

THE ORTHO-PARA HYDROGEN CONVERSION ON
IRON OXIDE-ZINC OXIDE CATALYSTS

by

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A THESIS

submitted to


OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY


June 1955

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Date thesis is presented May 13, 1955

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ACKNOWLEDGEMENT

I wish to thank Dr. Allen B. Scott for his
encouraging words and suggestions while this
work was in progress.

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THE ORTHO-PARA HYDROGEN CONVERSION ON IRON OXIDE-ZINC OXIDE CATALYSTS

INTRODUCTION

INTRODUCTORY REMARKS. Among the many items which one must take into consideration when studying solid-gas catalysis is the magnetochemical nature of the solid which may affect that particular reaction under consideration. Pierce W. Selwood has published an excellent review of this aspect of catalysis (23). Of the many examples given, two can be cited which have direct application to the work at hand. First, the work of Gustav F. Hüttig and his co-workers must be mentioned. Working with equimolar iron oxide-zinc oxide mixtures, Huttig has studied the variation of several properties with pretreatment temperature. Using the reactions $2\text{N}_2\text{O} \text{ ----> } 2\text{N}_2 + \text{O}_2$ and $2\text{CO} + \text{O}_2 \text{ ----> } 2\text{CO}_2$, two peaks of catalytic activity were found, one after heating the catalyst mixture at 400°C , and one after heating at $600 - 650^\circ \text{C}$. Simultaneous measurements of magnetic susceptibility show a sharp rise after the heat treatment has reached 550°C , and incipient ferromagnetism at about 650°C . The surprising feature of these magnetic results is that x-ray diffraction studies show no trace of the zinc ferrite lattice before about 650°C . Many other physical properties point to the same conclusion, namely,

that active intermediates are formed during the course of the transformation of mixed oxides into spinels which are responsible for the enhanced catalytic activity. This and many other studies are extensive in their scope and have been given attention in reviews other than Selwood's (14, pp. 172-176) (15, pp. 151-160).

Another example of the importance of the magnetic state of the catalyst is that of the low temperature ortho-parahydrogen conversion. Taylor and Diamond (26) have shown that the ortho-parahydrogen conversion is much more rapid on paramagnetic oxides than on chemically similar ones which are diamagnetic.

Another item which one would expect to affect the catalytic efficiency of a solid is the absolute magnitude of the surface area. That paramagnetic heterogeneous ortho-parahydrogen conversion and strong hydrogen adsorption go together has been shown by the experiments of Turkevich and Selwood (28). These experiments showed very clearly that a solid free radical, α, α -diphenyl- β -picryl hydrazyl does not appreciably catalyze the ortho-parahydrogen conversion although the radical is 100 percent dissociated (paramagnetic). Diamagnetic zinc oxide was also relatively inactive but strongly absorbed the hydrogen. When the free radical and the zinc oxide were mixed, a rapid conversion took place. This is interpreted to mean that two factors are necessary for the heterogeneous conversion of ortho to

parahydrogen at low temperatures, namely the existence of a field which is inhomogeneous in molecular dimensions and a very long contact of hydrogen with the field ensured by van der Waal's adsorption of hydrogen on the zinc oxide.

Beeck (3) has pointed out the necessity of more direct measurements beyond simple kinetic procedures. The many complex phenomena occurring at the interface of a heterogeneous reaction must be adequately controlled or maintained constant. The control of all these phenomena may be nearly impossible, but at least those properties thought to influence the reaction should be determined.

THE PROBLEM. Recently, Bupp and Scott (6, 7) developed a method which accomplished some of Beeck's requirements in that the magnetic susceptibility, surface area and catalytic efficiency for solid catalysts in situ could be determined. For this study the decomposition of nitrous oxide at 500°C and at one atmosphere pressure was chosen to serve as an index of efficiency for various iron oxide-zinc oxide catalysts pretreated for six hours at several elevated temperatures.

Several interesting questions arise in connection with this work. Perhaps the foremost is the selection of the reaction used as the index of catalytic efficiency. The reaction was carried out at an elevated temperature at which either or both the magnetic susceptibility and the surface area of the catalysts were undergoing a change.

From this standpoint it seemed desirable to use a reaction which proceeded at a low enough temperature to eliminate as much change as possible in the catalysts during the reaction period. The reaction also had to be one in which either the magnetic properties of the catalyst or the surface area, or both, played a role. The conversion of normal hydrogen (3 ortho:1 para) to equilibrium hydrogen at -195°C (approximately 1 ortho:1 para) seemed to fit these prescribed conditions and consequently was chosen to serve as an index of efficiency for the catalysts used.

The catalysts chosen for this purpose were some of the equimolar iron oxide-zinc oxide mixtures pretreated for six hours at elevated temperatures. Significant changes in magnetochemical properties as well as changes in specific surface are observed following this thermal treatment which in turn should influence the efficiency of the catalyst.

The second question which arises when studying the work of Bupp and Scott is one of experimental technique. In short, they reported a principal error in their efficiency determinations due to nitrous oxide by-passing the catalyst bed. This feature would impose a limitation on the accuracy of any kinetic information taken. In their case, however, the spread in efficiencies from one catalyst to the next was so great that the significance of the error was minimized. Nevertheless, for other reactions

this may not be true. It was felt that a change in design could eliminate this difficulty. This change in design is discussed under the section entitled EXPERIMENTAL METHOD.

A third question arising from the work of Bupp and Scott is one of incompleteness. There is presented a plot showing that the catalytic efficiency varies linearly with the specific surface area of the iron oxide-zinc oxide catalysts whose surfaces have been changed by the use of various pretreatment temperatures for six hours. However, no weight was given to the fact that the magnetochemical nature of the catalyst also changed. It was proposed that an attempt be made to at least partially rectify this if the need should arise in using the ortho-parahydrogen conversion.

Gustav F. Hüttig reported that after pretreating equimolar iron oxide mixtures at 410°C , a catalytically active phase was formed. Doubt has been expressed about the significance of this as the reaction was run at a temperature above that of the pretreatment temperature. Nevertheless, it was further proposed in this research to run a reaction on a catalyst so prepared to check this point.

The most striking work done with the low temperature heterogeneous ortho-parahydrogen conversion is the previously cited work of Taylor and Diamond in which evidence is presented which indicates that the ortho-parahydrogen

conversion is really much more rapid on catalysts having a paramagnetic moment. Although striking, this work brings to mind two important questions. The first question being the justification in using the magnetic susceptibilities reported at 25°C in some cases and not at -195°C , the reaction temperature. Also, in many cases the magnetic susceptibility data used were not those of the samples used but values extracted from the literature. Also, one may note that no surface measurements were made, although it was conceded that the magnitude of the surface was a determining factor.

In summarizing, the purpose of this study was to investigate the catalytic properties of ignited iron oxide-zinc oxide mixtures toward the ortho-parahydrogen conversion using an adaptation of the method of Bupp and Scott in which measurements of magnetic susceptibility, surface area and catalytic efficiency can be determined on the same sample (or another sample treated in the same way) in situ. It was hoped that a series of determinations of this sort could be used to correlate the efficiency of the catalyst with surface area and its magnetochemical properties.

ORTHO AND PARAHYDROGEN. Hydrogen has two distinct states owing to the fact that the proton has spin properties. One state has a total spin of 0 (parahydrogen) and

even rotational quantum numbers. The other state has a total spin of 1 (orthohydrogen) and odd rotational quantum numbers. A good review of the ortho and parahydrogen system may be found in Farkas' book, Light and Heavy Hydrogen (9). Nevertheless, some of this material will be briefly stated here in order to develop the material needed for this work.

As early as 1912, Eucken observed that the specific heat of hydrogen having at room temperature the value $5/2 R$ in agreement with the classical theory for diatomic molecules, gradually decreased when the temperature was lowered to $50^{\circ} K$. Below $50^{\circ} K$ the specific heat had the value of $3/2 R$ characteristic of monatomic gases. However, no exact formula representing the specific heat at low temperatures could be obtained. It was not until Heisenberg and Hund considered the spin properties of the proton that progress was made in explaining quantitatively the specific heat curve for hydrogen. Hund's attempt to derive an exact quantitative agreement failed because of an incorrect assumption that transitions between the two states were possible when only the temperature was changed. The alternating intensity in the line spectrum of hydrogen observed by Mecke in 1924 was readily explained however on the assumption that the spectrum really consisted of two sets of lines, one due to each modification. From the intensity ratio, it was calculated that at room temperature the ratio

of the two forms was three to one. The solution of the specific heat problem was achieved by Dennison who pointed out that if the correct value of the moment of inertia and correct statistical weights as found from band spectra were employed, the formula did not even represent qualitatively the form of the experimental curve. He showed however, that perfect agreement between experiment and theory could be obtained if hydrogen was considered as a mixture of the two different modifications whose ratio did not change although the temperature did. The fact that these two different modifications can be considered as different gases having different specific heats is the basis for distinguishing between ortho and parahydrogen.

When the temperature is changed in the presence of a catalyst, the ratio of ortho to parahydrogen will be determined by the temperature. These proportions are given in Table 1.

Table 1.

Ortho-Para Equilibria for Molecular Hydrogen

<u>Temperature, °K</u>	<u>Percentage of Parahydrogen at Equilibrium</u>
20	99.82
30	96.98
40	88.61
50	76.89
60	65.39
70	55.83
78	49.73
80	48.39
90	42.75
100	38.51
150	28.54
∞	25.00

In the hydrogen molecule itself the bond distance is 0.74 angstroms. The radius of the hydrogen atom is 0.37 angstroms (20, p. 168).

Although the proportions of ortho to parahydrogen are temperature dependent, the transition is forbidden if only the temperature is changed. Calculations indicate a transition probability of 1 in 300 years eliminating this as an important method of interconversion. Nevertheless, many materials act as catalysts for the change and this must be considered before assembling an experimental system.

Conversion by collision with other molecules may arise by a simple interchange of nuclei. However, calculations have indicated a half life for the transition to

be three years at atmospheric pressure. Thus, this mechanism can be ruled out as an important one under normal experimental conditions.

Conversion by collision with hydrogen atoms is possible but not plausible under normal experimental conditions.

Magnetic perturbation can cause a certain amount of spin reversal. This was first observed by Farkas and Sachsse (9, p. 79) with mixtures of parahydrogen and oxygen. This does become the important method of conversion if paramagnetic materials are in the system.

The heterogeneous conversion in which we are interested has been studied extensively. Nevertheless, a small amount of background material needs to be repeated here. Early studies indicated that some catalysts are effective only at low temperatures while others are effective only at higher ones. The same catalyst, such as charcoal, may exhibit both positive and negative temperature coefficients according to the temperature range investigated. The negative temperature coefficient is found at low temperatures, and the positive one is found at higher temperatures (9, p. 90). Due to this minimum activity range, two separate mechanisms have been proposed for the conversion; one is effective at low temperatures and has a negative temperature coefficient while the other is effective at high temperatures and has a positive temperature

coefficient. The similarity between the temperature dependence of the conversion and that of hydrogen sorption (25) suggested that the two mechanisms involved van der Waal's adsorption at low temperatures and activated adsorption at high temperatures.

Among other facts which support the contention that the conversion of parahydrogen occurs at low temperatures among molecules adsorbed on the surface by van der Waal's forces and at high temperatures by activated adsorption is the work of Harkness and Emmett (12). They found that, on magnetite at -190°C with a space velocity of 12,000, the parahydrogen conversion, which is nearly complete on a clean surface, is reduced to 12 percent if the catalyst is cooled from 450°C in an atmosphere of hydrogen. This may be explained by the diminution of van der Waal's adsorption.

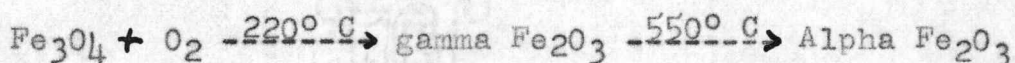
Also, one may cite work using the isotope reaction $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$ (22, p. 215). It is assumed that the isotope reaction cannot be achieved in adsorbed layers when the binding to the surface is by van der Waal's forces. On the other hand, if the reaction does occur, it is to be assumed that activated hydrogen exists on the surface. In comparison with the rapid conversion of ortho to parahydrogen on Cr_2O_3 gel surfaces at liquid nitrogen temperatures, the isotope exchange is slow. This indicates that the rapid spin isomerization at liquid nitrogen

temperatures is not due to any marked degree to activated adsorption, but is rather to be ascribed to magnetic forces on the surfaces.

According to a theory proposed by Wigner (30), the ortho-parahydrogen interconversion cannot take place unless there is a perturbation introduced which depends both on nuclear spins and on position of the nuclei. An inhomogeneous magnetic field of molecular dimensions satisfies both these criteria. Continuing further, it was shown on theoretical grounds that the velocity of the conversion should be proportional to the square of the Bohr magneton number. Many experiments using ionic solutions and paramagnetic gases have borne out the validity of this thinking.

The fact that Wigner's theory could be applied at least qualitatively to the heterogeneous case gained support from the results furnished by Taylor and Diamond. It is the purpose of this work to furnish additional experimental evidence along this line.

THE OXIDE CATALYSTS. Before continuing further, it is well to look upon some of the physical relationships between the iron oxides, some properties of zinc oxide, and the properties of equimolar iron oxide-zinc oxide mixtures. Welo and Baudisch (29) have published an extensive review on the oxide hydrates and the oxides of iron. An interesting set of transitions is discussed:

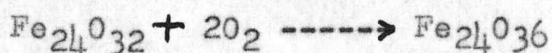


The Fe_3O_4 (magnetite) and gamma Fe_2O_3 are strongly ferromagnetic. Alpha Fe_2O_3 is generally thought of as being paramagnetic although careful studies have shown that it may actually be ferromagnetic with a low saturation permeability.

Katzoff and Ott (15) have made a study of alpha ferric oxide. They found the structure to be rhombohedral with the lattice constant a_0 to be 5.413 angstroms. The angle α was found to be $55^\circ 17.5'$.

Holgerson (14) has studied by x-ray methods many spinels isomorphous to magnetite and gamma ferric oxide. Magnetite is reported to have a lattice constant of 8.417 angstroms. Among other materials he studied is zinc ferrite. The cube edge is reported as 8.403 angstroms.

Gamma ferric oxide has been investigated by Thewlis (27) and he found the lattice constant to be identical to that of magnetite except that in the gamma ferric oxide structure four oxygen positions are vacant in each unit cube. The lattice constant was found to be 8.40 angstroms with the structure being a face centered cube. Haul and Schoon (24, p. 223) have shown that the unit cell of gamma ferric oxide is $\text{Fe}_{24}\text{O}_{36}$. The oxidation is therefore



Zinc oxide has a hexagonal structure with a_0 equal to 3.25 angstroms and c_0 equal to 5.23 angstroms. It is

slightly diamagnetic in character.

