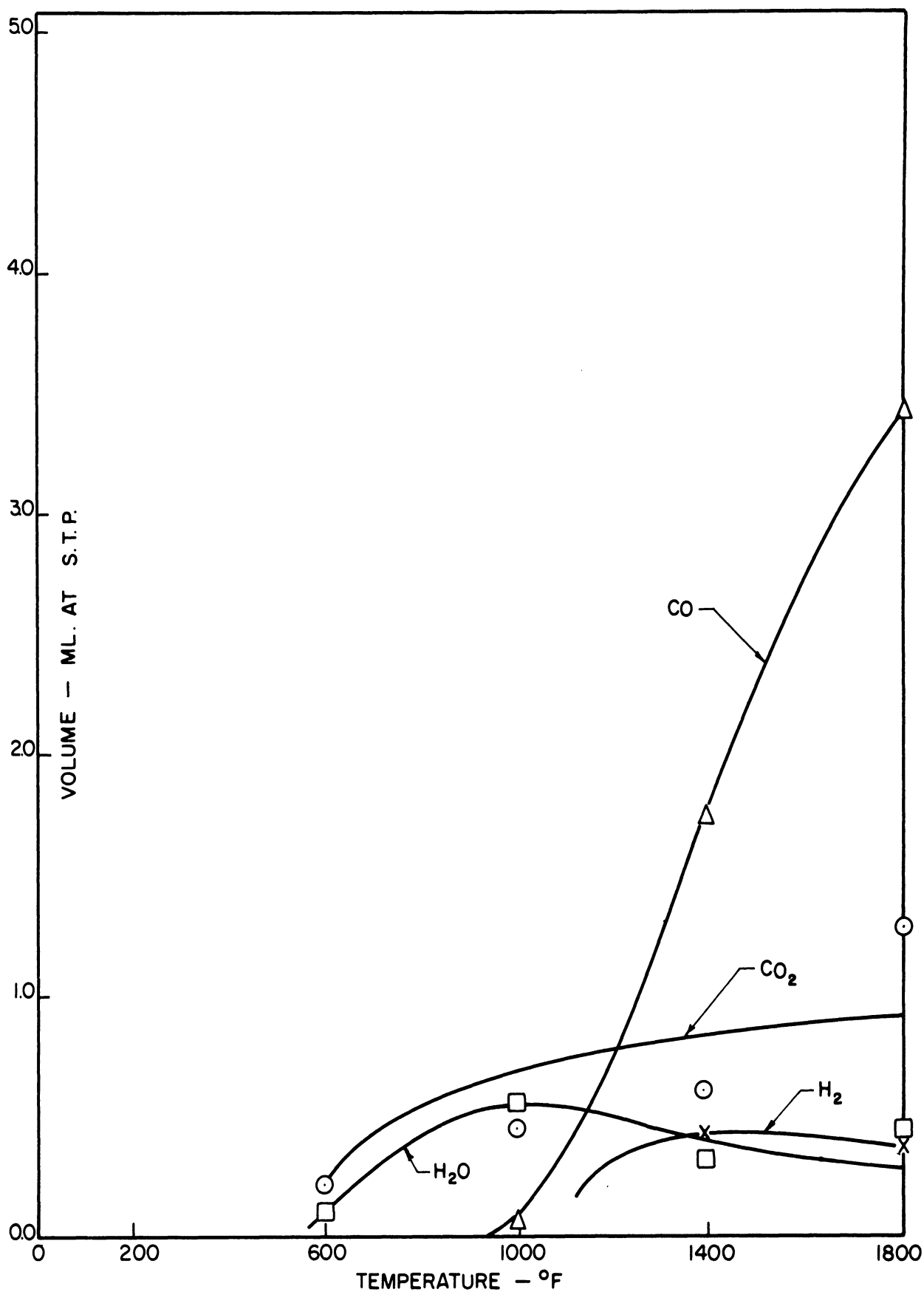


Figure 14. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Plastic Metals Company Powder in the As Received Condition; -100 +200 Mesh Fraction.

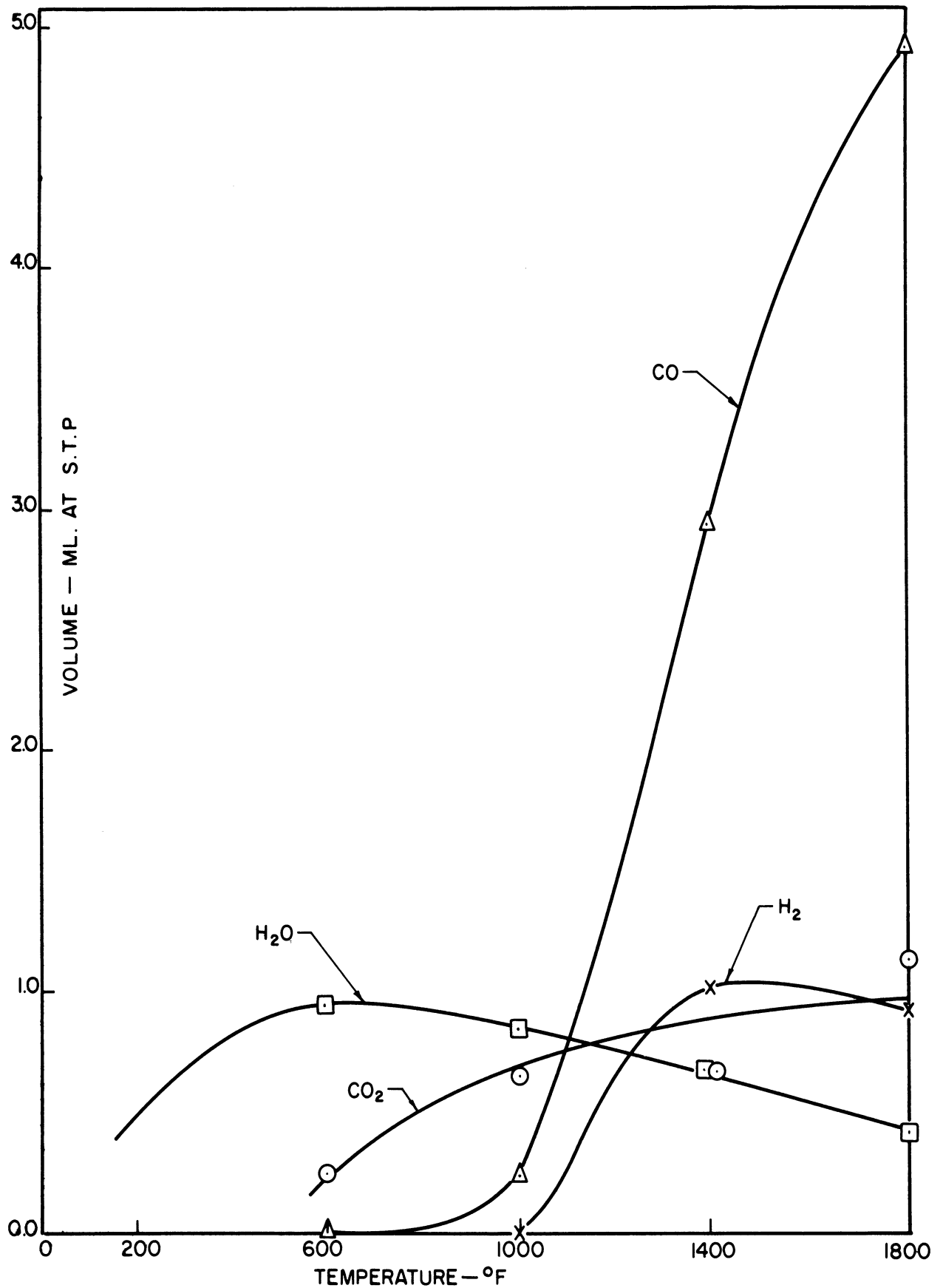


Figure 15. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Plastic Metals Company Powder in the As Received Condition; -200 +325 Mesh Fraction.

TABLE XIII

CUMULATIVE VOLUMES OF GASES EVOLVED FROM A TEN GRAM SAMPLE OF
PLASTIC METALS COMPANY POWDER IN THE AS RECEIVED CONDITION;
- 70 + 100, - 100 + 200, AND - 200 + 325 MESH FRACTIONS

<u>Mesh Fraction</u>	<u>Temperature °F</u>	<u>Volume, ml. at STP</u>				
		<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>Total</u>
- 70 + 100	600	0.0	0.5	0.0	0.1	0.6
	1000	0.0	0.6	0.1	0.4	1.1
	1400	0.6	0.2	2.3	0.4	3.5
	1800	0.6	0.2	5.0	0.4	6.2
- 100 + 200	600	0.0	0.1	0.0	0.2	0.3
	1000	0.0	0.6	0.1	0.5	1.2
	1400	0.5	0.3	1.8	0.6	3.2
	1800	0.3	0.5	3.4	1.3	5.5
- 200 + 325	600	0.0	0.9	0.0	0.3	1.2
	1000	0.0	0.9	0.2	0.6	1.7
	1400	1.0	0.7	3.0	0.7	5.4
	1800	0.9	0.4	4.8	1.0	7.1

TABLE XIV

TOTAL AND CUMULATIVE GAS VOLUMES FOR TEN GRAM SAMPLES OF SHERRITT GORDON MINES LTD. POWDER HEATED TO 1800°F IN THE AS RECEIVED CONDITION; - 100 + 200, AND - 200 + 325 MESH FRACTIONS

<u>Mesh Fraction</u>	<u>Total Volume</u>					
	<u>Volume, ml. at STP</u>					
	<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	<u>Total</u>
- 100 + 200	0.0	3.9	0.1	1.8	0.4	6.2
- 200 + 325	0.0	3.1	0.3	2.0	0.3	5.7

