THE SURFACE CATALYSIS OF THE ORTHO-PARA CONVERSION IN
LIQUID HYDROGEN BY PARAMAGNETIC OXIDES ON ALUMINA

DISSERTATION

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THE SURFACE CATALYSIS OF THE ORTHO-PARA CONVERSION IN
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INTRODUCTION

Statement of Problem

The purpose of this research was the investigation of factors affecting the surface catalysis of the ortho-para conversion in liquid hydrogen.

Scope of Problem

The ortho-para conversion in hydrogen is of interest for several reasons. The composition of normal hydrogen is 75% ortho and 25% para. When normal hydrogen is liquified its composition is almost equal to that of normal hydrogen; however, on standing it slowly reaches an equilibrium concentration of 99.8% para and 0.2% ortho. The heat of this conversion was calculated by Giauque (1) and found to be 337.17 calories per mole. Simon and Lange (2) found the heat of vaporization of normal hydrogen to be 216.0 calories per mole at 20.3° K. It is apparent that the heat of conversion is a very important factor to be considered in the storage of liquid hydrogen.

The ortho-para conversion in hydrogen is also of interest because this conversion is catalyzed by

-
- (1) W. F. Giauque, J. Am. Chem. Soc., 52, 4808 (1930).
(2) F. Simon and F. Lange, Z. Physik, 15, 312 (1923).

paramagnetic ions or sites. If the factors affecting the rate of the conversion could be established this reaction would be very useful in investigating the paramagnetic character of surfaces.

The investigations in this work were confined to two paramagnetic oxides, Cr_2O_3 and Fe_2O_3 , on two different types of alumina carriers. One series of catalysts was prepared by impregnating an alumina carrier and will be referred to as impregnated catalysts. The other series was prepared by the co-precipitation of $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ from dilute solutions of these cations. These catalysts will be referred to as solid solutions although in a strict sense they may not be true solutions.

Review of Recent Developments

Since the discovery that hydrogen molecules exist in two magnetic forms, para-hydrogen with the spin moments of the nuclei oriented anti-parallel and ortho-hydrogen with the spin moments of the nuclei oriented parallel, there have been numerous studies made of the kinetics of the interconversion between these two forms. A review of developments up to 1935 was given by A. Farkas (3). Most of the early investigations as well as

(3) A. Farkas, "Ortho-hydrogen, Para-hydrogen, and Heavy Hydrogen," Cambridge University Press at Cambridge, 1935, pp. 60 - 101.

most of the more recent studies have been concerned with the gas phase conversion. The gas phase catalysis can be divided into two mechanisms (4).

The so-called high temperature mechanism postulates there is a rearrangement of the atoms making up the hydrogen molecules. This rearrangement can result from the interaction of hydrogen atoms with hydrogen molecules or, as Taylor (5) suggested in the case of heterogeneous catalysis, by chemisorption of hydrogen molecules on a surface. In the latter system the H-H bonds of the chemisorbed hydrogen molecules are weakened, and on desorption bonds are formed between different pairs of hydrogen atoms. In the low temperature heterogeneous catalysis the hydrogen molecules are held on the surface by van der Waals' adsorption. Rummel (6) has pointed out that this is analogous to the homogeneous conversion occurring in liquid and solid hydrogen (7) or to that caused by paramagnetic substances.

The low temperature mechanism for the magnetic mechanism does not require that the atoms of the hydrogen molecules be rearranged, but allows transitions by radiation

(4) A. Farkas, ibid., p. 91.

(5) H. S. Taylor, J. Am. Chem. Soc., 53, 578 (1931).

(6) K. W. Rummel, Z. physik. Chem., A167, 221 (1933).

(7) E. Cremer and M. Polanyi, ibid., B21, 459 (1933).

between odd and even rotational levels. Selection rules forbid this transition unless the molecules of hydrogen are perturbed by a heterogeneous magnetic field such as that found in the vicinity of a paramagnetic substance. The theoretical equation for the transition probability for conversion by collision with paramagnetic substances has been developed by Wigner (8). Harrison and McDowell (9) have modified the Wigner theory and have applied it to the surface catalysis of the ortho-para conversion of hydrogen at low pressures. Recently Chapin (10) has found that the Harrison and McDowell equation applied at pressures as high as 100 atmospheres at liquid nitrogen temperatures.

Until the present time very few investigations have been conducted on the heterogeneous ortho-para conversion in liquid hydrogen. Cremer and Polanyi (7) investigated the liquid and solid homogeneous conversion. They found that the half-life of the liquid conversion was 109 hours and that the reaction was second-order with respect to the concentration of ortho-hydrogen. The catalysis of the ortho-para conversion in liquid hydrogen by charcoal and silica gel was investigated by Swenson (11). By

(8) E. Wigner, Z. physik. Chem., B23, 28 (1933).

(9) L. G. Harrison and C. A. McDowell, Proc. Roy. Soc., A220, 77 (1953).

(10) D. S. Chapin, Ph.D. Dissertation, The Ohio State University, 1954.

(11) C. A. Swenson, J. Chem. Phys., 18, 520 (1950).

following the conversion by the vapor pressure change
Swenson reported that the rate of conversion is first-
order with respect to the concentration of ortho-hydrogen.

EXPERIMENTAL

Apparatus

The experimental apparatus used in this work consisted of a purification and reaction system, a sample storage and analytical system, and an apparatus for measuring surface area.

Purification and reaction system. The hydrogen purification system was designed to remove oxygen, nitrogen, water vapor, and traces of helium and other gases. The system is shown schematically in Fig. 1.

The Cryogenic Laboratory's liquifier was used to produce cylinders of C. P. hydrogen gas. To do this commercial hydrogen was passed through a "Deoxo" purifier, a refrigeration dryer and was then liquified. The liquid was evaporated, compressed, and again dried in the refrigeration dryer before being put into cylinders. This gas was further purified by passing it through the system shown in Figs. 1 and 2 with cryostat baths E, F, and G filled with liquid hydrogen.

Water was removed in liquid nitrogen traps B and D. Oxygen was removed by a platinized asbestos catalyst, C, which was heated to 400° C. The hydrogen was condensed on copper turnings in a copper tube, a, passed through a glass wool filter, b, and was collected in a glass bulb, c. The liquid passed from c through a sintered

- A.-CP hydrogen source
- B and D. Liquid nitrogen traps.
- C. Platinized asbestos at 400°C.
- E. Liquid hydrogen condenser-filter
- F. Liquid hydrogen condenser-still
- G. To reaction cryostat
- I. Thru liquid nitrogen trap to Hg bubbler

FIG. 1. SCHEMATIC DIAGRAM OF HYDROGEN PURIFICATION TRAIN

FIG. 2. SCHEMATIC DIAGRAM OF REACTION CRYOSTAT AND SAMPLING SYSTEM

glass filter, d, and then into cryostat F. Again the gas was condensed on copper turnings, e, and collected in bulb f. A piece of copper tubing 1/4" by 3", g, extending from the bottom of f, served to increase the rate of heat transfer during the distillation stage that followed. Up to this point the purification of the gas from the C. P. hydrogen storage was continuous. When about 200 ml of liquid had been collected in f the flow of gas into this bulb was stopped.