A study of zinc oxide and alpha ferric oxide mixtures pretreated at various temperatures has yielded some interesting results. Some of the reported magnetic properties for the pretreated equimolar mixtures are shown in the following table:

Table 2.

Magnetic Susceptibility Data For Equimolar Alpha Ferric Oxide-Zinc Oxide Mixtures at 25° C

Sample	Pretreatment Temperature, °C	$\chi_g \times 10^6$ cgs units By Kittell (16)	$\chi_g \times 10^6$ cgs units By Bupp (6)
Fe ₂ O ₃	None	37.6	20.4
Mixture	20	19.33	13.9
	400	21.39	
	500	21.77	16.7
	530		18.7
	600	21.74	
	650	47.76	
	670		47.0

Kittell and Hüttig (16) have shown that similar oxide mixtures do not display field strength dependency of magnetic susceptibility until pretreatment temperatures are in excess of 650° C. The enhanced magnetic properties appearing between 600 and 650° C were thus attributed to the appearance of a phase in the system which was not zinc ferrite.

EXPERIMENTAL METHOD

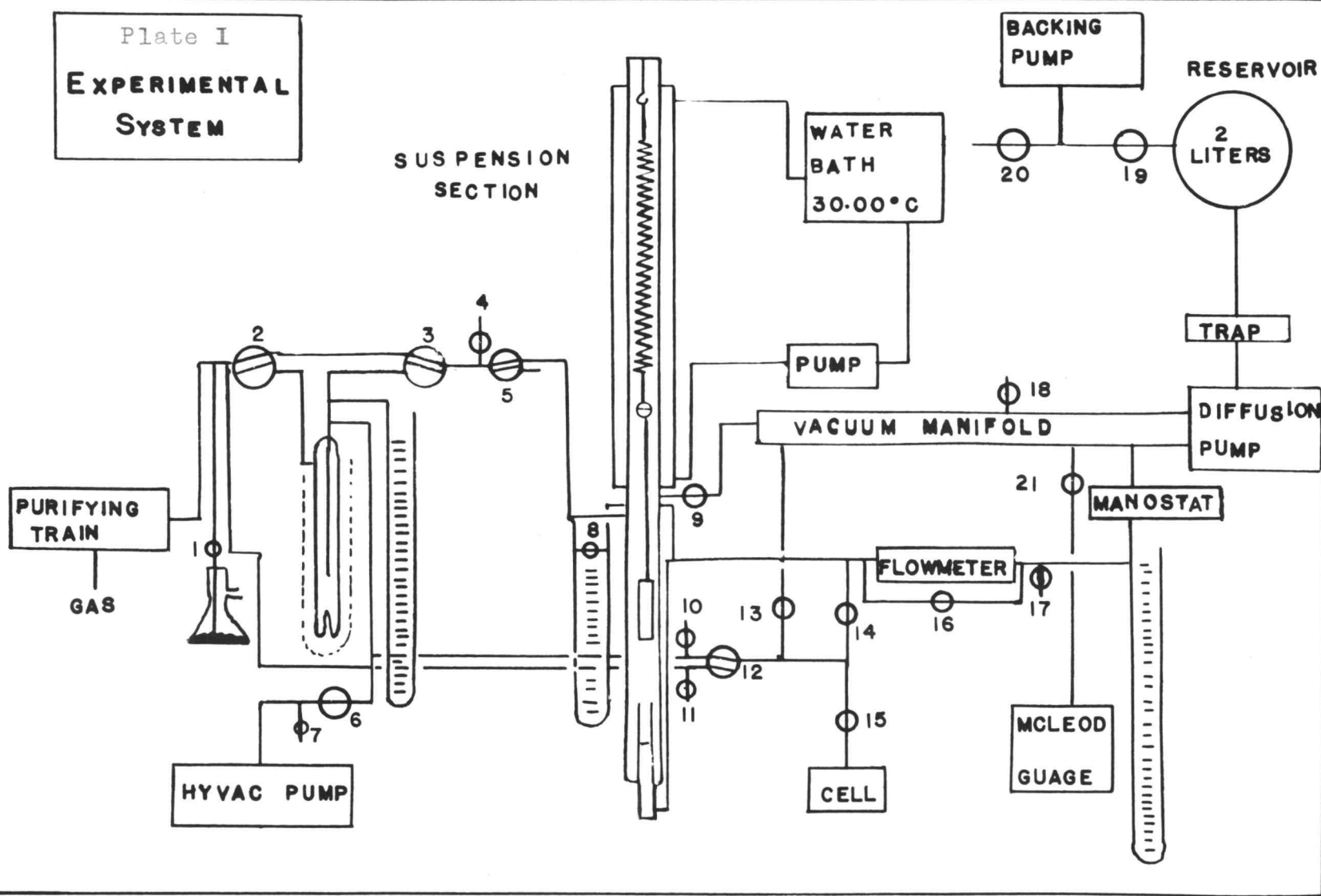
INTRODUCTORY REMARKS. An adaptation of the method of Bupp and Scott was used for the experimental work reported herein. This method approaches the ideal set forth by Selwood in his review on "Magnetism and Catalysis" in which he states the necessity of designing an experimental system in which the magnetic susceptibility, specific surface, and the catalytic activity of a solid substance can be determined simultaneously for one sample in situ. As the experimental set-up used was very similar to that one set up by Bupp for his PhD thesis work (5), only a brief description of the apparatus will be given where no important changes have been made. A more detailed discussion will be given of those parts of the apparatus either peculiar to this problem or to those parts which have been altered to improve the experimental method.

APPARATUS. Plate I is a schematic diagram of the entire experimental system. A brief account of the experimental procedure will now be given in order to orient the reader before going into greater detail of either procedure or equipment.

Briefly, the system was used in this manner. About five grams of uniform powder was contained in a sample tube which will be referred to as the reference vial. This

Plate I
EXPERIMENTAL
SYSTEM

SUSPENSION
SECTION



vial, confined by the reaction chamber, was freely suspended from a glass fiber which in turn was hung from a fine copper beryllium spring. Below this reference vial the reaction chamber was designed in such a manner that gas could pass through a bed of several grams of the same catalyst. It is to be noted that this arrangement allows both the catalyst bed and the reference vial, each filled with the same catalyst, to be treated in the same manner. The function of the catalyst bed is to serve as a catalyst for the reaction while the function of the reference vial filled with catalyst powder is to serve as a means of determining magnetic susceptibilities and surface areas by detecting the magnitude of any forces acting on the sample by means of a traveling microscope.

The amount of conversion was measured by use of a thermal conductivity cell which will be discussed later. Likewise to be discussed later is the flowmeter which was used to meter the gas flowing through the catalyst bed.

The pressure in the system was read from the difference between an open mercury manometer and a barometer. A closed manometer indicated any pressure drop across the catalyst bed. The pressure in the system varied from less than 5×10^{-3} mm to atmospheric pressure depending upon the operation being conducted. A cartesian diver type of manostat was used to control the pressures in the range of 30 - 400 mm during the nitrogen adsorption runs in

determining the surface areas. The system was evacuated through a 28 mm outside diameter vacuum manifold by means of a two stage mercury diffusion pump backed by a Cenco-Hyvac mechanical pump. (Henceforth, all sizes of glass tubing given will refer to the outside diameter.) A McCleod guage was attached to the manifold to read the lower pressures.

The glass throughout the system was pyrex and all tubing, unless otherwise noted, was 8 mm. Stopcocks 1, 2, 3, 5, 7, 8, 10, 17 and 21 were 2 mm bore with 8 mm tubing. Stopcocks 13, 14 and 15 were also 2 mm bore but with 8 mm capillary tubing. Stopcocks 4, 16, 18 and 20 were of 1 mm bore. Stopcocks 6, 9 and 19 were of 4 mm bore.

Suspension Section. The suspension section was similar to that one used by Lamar P. Bupp. The major change incorporated was that the male joints on both ends of the 125 mm condenser were 24/40 standard taper. A bath thermostated at 30.00° C was passed through the jacket.

A 24/40 standard taper female joint was used to make a cap for the top of the suspension section. This cap had a 3 mm glass hook sealed in to extend downward. This glass hook served as the support for a fine copper beryllium spring having the following characteristics:

Table 3.

Spring Constants

weight:	4.99g
number of turns:	410
length closed:	10.7 mm
outside diameter:	0.85 cm
wire diameter:	0.027 cm

The reference vial and catalyst were attached to the spring by means of a glass rod 1 mm in diameter which had small hooks on both ends. About five cm below the top of this glass rod was a glass circle 6 mm in diameter in which there was a cross hair made of Duco cement. This cross hair was followed by means of a traveling microscope (having a 6 cm range) when the sample was acted on by an outside force. The micrometer screw on this microscope was graduated to 0.01 mm.

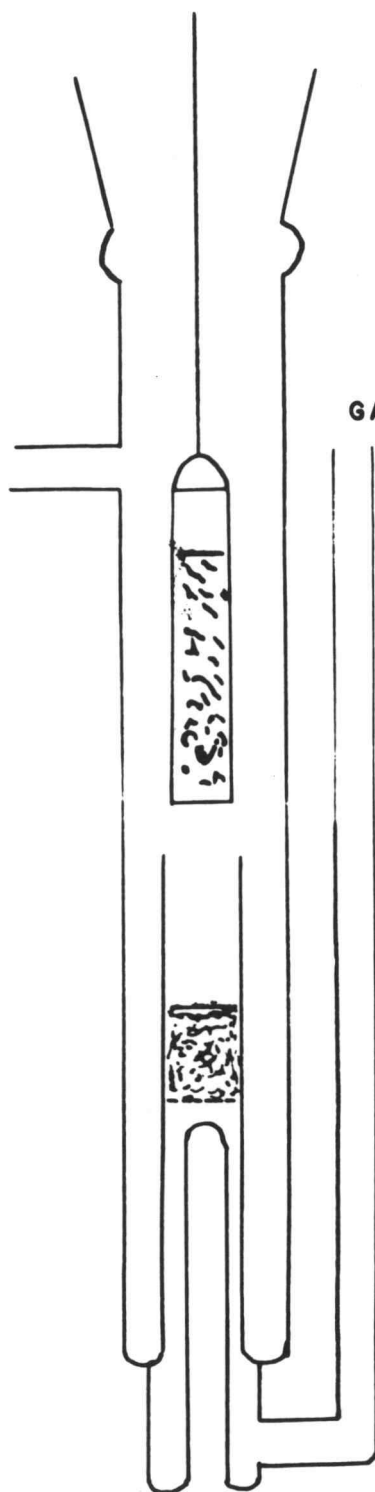
The spring was calibrated by adding standard weights in the same manner as was done by Bupp. The sensitivity was found to be 20.8 mg/mm.

Reaction Chamber. The reaction chamber was considerably redesigned from that used by Bupp. It is shown in cross section in Plate II with the reference vial containing the catalyst in position. It consisted of a body made of a 24 mm pyrex tube 45 cm in length with a 24/40 standard taper female joint on top. A 13 cm length of 10 mm tubing, with a coarse grade fritted disc dividing this tube into

Plate II
REACTION
CHAMBER

GAS INLET

GAS OUTLET



two compartments, was joined to the bottom of the body on the inside by means of a ring seal. This 10 mm tube was continued to the outside of the body with a 12 mm tube 12 mm long. A 4 mm thermocouple well extended through the length of the 12 mm tubing into the 10 mm tubing nearly up to the fritted disc which was about 5 cm in the main body of the reaction chamber.

Incoming gas entered the reaction chamber 12 cm below the 24/40 standard taper joint. The standard taper joints of the sample section and that of the suspension section were sealed with apiezon "W" wax. The 8 mm tubing for the incoming gas was directly sealed to the remainder of the system and had to be broken each time the reaction chamber was removed.

The gas escaped through the catalyst bed by way of an 8 mm tube which was attached to the 12 mm tubing at the bottom of the reaction chamber. This exit tube was also directly sealed to the system and had to be broken each time the system was disassembled.

The sample section was heated for outgassing purposes by means of a removable tubular electric oven. This was constructed from a copper tube base 33 mm in length and 4 cm in diameter. This base was wrapped in asbestos followed by a wrapping of 1/8 inch asbestos rope. It was then painted with sodium silicate. After drying, another wrapping of asbestos rope was applied. Between these

grooves number 18 nichrome wire was then wrapped to give a total resistance of 19 ohms. The cylinder was then given a third wrapping of asbestos rope followed by another wrapping of asbestos. This was painted once again with sodium silicate and allowed to dry.

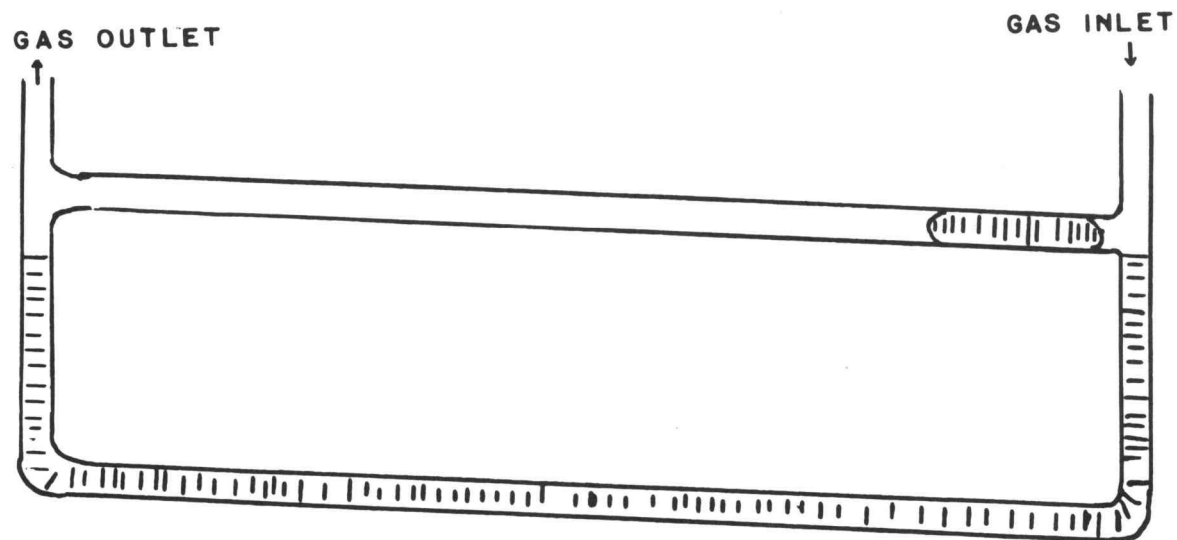
The reference vial was constructed by flattening out the bottom of a 3 inch pyrex test tube and adding a glass hook on top. The reference vial weighed 4.92 grams, had a total height of 70.9 mm and had a volume of 0.486 ml/cm. The volume versus height determination was made by weighing mercury which was added to various heights in the vial.