<u>Mesh Fraction</u>	<u>Cumulative Volume</u>					
	<u>Volume, ml. at STP</u>					
	<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	<u>Total</u>
- 100 + 200	1.1	1.6	0.2	1.5	0.1	4.5
- 200 + 325	0.5	1.5	0.1	1.6	0.3	4.0

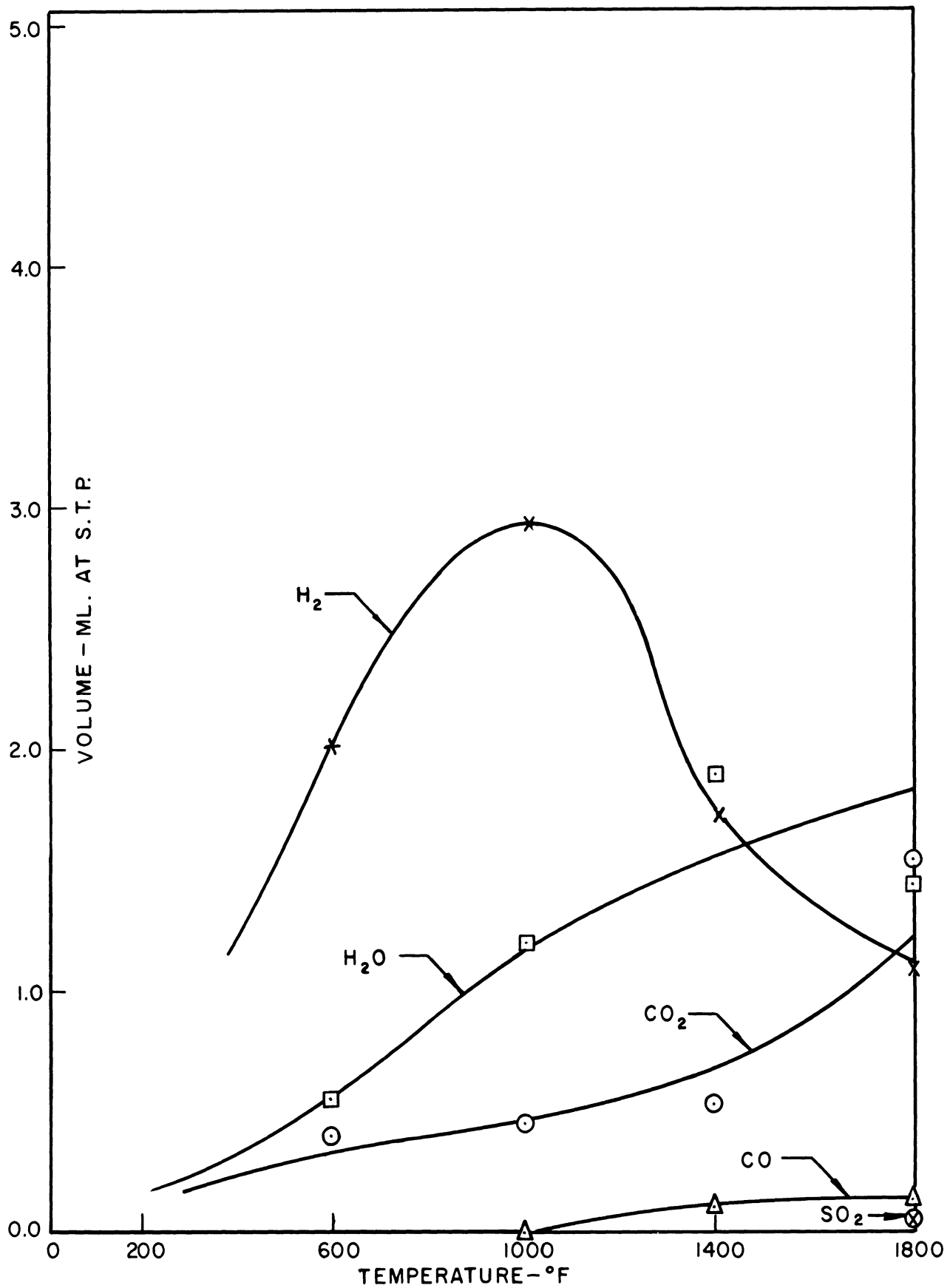


Figure 16. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Sherritt Gordon Mines Ltd. Powder in the As Received Condition; -100 +200 Mesh Fraction.

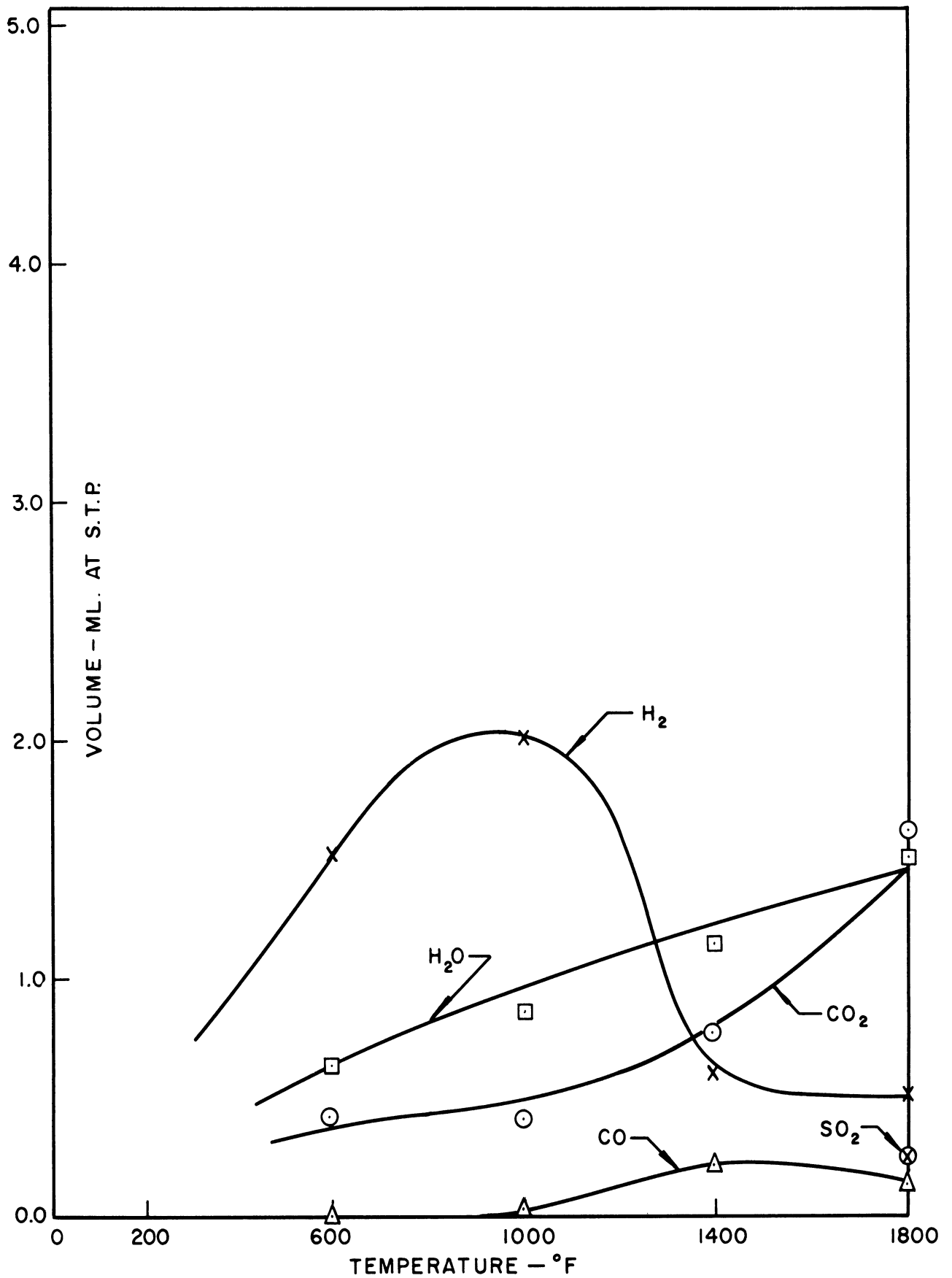


Figure 17. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Sherritt Gordon Mines Ltd. Powder in the As Received Condition; -200 +325 Mesh Fraction.