The cryostating liquid in F was pressurized to approximately one-third of an atmosphere. Approximately 10 ml of the liquid in bulb f were boiled off and discarded. Twenty-five ml of liquid hydrogen were distilled into each of the upper chambers, h, Fig. 2.

Fig. 3 shows the dump valve, the upper chamber, and the lower chamber in detail. The reaction cryostat contained four of these assemblies, so that four catalysts could be investigated per run. Three rubber "O" rings were used as packing for the dump valve, Fig. 3, section A. The body for the packing, b, the handle, c, and the upper section of the stem, d, were made of brass. Copper was used in fabricating the upper chamber, h, and valve seat, section B. The needle valve, e, was made of stainless steel. In order to conduct the heat of conversion from the reaction chamber more rapidly, the bottom of the lower

FIG. 3. LIQUID ORTHO-PARA CONVERSION CHAMBER

chamber, section C, i, was made of copper. The upper part of the lower chamber and the sight glass, f, were made of pyrex. The Litton Industries, San Carlos, California, made the copper-glass seal in the lower chamber. All other metal to glass seals were "Kovar" - glass seals made by H. S. Martin and Co., 1916-1920 Greenleaf Street, Evanston, Illinois. All connecting metal tubing, including the valve stems, were made of thin wall Monel.

At time zero the dump valve between the upper and lower chambers, h and i, Fig. 2, was opened. Samples were extracted through a 0.0035 inch O.D., 0.0010 inch wall stainless steel capillary tube, j, by opening a 1/4" Hoke needle valve, k, and placed in one of the 52 sample bulbs. A purge was taken immediately before each sample to remove the stagnant liquid that was held in the tube out of contact with the catalyst. Each sample taken with its preceeding purge removed approximately 0.25 ml of liquid hydrogen or 1% of the initial amount of liquid placed in the reaction chamber. It was estimated that the error in the rate constant, k, resulting from the removal of hydrogen as samples and purges was less than 5%. This was within other experimental errors.

A schematic diagram of the venting system for the hydrogen gas from the cryostat baths and the storage dewar is shown in Fig. 4. Cryostats K or L were pressurized to one-third of an atmosphere gauge, by closing valves C or

A. To Kinney vacuum pump	H. Transfer tube
B. Vent pipe ($1\frac{1}{2}$ ")	I. Liquid H ₂ Dewar
C. Pressurizing valves for K	J. Hg bubbler $\frac{1}{3}$ atm.
D. Pressurizing valves for L	K. Cryostat for liq. H ₂ filter
E. Pressurizing throttle valve	L. Cryostat for distillation
F. Transfer H ₂ 2-5 psig	M. Cryostat for catalyst
G. Transfer - vent valve	N. Rubber connectors

FIG. 4. LIQUID HYDROGEN TRANSFER, VENT AND PRESSURIZING SYSTEM FOR DISTILLATION

D respectively and throttling needle valve E until gas bubbled through the mercury in J. Transfer of liquid hydrogen from the storage dewar was accomplished through a vacuum-jacketed transfer tube, H, by closing valve G. The pressure in the storage dewar, I, was raised to 2-5 p.s.i.g. by passing hydrogen from a storage cylinder into F.

The sampling and analytical system. The sampling system is shown schematically in Fig. 2. The analytical system is shown in Fig. 5. The ortho-para content of the samples was determined by the macrothermal-conductivity method as described by Bonhoeffer and Harteck (12) and modified by Geib and Harteck (13) and Grilly (14). A further modification was made by replacing the micro-ammeter used by Grilly with a Rubicon portable potentiometer to measure the unbalance of the bridge.

Both cells were filled with normal hydrogen at approximately 5 cm pressure. The pressure was adjusted to the same value for each sample by raising or lowering the mercury in the Toepler, D. The correct pressure adjustment was indicated by the closure of the dark section of an electron-ray tube whose grid was connected across

(12) K. F. Bonhoeffer and P. Harteck, Z. physik, Chem., B4, 113 (1929).

(13) K. H. Geib and P. Harteck, Z. physik. Chem., Bodensteinband 849, (1931).

(14) E. R. Grilly, Rev. Sci. Instr., 24, 72-3. (1953).

- A. Normal hydrogen storage
- B. Para hydrogen storage
- C. Sample storage (52 bulbs)
- D. Mercury Toepler for pressure adjustment
- E and H. High vacuum
- F. Macro thermal conductivity cells
- G. Manometer for pressure regulation
- I. Remote control for Toepler
- J. To electron - ray tube
- K. To analytical bridge

FIG. 5. SCHEMATIC DIAGRAM FOR THE ORTHO-PARA - HYDROGEN ANALYTICAL SYSTEM.

two electrical contacts placed in manometer G. The Wheatstone bridge was adjusted to give a potential of less than 0.001 volts across the potentiometer, and this voltage was recorded as V_n . Normal hydrogen was replaced in the right cell by para-hydrogen, and the pressure was adjusted. The voltage across the potentiometer was recorded as V_p . Then the para sample was removed, and an unknown sample was placed in the right cell. Again the pressure was adjusted, and the voltage was recorded as V_s . The fraction converted, x , was calculated from the equation,

$$x = (V_s - V_n) / (V_p - V_n). \quad (1)$$

In practice these voltages were not strictly constant but changed as the height of liquid in the nitrogen bath changed. To correct this effect several determinations of V_n and V_p were made, and the time was recorded. V_n and V_p were plotted against time, and by interpolation the values of these voltages were determined at the time V_s was measured.

The cells were calibrated with known mixtures of ortho- and para-hydrogen. The calibration correction curve is given in Fig. 6. Reproducibility was better than 0.5% of para-hydrogen.

Surface area apparatus. The surface areas of the catalysts were determined by the B. E. T. adsorption

FIG. 6. CALIBRATION CURVE FOR THE MACRO THERMAL CONDUCTIVITY CELLS

method using both hydrogen and nitrogen. The system used is shown schematically in Fig. 7.

Helium was purified by passing it over bright copper, H, at 350° C, through a liquid nitrogen trap, G, and through the activated charcoal tray, F, which was submerged in liquid nitrogen. The purified gas was stored in bulb A. Hydrogen and nitrogen were purified in a like manner except the charcoal trap was not used. These gases were stored in bulb B.