The dotted circle shown in Plate II represents the position of the poles of a permanent magnet which was employed for making magnetic susceptibility measurements. This magnet had a field strength of about 1600 oersteds with a gap of 38 mm and pole diameter of 40 mm. The magnet was mounted so that it could be swung transverse to the reference vial inside the reaction chamber. When magnetic measurements were made at -195°C using liquid nitrogen, a styro-foam block 30 cm x 6.5 cm x 3.8 cm was hollowed out in such a manner so that it could be slipped around the reaction chamber and kept filled with liquid nitrogen long enough to determine the magnetic susceptibility at this temperature.

Flowmeter. Plate III shows the type of flowmeter used in this study. This is a design similar to one

Plate III

MERCURY SLUG FLOWMETER



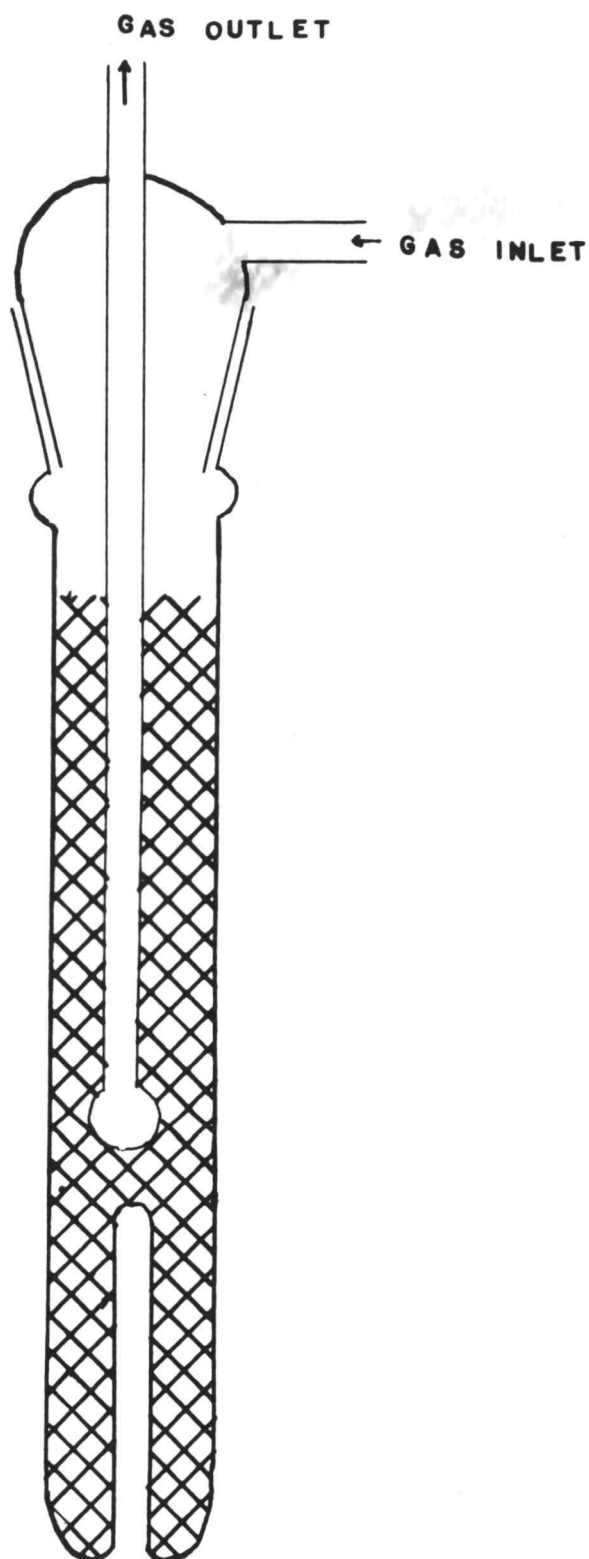
proposed by Appleby and Avery (1). Incoming gas passed through a mercury trap and through a 45 cm length of 6 mm tubing. The outlet was 2-3 mm above the inlet providing a constant gradient along the horizontal path. The large U tube was filled to such an excess that a new slug would close the entrance before the original slug completely left the slightly inclined tube. At all times therefore, the system was closed to gas flow and the volume of gas flowing could be measured by the number of slug cycles. This flowmeter was very satisfactory and proved more suitable than some others using this same principle in that it was easy to dismount and clean. It was very rugged and easy to construct.

The flowmeter was calibrated by means of a gas burette and found to contain 5.92 ml/cycle. It should be pointed out here that the flowmeter calibration is not critical in this work. The only limitation being that the volume displaced per cycle does not change. This is true since we are interested not in the absolute rate of reaction, but we are interested in comparing reaction rates between the different catalysts used.

Manostat. The manostat used was the same one that was used by Bupp, based on the design of R. Gilmont (10).

Parahydrogen Generator. The preparation of 1:1 hydrogen (1 ortho:1 para) was carried out in a pyrex vessel containing finely ground coconut charcoal. Plate IV

Plate IV
**PARAHYDROGEN
GENERATOR**



shows this generator in cross section. This generator consisted of a 25 mm pyrex tube 30 cm long with a 24/40 standard taper female joint on top and a 4 mm thermocouple well extending 5 cm through the base into the body. The construction was such that the incoming gas arriving through a 24/40 standard taper male joint which was sealed with Apiezon "W" wax to the main body of the generator had to come into contact with the entire charcoal column before leaving the generator by way of an 8 mm tube which led from near the base of the generator through the male joint on top.

The charcoal was evacuated through the hydrogen outlet (at 400° C) by means of a Cenco-Hyvac mechanical pump. The generator was heated by a removable electric furnace similar to that for the reaction chamber. The base was a 30 mm aluminum cylinder 23 cm long. Number 23 nichrome resistance wire was wound around this base in analogous manner to that for the reaction chamber furnace. A total resistance of 14 ohms easily gave temperatures greater than 400° C when current was supplied to it from a variable transformer. A five ampere AC ammeter was included in series with the resistance wire.

Temperature control. The temperatures were controlled by use of thermocouples made from chromel-alumel thermocouple wire. A millivoltmeter was calibrated using a Dewar flask of crushed ice and water in which a reference

couple was always immersed. A plot of scale reading of the millivoltmeter employed versus the temperature of the reference bath resulted in a linear relationship. The reference temperatures were the boiling point of water (100°C), the melting point of tin (231.8°C), the melting point of lead (327.4°C) and the melting point of zinc (419.5°C).

Thermal Conductivity Cell. The thermal conductivity cell and accompanying Wheatstone bridge arrangement was taken from an article by Bolland and Melville (3). This method of distinguishing between the two forms of hydrogen is based on the principal that a wire with low temperature coefficient of resistance should give a different resistance when the same amount of voltage is applied to the wire which is in the presence of gases of different thermal conductivities. In this case parahydrogen has a greater heat conductivity than orthohydrogen, i.e. the resistance of the wire should be measurably greater in the presence of normal hydrogen than in the presence of 1:1 hydrogen when observed at low temperatures where the differences in thermal conductivities is a maximum.

The cell was constructed using a filament from a $7\frac{1}{2}$ watt G. E. light bulb. The filament had a resistance of 190 ohms at 25°C . Each end of the filament was spot-welded onto a short length of number 36 tungsten wire. This arrangement was mounted in an 8 mm capillary tube as

shown in Plate V. An 8 mm tube led gas into or away from the cell through a doser arrangement (see Plate I). This doser arrangement was set up in order to insure the fact that the same amount of gas entered the conductivity cell each time it was filled. This was estimated to be about 100 mm of pressure.

Toward the end of this research a conductivity cell was constructed by sealing an outlet of soft glass directly to the light bulb itself. This in turn was attached to the doser arrangement by means of rubber tubing. A cell constructed in this manner seemed to work as well as the one illustrated in Plate V.

The resistance of the cell was measured while bathed in liquid nitrogen by the standard Wheatstone bridge method whose arrangement is shown in Plate V. The resistance of the cell was calculated from the resistances of the other three legs of the bridge by the following equation which is evident from the arrangement of the resistances shown in Plate V:

$$R_{(\text{cell})} = (100/1000) (R) = 0.1 R \quad (1)$$

With a slightly altered design which included a manometer to measure the absolute pressure in the cell, it was shown that there was a linear relationship between the resistance of the cell and the parahydrogen content. The

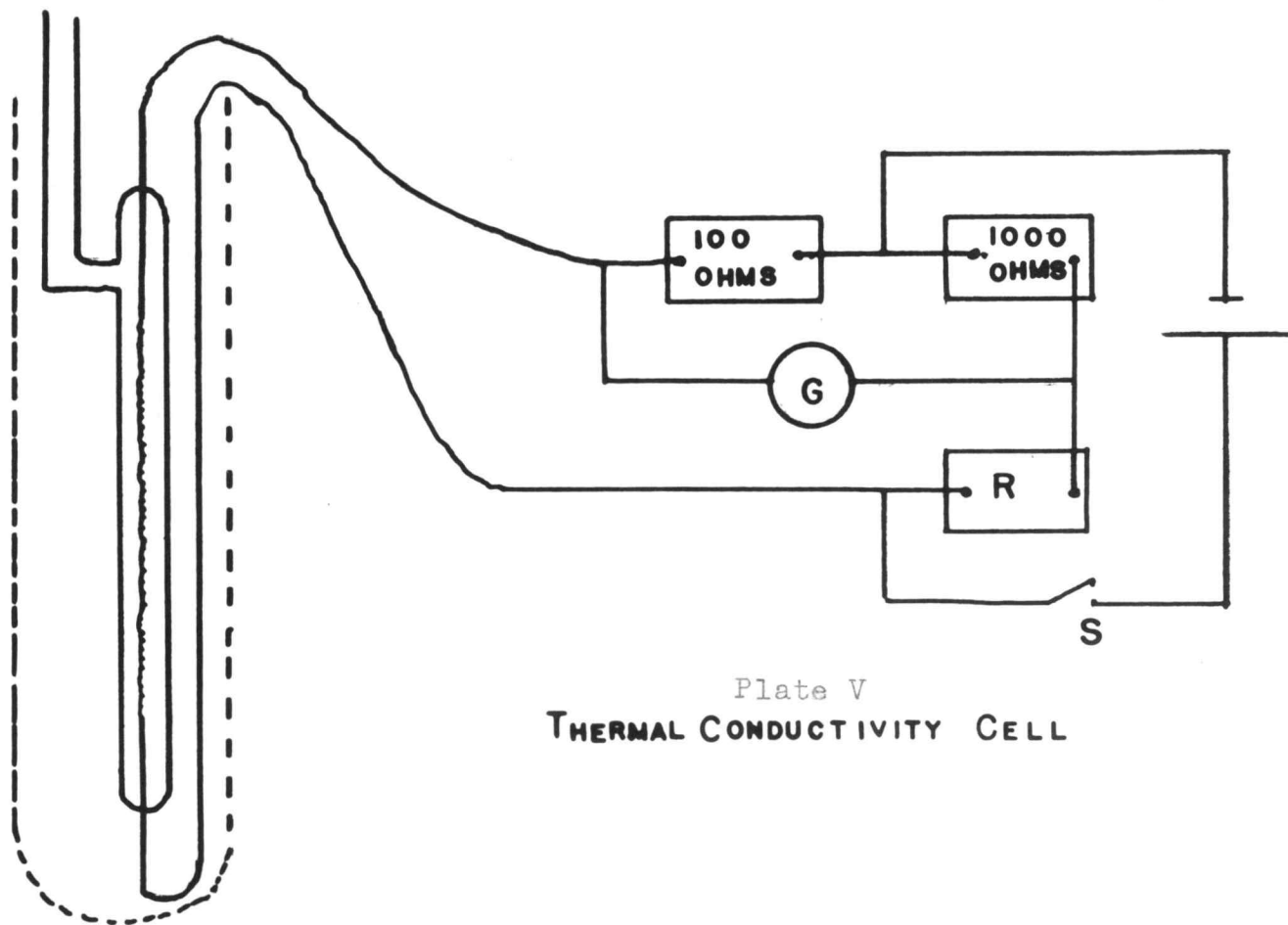


Plate V
THERMAL CONDUCTIVITY CELL

procedure for using the cell will be described later, but it may be said here that the cell was often extremely difficult to stabilize.

Enough voltage was applied to the Wheatstone bridge to give a total resistance of about 70 ohms to the hydrogen filled cell. The cell resistance was about 2.2 ohms less when surrounded by 1:1 hydrogen than when surrounded by normal hydrogen. That equilibrium hydrogen was obtained over the charcoal is verified by the fact that in increasing the contact time over some of the catalysts which were very active, no conversion over 100 percent was observed when referred to that hydrogen coming from the parahydrogen generator.

REAGENTS. The reagents listed below were specially prepared for this work in the same manner as done by Bupp. The reagents prepared are listed below with only little additional comment which is deemed worthwhile for the completeness of this work.

Gamma ferric oxide. This material was prepared by the oxidation of magnetite. Pure magnetite was made by coprecipitation of ferric and ferrous ions using the method of Lefort (29, p. 397) which involved the precipitation of ferrous and ferric ions from solution with the use of ammonia. This method was followed explicitly and will not be repeated here. The conversion to gamma ferric oxide

was carried out by passing nitrous oxide through a bed of this magnetite at 500°C . The resulting product was a dark red powder which showed no x-ray diffraction lines due to alpha ferric oxide.

Alpha ferric oxide. The alpha ferric oxide was synthesized using a method devised by the Bureau of Standards (8). This method is based on the precipitation of ferric ions with ammonia from an aqueous solution of nitrate which had been recrystallized several times. Bupp and Scott reported the major impurities of alpha ferric oxide prepared in this manner to be a trace of molybdenum and a trace of manganese.

Zinc Oxide. The zinc oxide was prepared by a method suggested by Roscoe and Schorlemmer (21, pp. 642-643). This was based upon a precipitation of zinc carbonate from a freshly prepared zinc sulfate solution. Ignition of the precipitate resulted in zinc oxide which was yellow when hot and white after it cooled. Bupp and Scott reported a purity of 99.8 percent for zinc oxide prepared in this manner. The major impurities were listed as being aluminum, calcium, magnesium and silicon.

Hydrogen. The hydrogen used throughout this study was obtained from a compressed gas cylinder supplied by the National Cylinder Gas Company. The principle impurities were small amounts of oxygen and water vapor.

Nitrogen. The nitrogen used for the surface area determinations was obtained from a compressed gas cylinder supplied by the National Cylinder Gas Company. The major impurity was oxygen.

Before entering the system both the hydrogen and nitrogen were passed through a bubbler containing 10 percent alkaline pyrogalllic acid followed by a furnace tube held at 400°C to remove all of the oxygen. Following this treatment, the gases were passed through a calcium chloride tower and a liquid nitrogen trap to remove all moisture and condensable gases.