TABLE XV

CUMULATIVE VOLUMES OF GASES EVOLVED FROM A TEN GRAM SAMPLE OF SHERRITT GORDON MINES LTD. POWDER IN THE AS RECEIVED CONDITION; - 100 + 200, AND - 200 + 325 MESH FRACTIONS

<u>Mesh Fraction</u>	<u>Temperature, °F</u>	<u>Volume, ml. at STP</u>					<u>Total</u>
		<u>H₂</u>	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>	
- 100 + 200	600	2.1	0.6	0.0	0.4	0.0	3.1
	1000	3.0	1.2	0.0	0.4	0.0	4.6
	1400	1.7	1.9	0.1	0.5	0.0	4.2
	1800	1.1	1.6	0.2	1.5	0.1	4.5
- 200 + 325	600	1.5	0.6	0.0	0.4	0.0	2.5
	1000	2.0	0.9	0.1	0.4	0.0	3.4
	1400	0.6	1.2	0.2	0.8	0.0	2.8
	1800	0.5	1.5	0.1	1.6	0.3	4.0

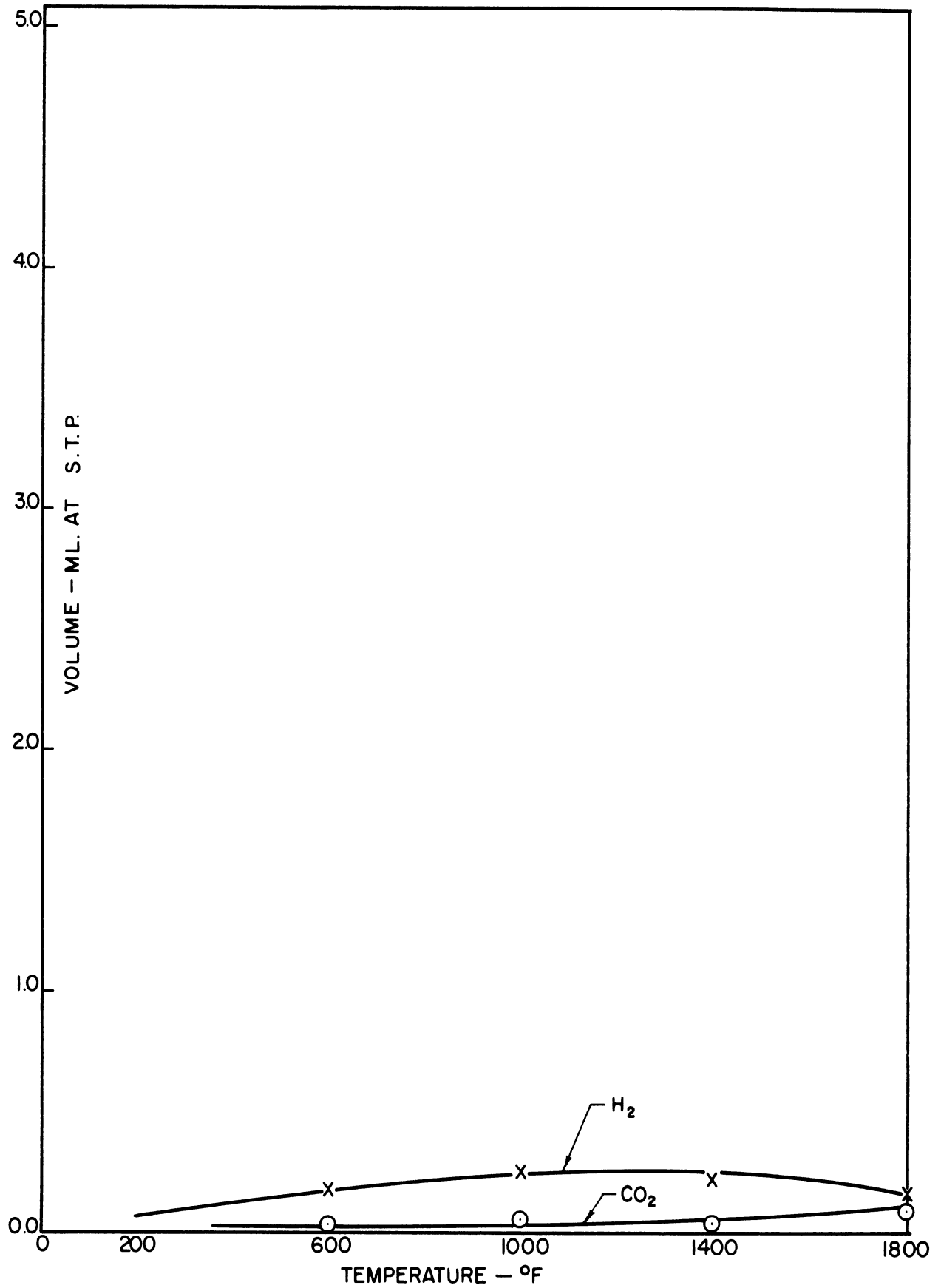


Figure 18. Cumulative Gas Volumes as a Function of Temperature for a Ten Gram Sample of Federal Mogul Company Powder in the As Received Condition; -70 +100 Mesh Fraction.

TABLE XVI

CUMULATIVE VOLUMES OF GASES EVOLVED FROM A TEN GRAM SAMPLE
OF FEDERAL MOGUL COMPANY POWDER IN THE AS RECEIVED CONDITION;
- 70 + 100 MESH FRACTION

Temperature, °F	Volume, ml. at STP	
	<u>H₂</u>	<u>CO₂</u>
600	0.2	0.1
1000	0.3	0.1
1400	0.2	0.1
1800	0.1	0.1

TABLE XVII

VACUUM FUSION ANALYSIS OF FEDERAL MOGUL POWDER IN THE AS
RECEIVED CONDITION; - 70 + 100
MESH FRACTION

	<u>Gas Content</u>					
	<u>Wt. %</u>			<u>ml. per 10gm. (S.T.P.)</u>		
	<u>N₂</u>	<u>O₂</u>	<u>H₂</u>	<u>N₂</u>	<u>O₂</u>	<u>H₂</u>
Sample No. 1	0.0009	0.284	0.0023	0.1	19.9	2.6
Sample No. 2	0.0007	0.304	0.0013	0.1	21.2	1.5

Comparison of Gas Analysis Techniques

As a means of comparing the gas analyses made by vacuum fusion and mass spectrographic techniques, identical gas samples were analyzed by both methods. The gas samples were obtained from Metals Disintegrating Company powder and Federal Mogul Company powder. The two comparisons made in every case were based on the analysis for oxygen plus carbon monoxide plus carbon dioxide, and hydrogen plus water vapor. The data resulting from these tests are presented in Table XVIII.

TABLE XVIII

COMPARISON OF GAS ANALYSES PERFORMED BY MASS SPECTROSCOPY
AND VACUUM FUSION

<u>Sample</u>	<u>Components</u>	<u>Mass Spectrometer Analysis, Vol. %</u>	<u>Vacuum Fusion Analysis, Vol. %</u>
MD9119 Ni	O ₂ + CO + CO ₂	86.8	96.9
"	"	96.8	97.8
"	"	98.7	97.8
"	"	95.3	90.8
"	"	96.3	99.0
"	"	96.0	98.0
MD9119 Ni	H ₂ + H ₂ O	13.2	2.5
"	"	3.2	2.3
"	"	2.7	2.1
"	"	4.7	8.0
"	"	3.7	2.1
"	"	4.0	1.1
FM Ni	O ₂ + CO + CO ₂	94.7	94.4
"	"	93.3	93.8
"	"	90.5	95.9
FM Ni	H ₂ + H ₂ O	5.3	3.2
"	"	6.7	5.9
"	"	9.3	3.9

CHAPTER V

ANALYSIS OF RESULTS

The volumes and analyses of the gases liberated from the various nickel powders studied throughout the course of this investigation were found to be dependent upon the method of powder manufacture. The gases evolved were found to be mixtures of one or more species from a group composed of H_2 , CO_2 , CO , SO_2 , and H_2O . The number of different gases evolved and their relative abundance was found to vary widely between different powders, and also varied with temperature for a given powder.

The mechanisms of gas desorption were also found to be influenced by the manufacturing technique. Powder atomized in air without further treatment was observed to liberate gas by surface desorption. Powders heat treated in hydrogen bearing atmospheres after atomization evolved gases whose source was believed to be dissolved hydrogen, oxygen and carbon. The heat treatments were performed at temperatures sufficiently high to cause the evolution of any gases adsorbed during the manufacturing process. These treatments in hydrogen bearing atmospheres also increased the dissolved hydrogen content of the annealed powders.

Structural studies of both powdered and massive nickel surfaces by electron diffraction techniques were unsuccessful. No diffraction rings were obtained from fine, -325 mesh, powder, because of charging phenomena. Very faint and diffuse diffraction rings were obtained from massive nickel surfaces which had been polished, etched,

and reexposed in air, but no positive identifications could be made. Diffuse diffraction rings of this type have also been observed by other investigators. Phelps, Gulbransen, and Hickman observed very diffuse diffraction rings while studying oxide films formed on nickel under controlled conditions of temperature, time, and oxygen pressure (41). Schlier and Farnsworth studied low-energy electron diffraction patterns obtained from single crystal nickel surfaces which had been outgassed at elevated temperatures, and then reexposed to several gases for various times under controlled pressures (47). When only enough gas to form a monolayer was admitted to the sample tube, electron diffraction patterns were obtained, indicating that the nickel surface was covered by a residual gas lattice. As increasing amounts of gas were admitted to the sample tube, intensities of the diffracted beams decreased, and were finally extinguished, indicating that the surface layers had no oriented lattice structure. Other surface film studies have been made by Rhodin (42) (43) (44). In view of these results obtained by other investigators, the diffuse rings obtained in this investigation are probably the result of fairly thick adsorbed films whose outer layers had very little orientation in their structure.

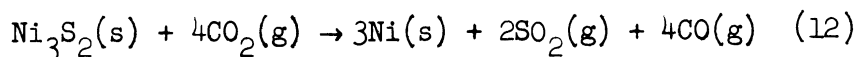
Metals Disintegrating Company Powder

This powder, produced by steam scattering in air, was studied in the greatest detail. It exhibited the greatest variety of desorption mechanisms, and for this reason received more study than the other powders.

Figure 10 shows that there is a correlation between gas volumes evolved and apparent surface area. This established the primary mechanism of gas evolution as surface desorption. This conclusion was further substantiated by tests wherein the influence of surface preparation on gas evolution was studied.

The total volume gas desorption studies, wherein evolved gases were condensed in a cold trap, show, in Table IV, that CO₂ was the major constituent of the gases evolved at 1800°F. These data also demonstrate that the volumes of CO, CO₂ and SO₂ evolved were related to the surface area, which established their mechanism of evolution as a surface phenomenon. The amount of water vapor liberated was erratic, and this was believed to be due to the low strength of the physical adsorptive bond by which water is known to be adsorbed on nickel (55) (62).