A constant volume manometer, K, a precision manometer, N, and a water-jacketed buret were placed inside a special cabinet. A standard meter bar was hung between the two manometers. The mercury maniscuses and bar references were read to ± 0.02 mm with a Wild cathetometer. Temperature readings taken at T_1 and T_2 were used to correct the meter bar for temperature changes. The reference point of K was a fine tungsten needle which was connected to the grid of an electron-ray tube. The plate of the tube was connected to the mercury in the manometer at a lower point by another tungsten contact. Thus the reference point was indicated by the mercury meniscus making contact with the upper needle causing the shadowed area of the tube to close. The reproducibility of this adjustment was ± 0.02 mm.

The gas buret consisted of five calibrated glass bulbs whose volume ranged from 7 to 150 ml. These bulbs were mounted in a water jacket and their temperature

FIG. 7. SCHEMATIC DIAGRAM OF THE SURFACE AREA APPARATUS.

determined by thermometer T_3 . Thus temperatures T_1 , T_2 , T_3 , and T_4 were used to determine the volume of gas outside the adsorption bulb containing the sample. The value of P_0 , the vapor pressure of the gas used at the temperature of the bath, was determined by manometer N.

The mercury in the constant volume manometer, K, and the buret were adjusted approximately by Hoke stainless steel needle valves. Fine adjustments were made by depressing or expanding the neoprene diaphragms of Hills-McCanna stainless steel valves.

Preparation of Catalysts

Solid solutions. Stock solutions of ferric nitrate, chromic nitrate, and aluminum nitrate containing approximately one mole per liter were prepared using Mallinckrodt Analytical Reagents. The manufacturer's control numbers were XVM-1 for the $\text{Cr}(\text{NO}_3) \cdot 9\text{H}_2\text{O}$, RMX for the $\text{Al}(\text{NO}_3) \cdot 9\text{H}_2\text{O}$, and SMK-1 for the $\text{Fe}(\text{NO}_3) \cdot 9\text{H}_2\text{O}$. The ferric nitrate solution was made 0.1 N acid with nitric acid. These stock solutions were quantitatively analyzed in the following manner:

The iron in the ferric nitrate was estimated by the method described by Olson, Orleman, and Koch (15).

The chromic nitrate was estimated by oxidizing the

(15) A. R. Olson, E. F. Orleman, and C. W. Koch, "Introductory Quantitative Analysis," W. H. Freeman and Co., San Francisco, Calif., 1948, p. 228.

chromium to the plus six oxidation state with sodium peroxide. The excess peroxide was boiled off, and an excess of standard ferrous sulfate solution was added. The excess ferrous sulfate was estimated by the same method used for the estimation of iron (15).

Aluminum in the aluminum nitrate solution was estimated by precipitating the oxime as described by Rieman, Neuss, and Neiman (16).

A measured quantity of the ferric nitrate or chromic nitrate solution was added to 400 ml of aluminum nitrate and diluted to 4 liters. These solutions were constantly stirred while five liters of 0.3 N ammonium hydroxide were added at the rate of sixty to one hundred drops per hour. The precipitates were allowed to settle, decanted, and washed until the ammonium nitrate concentration was less than 0.01 grams. The final separation was made by centrifuging for thirty minutes at 2500 rpm. The precipitates were dried in air first for three days at 90° C, then for one day at 130° C, and finally for two hours at 400° C. An Al₂O₃-blank was prepared in the same manner without the addition of ferric or chromic nitrate.

Impregnated catalysts. A series of catalysts in several concentrations was prepared by impregnating alumina

(16) W. Rieman III, J. D. Neuss, and B. Neiman, "Quantitative Analysis," 3rd Edition. McGraw Hill Book Co., Inc., New York, N. Y., 1951, p. 369.

pellets with solutions of chromium or iron.

The Harshaw Chemical Company of Cleveland, Ohio, prepared on special order 50 pounds of a special Bayer-process low iron alumina carrier in 1/8 inch pellets. The manufacturer furnished the following analysis based on a 750° C ignition temperature: Al_2O_3 - 99.5%, Na_2O_3 - 0.6%, Fe_2O_3 - 0.01%, SiO_2 - 0.05%, and L.O.I. (750° C) 1.39%. These pellets were heated at 600° C for 16 hours to remove slight traces of carbonized material. The carrier thus treated is termed unleached and was used in the preparation of those catalysts which are described as being on unleached carriers. The leached carrier was prepared by treating the ignited pellets with nitric acid as follows:

Five hundred ml of 1 N HNO_3 and 450 grams of unleached carrier were sealed in a one liter bottle and rolled for 16 hours on a slow speed (about 2 rpm) bottle roller. The pellets were washed in a 15 cm Buchner funnel with 20 half-liter portions of double-distilled water. The outlet of the funnel was partially restricted and five gallons of double-distilled water were slowly passed over the pellets. The gross water was removed by suction; then the pellets were heated in an air oven at 110° C for several hours. Again the carrier was ignited for 16 hours at 600° C and stored in ground glass stoppered bottles until ready for use.

Stock solutions of several concentrations of chromic acid were prepared from Baker and Adamson reagent-grade Chromic Acid, lot No. F117. Two hundred ml of stock chromic acid solution and 228.3 g of carrier were sealed in a 500 ml bottle with Apiezon "W" wax and rolled on a slow speed bottle roller for 16 hours. The bottle was carefully opened, the wax removed, and a portion of the liquid removed and analyzed by the method described for the solid solutions. The pellets were filtered on a Buchner funnel and washed with about four liters of double-distilled water.

The gross water was removed by suction, and then the pellets were dried for several hours at 110°C and for 16 hours at 300°C . The bright yellow pellets were reduced by passing hydrogen over them for five hours at 350°C . A light green uniform product was obtained.

In determining the concentration of Cr_2O_3 on the pellets two methods were used. In the case of the higher concentration, a weighed portion of the finely ground catalyst was fused with ten times its weight of sodium peroxide in a nickel crucible. The solution was neutralized carefully with 6 N sulfuric acid and boiled to expel the excess peroxide. The chromium was analyzed as previously described. The chromium content of the low chromium catalysts was determined by carefully saving all the liquid that was washed from the catalyst. This was concentrated

and analyzed for chromium. Knowing the volume and concentration of the initial stock solution and the chromium in the wash water, the chromium adsorbed by the pellets was calculated by difference. The two methods gave checks within one per cent.

The ferric oxide impregnated catalyst (2 Fe) was made from a freshly prepared ferrous nitrate solution. Ferrous nitrate was prepared by mixing stoichiometric amounts of Merck reagent-grade ferrous ammonium sulfate and Mallinckrodt reagent-grade barium nitrate in a separatory funnel with 100 ml of boiled distilled water. The end of the separatory funnel was fastened to a medium sintered glass filtering funnel by means of a rubber stopper. The filtering funnel was fastened to a suction flask and the system evacuated up to the stopcock on the separatory funnel. The stopcock was opened and the liquid filtered into the suction flask. At the end of the filtration dry nitrogen was used in breaking the vacuum, thus keeping the ferrous nitrate from coming in contact with oxygen.