PROCEDURES. The methods used to ready the system for experimental determinations and the manner in which various units of the apparatus were calibrated are given as follows:

Mounting the catalysts. The catalysts were finely divided powders which were packed in both the reference vial and the catalyst bed. The catalysts were well ground, weighed and transferred to the reference vial by means of a glazed paper funnel. The reference vial was then tapped about 100 times on a hard surface and then packed with pyrex glass wool to prevent exploding of the samples on evacuation. The height of the packing was observed with a millimeter rule and the tube hung on the spring suspension. In order for the cross hairs to be in the range of the

microscope, small spacer rods were used to shorten or lengthen the entire suspension system.

The catalyst bed support was filled with previously weighed catalyst with the aid of a long stemmed glass funnel which reached down into it at the bottom of the reaction chamber. The catalyst bed was then also packed with a small amount of pyrex glass wool. The reaction chamber was then fitted into place and the height of the catalyst bed was read by means of a millimeter scale.

Surface Area Determinations. The method of determining the extent of the interfacial surface on the solid catalysts was the same as used by Bupp and Scott who made use of the well known relationship derived by Brunauer, Emmett and Teller commonly known as the BET relationship (4). In brief, the adsorption data was obtained by weighing the amount of nitrogen adsorbed on the catalyst in the reference vial at -195° C while the system was held at constant pressure by means of a manostat.

In greater detail, referring to Plate I, stopcocks 5, 13, 18 and 20 were closed and stopcocks 8, 9, 16 and 19 were opened while the suspension section and reaction chamber were evacuated to $< 5 \times 10^{-3}$ mm. While heating the reaction chamber at an elevated temperature (see the section on EXPERIMENTAL RESULTS for outgassing temperatures used), the catalyst was weighed by means of the traveling microscope. When the weight showed no more

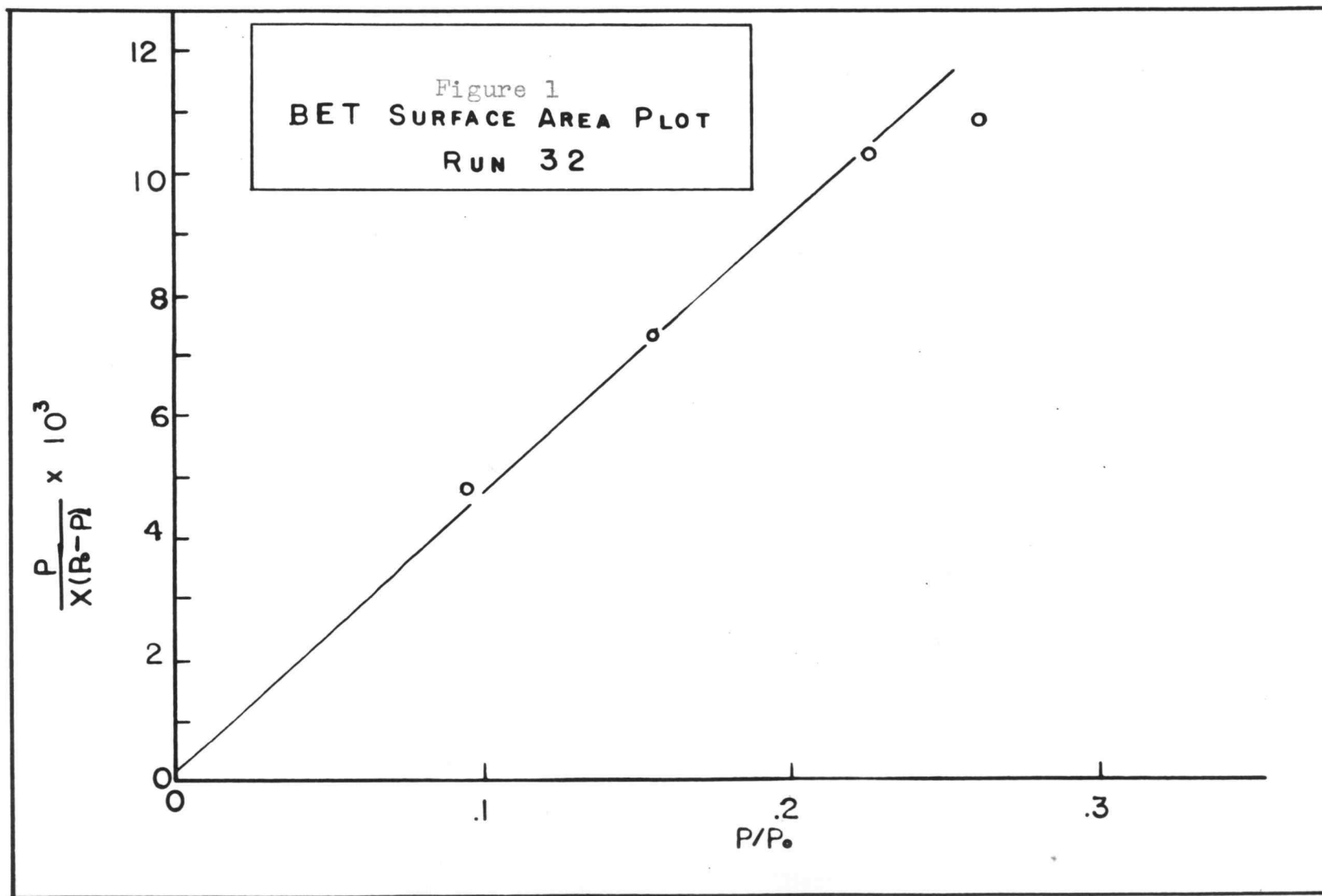
decrease with time, the reference sample was considered outgassed. The same assumption was made for the catalyst bed. The furnace was then turned off and removed. A one liter Dewar flask of liquid nitrogen was slipped around the reaction chamber after it had cooled to room temperature.

Purified nitrogen was then admitted into the system with stopcocks 2, 5, 8 and 16 open and stopcock 9 closed. When the desired pressure was reached, the manostat was set and allowed to take control. It was necessary for about 20 ml/min of nitrogen to bleed into the system for the manostat to operate properly.

In this manner the weight of the nitrogen at each of various pressures was obtained. These weights could then be used in the BET equation:

$$\frac{P}{X(P_0 - P)} = \frac{1}{X_m C} + \frac{(C-1)}{X_m C} \cdot \frac{P}{P_0} \quad (2)$$

where P is the pressure of the system, P_0 the atmospheric pressure, X is the mg of nitrogen adsorbed, X_m is the number of mg of nitrogen which would form a monomolecular layer over the surface of the sample, and c is a constant. From the data a graph, such as shown in Figure 1, was constructed using P/P_0 as the abscissa and $P/X(P_0 - P)$ as the ordinate. The plots obtained were such that the



intercepts of the straight lines always were near the origin making the value of c large compared to 1. Hence the slope of the line could be taken as the reciprocal of X_m with little error. Once having the value of X_m , the specific surface in square meters per gram could be calculated from equation (3):

$$\sigma = \frac{AxNxX_m}{10^7MxW} \quad (3)$$

where σ is the specific surface in square meters per gram, A is the cross sectional area of the nitrogen molecule which was taken as 16.3 square angstroms (8, p. 1559), X_m is the number of mg of nitrogen in the monomolecular layer, N is Avogadro's number, M is the molecular weight of the nitrogen, and W is the sample weight.

A correction was made for self adsorption as well as buoyant effect on the vial and suspension system. This correction was determined by making a blank adsorption investigation at several pressures on the sample tube. This buoyant effect was added to the apparent weight adsorbed. Another correction was due to the buoyant effect of the sample itself. This was corrected for by adding 4.9 mg per ml of sample (18), for a pressure of 760 mm, to the apparent amount of nitrogen adsorbed.

Catalytic Efficiency Determinations. The surfaces of the catalysts were degassed under $< 5 \times 10^{-3}$ mm at an elevated temperature. For details concerning this degassing, the section under EXPERIMENTAL RESULTS should be consulted.

Hydrogen was passed from a compressed gas cylinder through a reduction valve. The hydrogen at the reduced pressure then passed directly into the leads which go into the system. Before any gas was allowed to come into contact with the catalyst already at -195° C, the leads were completely flushed by alternately opening and closing stopcocks 1, 4, 5 and 11 to the atmosphere. After the leads were flushed for some time, hydrogen was admitted into the system to atmospheric pressure with stopcock 9 closed. This was done by keeping stopcock 1 open using enough hydrogen pressure so that hydrogen was going through the mercury bubbler as well as into the system. This insured that no air was drawn into the system when it was opened to the hydrogen stream.

The parahydrogen generator, having previously been evacuated by a Cenco Hyvac mechanical pump for two hours or more at 400° C, was immersed in a one quart Dewar flask of liquid nitrogen. The charcoal was then saturated with hydrogen at -195° C by opening stopcock 2, keeping stopcock 1 open to a mercury bubbler such that the pressure of the hydrogen in the leads was always slightly greater

than atmospheric pressure. When the charcoal became saturated with hydrogen, the flowrate was decreased and stopcock 10 was opened such that 1:1 hydrogen might flush out the outlet. After several minutes of flushing stopcock 10 was closed and stopcock 2 opened into the system again.

After opening stopcock 17, the hydrogen flowrate was adjusted to a desired rate, the flowmeter was placed into operation by closing stopcock 16, and stopcock 8 was closed forcing the normal hydrogen to pass through the catalyst bed. The pressure drop across the catalyst bed was noted by observing the difference in the readings of the two arms of the closed mercury manometer. The barometric pressure was also recorded for each series of runs. When the flowrate became constant, the number of slugs of mercury passing a given mark per unit time was recorded as determined with the aid of a stopwatch. From this and the volume of the catalyst bed, the contact time of the gas with the sample was calculated.

The thermal conductivity cell was then balanced. The cell was evacuated through the manifold by opening stopcocks 13 and 15 while keeping stopcocks 12 and 14 closed. After a short evacuation time, stopcocks 15 and 13 were closed and stopcock 12 opened to allow normal hydrogen to enter the doser. Stopcock 12 was then closed and stopcock 15 was opened allowing the trapped hydrogen to be expanded into the conductivity cell which was immersed in liquid

nitrogen. The resistance value of the cell was taken exactly three minutes after switch S of the Wheatstone bridge circuit was closed. This procedure was then repeated and the resistance of the wire was determined in the presence of 1:1 hydrogen obtained from the parahydrogen generator by opening stopcock 12 in that direction. This procedure was continued until a maximum reproducible value of ΔR (the resistance difference of the tungsten wire in the presence of normal hydrogen and that in 1:1 hydrogen) was obtained. This procedure took anywhere from two hours up to twenty or thirty. In general, the resistance of the cell decreased each time the cell was refilled before a near constant value for the resistances was obtained. If the cell resistance ever increased markedly above the preceding time, this was an indication that the cell had lost its stability. When this happened, the cell was discarded and efforts to balance a new cell were begun.

After the cell was once balanced, catalytic efficiency data was taken. For any given flowrate (contact time), the resistance of the wire in the cell surrounded by normal hydrogen was first measured. This was then followed by a measurement of the resistance of the wire in the cell when it was surrounded by hydrogen which had been extracted from the system into the doser by stopcock 14. This was then followed by a determination of the resistance of the wire surrounded by 1:1 hydrogen. The efficiency of the

catalyst, (amount of conversion toward 1:1 hydrogen) was calculated by linear interpolation. This procedure was repeated for each flowrate several times until nearly constant conversion values were obtained. It should be pointed out that at times the conductivity cell worked very well and the data was reasonably reproducible. At other times the cell worked very poorly and the data was widely scattered.

When the flowrates were changed, some time elapsed before constant conversion values were obtained, since the line had to be swept out with a gas of different composition. This was a very bothersome feature in the case of very small flowrates.

Magnetic Calibrations. The experimental method used for determining the magnetic susceptibilities of the catalysts was an adaptation of the Gouy method. The Gouy equation, which relates the variables involved in the determination, may be expressed as

$$f = g\Delta w = \frac{1}{2}(k_1 - k_2)(H_1^2 - H_2^2)A \quad (4)$$

where f is the force exerted on the sample perpendicular to the homogeneous magnetic field, k_1 is the magnetic susceptibility per ml of the surrounding medium, H_1 is the maximum field to which the sample is subjected, H_2 is the minimum field to which the sample is subjected, g is the

gravitational constant, A is the cross sectional area of the sample material, and Δw is the apparent change in weight of the sample on application of the magnetic field.

The magnet was calibrated in terms of $(H_1^2 - H_2^2)A$ versus the height of hydrated ferrous ammonium sulfate. This was done by packing the sample tube to different heights with weighed amounts of the sulfate and positioning the magnet transversely to the sample such that the maximum force exerted on a sample could be noted. From such a series of measurements made at room temperature as well as at -195°C , the quantity $(H_1^2 - H_2^2)A$ was calculated for the various sample heights.

In greater detail, equation (4) was solved for $(H_1^2 - H_2^2)A$ to give

$$(H_1^2 - H_2^2)A = \frac{2g\Delta w}{k_1} \quad (5)$$

since the volume susceptibility k_2 of the vacuum in which these determinations were made can be taken as 0.

If ΔM is the observed difference in mm on the traveling microscope for the maximum displacement of the sample when the magnet was swung transverse to the sample, Δw in grams could be calculated from

$$\Delta w = 20.8 \Delta M / 1000 \quad (6)$$

By definition $k = D\chi_g$ (7)

where χ_g is the magnetic susceptibility per gram and D is the apparent density in g/ml. Substituting equations (6) and (7) into equation (5), one arrives at

$$(H_1^2 - H_2^2)A = 41.6 \text{ g M}/(\chi_g D) \quad (8)$$

Since we are dealing with powders whose packing densities are not equal to 1, equation (8) has to be divided by the packing density defined by

$$\text{Packing density} = \frac{\text{Apparent density}}{\text{True density}} = \frac{D}{d}$$

where d is the true density. On dividing equation (8) by this packing density, assigning the gravitational constant g the accepted value of 980, and remembering that $D = W/V$ where W is the weight of the sample and V is the sample volume, equation (8) then becomes

$$(H_1^2 - H_2^2)A = (40,768 \text{ MdV}^2)/(\chi_g W^2) \quad (9)$$

For hydrated ferrous ammonium sulfate (24, p. 29)

$$\chi_g = (9500 \times 10^{-6})/(T + 1) \quad (10)$$

where T is the absolute temperature. Eliminating in equations (9) and (10) and assigning the density d a value of 1.86 g/ml (17, p. 189) for the hydrated ferrous ammonium sulfate, one arrives at

$$(H_1^2 - H_2^2)A = \frac{8000 MV^2(T + 1)}{W^2} \quad (11)$$

The term $(H_1^2 - H_2^2)A$, as calculated from equation (11), was plotted against the sample height. This procedure gave a curve from which the maximum value of $(H_1^2 - H_2^2)A$ could easily be obtained for the desired sample height. Eighteen points were determined between the heights of 30 and 60 mm. The term $(H_1^2 - H_2^2)A$ became independent of the sample height at heights greater than about 50 mm. The standard deviation for the seven determinations at heights of 50 mm or more was 0.21. In order to check the value of $(H_1^2 - H_2^2)A$, the sample vial was filled with a solution of 30.28 percent $NiCl_2 \cdot 6H_2O$ solution. The term $(H_1^2 - H_2^2)A$ was calculated to be 22.7×10^5 versus 22.9×10^5 obtained by the use of the hydrated ferrous ammonium sulfate. Values of the term $(H_1^2 - H_2^2)A$ determined at $-195^\circ C$ lay on the same curve as those determined at room temperature. This indicated that the surrounding styro-foam container and liquid nitrogen had no appreciable effect on the magnetic field.