The amounts of SO₂ liberated in the total volume studies are shown to be considerably higher than those amounts liberated in the cumulative volume studies in Table IV. This was caused by the non-equilibrium nature of the experimental procedure, wherein the SO₂ was frozen out as soon as it was formed, thus allowing the reaction producing it to proceed to completion. This reaction is believed to be as follows:

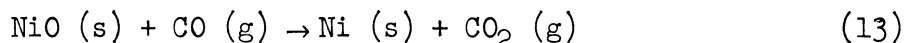


In the cumulative volume procedure, however, the gas system approached equilibrium and the amount of SO₂ produced was limited.

The cumulative volume gas desorption studies, shown in

Figures 7, 8, and 9 and Table VII, indicate the temperatures at which the various gases were evolved, and again show that CO₂ was the major constituent in the evolved gas mixture. Because these cumulative plots show the total volumes of the various gases evolved to a given temperature, it is apparent that a curve which shows a decreasing volume with increasing temperature indicates that the gas is reacting in some way so as to reduce its total volume at the higher temperature. It is believed that water vapor was undergoing a reaction to produce hydrogen and oxygen in the temperature range of 600°F to 1400°F, and that CO was undergoing a reaction to produce CO₂ between 1400°F and 1800°F. The amount of CO₂ evolved is seen to be decreasing at 1800°F, and it is believed that very little further gas evolution would have occurred between this temperature and the melting point. It should also be noted that very small amounts of SO₂ were liberated only at 1800°F.

The primary reaction involving CO is as follows:



The reduction of the nickel oxide is confirmed by the data of Table IX, which presents the x-ray diffraction results on the ball mill fines milled from the powder after a cumulative test as well as in the as received condition. The surface material milled from the as received powder indicated the presence of nickel oxide on the surface of the powder. Surface material milled from the powder in the same way after a cumulative gas desorption test showed that all of the nickel oxide had been removed from the surface of the

powder. That the CO was acting as the reducing agent is shown in all three of the cumulative studies, Figures 7, 8, and 9, where the CO is seen to reach a maximum at about 1400°F and then decrease. The CO₂ which was a product of this reaction was indistinguishable from the CO₂ produced by surface desorption, but the upward trend of the CO₂ curve between 1400°F and 1800°F in each of these three figures is probably due largely to the CO₂ produced by the reduction reaction.

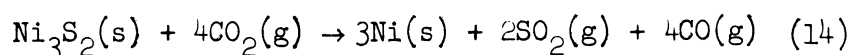
A comparison of the total and cumulative gas desorption studies at 1800°F, presented in Table IV, shows that the CO and CO₂ values are about the same in both runs. This was caused by the fact that the CO was not frozen out in the total volume runs, because it did not condense at the temperature of liquid nitrogen under the manifold pressure. Thus the CO was free to react with the hot nickel oxide, with the result that the CO volume was reduced to the same low level as observed in the cumulative run. The CO₂ produced by the reduction reaction in the total volume test was frozen out, and this had the effect of allowing the reaction to continue until all of the nickel oxide had been reduced. In both cases the powder was appreciably brighter after the desorption runs than in the as received condition, which also indicated the occurrence of an oxide reduction reaction.

The desorbed water vapor underwent a reaction at higher temperatures which involved a breakdown of the water molecule with a subsequent solutioning of the hydrogen in the nickel, and a probable reaction of the oxygen with CO to form CO₂. The solu-

tioning of the hydrogen is established by the vacuum fusion data of Table X which indicate that the powder contained significantly more dissolved hydrogen after the cumulative run than in the as received condition. The nickel did not show a significantly higher dissolved oxygen content after the cumulative run, which led to the hypothesis that the oxygen reacted with CO to form CO₂. The desorption of water vapor at relatively low temperatures was consistent with the literature which indicates that water is very weakly bonded to nickel by a physical adsorption bond, and should therefore be desorbed at a relatively low temperature (55) (62).

As a means of further investigating the surface dependence of the desorbed gases, powder surfaces were treated by ball milling and by rinsing in acid before total gas desorption runs were performed. Table V shows that both treatments effected the desorbed gas volumes significantly. The nitric acid rinse reduced the CO₂, CO and SO₂ volume desorbed, which again indicated that the desorption mechanism for these gases was a surface phenomenon.

The ball milling operation lowered the CO₂ gas volume desorbed, but increased the SO₂ volume. These data support the surface desorption mechanism for CO₂, and indicate that the SO₂ is the product of a reaction involving the oxidation of a nickel sulphide. The presence of the nickel sulphide was to be expected because sulfur was present in excess of its solubility limit. Apparently the ball milling brought more nickel sulphide into contact with the atmosphere where SO₂ was produced according to the reaction:



Both the ball milling and acid rinse increased the surface activity of the powder, as evidenced by a tendency for the powder to cling to the sides of the sample tube. That this surface activity was caused by unsatisfied surface forces of the type which cause adsorption was demonstrated by the fact that powders in both conditions desorbed nitrogen upon heating. Of all the samples investigated, there were the only ones to desorb nitrogen, which was presumably adsorbed during loading when the "active" powder was briefly exposed to air.

This tendency for the cleaned powder to readsorb gases was studied by exposing powder rinsed in nitric acid to air for periods of time up to 96 hours. The results of these tests are presented in Figure 6 and Table VI, and show that readsorption was completed in about 24 hours. This readsorption was limited primarily to CO_2 and smaller amounts of nitrogen. It is believed that both of these gases were adsorbed directly from the atmosphere. The water data again tend to be erratic because of the weak adsorptive bond. The SO_2 curve shows no definite trend, which lends support to the hypothesis that the SO_2 was produced by the oxidation of a nickel sulphide distributed throughout the powder matrix.

To check the readsorption characteristics of CO, whose concentration is believed to be too low in the atmosphere to cause appreciable adsorption, a separate test was performed. A powder sample was heated at 1800°F for one hour under vacuum and then cooled to room temperature. The sample was then exposed to a pure CO atmosphere at 300 millimeters pressure for one hour, and then the

sample was reevacuated for another hour. Following this treatment, the normal total gas desorption technique was used to obtain a sample of the desorbed gases. The desorption data are given in Table XI. The gas sample contained only CO and a trace of water vapor which was probably an impurity in the CO. A volume of 0.1 milliliters per ten grams of powder of CO was obtained, which is about the same as the amount of this gas evolved from a sample in the as received condition. This test demonstrated that CO is adsorbed by this type of powder and that the postulated source of CO, surface desorption, is reasonable. The as received samples probably adsorbed their CO and CO₂ during manufacturing when these gases could have been formed from reactions between dissolved carbon and oxygen.

In Figure 11 the logarithms of the partial pressures of the desorbed gases are plotted as a function of temperature. This plot was derived from the data of Figures 7, 8, and 9 and Table VIII, and was used to determine the heat of desorption for the various gases over the temperature range of 600°F to 1800°F. Data from this plot were used to solve an integrated form of the van't Hoff equation for the heat of desorption. This equation may be written:

$$\log P_2/P_1 = (\Delta H/2.3 R) (T_2 - T_1/T_1T_2) \quad (15)$$

P_1 and P_2 are the equilibrium pressures of the gas at absolute temperatures T_1 and T_2 . The gas constant is R , and the heat of desorption is ΔH . Figure 8 shows that only CO₂ exhibits

a linear plot over this temperature range, and its ΔH value is about +8.2 kcal. per mole. The linearity of the plot would indicate that the CO_2 was being liberated by some sort of a surface compound, and the magnitude of the heat of desorption would indicate that the bonding forces were appreciably smaller than those present in bulk compounds.

The vacuum fusion data of Table X show that the oxygen content of the powder in all conditions of treatment is substantially higher than that which could be accounted for by the desorbed gases. As mentioned previously, CO and CO_2 adsorbed on the powder would analyze as oxygen. The excess of oxygen was due to dissolved oxygen, and oxygen present as nickel oxide, which can be seen in the photomicrographs of Figure 2. The solubility of oxygen in nickel is .020 weight percent at 600°C (66). Additional amounts of oxygen result in the formation of nickel oxide. If the nickel were free of oxygen and nickel oxide, the vacuum fusion analysis would theoretically show the maximum amount of CO and CO_2 that would be liberated if the powder were heated to its melting point. Then a subtraction of the CO and CO_2 desorbed at 1800°F would leave a remainder which would be the amount of CO and CO_2 that would be evolved if the powder were heated from 1800°F to its melting point. The powder, however, contained excessive amounts of dissolved oxygen and nickel oxide which made such calculations meaningless.

A comparison of the various nitrogen and oxygen analyses shows that the within sample variation exceeds the between sample

variation, which means that the between sample analyses are not significantly different. As mentioned previously, the samples tested after cumulative analysis had a higher hydrogen content than did the as received samples. This difference was attributed to the solutioning of hydrogen from reacted water vapor in the powder during the cumulative run.

Of secondary interest is the check made between gas analysis by vacuum fusion techniques and mass spectrographic techniques. These checks were made on identical samples of gas, and the data are presented in Table XVIII. It is seen that the vacuum fusion analysis for O_2 , CO and CO_2 checks very well with the mass spectrographic analysis for the sum of these gases. The vacuum fusion analysis for hydrogen, which includes water, does not check favorably with the mass spectrographic analysis for the sum of these two gases, although the smaller percentages present may account for the greater apparent error. The greatest single source of error in these calculations probably arises from the adsorption of the water vapor on the inner surfaces of the Pyrex tubing in the vacuum fusion apparatus, where it escapes analysis. This error does not effect the mass spectrographic analysis for water, because in this technique water contents are calculated by difference. This explains why the mass spectrometer analysis for hydrogen plus water exceeds the vacuum fusion analysis in all cases except one.