In the meantime the carrier was prepared by passing dry nitrogen over the leached carrier for 16 hours at 300° C in a U-tube. A 500 ml bottle was evacuated and filled with nitrogen and the carrier was poured directly into the bottle from the U-tube with a slow stream of nitrogen still flowing through the U-tube. The ferrous

ammonium nitrate solution was diluted to 200 ml with 100 ml of 1 N HNO_3 and added to the bottle with the carrier. The bottle was closed quickly and rolled slowly for 16 hours. The catalyst was washed and dried in the same manner as the chromium catalyst. Finally the catalyst was placed in a U-tube and heated for five hours at 300°C in a stream of oxygen. A uniformly impregnated substance was obtained.

These precautions were found to be necessary in order to prevent oxidation of the ferrous ions to ferric before they are adsorbed on the carrier. It was found that adsorbed oxygen on the carrier oxidized the ferrous ions forming the brown, colloidal ferric hydroxide. This colloid was adsorbed on the outer surface of the pellets leaving the centers unimpregnated.

To analyze this catalyst for iron, a weighed, finely-ground sample was fused with sodium carbonate in a platinum crucible. The fused mass was dissolved in concentrated HCl , and the iron was estimated colorimetrically (17). A portion of this catalyst was ignited for 16 hours at 600°C and is designated as 2 Fe*.

Catalytic Runs

The lower catalytic reaction chambers were removed

(17) W. M. MacNevin, and T. R. Sweet, "Quantitative Analysis," Harper and Brothers, New York, N. Y., 1952, p. 169.

and the catalysts were placed in the chambers. The quantity of catalyst used was such that 25 ml of liquid hydrogen would completely cover the catalyst leaving about one ml of liquid in excess. After carefully soldering the catalytic chambers in place they were tested for leaks and then heated to 200° C for 24 hours with continuous pumping. All chromia catalysts were reduced for three hours at 200° C in a stream of hydrogen and then the heating and pumping repeated for two more hours. All stopcocks at the top of the catalytic apparatus were closed, and the apparatus was placed in the cryostat.

The apparatus was cooled with liquid hydrogen, and 25 ml of purified hydrogen were collected in the upper chamber, Figs. 1, 2, and 3. Approximately one and one-third atmospheres, absolute of helium were placed on the surface of the liquid in the upper chamber to help force the liquid into the lower chamber. At time zero the needle valve between the upper and lower chambers was opened, and twelve samples were taken as scheduled.

THEORETICAL DEVELOPMENT

The following assumptions are made in developing the rate law for the surface catalysis of the ortho-para conversion in liquid hydrogen:

(1) The ortho-para conversion takes place only in the first layer on the surface of the catalyst. This is neglecting the homogeneous conversion which is very small compared to the very fast heterogeneous conversion on these catalysts.

(2) There is a preferential adsorption of ortho-hydrogen by the surface. It is assumed that all liquid hydrogen in the chamber except the first adsorbed layer is the same ortho concentration and that the first adsorbed layer is ortho rich. Sandler (18) has given evidence for preferential adsorption of ortho-hydrogen on the surface of TiO_2 and charcoal at 77.8°C .

(3) The conversion within the first layer is first-order and rate determining.

The chemical equation for the ortho-para conversion on a para-magnetic surface can be written as follows:

where k_1 is the forward reaction rate constant and k_2 is the reverse rate constant. From the above assumptions the

(18) Y. L. Sandler, J. Phys. Chem., 58, 58 (1954).

differential rate equation becomes:

$$-dO_b/dt = O_s k_1 - (1-O_s) k_2, \quad (2)$$

where

O_b = the mole fraction of ortho in the body of the liquid at time t ,

O_s = the mole fraction of ortho on the surface at time t ,

t = time.

By defining the separation coefficient as

$$s = [O_s/(1-O_s)] / [O_b/(1-O_b)], \quad (3)$$

and letting $-dO_b/dt$ in equation (2) approach zero at infinite time, O_s and k_2 may be expressed as follows:

$$O_s = s O_b / [1 + O_b(s-1)], \quad (4)$$

and

$$k_2 = k_1 O_s^\infty / (1-O_2^\infty) = k_1 s O_b^\infty / (1-O_b^\infty), \quad (5)$$

where the superscript, ∞ , denotes the mole fraction of ortho at infinite time.

Substituting equation (4) and (5) into (2) gives

$$\frac{-dO_b}{dt} = \left[\frac{s k_1}{1 + O_b(s-1)} \right] \left[\frac{O_b - (1-O_b) O_b^\infty}{1 - O_b^\infty} \right], \quad (6)$$

which on integration and substitution of limits becomes:

$$[1 + (s-1) O_b^\infty] \frac{\ln O_b^\infty - O_b^0}{O_b^\infty - O_b^0} + (s-1)(O_b^0 - O_b^\infty) = \frac{s k_1 t}{1 - O_b^\infty}. \quad (7)$$

O_b^0 is the mole fraction of ortho in the liquid at time zero.

At 20.3° K O_b^∞ is 0.002 and may be neglected without causing serious error. Substituting

$$x = (O_b^o - O_b) / (O_b^o - O_b^\infty) = \text{mole fraction converted),} \quad (8)$$

where

$$O_b^o = 0.75, \quad (9)$$

and

$$k_1 + k_2 \cong k_1 / (1 - O_b^\infty) \cong k \quad (10)$$

into equation (7) we obtain

$$[\ln 1/(1-x)] + (s-1)(0.75)x = skt. \quad (11)$$

If equation (11) is expressed in the form

$$\frac{\ln 1/(1-x)}{x} + (s-1)(0.75) = skt/x, \quad (12)$$

one may solve for s by plotting $[\ln 1/(1-x)]/x$ vs. t/x . It must be noted that as $t \rightarrow 0$, $[\ln 1/(1-x)]/x \rightarrow 1$ as a limit. Then

$$s = [(SI-1)/0.75] + 1, \quad (13)$$

where the slope, $S = sk$, and the intercept, $I = t/x$ as $t \rightarrow 0$.

Although k could be calculated from equation (13), it is more accurate to use equation (11) and plot $[\ln 1/(1-x)] + (s-1)(0.75)x$ vs. t using the value of s obtained from equation (13).

In order to compare the solid solution catalysts with the impregnated catalysts it is necessary to determine the amount of paramagnetic oxide on the surface. It

might be assumed that all the paramagnetic molecules in the impregnated catalysts are on the surface; however, there is some evidence (see Discussion of Results) that this is not exactly true. To estimate the paramagnetic oxide concentration on the surface of the solid solution catalysts several assumptions must be made.