Magnetic susceptibility determinations. No significant changes need to be discussed here in measuring the magnetic susceptibilities of the catalysts. In this case equation (9) was used after solving for $\chi_g \cdot \Delta M$, V, and W were the observed quantities. The density d was estimated at 5.1 g/ml for all the catalysts used. The value of $(H_1^2 - H_2^2)A$ for the particular sample height was taken from the plot previously discussed.

EXPERIMENTAL RESULTS

The results to be presented in this section will be classified according to series. The powdered sample catalysts were mixed and mounted as given in the section on procedures. The order of determinations for each run is the order in which the data is presented. Briefly stated, the sample was slowly heated to an elevated temperature in a vacuum until there was no more decrease in weight with time. The surface adsorption of nitrogen was observed at -195°C . The symbol σ_T is used to designate the specific surface, the T referring to the outgassing temperature. The reason for this will become apparent later. The sample was always outgassed before allowing it to come in contact with the normal hydrogen at -195°C . The catalytic efficiency determinations were then completed. At various times the magnetic susceptibility determinations were made both at -195°C and at room temperature. The order of determinations was not always the same, but became more standardized as the work progresses.

SERIES I. This investigation was primarily made to check the equipment and to get an idea as to what kind of results could be expected.

Run 1. For this investigation the reference vial was filled to a height of 49.0 mm with 5.07 grams of alpha

ferrie oxide. The catalyst bed was filled to a height of 14 mm with 1.11 grams of the same catalyst. The following results were obtained:

$$\sigma_{350} \dots \dots \dots 24.1 \text{ m}^2/\text{g}$$

$$\chi_g \text{ at } 25^\circ \text{ C} \dots \dots \dots 28.0 \times 10^{-6}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
.58	25
.76	31
1.2	42
2.4	50

After the run it was discovered that the base of the catalyst bed container was cracked which caused a portion of the hydrogen to bypass the catalyst bed. This rendered the data only useful for the qualitative interpretation that the reaction was very rapid.

Run 2. For this investigation the reference vial was filled to a height of 55.0 mm with 2.69 grams of the prepared zinc oxide. The catalyst bed was filled to a height of 28 mm with 1.33 grams of the same material. The following results were obtained:

$$\sigma_{300} \dots \dots \dots 4.1 \text{ m}^2/\text{g}$$

$$\chi_g \text{ at } 25^\circ \text{ C} \dots \dots \dots -0.35 \times 10^{-6}$$

Less than 10 percent conversion was observed with contact times ranging up to 10.5 seconds.

Run 3. For this investigation the reference vial was filled to a height of 28.0 mm with 4.44 g of alpha ferric oxide which had previously been heated at more than 600° C for 12 hours. (The exact pretreatment temperature for all the catalysts in series I was not exactly known, since it was discovered after this series of runs was completed that the electric furnace in which these were heated was not functioning properly.)

The catalyst bed was filled to a height of 12 mm with the same sample. The following results were obtained:

σ_{300} less than 1 m²/g

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
1.0	0
1.1	0
3.1	2
3.5	0

χ_g at 20° C..... 37.7 x 10⁻⁶

The high magnetic susceptibility per gram prompted an investigation of the sample. A small magnet was held close to the powder. Some of the particles appeared to be more markedly magnetic than others.

Run 5. For this investigation the reference vial was filled to a height of 34.0 mm with 4.99 g of alpha ferric

oxide which had been heated at an elevated temperature for 10 minutes. The catalyst bed was filled to a height of 23 mm with 3.15 g of the same sample. The following results were obtained:

σ_{300} less than 1 m²/g

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
1.1	7
4.2	19
7.7	34

χ_g at 25° C..... 24.7 x 10⁻⁶

Run 6. For this investigation the reference vial was filled to a height of 50.0 mm with 3.76 g of an equimolar mixture of alpha ferric oxide and zinc oxide which had been heated for six hours at more than 500° C. The catalyst bed was filled to a height of 12 mm with 0.84 g of the same catalyst. The sample was degassed at 300° C and the following results were obtained:

χ_g at 25° C..... 31.0 x 10⁻⁶

σ_{300} 12.3 m²/g

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.37	32
0.72	52

Unfortunately the cell burned out before more data could be obtained.

Run 7. For this investigation the reference vial was filled to a height of 53.0 mm with 4.06 g of equimolar alpha ferric oxide and zinc oxide which had been heated for six hours at more than 600° C. The catalyst bed was filled to a height of 25 mm with 1.47 g of the same sample. The following results were obtained:

$$\sigma_{300} \dots \dots \dots 4.9 \text{ m}^2/\text{g}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
2.5	30
3.6	50

At this point air accidentally entered the system. Thus no more reliable data could be taken.

$$\chi_g \text{ at } 20^\circ \text{ C.} \dots \dots \dots 70.7 \times 10^{-6}$$

Run 8. For this investigation the reference vial was filled to a height of 50.0 mm with 4.07 g of an equimolar mixture of alpha ferric oxide and zinc oxide which has previously been heated for six hours at a temperature greater than 550° C. The catalyst bed was filled to a height of 23 mm with 1.47 g of the same sample. The following results were obtained:

$$\sigma_{300} \dots \dots \dots 2.0 \text{ m}^2/\text{g}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.77	10
2.3	18
3.9	27

$$\chi_g \text{ at } 23^\circ \text{ C} \dots \dots \dots 32.6 \times 10^{-6}$$

After this series of runs, the styro-foam block previously described was obtained and the magnetic determinations were repeated; these are tabulated in Table 3. Column I refers to the run number, column II refers to the susceptibility obtained at room temperature for the catalyst the first time, column III refers to the magnetic susceptibility obtained the second time at room temperature when the samples were remounted, and column IV refers to the magnetic susceptibility obtained at -195° C when the samples were remounted.

Table 3.

<u>Run</u>	<u>χ_g the first time at 25° C</u>	<u>χ_g after remounting</u>	<u>χ_g at -195° C after remounting</u>
1	28×10^{-6}	34.3×10^{-6}	34.9×10^{-6}
6	31×10^{-6}	37.5×10^{-6}	76.8×10^{-6}
8		32.6×10^{-6}	68.6×10^{-6}
7	70.7×10^{-6}	79.4×10^{-6}	360×10^{-6}

SERIES II. This series of runs was made with a fresh stock of alpha ferric oxide. The largest change made for

this group of runs was that the magnetic susceptibility was determined alongside that determined at room temperature. It was hoped that this series of runs would give some information on the cause of the odd magnetic behaviour observed with those catalysts used in series I.

Run 9. For this investigation the reference vial was filled to a height of 45.0 mm with 4.87 g of alpha ferric oxide. The catalyst bed was filled to a height of 20 mm with 1.88 g of the same sample. The following data was obtained:

τ_{300}	12.3 m ² /g
χ_g at 25° C.....	28.5 x 10 ⁻⁶
χ_g at -195° C.....	24.5 x 10 ⁻⁶

After outgassing at 300° C, the following efficiencies were obtained:

<u>Secs.</u>	<u>Efficiency</u>
0.35	45
0.80	64
1.1	62
2.0	83
3.4	100

After the run the sample was found to be extremely magnetic.

Run 10. For this investigation the reference vial was filled to a height of 50.0 mm with 3.97 g of equimolar ferric oxide and zinc oxide which had no previous heat treatment. The catalyst bed was filled to a height of 11 mm with 0.84 g of the same material. The sample was

outgassed at 300° C and the following results were obtained:

χ_g at 25° C..... 55.9 x 10⁻⁶
 χ_g at -195° C..... 55.9 x 10⁻⁶
 σ_{300} 9.9 m²/g

The sample was again outgassed at 300° C and the following efficiencies were observed:

<u>Secs.</u>	<u>Efficiency</u>
0.34	39
0.39	33
0.60	38
1.3	59
1.4	63
2.5	75

χ_g at 25° C..... 55.9 x 10⁻⁶
 χ_g at -195° C..... 55.6 x 10⁻⁶

The magnet was swung into position and the sample was found to be extremely attracted by the magnet at room temperature.

Run 13. For this investigation the reference vial was filled to a height of 45.0 mm with 2.46 g of gamma ferric oxide. The catalyst bed was filled to a height of 35 mm with 1.89 g of the same sample. The following observations were made:

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.57	100
0.89	100
σ_{400}	32.7 m ² /g

SERIES III. It appeared from the previous runs that the samples often became ferromagnetic upon heating. This suggested small amounts of reducing material in the alpha ferric oxide. In order to check this possibility, a new source of alpha ferric oxide needed to be prepared. In the meantime, the following runs were made from a mixture of the alpha ferric oxides used in series I and II.

Run 14. For this investigation the reference vial was packed to a height of 43.0 mm with 4.77 g of alpha ferric oxide. The catalyst bed was packed to a height of 19.0 mm with 1.76 g of the same sample. The following results were obtained:

χ_g at 25° C.....	29.7 x 10 ⁻⁶
χ_g at -195° C.....	26.0 x 10 ⁻⁶
σ_{400}	16.3 m ² /g

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.39	71
0.64	96
χ_g at 25° C.....	28.1 x 10 ⁻⁶
χ_g at -195° C.....	23.4 x 10 ⁻⁶

Run 16. For this investigation the reference vial was packed to a height of 50.0 mm with 3.74 g of an equimolar mixture of alpha ferric oxide which had been treated at 700° C. The catalyst bed was packed to 37 mm with 2.03 g of the same catalyst. The following results were obtained:

$$\begin{aligned}\chi_g \text{ at } 20^\circ \text{ C} &\dots\dots\dots 35.0 \times 10^{-6} \\ \chi_g \text{ at } -195^\circ \text{ C} &\dots\dots\dots 100 \times 10^{-6} \\ \sigma_{300} &\dots\dots\dots 2.7 \text{ m}^2/\text{g}\end{aligned}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
1.8	17
2.1	20
6.3	40
8.9	49

The sample was found to be ferromagnetic after the run. It was divided into several portions. The top portion was found to be more strongly attracted to a magnet than the lower portions.

SERIES IV. This group of runs was investigated using freshly prepared zinc oxide and freshly prepared alpha ferric oxide to eliminate the possibility that a reducing impurity was present which might have been reducing the ferric oxide to a more paramagnetic or ferromagnetic constituent. All samples for this and the following series were heated in an oven whose temperature was

checked with an alternate thermocouple.

Run 17. For this investigation the reference vial was packed to a height of 54.0 mm with 2.78 g of zinc oxide. The catalyst bed was packed to a height of 40 mm with 1.54 g of the same sample. The following results were obtained:

χ_g at 25° C..... negligible

χ_g at -195° C..... negligible

σ_{400} 3.0 m²/g

Catalytic Efficiency

Secs.

1.4

4.9

Efficiency

negligible

negligible

χ_g at 25° C..... negligible

Run 18. For this investigation the reference vial was packed to a height of 47.0 mm with 4.46 g of alpha ferric oxide. The catalyst bed was packed to a height of 23 mm with 1.75 g of the same sample. The following results were obtained:

χ_g at 22° C..... 27.7 x 10⁻⁶

χ_g at -195° C..... 27.9 x 10⁻⁶

σ_{400} 27.5 m²/g

Catalytic Efficiency

Secs.

0.60

5.9

Efficiency

100

100

χ_g at 22° C..... 27.2 x 10⁻⁶

χ_g at -195° C..... 27.0 x 10⁻⁶

Run 19. For this investigation the reference vial was packed to a height of 53.5 mm with 4.47 g of an equimolar mixture of alpha ferric oxide and zinc oxide. The catalyst bed was packed to a height of 16 mm with 1.00 g of the same sample. The following results were obtained:

χ_g at 20° C..... 22.6 x 10⁻⁶

σ_{400} 20.6 m²/g

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.26	44
0.47	63
0.77	71
2.1	92

χ_g at 22° C..... 24.6 x 10⁻⁶

Run 20. For this investigation the reference vial was packed to a height of 50.0 mm with 4.38 g of an equimolar mixture of alpha ferric oxide and zinc oxide pretreated at 700° C for six hours. The catalyst bed was packed to a height of 33 mm with 2.00 g of the same sample. The following results were obtained:

χ_g at 23° C..... 41.6 x 10⁻⁶

χ_g at -195° C..... 195 x 10⁻⁶

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
1.6	20
4.5	50
12	equilibrium was never reached
χ_g at 23° C.....	41.6×10^{-6}
χ_g at -195° C.....	220×10^{-6}
σ_{400}	$2.0 \text{ m}^2/\text{g}$

Run 21. This is a repeat of run 19. The reference vial was packed to a height of 50.0 mm with 4.04 g of the sample. The catalyst bed was packed to a height of 19 mm with the same sample. The following data were obtained:

χ_g at 23° C.....	23.8×10^{-6}
χ_g at -195° C.....	23.8×10^{-6}

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.34	47
0.50	65
0.72	52
0.97	86
χ_g at room temperature....	23.8×10^{-6}
χ_g at -195° C.....	23.8×10^{-6}
σ_{400}	$19.9 \text{ m}^2/\text{g}$

Run 22. For this investigation the reference vial was packed to a height of 48.0 mm with 3.74 g of an equimolar

mixture of zinc oxide and alpha ferric oxide which had been pretreated at 500° C for six hours. The catalyst bed was packed to a height of 18 mm with 1.08 g of the same sample. The following results were obtained:

χ_g at 21° C..... 24.4×10^{-6}

χ_g at -195° C..... 24.4×10^{-6}

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.48	33
1.1	48
1.6	78

χ_g at 21° C..... Strongly magnetic

σ_{400} -----

The sample was divided into four layers. The top layer was found to be more ferromagnetic than the remainder of the layers. This was also found to be true for the catalyst bed. An analysis for iron by the dichromate method showed no difference in iron content between the different layers. An x-ray determination did not indicate the presence of anything other than alpha ferric oxide. When the magnetic portion was viewed through a Greenough binocular microscope, small black granules were observed among the many brown ones characteristic of the alpha ferric oxide. The small black granules moved when a small magnet was brought near.