A final piece of interesting data pertaining to the growth of pressed nickel powder compacts at elevated temperatures

has been presented in the literature and part of the experimental work is reproduced in Figure 9 (15). It is seen that the growth curve exhibits two maxima. The author postulates that the lower temperature peak is due to the relief of internal stresses, while the higher temperature peak is caused by the evolution of adsorbed gases. The sum of the gas volumes liberated in a cumulative gas desorption test from this investigation have been plotted on this same graph, and it is seen that two maxima occur at about the same temperatures as the two growth maxima in the previously cited work. Because the powder used in the compacts was previously annealed in hydrogen, a better explanation of the two growth peaks, based on the results of this investigation, would be that the low temperature growth peak is caused primarily by desorbed water vapor, and the high temperature growth peak is caused primarily by desorbed CO₂.

Plastic Metals Company Powder

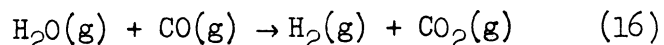
This powder was of interest because it was manufactured in the same way as the MD9119 powder, but had had an additional annealing treatment of 45 minutes in a cracked ammonia atmosphere. The x-ray data of Table IX show that this annealing treatment reduced the surface oxides, because no nickel oxide was present in the ball mill fines milled from the surface of a sample of this powder in the as received condition. The most noticeable feature of the gas evolution from this powder was that the volume desorbed was not a function of the apparent surface area; thus the mechanism

of surface desorption was eliminated as the major source of gas. It is believed that dissolved elements, H, O, and C, were responsible for the evolved gases. This mechanism is reasonable in view of the fact that this annealing treatment would result in the desorption of the greater part of any adsorbed gases present on the atomized, unannealed powder.

Table XII shows that the gas volumes released during both the total and the cumulative desorption tests were not related to surface area, and that the gas mixtures evolved contained H_2 , H_2O , CO , and CO_2 . Carbon monoxide is seen to be the major constituent of the desorbed gases, with CO_2 , H_2 , and H_2O representing smaller fractions of the total.

The cumulative volume gas desorption studies for three mesh fractions of this powder are shown in Figures 13, 14, and 15. The outstanding feature of the gas desorption was that the evolution of CO did not occur until a temperature in excess of $1000^\circ F$ was attained. This is further evidence that the CO was formed from dissolved carbon and oxygen, because these higher temperatures are required before diffusional mechanisms will transport carbon and oxygen atoms to the surface at an appreciable rate.

Another feature of the cumulative plots was the general decrease in the water volumes at a temperature where the hydrogen volumes increased. These facts are best explained by a reaction of the type:

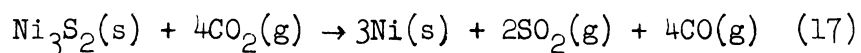


where the H₂O and CO were both originally formed from dissolved elements.

The correlation between total and cumulative volumes evolved is seen to be quite good in Table XII, primarily because the only gases which could be frozen out, H₂O and CO₂, were present in minor amounts. The major constituent, CO, was not frozen out and therefore participated in the same reactions in both types of desorption runs. Thus the CO and CO₂ volumes checked very well in both runs.

The annealing treatment in cracked ammonia would result in the powder being saturated with dissolved hydrogen. Thus, when the reaction of water vapor with CO yielded hydrogen, this hydrogen could not dissolve and was liberated in the gaseous state, as contrasted to the MD9119 powder wherein the hydrogen resulting from the dissociation of water vapor was dissolved in the powder.

A final point of interest concerning the gases liberated from this powder pertains to the lack of SO₂ evolution. This powder contained sulfur in excess of the solubility limit, indicating that some nickel sulphide must have been present. No SO₂ was produced by an oxidation reaction of the sulfide with CO₂ because the CO present in large amounts shifted the equilibrium in the opposite direction. This postulated reaction is:



Sherritt Gordon Company Powder

This powder, manufactured by hydrogen reduction from an aqueous solution, represented a completely different method of manufacture, and was of interest as a means of determining the effect of manufacturing technique on the evolved gases.

Neither the cumulative nor total gas volumes correlate with apparent surface area, as seen in Table XIV, so again the mechanism of surface desorption as a source of gas was eliminated. Dissolved hydrogen, oxygen and carbon are believed to be the source of the evolved gases. In Table XIV the total volumes desorbed are seen to be substantially greater than cumulative volumes. The difference is due mainly to the higher water volumes in the total volume tests. The water was frozen out in the total volume tests, but reacted during the cumulative runs with dissolved carbon to form both molecular and dissolved hydrogen and a mixture of CO and CO₂. A comparison of the gases evolved during both cumulative and total desorption runs, shown in Table XIV, indicates that no hydrogen is evolved during the total volume runs, but is seen to be present in the cumulative runs. This would indicate that no hydrogen is evolved as such, but is produced by a reaction with the water vapor.

The cumulative plots, Figures 16 and 17, show that fairly large amounts of hydrogen are liberated at temperatures up to 1000°F, but that the hydrogen volume decreases above this temperature. This is taken as an indication that hydrogen is

dissolving in the nickel powder at higher temperatures, because the solubility of hydrogen in nickel increases rapidly at elevated temperatures. Solutioning would not be expected at lower temperatures because the powder was manufactured at 350°F by bubbling hydrogen through a solution from which the nickel powder was precipitated. These manufacturing conditions would saturate the powder with hydrogen at this temperature, and preclude further solutioning of hydrogen until the solubility limit was increased by raising the temperature.

Dissolved carbon was held to relatively low levels in this process, so that the reaction between dissolved carbon and oxygen would not be expected to yield large quantities of CO or CO₂. The small amounts of CO and CO₂ actually evolved during the cumulative runs was taken as indirect evidence supporting the existence of this type of reaction in the PM273 powder which contained larger amounts of dissolved carbon.

Evolution of SO₂ was observed at 1800°F, and again the existence of a nickel sulphide was postulated, which upon oxidation yielded SO₂. The same reaction was involved with the MD9119 and PM273 powders, and in this case the CO/CO₂ ratio favors the reaction producing the SO₂.

Federal Mogul Company Powder

This powder, manufactured by water atomization in a nitrogen atmosphere, followed by an annealing treatment under a hydrogen atmosphere, offered a means of checking the effects of manufacturing

variations, as well as heat treatment variables. Only a limited amount of this powder was available, so only one cumulative volume test and duplicate vacuum fusion analyses were made. The cumulative volume run, Figure 18, shows that only very small amounts of hydrogen and CO_2 were liberated from this powder. The relatively minor amounts of gas liberated from this powder would indicate that this method of manufacture yields the cleanest product of any of those tested.

The vacuum fusion data of Table XVII show that annealing this powder under a hydrogen atmosphere for one hour at 1200°F resulted in a dissolved hydrogen content about one order of magnitude above that obtained in the unannealed MD9119 powder. The amount of dissolved hydrogen observed approaches the solubility limit at room temperature.

CONCLUSIONS

1. The mechanism of gas evolution and the type of gas evolved from nickel powder heated to 1800°F is dependent upon how the nickel powder is produced.
2. Nickel powder produced by steam scattering in air desorbs CO₂, H₂O, CO, and SO₂. The mechanism of gas evolution is surface desorption. The H₂O and CO are physically adsorbed, while the CO₂ is present as a weakly bonded surface compound. The SO₂ is the product of the oxidation of a nickel sulphide which is distributed throughout the powder matrix.
3. Nickel powder produced by steam scattering, followed by an annealing treatment in cracked ammonia, evolves CO and minor amounts of H₂O, H₂, and CO₂. The CO and H₂O are formed from dissolved O, C, and H, while the H₂ and CO₂ are products of reactions between H₂O and CO.
4. Nickel powder produced by precipitation from aqueous nickel ammonia complex solutions evolves H₂, H₂O, CO₂, and minor amounts of CO and SO₂. The gases are formed from dissolved gases.
5. Nickel powder produced by water atomization in a hydrogen atmosphere followed by an annealing treatment in hydrogen for one hour at 1200°F yields a very clean powder which evolves only minor amounts of H₂ and CO₂ upon heating to 1800°F.

6. If these gases, which were shown to be liberated at elevated temperatures, were evolved within a powder compact after the interior voids had closed, complete densification of the compact would be impossible. The best means of preventing excessive porosity due to gas evolution would be to heat the compact slowly, thus allowing the desorbed gases to escape before the pores were closed. Vacuum annealing treatments prior to sintering would be effective in reducing the H_2 and H_2O gases generated from the dissolved hydrogen.
7. In the case of desorption from steam scattered powders the following statements can be made: water vapor is desorbed at low temperatures indicating weak bonding to the nickel surface; surface oxides are reduced at elevated temperatures by desorbed CO; desorbed water vapor reacts with the hot metal powder and other desorbed gases at high temperatures to form H and CO_2 .
8. The steam scattered powder, when subjected to various surface treatments, exhibits different desorption characteristics. Mechanically or chemically cleaning the surface significantly decreases the subsequent gas evolution. Reexposure to air causes readsorption of CO_2 and N_2 which is complete in twenty-four hours.
9. Annealing treatments of steam scattered powder in hydrogen-bearing atmospheres remove adsorbed gases, and increase the dissolved hydrogen content of the powder while reducing the surface oxides.

10. Electron diffraction studies on massive nickel surfaces indicate the presence of weakly oriented surface films.
11. A comparison of vacuum fusion and mass spectrographic analyses performed on identical samples shows that the two methods of analysis check very well for the combination of O_2 plus CO plus CO_2 . The combined analyses for H_2 plus H_2O do not check, probably because of water adsorption on the tubing in the vacuum fusion apparatus.