The unit cell for $\gamma\text{-Al}_2\text{O}_3$ is composed of 32 oxygen atoms in cubic close pack with $a = 7.895 \text{ \AA}$. It is assumed that the surface is composed of a plane of closely packed oxygen atoms. From this model we obtain for the area covered by a molecule of Al_2O_3 the following equation:

$$A = 4(0.866)^3 [a^3/(128\sqrt{2})]^{2/3}. \quad (14)$$

Next it is assumed that replacing some of the aluminum ions with ferric or chromic ions does not change the area per M_2O_3 molecule and that the mole fraction of paramagnetic ions in the bulk of the solid. From these assumptions it follows that the moles of paramagnetic oxide on the surface, M^* , can be calculated from the equation:

$$M^* = \frac{A_s \times W \times M_F}{A \times N_A}, \quad (15)$$

where

A_s = Surface area per gram,

W = Weight of catalyst in cell in grams,

M_F = Mole fraction of paramagnetic oxide in catalyst,

-30-

A = Area per molecule,

N_A = Avogadro's number.

RESULTS

Characteristics of Catalysts

Adsorption of chromic acid. Since Eischens and Selwood (19) had reported that chromia was adsorbed on alumina in small piles, it was decided to make a preliminary study of the adsorption of chromic acid on alumina. The adsorption was studied on both leached and unleached material. Because the pH is dependent upon the initial chromic acid concentration, it was also decided to study the effect of nitric acid on the amount of chromium adsorbed. Table I and Figs. 8 and 9 summarize the results. The addition of acid greatly changes the amount of chromium adsorbed on the unleached carriers but had little effect on the amount adsorbed by the acid leached carriers. Four low chromia catalysts were selected for the ortho-para studies in this work with the hope that the adsorbed chromia would be distributed uniformly. The conversion experiments indicated that this was realized.

Surface area and adsorption isotherms. Hydrogen surface areas were determined for all the solid solutions, the Al_2O_3 -blank, the leached carrier, and 20 Cr. Complete hydrogen isotherms at liquid hydrogen temperature were determined for the leached carrier, 20 Cr, Fe_2O_3 (25), and Cr_2O_3 (25). The results of these determinations are

(19) R. P. Eischens and P. W. Selwood, J. Am. Chem. Soc., 70, 2271 (1948).

Table I

Adsorption of Chromic Acid on Alumina

Catalyst ^a	HNO ₃	Chromium Concentration		
	Concentration Initial	Initial	Final	Apparent Adsorption ^b %
2 Cr		0.996	0.730	1.74
3 Cr		0.4980	0.226	1.78
4 Cr		0.0996	0.0403	0.393
5 Cr	0.1	0.0996	0.0095	0.596
6 Cr		0.1992	0.0670	0.873
7 Cr		0.3984	0.1489	1.633
8 Cr	0.1	0.1992	0.0353	1.080
9 Cr	0.2	0.1992	0.0182	1.190
10 Cr L ^c		0.1992	0.0132	1.223
11 Cr L ^c	0.1	0.1992	0.0107	1.240
12 Cr	0.3	0.1992	0.0279	1.128
13 Cr	0.3	0.1992	0.0214	1.170
14 Cr	0.2	0.1992	0.0165	1.202
15 Cr L		0.00996	0.000803	0.0616
16 Cr L		0.0996	0.00436	0.630
17 Cr L		0.04980	0.00251	0.314
18 Cr L		0.03984	0.00213	0.250
19 Cr L		0.00996	0.00120	0.0583
20 Cr L		0.0996	0.00453	0.629
21 Cr L		0.03984	0.00257	0.248
22 Cr L		0.01992	0.00425	0.104
23 Cr L ^c		0.1992	0.0220	1.122
24 Cr		0.01992	0.0150	0.0325
25 Cr		0.0996	0.0398	0.397

^a The leached carriers are designated by the letter L.

^b Expressed as % by weight as Cr₂O₃.

^c The leached carrier was prepared using 450 ml of 1 N HNO₃ on 500 g of unleached carrier.

FIG. 8. Apparent Adsorption of Chromic Acid on Alumina

FIG. 9. Apparent Adsorption of Chromic Acid on Alumina

given in Tables II and III and in Figs. 10 and 11. A nitrogen isotherm at liquid nitrogen temperature was determined for the Al_2O_3 -blank; the results are given in Table IV and Fig. 12. Table IV also gives the surface area for the unleached carrier. Chapin (20) determined the nitrogen surface area for several leached catalysts and found that in this concentration range the surface area is unaffected by impregnation. He found the average value to be $87.2 \text{ m}^2/\text{g}$. The ratio of the hydrogen to nitrogen surface area was found to be 1.6 to 1 for the impregnated catalysts and 1.4 to 1 for the solid solution catalysts.

Both the hydrogen and nitrogen isotherms for the solid solution type catalysts are Type I. Type I isotherms are described by Brunauer (21) as resulting from monomolecular adsorption in pores whose width is not more than two molecular diameter. The hydrogen isotherm for the leached impregnated catalysts is the Type II isotherm (22) which is characteristic of multimolecular adsorption.

In determining the surface areas the B. E. T. equation, (2

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{P}{P_0}, \quad (16)$$

(20) D. S. Chapin, Dissertation, The Ohio State University, 1954, p. 41.

(21) Stephen Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Physical Adsorption, Princeton University Press, Princeton, New Jersey, 1945, p. 166.

(22) Ibid., p. 155.

(23) Ibid., p. 153.

Table II

Hydrogen Adsorption on Impregnated Catalysts at 20.3° K

<u>Leached Carrier</u>		<u>20 Cr</u>	
P/P _o	Volume Adsorbed per g, cc s.t.p.	P/P _o	Volume Adsorbed per g, cc s.t.p.

1st Determination

0.0247	31.58	0.0563	34.79
0.0413	33.26	0.1016	38.79
0.0553	35.44	0.1419	41.48
0.0712	36.91	0.1913	44.57
0.0804	37.93	0.2270	46.69
0.0886	38.47	0.2525	48.13
0.1002	39.63	0.1391	41.28
0.1845	45.56	0.2627	48.53
0.2601	50.06	0.3734	54.87
0.3507	55.35	0.4994	63.06
0.4060	59.56	0.5801	69.48
0.4498	62.01	0.6280	74.38
0.4604	63.06	0.6580	77.54
0.7845	106.97	0.8148	112.14
0.8873	162.98	0.8826	151.46
0.0678	207.01	0.9200	170.33
0.9848	230.55		
0.9918	243.61		

Surface Area = 138 m²/g

2nd Determination

0.0979	40.62
0.1815	45.89
0.2561	50.23
0.3444	55.37
0.4038	59.21
0.4436	61.86
0.4613	62.96
0.7867	108.24
0.8960	164.89
0.9703	210.89

Surface Area = 142 m²/g

FIG. 10. Hydrogen Adsorption Isotherm on Leached Carrier and Catalyst 20Cr at 20.3°K.