Run 23. For this investigation the reference vial was packed to a height of 45.0 mm with 4.83 g of an equimolar mixture of alpha ferric oxide and zinc oxide. The catalyst bed was packed to a height of 14 mm with 1.00 g of the same material. The following results were obtained:

$$\begin{aligned} \chi_g \text{ at } 22^\circ \text{ C} &\dots\dots\dots 19.6 \times 10^{-6} \\ \chi_g \text{ at } -195^\circ \text{ C} &\dots\dots\dots 20.3 \times 10^{-6} \end{aligned}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.57	55
0.72	59
2.1	100
2.6	96
τ_{330}	20.0

The sample was found to be very magnetic after the surface area determination. The sample was divided into five nearly equal portions from the top down. The top two portions were responsible for the odd magnetic behaviour.

SERIES V. For this series of runs all operations were carried out as before, except the outgassing operation, which was carried out at a lower temperature, 200° C .

Run 24. For this investigation the reference vial was packed to a height of 48.0 mm with 4.33 g of an equimolar mixture of alpha ferric oxide and zinc oxide. The catalyst bed was packed to a height of 14 mm with 1.00 g of the

same catalyst. The following results were obtained:

$$\chi_g \text{ at } 22^\circ \text{ C} \dots\dots\dots 20.2 \times 10^{-6}$$

$$\chi_g \text{ at } -195^\circ \text{ C} \dots\dots\dots 19.9 \times 10^{-6}$$

The sample was outgassed at 200° C and the magnetic susceptibility determination was repeated:

$$\chi_g \text{ at } 24^\circ \text{ C} \dots\dots\dots 20.2 \times 10^{-6}$$

$$\chi_g \text{ at } -195^\circ \text{ C} \dots\dots\dots 19.9 \times 10^{-6}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.45	58
0.82	62
1.6	91

$$\sigma \dots\dots\dots 18.9 \text{ m}^2/\text{g}$$

Run 25. For this investigation the reference vial was packed to a height of 49.0 mm with 4.51 g of an equimolar alpha ferric oxide zinc oxide mixture which had been pre-treated at 600° C for six hours. The catalyst bed was packed to a height of 37 mm with 2.65 g of the same sample. The following results were obtained:

$$\chi_g \text{ at } 22^\circ \text{ C} \dots\dots\dots 25.4 \times 10^{-6}$$

$$\chi_g \text{ at } -195^\circ \text{ C} \dots\dots\dots 52.9 \times 10^{-6}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.52	37
0.76	50
1.0	55
1.3	88
2.4	98
σ	$10.5 \text{ m}^2/\text{g}$

Run 26. For this investigation the reference vial was packed to a height of 48.0 mm with 4.44 g of an equimolar mixture of alpha ferric oxide and zinc oxide which had been pretreated at 700° C for six hours. The catalyst bed was packed to a height of 38 mm with 2.67 g of the same material. The following results were obtained:

χ_g at 21° C.....	36.2×10^{-6}
χ_g at -195° C.....	198×10^{-6}

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.66	18
1.4	30
2.8	49
3.9	60
4.1	63

σ	$3.3 \text{ m}^2/\text{g}$
χ_g at 21° C.....	37.5×10^{-6}
χ_g at -195° C.....	200×10^{-6}

Run 27. For this investigation the reference vial was packed to a height of 40.0 mm with 4.60 g of an equimolar

mixture of alpha ferric oxide and zinc oxide which had been pretreated at 900° C for six hours. The catalyst bed was packed to a height of 42 mm with 3.61 g of the same material. The following results were observed:

$$\chi_g \text{ at } 24^\circ \text{ C} \dots\dots\dots 514 \times 10^{-6}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
2.2	11
5.3	21

$$\sigma \dots\dots\dots 1.4 \text{ m}^2/\text{g}$$

Run 28. For this investigation the reference vial was packed to a height of 44.0 mm with 4.65 g of alpha ferric oxide. The catalyst bed was packed to a height of 14 mm with 1.00 g of the same material. The following results were obtained:

$$\chi_g \text{ at } 20^\circ \text{ C} \dots\dots\dots 24.4 \times 10^{-6}$$

$$\chi_g \text{ at } -195^\circ \text{ C} \dots\dots\dots 25.0 \times 10^{-6}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.17	58
0.28	73
0.62	82
0.72	89

$$\sigma \dots\dots\dots 26.8 \text{ m}^2/\text{g}$$

Run 29. For this investigation the reference vial was packed to a height of 51.0 mm with 4.46 g of an equimolar mixture of alpha ferric oxide and zinc oxide which had been pretreated at 500° C for six hours. The catalyst bed was packed to a height of 34 mm with 2.00 g of the same material. The following results were obtained:

$$\chi_g \text{ at } 24^\circ \text{ C} \dots\dots\dots 20.6 \times 10^{-6}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
1.1	71
1.6	91
6.5	100

$$\chi_g \text{ at } 23^\circ \text{ C} \dots\dots\dots 21.7 \times 10^{-6}$$

$$\chi_g \text{ at } -195^\circ \text{ C} \dots\dots\dots 19.1 \times 10^{-6}$$

$$\sigma \dots\dots\dots 13.1 \text{ m}^2/\text{g}$$

Run 30. For this investigation the reference vial was packed to a height of 47.1 mm with 3.90 g of an equimolar mixture of zinc oxide and alpha ferric oxide. The catalyst bed was filled to a height of 8.0 mm with 0.50 g of the same material. The following results were obtained:

$$\chi_g \text{ at } 22^\circ \text{ C} \dots\dots\dots 22.4 \times 10^{-6}$$

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.43	55
0.96	70

χ_g at 22° C.....	20.6 x 10 ⁻⁶
χ_g at -195° C.....	17.2 x 10 ⁻⁶
σ	18.0 m ² /g

Run 31. For this run a few grams of the alpha ferric oxide were heated at 700° C for four hours. This was then mixed with equimolar zinc oxide and heated at 600° C for six hours. The resulting powder was gray in color in contrast to a chocolate brown color of various shades for the other mixed catalysts used. The reference vial was packed to a height of 54.0 mm with 5.36 g of this material. The catalyst bed was packed to a height of 54 mm with 3.39 g of the same sample. The following results were obtained:

χ_g at 25° C.....	40.7 x 10 ⁻⁶
χ_g at -195° C.....	33.3 x 10 ⁻⁶
σ	less than 1 m ² /g
χ_g at 23° C.....	41.0 x 10 ⁻⁶
χ_g at -195° C.....	33.5 x 10 ⁻⁶

No conversion was observed after 35 seconds contact time.

χ_g at 23° C.....	41.0 x 10 ⁻⁶
χ_g at -195° C.....	34.7 x 10 ⁻⁶

Run 32. For this investigation the reference vial was packed to a height of 59.0 mm with 5.25 g of an equimolar mixture of alpha ferric oxide and zinc oxide which had

previously been heated at 410°C for six hours. The catalyst bed was packed with the same sample to a height of 10 mm with 0.50 g of the same sample. The following results were obtained:

χ_g at 22°C	22.0×10^{-6}
χ_g at -195°C	21.5×10^{-6}
Catalytic Efficiency	

<u>Secs.</u>	<u>Efficiency</u>
0.25	33
0.78	61
1.5	43
1.9	81

χ_g at 25°C	22.0×10^{-6}
χ_g at -195°C	21.5×10^{-6}
σ	$15.6 \text{ m}^2/\text{g}$

The catalytic efficiency determination was repeated once again:

<u>Secs.</u>	<u>Efficiency</u>
0.13	22
0.24	19
0.28	44
0.38	57
1.5	47
2.3	62

σ	$14.3 \text{ m}^2/\text{g}$
χ_g at 22°C	22.6×10^{-6}
χ_g at -195°C	21.5×10^{-6}

Run 33. For this investigation equimolar alpha ferric oxide and zinc oxide were heated together for $5\frac{1}{2}$ hours at

900° C. The resulting powder was then moistened and followed by alternately freezing and thawing the paste several times. This was followed by drying at 350° C for three hours. The reference vial was filled to a height of 43.0 mm with 5.57 g of this sample. The catalyst bed was packed with the same sample to a height of 46 mm. The following results were obtained:

χ_g probably ferromagnetic
 σ less than 1 m²/g

Run 34. Equimolar alpha ferric oxide and zinc oxide were heated for six hours at 650° C and this was followed by a treatment similar to the one described in the preceding run. The reference vial was filled to a height of 49.0 mm with 4.20 g of this material. The catalyst bed was filled with 1.11 g of the same material to a height of 14 mm.

χ_g at 25° C 54.6 x 10⁻⁶
 χ_g at -195° C 257 x 10⁻⁶
 σ 9.6 m²/g

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.86	28
2.4	40
6.2	67

The system was left intact but the sample was outgassed again the following day. An efficiency run yielded these results.

<u>Secs.</u>	<u>Efficiency</u>
0.57	17
2.2	37
8.0	76

Run 35. For this investigation the reference vial was packed to a height of 55.0 mm with 5.18 g of an equimolar mixture of alpha ferric oxide and zinc oxide which had been pretreated at 650° C for six hours. The catalyst bed was packed to a height of 14.8 mm with 1.34 g of the same sample. The following results were obtained:

χ_g at 20° C..... 28.9 x 10⁻⁶

χ_g at -195° C..... 88 x 10⁻⁶

Catalytic Efficiency

<u>Secs.</u>	<u>Efficiency</u>
0.33	16
0.62	24
1.16	55
1.24	47
7.4	90

χ_g at 21°C 28.9×10^{-6}
 χ_g at -195°C 93.0×10^{-6}
 σ $8.6 \text{ m}^2/\text{g}$

Run 36. The reference vial was filled with alpha ferric oxide and its magnetic properties were checked:

χ_g at 23°C 27.4×10^{-6}
 χ_g at -195°C 26.1×10^{-6}

DISCUSSION OF RESULTS

INTRODUCTORY REMARKS. The results of this investigation are presented in five series. The results of all the series are consistent in the respect that the efficiencies of the catalysts decreased with decreasing surface area. For the first four series however, the magnetic data was very inconclusive since the magnetic properties of the catalysts changed during the experiment. Some of the catalyst's magnetic properties changed more than others. This apparently did not have too much effect on the catalytic efficiency. This is particularly striking when one views the results of runs 10 and 11. More will be said of this later.

It was found that the extreme changes in magnetic properties were due only to the top layer of the catalyst in the reference vial. This was also found to be true for the top layer of the catalyst bed indicating that both had been subjected to the same kind of treatment and those changes which occurred in the reference vial and the catalyst bed were of a similar nature. Several chemical and physical examinations failed to indicate the presence of anything other than alpha ferric oxide. The observation of the catalyst under a microscope showed the presence of black granules which moved when a small magnet was brought

near. This suggested that magnetite whose characteristic color is black might be responsible for the peculiar magnetic behaviour. It is suggested that this magnetite was formed by the decomposition of the alpha ferric oxide at low pressures and at temperatures of 300° C and above. Moissan (19, p. 23) has reported such a reaction, but an accurate estimate of the temperature and pressure at which this was carried out was not reported.

Bupp and Scott did not report such a phenomenon in their work. On studying some unpublished data (13, p. 62-63), one finds that, after heating a mixture of ferric oxide and zinc oxide at 400° C in a vacuum, the magnetic susceptibilities measured after each period of outgassing were 13.9×10^{-6} , 16.5×10^{-6} , 16.7×10^{-6} and 17.5×10^{-6} respectively. The important thing to notice is the increase in magnetic susceptibility after each heating. It is likely that he was not working at pressures as low as he thought since he had only a relative method of measuring pressure instead of an absolute one. The explanation is plausible since the transformation took place only on the uppermost layers of the catalyst samples, indicating that a moderately high vacuum is needed for the transformation, and that even the pressure drop throughout the sample was sufficient to prevent the reaction from occurring.

Since this work was initiated to correlate both the magnetic properties of the catalysts as well as the surface areas of the catalysts, the data presented in the runs under series V will be most closely followed. In this series of runs all outgassing operations were carried out at temperatures below 200°C , a temperature at which none of the catalysts had their magnetic properties change significantly.

THE CONVERSION OF ORTHOHYDROGEN ON GAMMA FERRIC OXIDE.

A sample of gamma ferric oxide which had a specific surface area of $32.7\text{ m}^2/\text{g}$ was found to be a very effective catalyst. Complete conversion was obtained for contact times as small as 0.57 seconds. Sufficient experiments were not performed to show whether its high activity was due to its extended surface, to its ferromagnetic properties or to both. Nevertheless the important thing to note is that gamma ferric oxide with an extended surface is an excellent material with which to catalyze the ortho to parahydrogen transformation at -195°C and at atmospheric pressure.

THE CONVERSION OF ORTHOHYDROGEN ON ALPHA FERRIC OXIDE.

The transformation of orthohydrogen to parahydrogen at atmospheric pressure, and at -195°C , took place rapidly on a sample of the alpha ferric oxide which had a specific surface area of $26.8\text{ m}^2/\text{g}$. Its magnetic susceptibility was 25.0×10^{-6} , but a later measurement on a sample from

the same source gave a value of 26.1×10^{-6} . Indications are that the surface plays a role in determining the efficiency of the catalyst. Such evidence is presented in Table 3 using data from runs besides group V. This data was derived in this manner: The catalytic efficiency was plotted against the contact time. The efficiency at 1 second was then obtained from the plot. These are the values tabulated in column 3.

Table 3.

Dependence of the Catalytic Efficiency on the Specific Surface Area of Alpha Ferric Oxide Catalysts

<u>Run</u>	<u>m²/g</u> <u>Specific Surface,</u>	<u>Efficiency</u> <u>at 1 Second</u>
3	1	0
5	1	6
9	12.3	61
14	16.3	100 (est)
18	27.5	100
28	26.8	100

A change of efficiency of nearly 100 fold strongly suggests that there is a relationship between the specific surface area and catalytic efficiency.

THE CONVERSION OF ORTHOHYDROGEN ON ZINC OXIDE. Run 2 was conducted using the prepared zinc oxide as the catalyst. This material had a rather low surface area of $4.1 \text{ m}^2/\text{g}$. Less than 10 percent conversion was obtained

for a contact time of 10.5 seconds. Slight diamagnetism was observed.

THE CONVERSION OF ORTHOHYDROGEN ON ALPHA FERRIC OXIDE-ZINC OXIDE MIXTURES. Equimolar mixtures of the prepared alpha ferric oxide and the prepared zinc oxide were mixed thoroughly and heated in alundum boats for six hours at 410° , 500° , 600° , 650° , 700° and 900° C. The results of these determinations (Series V) are shown in Figures 2, 3 and 4. That these results are in reasonable agreement with those of series I, II, III and IV will be pointed out shortly. Referring to Figures 2, 3 and 4, one notes that the efficiency of the catalysts falls off in a more or less regular manner with increasing pretreatment temperature. Simultaneously with this decrease in activity there can be noted a decrease in surface area as well as an increase in magnetic susceptibility.