BIBLIOGRAPHY

1. Baker, M. M. and Rideal, E. K., Trans. Faraday Soc., 51, 1592 (1955).
2. Baker, M. M., Jenkins, G. I. and Rideal, E. K., Trans. Faraday Soc., 51, 1594 (1955).
3. Barrer, R. M., MacKenzie, N., and MacLeod, D., J. Chem. Soc., 151, 1736 (1952).
4. Beeck, O., Givens, J. W. and Ritchie, A. W., J. Colloid Sci., 5, 141 (1950).
5. Boer, J. H., The Dynamical Character of Adsorption, Clarendon Press, Oxford (1953).
6. Boudart, M., J. Chem. Phys., 23, 753 (1955).
7. Brunauer, S., The Adsorption of Gases and Vapors, Princeton University Press (1943).
8. Brunauer, S., Emmett, P. H. and Teller, E., J. Am. Chem. Soc., 60, 309 (1938).
9. Cassel, H. M., J. Phys. Chem., 48, 195 (1944).
10. DeBoer, J. H., Advances in Catalysis, Vol. VIII, Academic Press, Inc., New York (1956).
11. Dillon, J. A., and Farnsworth, H. E., J. Chem. Phys., 22, 1601 (1954).
12. Duftschmid, F., Schlect, L., and Schubart, W., Stahl u Eisen, 52, 845 (1932).
13. Emmett, P. H., Catalysis, Vol. I, Rienhold Publishing Corp., New York (1951).
14. Eastwood, L. W., Gases in Metals, ASM, Cleveland, Ohio, (1953).
15. Fedorchenko, I., Zhur. Tekhn. Fiziki, 26, 2067 (1956).
16. Forward, F. A., C. I. M. Trans., 56, 373 (1953).
17. Freundlich, H., Kapillarchemie, Akademische Verlagsgesellschaft M. B. H., Leipzig (1923).

18. Gonzales, O. F. and Parravano, G., J. Am. Chem. Soc., 78, 4533 (1956).
19. Graham, D., J. Phys. Chem. 58, 869 (1954).
20. Griffith, R. H., Contact Catalysis, Oxford University Press (1946).
21. Hall, A. J., Metals Handbook, ASM, Cleveland (1948).
22. Halsey, G. D., J. Am. Chem. Soc., 74, 1082 (1952).
23. Harkins, W. D., The Physical Chemistry of Surface Films, Reinhold Publishing Co., New York (1952).
24. Harkins, W. D., and Jura, C., J. Am. Chem. Soc., 66, 1362 (1944).
25. Hill, T. L., Advances in Catalysis, Vol. IV, Academic Press, Inc., New York (1952).
26. Hill, T. L., J. Chem. Phys., 14, 263 (1946).
27. Jones, W., Principles of Powder Metallurgy, Metallurgy Press, London (1940).
28. Joy, A. S., Vacuum, 3, 254 (1953).
29. Kihlgren, T. E., and Eash, J. T., Metals Handbook, ASM, Cleveland (1948).
30. Kwan, T., J. Chem. Phys., 18, 1309 (1950).
31. Langmuir, I., J. Am. Chem. Soc., 40, 1361 (1918).
32. Ledoux, E., Adsorption, Chemical Publishing Co., Brooklyn, N. Y. (1945).
33. Lee, E. L., Sabatka, J. A. and Selwood, P. W., J. Am. Chem. Soc., 79, 5391 (1957).
34. Letnam, C., Adsorption, McGraw Hill Publishing Co., New York (1945).
35. Mackiw, V. N., Lin, W. C. and Kunda, W., J. Met., 9, 786 (1957).
36. Matsen, F. A., J. Chem. Phys., 22, 1800 (1954).

37. Maxted, E. B., J. Chem. Soc., 78, 1987 (1949).
38. Mignolet, J. C., J. Chem. Phys., 21, 1289 (1953).
39. Orr, C., Blocker, H. G. and Craig, S. L., Trans. AIME, 194, 657 (1952).
40. Pfeiffer, I., Z. Metallkunde, 46, 516 (1955).
41. Phelps, R. T., Gulbransen, E. A., and Hickman, J. W., Industr. Eng. Chem. (Anal.), 18, 391 (1946).
42. Rhodin, T. N., Anal. Chem., 27, 1857 (1955).
43. Rhodin, T. N., Annals of the New York Academy of Science, 58, 855 (1954).
44. Rhodin, T. N., Corrosion, 12, 123 (1956).
45. Ries, H. E., Catalysis, Vol. I, Reinhold Publishing Corp. New York (1951).
46. Rosenquist, T., J. Iron and Steel Inst., 176, 37 (1954).
47. Schlier, R. E. and Farnsworth, H. E., J. App. Phys., 25, 1333 (1954).
48. Selwood, P. W., J. Am. Chem. Soc., 78, 3893 (1956).
49. Skinner, E. N., Metals Handbook, ASM, Cleveland (1948).
50. Sloman, J. F., J. Inst. Metals, 71, 391 (1945).
51. Smithells, C. J., Metals Reference Book, Vol. II, Interscience Publishers, Inc., New York (1955).
52. Smithells, C. J., and Ransley, C. E., Proc. Royal Soc., A155, 195 (1936).
53. Starkweather, F. M. and Palumbo, D. T., J. Electrochem. Soc., 104, 287 (1957).
54. Stevenson, D. P., J. Chem. Phys., 23, 203 (1955).
55. Tingle, E. T., Trans. Faraday Soc., 46, 43 (1950).
56. Tobin, J. C. and Sinnott, M. J., Trans. AIME, Paper 140-E (to be published).
57. Tobin, J. C., PhD Thesis, University of Michigan, Ann Arbor (1956).

58. Uhlig, H. H., Annals of the New York Academy of Sciences, 58, 843 (1954).
59. Wahba, M. and Kemball, C., Trans. Faraday Soc., 49, 1351 (1953).
60. Wang, H. L., and Hackerman, N., J. Phys. Chem., 56, 771 (1952).
61. Warren, D. and Libsch, J. F., Trans. AIME, 191, 774 (1951).
62. Zettlemoyer, A. C. and Chessick, J. J., J. Phys. Chem., 58, 242 (1954).

APPENDIX A

Calibration of Gas Desorption Apparatus

A determination of the amounts of gas evolved during a desorption test required that the volume of gas liberated be measured under controlled conditions of pressure and temperature. This volume of gas was contained in the combined volume consisting of the measuring manifold, sample tube, and burette as shown in Figure 1. The calibration of this combined volume involved three separate calculations; the volume of the sample tube, the volume of the measuring manifold, and a correction factor for the apparent change in this calibrated volume as a function of the sample tube temperature.

Volume of the Sample Tubes

Two quartz sample tubes were used throughout the course of this investigation, and the volume of each was determined separately, so that the sample tubes could be used interchangeably without requiring separate calibrations of the desorption volume. The sample tube volumes were determined by placing the sample tubes on the manifold, and then evacuating the system composed of the sample tube, measuring manifold and burette. Upon evacuation valve S_7 was closed, and then a small amount of helium was bled into the manifold and burette through valve S_3 . After valve S_3 was closed, the manifold pressure was adjusted to about 20 mm, and then pressure and burette readings were made. Next, valve S_7 was opened, and then the mercury level in

the burette was raised until the manifold pressure was returned to its original value. The volume of the sample tube was then equal to the initial burette reading minus the final burette reading.

$$V_t = r_1 - r_2 \quad (A-1)$$

where:

V_t = volume of the sample tube, ml.

r_1 = initial burette reading, ml.

r_2 = final burette reading, ml.

The volumes of the two sample tubes are shown below:

Table A-1

Volume of Sample Tubes

	<u>Volume, ml.</u>	
	<u>Tube No. 1</u>	<u>Tube No. 2</u>
Reading No. 1	26.2	27.4
Reading No. 2	25.9	27.2
Reading No. 3	<u>26.1</u>	<u>27.5</u>
<u>V_t</u>	26.1	27.4

This calibration was repeated on sample tube number one after it had accumulated thirty hours at 1800°F under a pressure of about 20 mm, as a means of determining if the quartz had been plastically deformed under the combination of high temperature and low pressure. The calibration showed that no change in volume had occurred.

Volume of the Measuring Manifold

The calibration of the measuring manifold was based on

an ideal gas law calculation:

$$PV = nRT \quad (A-2)$$

In this case the volume under consideration was the manifold volume, V_M , plus the burette volume, r . Since n , R and T were held constant during calibration, the gas law could be re-written as:

$$P (V_M + r) = K \quad (A-3)$$

Upon conversion to the standard slope-intercept form, the equation becomes:

$$r = \frac{K}{P} - V_M \quad (A-4)$$

A plot of r versus $\frac{1}{P}$ yields a straight line whose slope is K , and whose intercept on the r axis is $-V_M$. The points on the plot were obtained by filling the measuring manifold and burette with about 150 mm of helium, and then measuring the pressure at the manometer, as r was varied by raising the burette leveling bottle. Three calibrations involving slightly different amounts of helium are shown in Figure A-1 and Table A-II. These calibrations yield an average manifold volume of 35.3 ml.