Table III

Hydrogen Adsorption on Solid Solution Catalysts at 20.3° K

P/P ₀	Volume Adsorbed per g, cc s.t.p.	P/P ₀	Volume Adsorbed per g, cc s.t.p.
Fe₂O₃(25)		Cr₂O₃(25)	
0.0719	122.7	0.0399	129.6
0.1093	132.2	0.0561	137.3
0.1349	139.3	0.0660	140.7
0.1599	144.6	0.0750	143.5
0.1747	147.7	0.0799	145.1
0.1836	149.5	0.0835	146.1
0.3776	178.7	0.0857	146.7
0.6780	206.2	0.1333	157.5
0.9360	227.4	0.1685	164.0
Surface area = 482 m ² /g		0.2061	169.7
		0.2306	173.0
		0.2588	176.1
Cr₂O₃(10)		0.4650	194.2
0.0648	147.0	0.6225	211.1
0.1096	160.5	0.7994	228.5
0.1471	168.7	0.9522	236.5
0.1939	176.6	Surface area = 511 m ² /g	
0.2294	181.6		
0.2567	184.8		
Surface area = 559 m ² /g			
		Al₂O₃ Blank	
		0.0548	130.0
		0.0912	141.7
		0.1204	148.8
		0.1543	156.1
		0.1770	160.2
		0.1931	163.0
		Surface area = 518 m ² /g	
Fe₂O₃(10)			
0.0499	127.8		
0.0807	138.7		
0.1043	145.3		
0.1296	151.4		
0.1460	155.3		
0.1571	157.8		
Surface area = 525 m ² /g

FIG. II. Hydrogen Adsorption Isotherm on Solid Solution Catalysts Cr_2O_3 (25) and Fe_2O_3 (25) at 20.3°K

Table IV

Nitrogen Adsorption on Alumina Catalysts at 77.8° K

<u>Unleached Carrier</u>		<u>Al₂O₃ Blank</u>	
P/P ₀	Volume Adsorbed per g, cc s.t.p.	P/P ₀	Volume Adsorbed per g, cc s.t.p.
0.0248	16.67	0.0352	63.87
0.0414	19.81	0.0623	71.06
0.0600	20.98	0.0852	76.43
0.0862	22.47	0.1118	82.33
0.1084	23.50	0.1294	86.16
0.1249	24.35	0.1417	88.72
		0.1773	96.22
Surface area = 99.3 m ² /g		0.3327	123.94
		0.5166	136.89
		0.8575	146.85
		0.9880	176.71
		Surface area = 327 m ² /g

FIG. 12. Nitrogen Adsorption Isotherm on Al_2O_3
Blank at 77.8°K

was used where V is the volume of adsorbed gas at pressure P , P_0 is the saturation pressure, V_m is the volume of gas for a monomolecular layer, and C is a constant. A graphical solution for V_m was made and this was multiplied by the area covered by one cc at s.t.p. of gas assuming mono-layer close packing. The values used for this area were 3.78 square meters for hydrogen and 4.38 m^2 for nitrogen.

Structural character. X-ray diffraction photographs were taken of $\text{Cr}_2\text{O}_3(25)$, $\text{Fe}_2\text{O}_3(25)$, Al_2O_3 -blank, unleached carrier, and 2 Cr. The unleached carrier and the 2 Cr diffraction photographs were identical and indicated that these carriers were principally γ -alumina. The diffraction photographs for the $\text{Cr}_2\text{O}_3(25)$, $\text{Fe}_2\text{O}_3(25)$, and Al_2O_3 -blank were identical and the principle lines were also those of γ -alumina. It was not possible from these photographs to establish that $\text{Cr}_2\text{O}_3(25)$ and $\text{Fe}_2\text{O}_3(25)$ were solid solutions of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ at room temperatures. The percent of ferric-oxide or chromic-oxide in the catalysts used in the present investigations was less than those prepared by Cirilli (24). It is believed that these catalysts also may be considered solid solutions.

(24) V. Cirilli, Gazz. Chim. Ital., 80, 347 (1950).

Conversion Results

The data used in determining the separation coefficients and rate constants are given in Tables VI to XVII in the Appendix. By substituting experimental values of x and t into equation (11) and plotting $[\ln 1/(1-x)] + (s-1)(0.75)x$ vs. t , a straight line was obtained, Figs. 13 to 18. The reaction rate constant, k , was found from the slope of this line and equation (11). The corrected time, t^* , was obtained by adding or subtracting the intercept of this plot from the observed time in order to make $t = 0$ correspond to $x = 0$. The corrected values for time and the observed values of x were substituted into equation (12) and $[\ln 1/(1-x)]/x$ was plotted against t^*/x in Figs. 19 to 21. The separation coefficients were calculated by using equation (13). In determining the rate constants from equation (11) and Figs. 13 to 18, and in making the calculated x vs. t^* plots, Figs. 22 to 27, an average value of $s = 16$ was used for all catalysts.

A summary of all experimental data is given in Table V and Figs. 28 and 29. The hydrogen surface areas are given in column 5 and the nitrogen surface area in column 6. Column 7 gives the total number of moles of the paramagnetic oxide in the reaction chamber. The number of moles of paramagnetic substance on the surface, column 8, was calculated in the case of the solid solutions by equation (15). A plot of moles (column 7) vs. k/μ^2 (Fig. 28) for

FIG. 13. Rate Constants and Time Zero for Leached Carrier and Al_2O_3 Blank

FIG. 14. Rate Constant and Corrected Time Zero on 19 Cr, Run L-V-1.

FIG. 15. Determination of Rate Constants and Corrected Time Zero for Catalysts 25 Cr, Run L-V-4 and 21 Cr, Run L-V-2.

FIG. 16. Determination of Rate Constants and Corrected Time Zero for Catalysts 20Cr, Run L-VI-1, 2 Fe, Run L-VI-2, and 2Fe*, Run L-VII-1.

FIG. 17. Determination of Rate Constants and Corrected Time Zero for Catalysts Fe_2O_3 (25), Run L-III-2 and Fe_2O_3 (10), Run L-III-1.

FIG. 18. Determination of Rate Constants and Corrected Time Zero for Catalysts Cr_2O_3 (25), Run L-II-4 and Cr_2O_3 (10), Run L-III-4

FIG. 19. Determination of Separation Factors on Catalyst 19 Cr, Run L-V-1 and 21 Cr, Run L-V-2.

FIG. 20. Determination of Separation Factors on Catalyst 20 Cr, Run L-VI-1 and 2 Fe, Run L-VI-2.

FIG. 21. Determination of Separation Factors on Catalyst Fe_2O_3 (10), Run L-III-1 and Fe_2O_3 (25), Run L-III-2.