In order to correlate the change in efficiency with specific surface and/or magnetic susceptibility, the efficiency at 1 second was obtained from Figures 2, 3 and 4. This was compared with the specific surface area and magnetic susceptibility as done in Table 4.

Figure 2

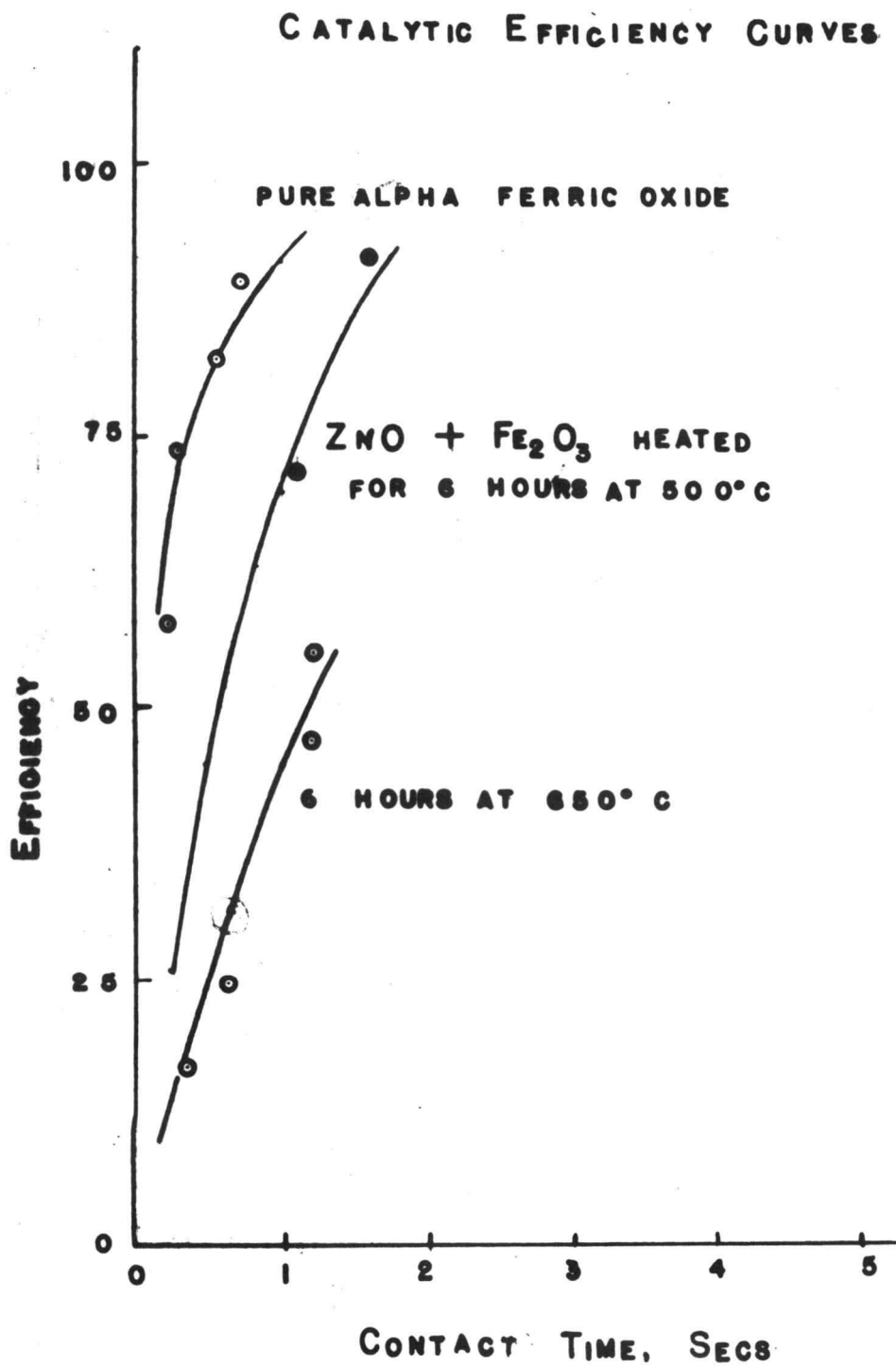


Figure 2
CATALYTIC EFFICIENCY CURVES
 $\text{Fe}_2\text{O}_3 + \text{ZnO}$

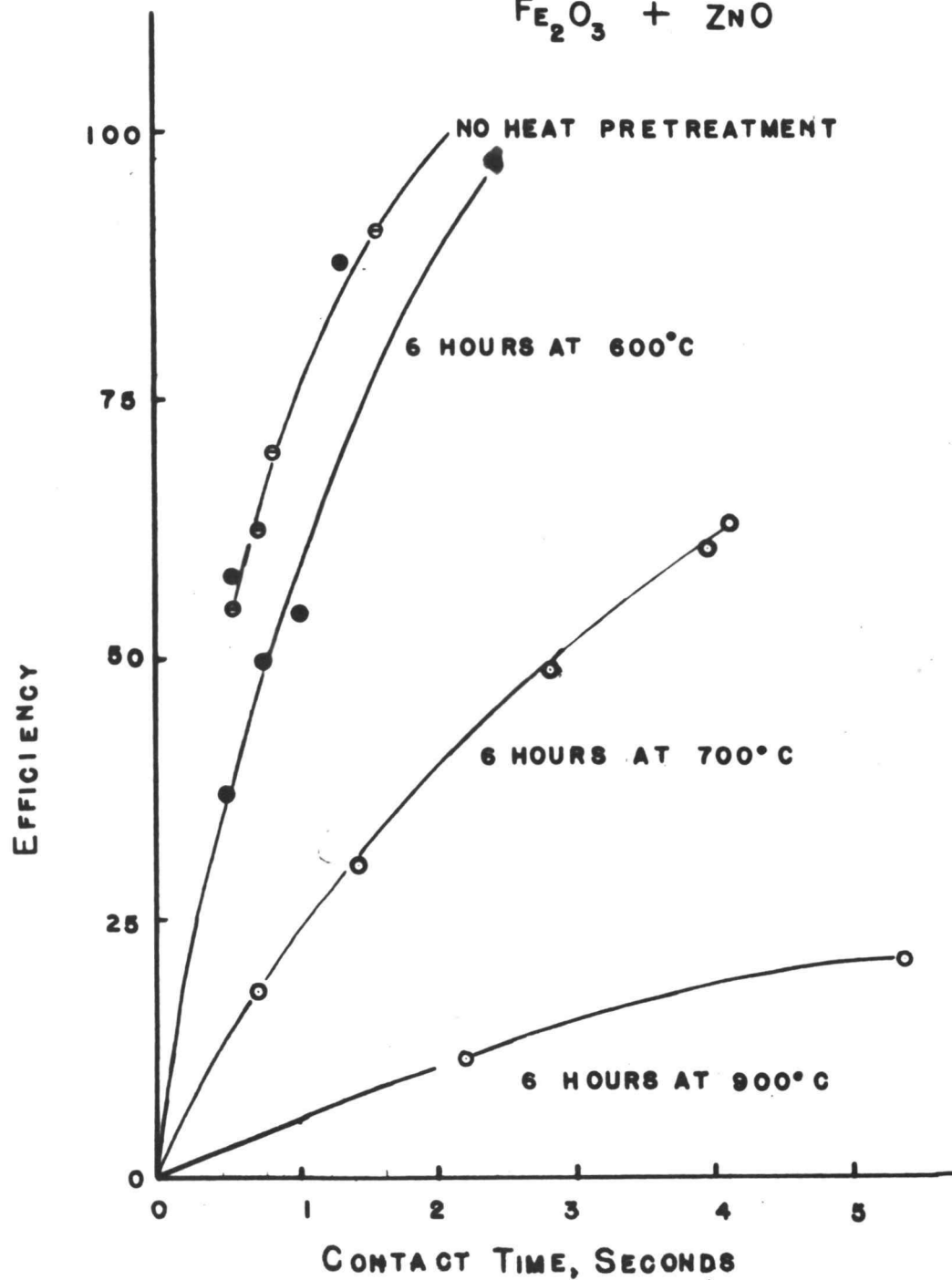


Figure 4

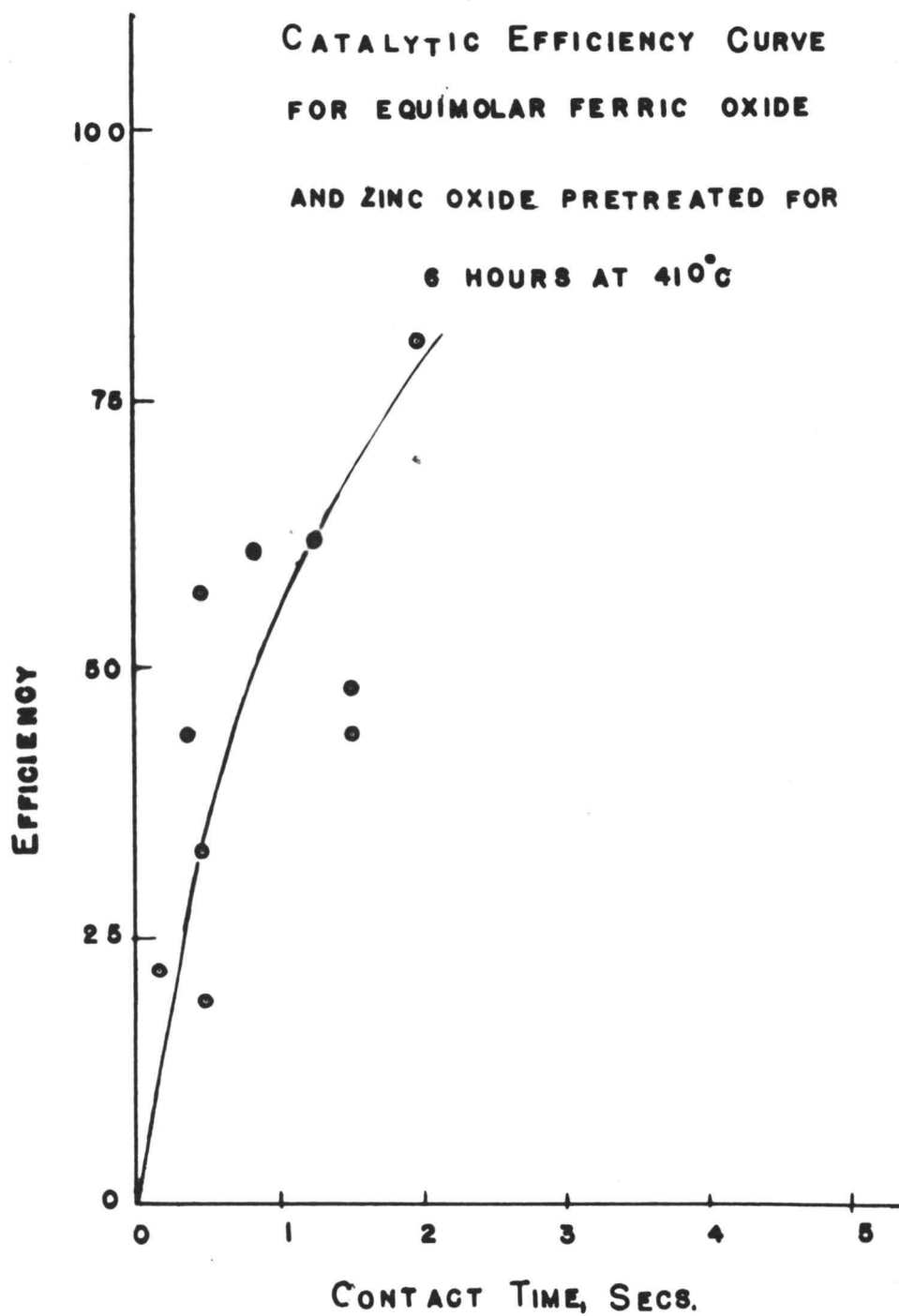


Table 4.

<u>Pretreatment Temperature, °C</u>	<u>Specific Surface, m²/g</u>	<u>$\chi_g \times 10^6$ at -195° C</u>	<u>Efficiency at 1 Second</u>
25	19.5	19.9	71
410	15.0	21.5	64
500	13.1	19.1	63
600	10.5	52.9	57
650	8.6	88.0	45
700	3.3	198	18
900	1.4	-	6
900	1	-	5
Pure alpha ferric oxide	26.8	25.0	98

For series I, II, III and IV the efficiency at 1 second was compared only with the specific surface area since the magnetic susceptibility data had no real meaning. This is presented below:

Table 5.