Temperature Correction

When the sample tube was heated, the apparent volume of the calibrated measuring manifold and sample tube decreased. To correct for this effect, the influence of sample tube temperature on the effective volume of the measuring manifold and sample tube was determined. Considering the calibrated volume

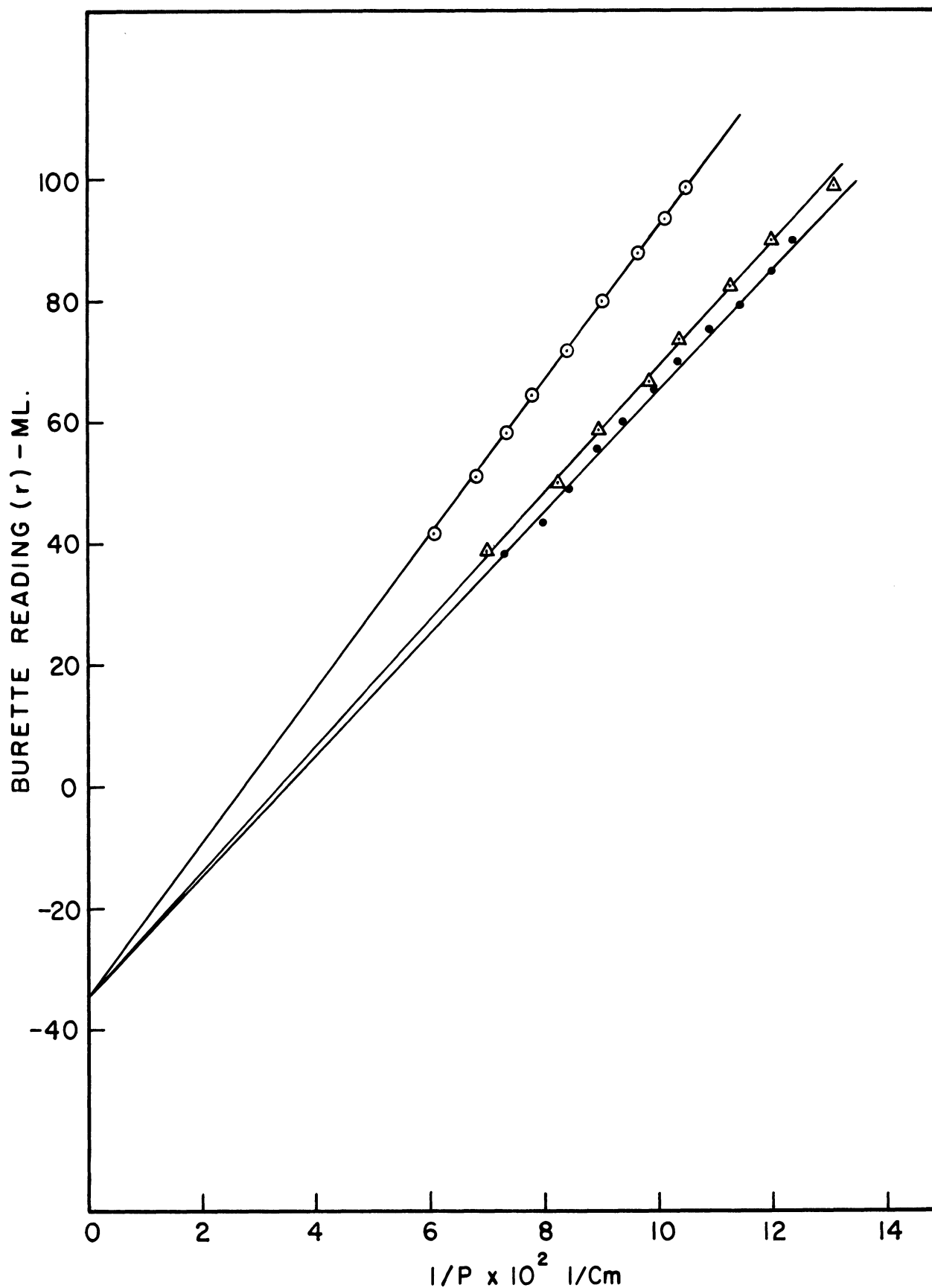


Figure A-1. Calibration of Measuring Manifold; Burette Reading (r), ml., as a Function of Reciprocal Manifold Pressure, $1/P \times 10^2$ $1/\text{cm}$.

TABLE A-II

CALIBRATION OF MEASURING MANIFOLD; BURETTE READING $\underline{r}$ AS A FUNCTION
OF RECIPROCAL MANIFOLD PRESSURE $1/P$

<u>Calibration No. 1</u>		<u>Calibration No. 2</u>		<u>Calibration No. 3</u>	
<u>$\underline{r}$, ml.</u>	<u>$1/P \times 10^2$ cm.</u>	<u>$\underline{r}$, ml.</u>	<u>$1/P \times 10^2$ cm.</u>	<u>$\underline{r}$, ml.</u>	<u>$1/P \times 10^2$ cm.</u>
39.05	7.37	42.60	6.18	38.70	7.23
44.30	7.94	50.65	6.84	50.05	8.29
49.80	8.41	57.80	7.35	58.20	9.06
55.50	8.97	64.20	7.82	66.15	9.86
59.90	9.37	72.10	8.45	74.00	10.49
66.02	9.96	80.20	9.05	82.05	11.28
70.28	10.40	88.30	9.69	90.02	12.01
75.30	10.91	94.00	10.15	98.50	13.05
80.03	11.39	99.42	10.56		
85.70	12.08				
90.33	12.41				

as containing two parts, one at room temperature, T_1 , and the other at elevated temperature T_2 , then V_1 and V_2 and n_1 and n_2 are the corresponding volumes and amounts of gas in the manifold respectively. The ideal gas law corresponding to this situation is:

$$PV = (n_1 + n_2) RT_1 \quad (A-5)$$

The amounts of gas in each section of the manifold are:

$$n_1 = \frac{PV_1}{RT_1} \quad (A-6)$$

and:

$$n_2 = \frac{PV_2}{RT_2} \quad (A-7)$$

The substitution of these values for n_1 and n_2 into Equation A-5 yields:

$$V_e = V_1 + V_2 \left(\frac{T_1}{T_2} \right) \quad (A-8)$$

This equation indicates that a plot of V_e versus $\left(\frac{T_1}{T_2} \right)$ yields a straight line. Points on this plot were obtained by first enclosing a sample of helium in the calibrated volume with the sample tube at room temperature. Then the effective volume, V_e , was determined by measuring the change in the burette reading, r , as the sample tube was heated to elevated temperature. These data are presented in Figure A-2 and Table A-III.

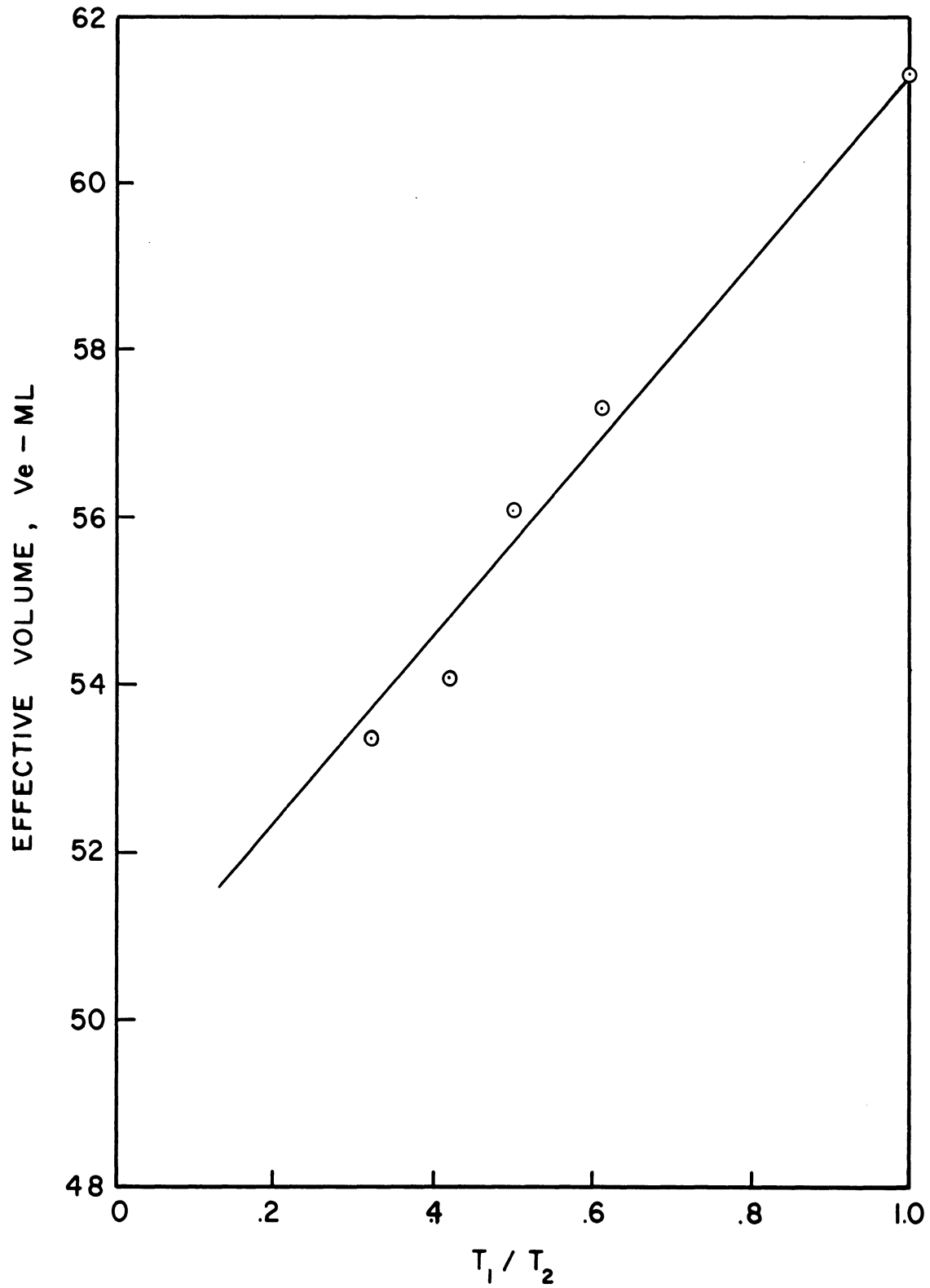


Figure A-2. Effective Volume of Measuring Manifold and Sample Tube, V_e , as a Function of Sample Tube Temperature, T_2 .