FIG. 22. Ortho-para Conversion on Leached Carrier and Al_2O_3 Blank

FIG. 23. Ortho-para Conversion of Liquid Hydrogen on Catalyst 19 Cr, Run L-V-1

FIG. 24. Ortho - para Conversion of Liquid Hydrogen on Chromia - Alumina Catalyst.

FIG 25. Ortho-para Conversion of Liquid Hydrogen on Chromia-Alumina and Ferric Oxide-Alumina Catalysts.

FIG. 26. Ortho-para Conversion of Liquid Hydrogen on Solid Solutions of Fe₂O₃ and Al₂O₃

FIG. 27. Ortho-para Conversion of Liquid Hydrogen on Solid Solutions of Cr_2O_3 and Al_2O_3

Table V

Summary of Rate Data

1	2	3	4	5	6	7	8	9	10	11
Catalyst	Wt. of Catalyst grams	Wt. % of Para-magnetic substance	Mol % of Para-magnetic substance	H ₂ Surface Area m ² /g	N ₂ Surface Area m ² /g	Moles of Para-magnetic substance M	Moles of Paramagnetic substance on surface M ² x10 ⁵	k Min. ⁻¹	k/M ² x 10 ⁴ Min. ⁻¹	k/M ² M Min. ⁻¹ Mole ⁻¹
Leached carrier	27.88	0.016	0.010	142	87.2 ^d	2.8x10 ⁻⁵	0.32	0.000586	0.167	5.6
19 Cr	27.83	0.0486	0.0326		87.2 ^d	8.91x10 ⁻⁵	4.71 ^c	0.00466	2.70	5.7 ^c
21 Cr	27.88	0.237	0.159		87.2 ^d	43.5x10 ⁻⁵	39.3 ^c	0.0343	22.3	5.7 ^c
25 Cr ^a	28.02	0.286	0.192		99.3 ^b	52.6x10 ⁻⁵		0.0468	31.0	5.9
20 Cr	28.01	0.627	0.420	138	87.2 ^d	115x10 ⁻⁵	111 ^c	0.099	66.0	5.9 ^c
2 Fe	28.02	0.238	0.152		87.2 ^d	41.7x10 ⁻⁵		0.056	16.0	3.84
2 Fe* ^e	27.95	0.238	0.152		87.2 ^d	41.6x10 ⁻⁵		0.0095	2.72	0.65
Fe ₂ O ₃ (25)	10.18		5.22	482		0.531	209	0.105	30.0	1.44
Fe ₂ O ₃ (10)	10.64		2.15	525		0.229	99	0.574	16.4	1.67
Cr ₂ O ₃ (25)	11.22		5.96	511		0.668	279	0.0564	37.3	1.32
Cr ₂ O ₃ (10)	9.32		2.47	559		0.230	105	0.0206	13.6	1.29
Al ₂ O ₃ Blank	13.48			518	327			0.000478		

^a On unleached carrier.^b Determined on the unimpregnated unleached carrier.^c Corrected for diffusion.^d Average of several determinations by Chapin (18).^e Heated for 16 hours at 600° C after impregnation.

FIG. 28. Ortho-para Conversion Rate per Unit Magnetic Moment vs Moles of Paramagnetic Oxide on Impregnated Aluminas.

FIG.29. Ortho-para Conversion Rate per Unit Magnetic Moment vs. Moles Paramagnetic Oxide on Surface of Solid Solution Catalysts:

the three chromia catalysts on leached carrier gives a straight line, but this line does not pass through the origin. For these three catalysts the intercept of this line with the y axis is subtracted from column 7, and the difference is given in column 8. Column 9 gives the experimentally determined first-order rate constants. In column 10, k is divided by the square of the effective magnetic moment for the various ions. The values, $\mu(\text{Cr}^{+3}) = 3.87$ and $\mu(\text{Fe}^{+3}) = 5.92$ Bohr magnetons, used in this work are those of Van Vleck (25). The results given in column 11 were obtained by dividing column 10 by column 8 where values are given in column 8 or by dividing column 10 by column 7 where no values are given in column 8.

(25) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford at the Clarendon Press, 1932, p. 285.

DISCUSSION OF RESULTS

The solid lines in Figs. 21 to 26 were calculated by substituting the experimentally determined rate constants and the average value for the separation coefficient into equation (11). This equation apparently explains the observed conversion satisfactorily. The value for $s = 16$ is very approximate, but an error of ± 5 in s causes less than 5% error in the determination of the first-order rate constant. Sandler (18) suggested that the preferential adsorption of ortho-hydrogen on a surface was due to hindered rotation. By assuming the molecules of hydrogen are restricted to rotation in a plane, he gives for the separation coefficient

$$s = 2/3 \exp(\epsilon_1/2kT), \quad (17)$$

where $\epsilon_1 = 338$ cal./mole, the molar heat of conversion of ortho- to para-hydrogen. This equation was developed for a gas system; however it might be applied to the liquid system by correcting ϵ_1 for the difference between the heats of vaporization of ortho- and para-hydrogen. An equation for calculating the heats of vaporization of ortho-para mixture was given by Woolley, Scott and Brickwedde (26). From their equation it was calculated that

(26) H. Woolley, R. B. Scott, and F. G. Brickwedde, J. of Res. N. B. S., 41, 466 (1948).

the heat of vaporization for ortho-hydrogen is 4.3 cal./mole higher than that for para-hydrogen. Thus for the liquid ortho-para conversion ϵ_1 was taken to be 334 cal./mole. Substituting this value into equation (17) it was found at 20.3° K that $s = 41$. If these assumptions are valid, apparently the first adsorbed layer is not entirely restricted to a plane rotator. The large separation coefficient found from these experiments suggests that alumina could be used at liquid hydrogen temperatures to prepare pure ortho-hydrogen.

Wigner (8) has obtained an expression for the over all collision efficiency of the homogeneous para-hydrogen conversion induced by paramagnetic molecules. Although this expression cannot be applied directly to this work, it does suggest that the rate of conversion is proportional to the square of the magnetic moment of the perturbing molecule. An examination of column 11, Table V will show this is approximately true in the case of the solid solutions.

However, in the case of the impregnated catalyst it must be noted that the 2 Fe catalyst had a much lower rate than was expected (Table V and Fig. 28). A portion of this catalyst was heated for 16 hours at 600° C and the rate again determined. The rate decreased to approximately one-fifth its original value. These experiments suggested that the ferric oxide diffused into the solid carrier. Although the surface area has not been determined

for this catalyst, it is believed that this decrease in rate could not possibly be due to a change in surface area. Measurements on other catalysts have shown that this treatment at most changes the surface area less than 10%. Further evidence for diffusion is offered by the fact that the rate vs. concentration curve for the leached chromia catalysts (Fig. 28) does not pass through the origin. Apparently chromic oxide also diffuses into alumina but not as rapidly as ferric oxide. The rapid diffusion of the ferric oxide is probably due to the very close similarity in the crystal structures of $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$.