Catalytic Efficiency for Zinc Oxide-
Ferric Oxide Mixtures for Runs in Series I - IV

<u>Run</u>	<u>Specific Surface, m²/g</u>	<u>Efficiency at 1 Second</u>
6	12.3	60 (est)
7	4.9	29 (est)
8	2.0	7
10	9.9	52
16	2.7	12
19 & 23	20.6	75
20	2.0	12

Figure 5 shows a relationship between the efficiency at 1 second and the surface area. It should be noted that

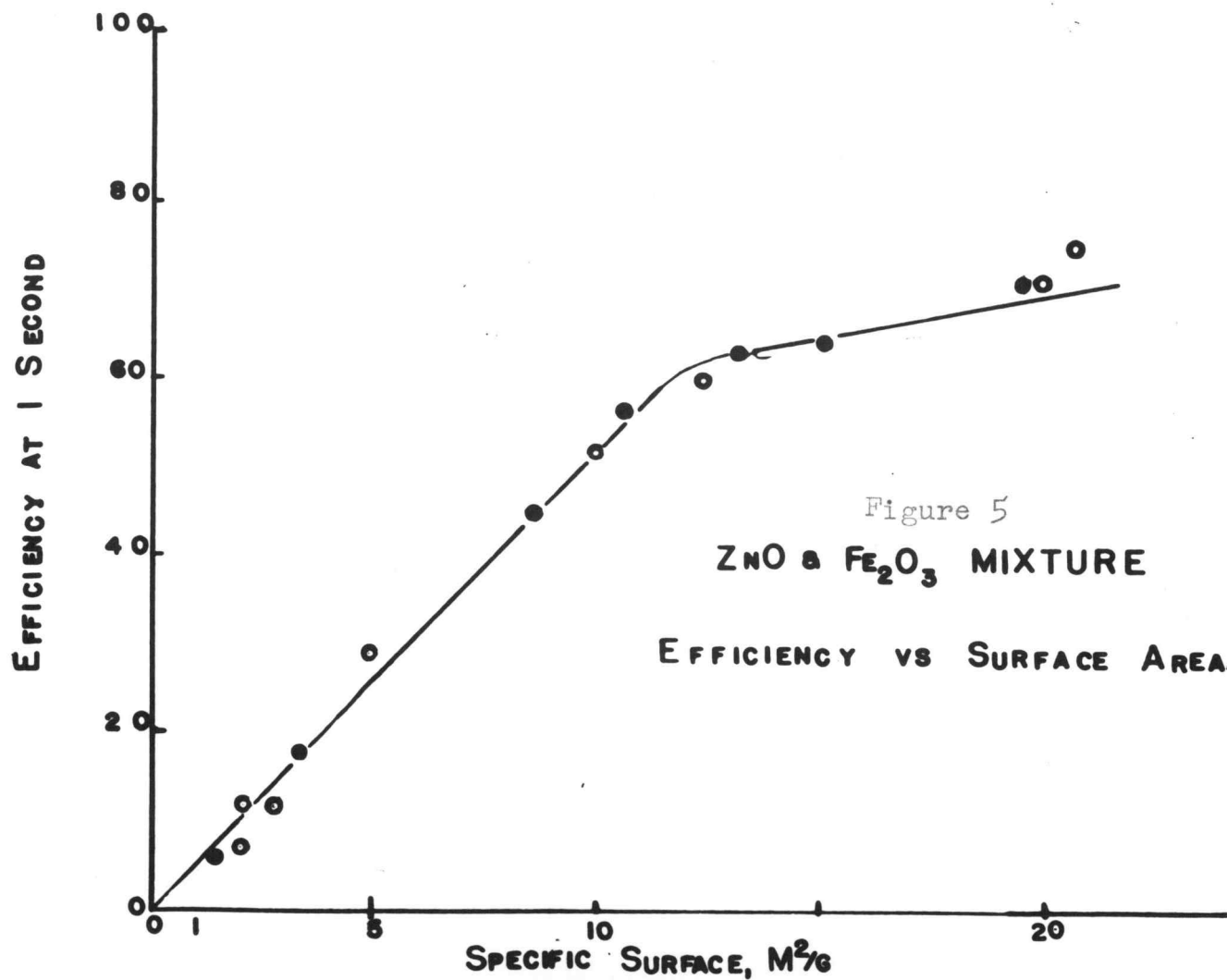


Figure 5
ZnO & Fe₂O₃ MIXTURE
EFFICIENCY VS SURFACE AREA

all the points from the same series fall on the same line. The points which are darkened are those points belonging to series V alone. The circles represent points belonging to the remaining series. It is of interest that the apparent change in magnetic properties of some of the other catalysts did not seem to affect the efficiency versus specific surface plot.

One quickly recognizes that for surfaces greater than about $13 \text{ m}^2/\text{g}$ the efficiency is nearly independent of the surface. Below a specific surface of $13 \text{ m}^2/\text{g}$ the efficiency is linearly dependent on the specific surface. This means that even if the surface is extended beyond $13 \text{ m}^2/\text{g}$ no more than the $13 \text{ m}^2/\text{g}$ is available for catalysis. In order to find what effect the magnetic susceptibility has on the catalytic efficiency, the efficiencies for points below $13 \text{ m}^2/\text{g}$ were corrected to efficiencies which they would have in the region where the efficiency is independent of the specific surface. This was done by multiplying the measured efficiencies for those points having specific surfaces less than $13 \text{ m}^2/\text{g}$ by $13/(\text{measured surface})$. These "corrected efficiencies" were then plotted against the magnetic susceptibilities of the corresponding samples. This resulted in a horizontal line as shown in Figure 6. This indicates that for this particular reaction on these particular catalysts the catalytic efficiency is independent of the magnetic properties of the catalyst.

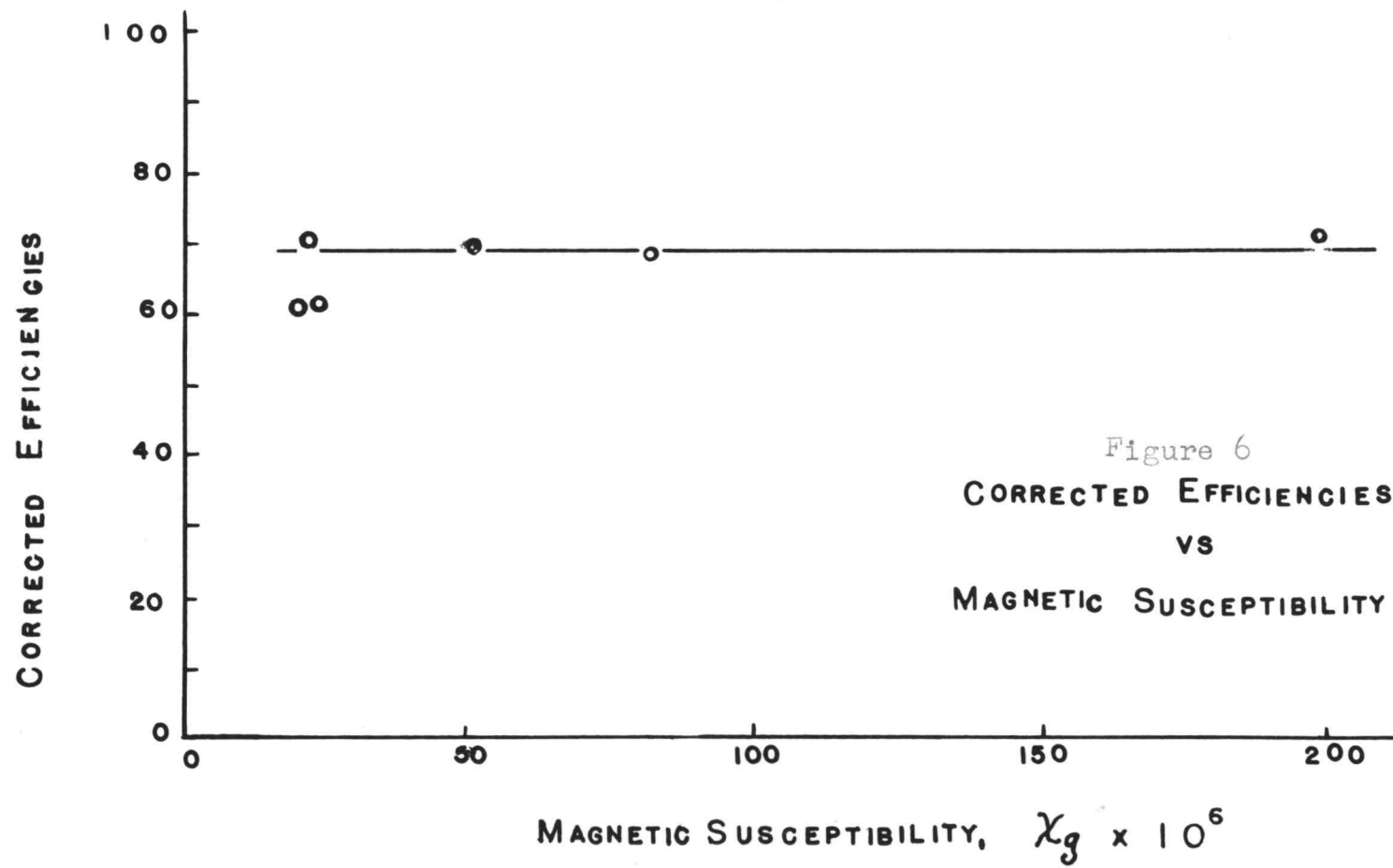


Figure 6
CORRECTED EFFICIENCIES
VS
MAGNETIC SUSCEPTIBILITY

Notwithstanding, the magnetochemical investigations of these oxide mixtures proved to be interesting. Table 6 compares the results of this study with those observed by Bupp and Scott. It also includes the values of the observed magnetic susceptibilities at -195°C .

Table 6.

Magnetic Susceptibilities for Zinc Oxide-
Alpha Ferric Oxide

Sample	Pretreatment Temperature, $^{\circ}\text{C}$	$\chi_g \times 10^{-6}$ at 25°C Bupp and Scott	$\chi_g \times 10^{-6}$ at 25°C Observed	$\chi_g \times 10^{-6}$ at -195°C Observed
Alpha ferric oxide	None	20.4	27.4	26.1
Equal molar mixture	20	13.9	20.2	19.9
	410	-	22.0	21.5
	500	16.7	21.7	19.1
	530	18.7	-	-
	600	-	25.4	52.9
	650	-	28.9	88.0
	670	47.0	-	-
	700	-	36.2	198
	900	-	High	High

It appears that the magnetic susceptibilities as measured at room temperature follow the same general trend as those reported by Bupp and Scott. The susceptibility data taken at -195°C shows that some sort of change in magnetic phase begins for mixtures pretreated for six hours at temperatures below 600°C , in contrast to the

work of Hüttig and Kittel who report a phase change between 600 and 650° C with ferromagnetism not setting in until pretreatment temperatures are in excess of 650° C.

Whether the new magnetic phase is paramagnetic or ferromagnetic cannot be conclusively determined. However a few considerations seem to be in order. The ratio of the magnetic susceptibilities measured at -195° C to that measured at room temperature for the catalyst pretreated at 600° C is about 2. This would be reasonable if a paramagnetic phase following Curie's Law were present to an extent of about 55 percent. For the catalyst which was treated at 650° C the ratio of the susceptibilities is about 3 which would be reasonable if one assumes that all the catalyst was changed to a paramagnetic form obeying Curie's Law. However, for the catalyst treated at 700° C the ratio of the magnetic susceptibilities is far too high to obey Curie's Law. Likewise it is far too high for the usual ferromagnetic behaviour. Thus the catalyst prepared at this pretreatment temperature represents an anomaly which should be more thoroughly investigated.

CONCLUSIONS. The following may be concluded from the experimental work presented here.

1. Alpha ferric oxide is a good catalyst for the conversion of ortho- to parahydrogen at -195° C and atmospheric pressure. The efficiency of the catalyst

seems to be very dependent on its surface area as measured by the BET nitrogen adsorption method. This change in efficiency may be due to a decrease in catalytically active areas on the ferric oxide which would occur on heating, or it may be due to strictly the surface area of the ferric oxide.

2. High area gamma ferric oxide serves as a good catalyst for the conversion of ortho- to parahydrogen at -195°C and atmospheric pressure. Its efficiency per unit surface is greater than 3 percent per square meter per gram. It is interesting to note that the velocity of conversion appears to be greater on the ferromagnetic form of ferric oxide than on the paramagnetic form.

3. The results of the investigation with equimolar mixtures of alpha ferric oxide and zinc oxide as catalysts for the conversion of ortho- to parahydrogen are similar in some respects to those obtained by Bupp and Scott for the decomposition of nitrous oxide over catalysts prepared in a similar manner. They found, as in this case, that increasing thermal treatment of the oxide mixture decreases the efficiency of the catalyst material. With increasing thermal treatment there occurs a decrease in the surface area of the mixture. Figure 4 shows that efficiency is dependent on the surface area for specific surfaces below $13\text{ m}^2/\text{g}$. Above this the catalytic efficiency seems to be independent of the surface. There is no dependence of

catalytic efficiency on the magnetic susceptibility. It must be conceded however that the catalysts are active because they are paramagnetic.

Our efficiency plot is dissimilar to that presented by Bupp and Scott in the respect that they found the catalytic efficiency to be directly dependent on the specific surfaces of the mixtures even at high specific surfaces. However, it appears that for high surface area alpha ferric oxide the efficiency was independent of the surface area.

The fact that at high surfaces the efficiency is independent of the surface area requires more discussion. For convenience let us consider 1 gram of sample in a catalyst bed occupying a volume of 0.5 ml. First let us consider a hydrogen molecule's experience in the catalyst bed for the 1 second that it is there. A simple calculation shows that the molecule has a velocity of 1,000 m/sec at -195° C, the reaction temperature. It is certain then that the molecule must collide with the surface many times during its stay in the catalyst bed.

If we assume that at least one hydrogen molecule is adsorbed wherever a nitrogen molecule was adsorbed in measuring the surface, a simple calculation shows us that there must be at least 2.0×10^{20} molecules adsorbed on the catalyst surface if it has a specific surface of $13 \text{ m}^2/\text{g}$. In our one gram of catalyst there is a dead

space of 0.3 ml as calculated from the true density. In this 0.3 ml there are roughly 2.8×10^{19} molecules. This means that there are roughly more than seven times as many molecules on the surface as there are in the gas phase.

We can also assume that most catalysis occurs when the hydrogen molecules collide with the surface or come very close to the surface since the energy of interaction between the nuclear spins of the hydrogen molecules and the inhomogeneous magnetic field falls off approximately as the cube of the distance.

With these facts in mind, this is what seems to happen. When the specific surface is $13 \text{ m}^2/\text{g}$ or greater, all the molecules get a chance to collide with the surface since only one-seventh or less have to leave the surface in order to give the ones in the gas phase a chance to collide with the surface. This does not necessarily mean that a conversion may be expected with each collision, but collisions happen so frequently that many conversions can be expected. The efficiency will be dependent on how fast adsorbed molecules leave the surface making room for others in the gas phase to land on the surface. Hence, a further increase in surface will not increase the catalytic efficiency.

For specific surfaces of less than $13 \text{ m}^2/\text{g}$, there begin to be relatively more molecules in the gas phase than in the adsorbed layer. In this case the molecules have

less chance of colliding with the surface and being converted than before. This collision frequency becomes less and less as the surface gets smaller accounting for the decreased efficiency at low surfaces.

If one assumes as Hüttig did (13, p. 155) and as followed by Bupp and Scott that the ferrite structure is formed by the diffusion of the ferric oxide lattice to the zinc oxide lattice, then the diffusional rate would increase with increasing temperature accounting for the lowering of the surface. The decrease in catalytic efficiency with increasing pretreatment temperature may be attributed to one of the following effects:

- a. to a decrease in the total extent of the surface area exposed.
- b. to an increase in surface regularity (which is accompanied by a decrease in surface area) which increasing temperature pretreatments would cause.

SUMMARY

The conversion of normal hydrogen over iron oxide and iron oxide-zinc oxide catalysts was studied under the fixed conditions of -195°C and atmospheric pressure so that the extent of the conversion might be used to judge the efficiency of the catalysts.

The mixed oxides were pretreated at various temperatures for six hours, which altered their physical and chemical properties. The catalytic efficiency of the mixtures decreased in a regular manner as the pretreatment temperature increased. The surface also decreased; the magnetic susceptibilities increased. A correlation was found between the catalytic efficiencies and specific surface area. The efficiencies of the catalysts per unit surface were not dependent on the magnetic susceptibilities.

High surface gamma ferric oxide was shown to be a very excellent catalyst for the reaction. High surface alpha ferric oxide also was found to be a good catalyst. However the efficiency of the alpha ferric oxide depended strongly on the measured surface area.

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