TABLE A-III

EFFECTIVE VOLUME OF THE MEASURING MANIFOLD AND SAMPLE TUBE
AS A FUNCTION OF TEMPERATURE

Temperature, °F	T_1/T_2	<u>r</u> , ml.	<u>Δr</u> , ml.	<u>V_e</u> , ml.
70	1.00	28.40	-	61.36
400	0.61	32.46	4.06	57.30
600	0.50	33.68	5.28	56.08
800	0.42	35.72	7.32	54.04
1200	0.32	36.40	8.00	53.36

APPENDIX B

Gas Volume and Pressure Calculations

Both the total and cumulative volume gas desorption calculations and the partial pressure calculations were derived from volume measurements and gas analyses. A typical gas analysis is shown, and representative total and cumulative volume calculations are given. Partial pressure data derived from these calculations are also presented.

Gas Analysis

The theory of gas analysis by mass spectroscopy has been previously outlined (see page 36). Data from a typical gas analysis are presented in Table B-I. The raw data consist of m/e peak height measurements and a total pressure measurement of the sample. The background intensity of these peaks, previously measured in blank runs, is subtracted from the gross peak height, to yield a net peak height. The partial pressures of the H₂, He, SO₂ and CO₂ in the inlet volume are calculated directly by dividing their net peak heights by their respective sensitivities. These sensitivities, measured in divisions of peak height per micron of gas pressure, were determined prior to the actual gas analyses by calibration of pure gas samples. Typical gas sensitivities are given in Table B-II. The partial pressure of N₂ in the inlet volume is calculated by first dividing the 14 peak height by the corresponding cracking pattern value of nitrogen, and then

TABLE B-1
TYPICAL GAS ANALYSIS

Sample No. 4248				<u>Inlet Pressure: 34.35 microns</u>		
<u>m/e</u>	<u>gross peak</u>	<u>background</u>	<u>net peak</u>	<u>Component</u>	<u>microns</u>	<u>volume %</u>
2	3	2	1	H ₂	0.00	0.0
4	1599	0	1599	He	27.62	0.0
14	31	1	30	-	-	-
28	414	13	401	-	-	-
44	1620	9	1611	CO ₂	3.69	54.8
64	431	0	431	SO ₂	1.18	17.5
				CO ₂	0.07	1.0
				<u>N₂</u>	<u>0.49</u>	<u>7.3</u>
					33.05	
				H ₂ O (diff)	<u>1.30</u>	<u>19.3</u>
					34.35	99.9
				Less He	<u>27.62</u>	
					6.73	

$$\text{div}_{28}^{N_2} : 30/0.16 = 178$$

$$\text{div}_{28}^{CO} : 401 - 178 - (1620) (0.12) = 30$$

TABLE B-II
TYPICAL GAS SENSITIVITIES

<u>Gas</u>	<u>Sensitivity, divisions per micron</u>
H ₂	366.1
He	70.77
CO	442.8
N ₂	414.5
CO ₂	500.3
SO ₂	412.3

TABLE B-III
MASS SPECTROMETER GAS MATRIX

<u>m/e</u>	<u>H₂</u>	<u>He</u>	<u>CO</u>	<u>N₂</u>	<u>CO₂</u>	<u>SO₂</u>
2	1.00	-	-	-	-	-
4	-	1.00	-	-	-	-
14	-	-	0.00	0.16	0.00	-
28	-	-	1.00	1.00	0.12	0.02
44	-	-	-	-	1.00	-
64	-	-	-	-	-	1.00

by dividing this value by the sensitivity of nitrogen. The cracking patterns of all the gases present are given in matrix form in Table B-III. The CO partial pressure is computed by first subtracting the N₂ and CO₂ contributions to the 28 peak from the net 28 peak. The remainder of the 28 peak height, due only to CO, is then divided by the CO sensitivity to yield the CO partial pressure. The sum of the partial pressures of H₂, He, CO, N₂, CO₂ and SO₂ is then taken, and this value is subtracted from the total pressure. This remaining pressure is attributed to water vapor. The volume percent of a gas is then simply the partial pressure of that gas divided by the total pressure. In total volume calculations, a helium free analysis was required. In these cases, the partial pressure of helium was subtracted from the total pressure, and the analysis was based on this remainder, rather than on the total pressure.

Total Volume Gas Desorption Calculations

The raw data from a total volume gas desorption run consisted of initial and final burette readings, and manifold temperature and pressure values. The difference between the initial and final burette readings was the total gas volume liberated. This volume was converted to standard conditions of temperature and pressure. The volumes of the component gases were computed by applying the gas analysis to the total volume as corrected to standard conditions. Typical data are given in Table B-IV.

TABLE B-IV

TOTAL VOLUME GAS DATA SHEET

Run No.:	121	Room Temperature:	25.9°C
Powder:	MD9119 Ni	Mesh Size:	-100 + 200
Pressure:	19.1 mm.	Tube:	quartz #1
Weight:	2 gm.	Date:	Sept. 20, 1957

<u>Temperature, °F</u>	<u>r, ml.</u>	<u>sample bulb</u>
1800	62.6	#2
1800	27.2	

$$V_0 = (62.6 - 27.2) (19.1/760) (273/299) (5) = 4.0 \text{ ml. STP/ 10 gm.}$$

<u>Component</u>	<u>Volume %</u>	<u>Volume, ml. STP/10 gm.</u>
H ₂	0.0	0.0
H ₂ O	8.1	0.3
CO	8.1	0.3
CO ₂	62.6	2.5
SO ₂	21.5	0.9

Cumulative Volume Gas Desorption Calculations

The cumulative gas volume calculations were based on the volumes of gas liberated at a series of temperatures, and the amounts of gas removed during sampling at lower temperatures. Tobin's relation was used in making this calculation as follows (57):

$$V_{nm} = f_{nm} (V_e + r) + G_{n1} + G_{n2} + G_{n(m-1)} \text{ (Equation B-1)}$$

where

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

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

$(V_e + r)$ = the total volume of the specimen manifold at a given temperature

G_{nm} = the volume of the nth component in the gas sample taken at the mth temperature point.
It is $f_{nm}V_{bm}$

V_{bm} = The volume of the gas sample taken at the mth temperature point

A sample calculation is given in Table B-V.

Partial Pressure Calculations

The partial pressure calculations, used to determine heats of desorption, were based on the gas analysis of samples collected at known pressures and temperatures. Thus the partial pressure of a given component at a certain temperature was simply the fraction of this gas present as determined by the gas analysis, times the manifold pressure. Typical partial pressure data are shown in Table B-VI.

TABLE B-V

CUMULATIVE VOLUME GAS DATA SHEET

Run No.:	118	Room Temperature:	24.0°C
Powder:	SG 321	Mesh Size:	- 100 + 200
Pressure:	20.8 mm.	Tube:	quartz #1
Weight:	2 gm.	Date:	Aug. 22, 1957

Temperature, °F	<u>r</u>	<u>V_e</u> , ml.	<u>sample vol.</u> , ml.	<u>sample bulb</u>	
600	52.8	-	-	-	
600	88.6	52.7	-	1	
600	51.2	-	37.4	-	
1000	69.8	53.3	-	2	
1000	46.2	-	23.6	-	
1400	51.9	54.1	-	3	
1400	37.2	-	14.7	-	
1800	44.6	55.2	-	4	
		<u>600°F</u>	<u>1000°F</u>	<u>1400°F</u>	<u>1800°F</u>
	<u>V_e</u>	55.2	54.1	53.3	52.7
	<u>r</u>	<u>88.6</u>	<u>69.8</u>	<u>51.9</u>	<u>44.6</u>
	(<u>V_e</u> + <u>r</u>)	143.8	123.9	105.2	97.3
					Vol. STP/10 gm.
Vol. H ₂	(600°F) = 0.113(143.8)				2.1
"	(1000°F) = 0.155(123.9) + .113(37.4)				3.0
"	(1400°F) = 0.055(105.2) + " + .155(23.6)				1.7
"	(1800°F) = 0.0017(97.3) + " + " + .055(14.7)				1.1
Vol. H ₂ O	(600°F) = 0.03(143.8)				0.6
"	(1000°F) = 0.069(123.9) + .03(37.4)				1.2
"	(1400°F) = 0.113(105.2) + " + .069(23.6)				1.9
"	(1800°F) = 0.073(97.3) + " + " + .114(14.7)				1.6
Vol. CO	(600°F) = 0.00(143.8)				0.0
"	(1000°F) = 0.00(123.9) + .00(37.4)				0.0
"	(1400°F) = .01(105.2) + " + .00(23.6)				0.1
"	(1800°F) = .01(97.3) + " + " + .01(14.7)				0.2
Vol. CO ₂	(600°F) = 0.02(143.8)				0.4
"	(1000°F) = .02(123.9) + .02(37.4)				0.4
"	(1400°F) = .02(105.2) + " + .02(23.6)				0.5
"	(1800°F) = .11(97.3) + " + " + .03(14.7)				1.5
Vol. SO ₂	(1800°F) = .01(97.3)				0.1

TABLE B-VI

TYPICAL PARTIAL PRESSURE DATA

Run No.:	106	Room Temperature:	25.3°C
Powder:	MD9119	Mesh Size:	-100 + 200
Pressure:	21.9 mm.	Tube:	quartz #1
Weight:	5 gm	Date:	July 30, 1957

<u>Temperature, °F</u>	<u>Partial Pressure, mm.Hg.</u>			
	<u>H₂O</u>	<u>CO</u>	<u>CO₂</u>	<u>SO₂</u>
600	6.35	0.02	0.21	0.00
1000	2.80	0.22	0.83	0.00
1400	0.00	2.08	5.40	0.00
1800	2.44	0.62	7.10	0.02

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