The value for k/η^2 per mole (column 11, Table V) for the solid solution was approximately one-fourth that for the impregnated catalysts. This is believed to be due to a difference in diffusion rates to and from the catalytic surfaces.

The impregnated carriers give a Type II adsorption isotherm which is characteristic of surfaces of wide pores (22). Such a surface would be favorable for a rapid rate of exchange between the surface layer and the body of the liquid. Also it must be remembered that these catalysts were prepared by the adsorption of chromic acid from water solution. Most of the adsorption probably took place in the wider pores, thus making practically all of the paramagnetic ions available on a surface where the

surface exchange reaction would be rapid.

In contrast with this the solid solutions give a Type I adsorption isotherm which is characteristic of surfaces composed of pores of less than two molecular diameters in width (21). The exchange rate between the adsorbed layer and the body of the liquid would be much slower, for much of the surface of the adsorbed layer is not in direct contact with the body of the liquid.

In the case of the chromia impregnated catalysts, Fig. 28, the linear dependence of k on the concentration of chromia indicates that the adsorbed chromia is distributed over the surface and not adsorbed in piles. This is not in contradiction with the findings of Selwood (19), for it must be remembered that the catalysts used in the present kinetic studies contained much less chromia than those of Selwood. Had the ortho-para conversion experiments been extended to the higher chromia catalysts evidence of piling might have been observed.

CONCLUSIONS

(1) The ortho-para conversion of liquid hydrogen on the surface of chromia-alumina and ferric oxide-alumina catalysts was approximately zero-order with respect to concentration of ortho-hydrogen below 70% completion and approached first-order above 70% completion.

(2) The experimental results were explained by assuming: (a) that the reaction took place only within the first adsorbed layer, (b) that there is preferential adsorption of ortho-hydrogen on the surface of the catalyst, and (c) that the reaction rate was first-order with respect to the ortho concentration in the first adsorbed layer.

(3) The first-order rate constant increased linearly with the concentration of chromic oxide on the chromic oxide impregnated catalysts.

(4) The first-order rate constant increased linearly with the concentration of paramagnetic oxide in solid solution of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ and as the square of the magnetic moment of the paramagnetic ion.

(5) The observed first-order rates for the impregnated catalyst and the solid solutions were brought into qualitative agreement by considering the differences in their adsorption isotherms.

(6) It was suggested that alumina could be used at liquid hydrogen temperature to prepare pure ortho-hydrogen.

A P P E N D I X

Table VI

The Ortho-Para Conversion of Liquid
Hydrogen by Special Harshaw Carrier

Frac- tion Conver- ted	Time in Min. t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75)x
<hr/>					
Run L-VI-3					
0.053	6.3	83.3	0.055	0.62	0.68
0.102	64	141	0.106	1.15	1.26
0.155	121	198	0.169	1.76	1.93
0.195	180	257	0.216	2.19	2.41
0.243	241	318	0.278	2.74	3.02
0.288	300	377	0.340	3.24	3.58
0.329	360	437	0.399	3.70	4.10
0.426	492	569	0.553	4.79	5.34
0.464	545	622	0.605	5.23	5.84
0.508	604	681	0.707	5.72	6.41
0.542	660	737	0.783	6.10	6.88
Run L-VII-3					
0.029	1	31	0.029	0.32	0.35
0.021	2	32	0.021	0.23	0.25
0.024	6	36	0.024	0.27	0.29
0.076	66	96	0.079	0.86	0.94
0.121	120	150	0.127	1.36	1.49
0.170	181	211	0.186	1.91	2.10
0.221	244	274	0.240	2.49	2.73
0.264	300	330	0.307	2.97	3.28
0.312	360	390	0.373	3.51	3.88

Table VII

The Ortho-Para Conversion of Liquid Hydrogen by Catalyst 19 Cr

Run L-V-1

Fraction Converted x	Time in Minutes t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75)x	$\frac{\ln 1/(1-x)}{x}$	t*/x
0.135	0	20	0.145	1.52	1.67	1.07	148
0.154	5	25	0.167	1.73	1.90	1.08	162
0.209	15	35	0.234	2.35	2.58	1.12	167
0.305	30.5	50.5	0.363	3.43	3.79	1.19	166
0.385	45	65	0.485	4.33	4.82	1.26	168
0.493	60	80	0.668	5.55	6.22	1.35	162
0.615	82	102	0.954	6.92	7.87	1.55	166
0.841	131	151	1.837	9.46	11.30	2.18	180
0.908	145.5	165.5	2.195	10.22	12.42	2.42	182
0.939	160	180	2.800	10.56	13.36	2.98	192
0.979	180	200	3.860	11.01	14.87	3.94	204
0.992	222	242	4.73	11.16	15.89	4.77	244

Table VIII

The Ortho-Para Conversion of Liquid Hydrogen by Catalyst 21 Cr

Run L-V-2

Fraction Converted x	Time in Minutes t	Corrected Time in Minutes t^*	$\ln 1/(1-x)$	$(s-1)(.75)x$ $s=16$	$\ln 1/(1-x)$ $+(s-1)(.75)x$	$\frac{\ln 1/(1-x)}{x}$	t^*/x
0.241	3.0	4.6	0.274	2.71	2.98	1.14	19.1
0.346	7.0	8.6	0.423	3.89	4.31	1.22	24.8
0.504	10.0	11.6	0.701	5.67	6.37	1.39	23.0
0.626	13.0	14.6	0.983	7.04	8.02	1.57	23.3
0.730	16.0	17.6	1.310	8.22	9.53	1.79	24.1
0.831	19.3	20.9	1.778	9.35	11.13	2.14	25.2
0.924	22.0	23.6	2.585	10.40	12.99	2.82	25.6
0.983	25.0	26.6	4.07	11.06	15.13	4.14	27.1

Table IX

The Ortho-Para Conversion of Liquid

Hydrogen by Catalyst 25 Cr

Run L-V-4

Frac- tion Con- verted $\bar{x}$	Time in Min. t	Corrected Time in Minutes t^*	$\ln 1/(1-x)$	$(s-1)(.75)x$ $s=16$	$\ln 1/(1-x)$ $+(s-1)(.75)x$
0.145	0.0	0.8	0.156	1.63	1.79
0.163	2.0	2.8	0.167	1.83	2.00
0.342	4.0	4.8	0.417	3.85	4.27
0.393	6.0	6.8	0.497	4.42	4.92
0.516	8.0	8.8	0.725	5.81	6.53
0.628	10.0	10.8	0.988	7.07	8.06
0.701	13.0	13.8	1.209	7.89	9.10
0.870	15.0	15.8	2.037	9.79	11.83
0.937	17.0	17.8	2.766	10.54	13.31
0.989	20.3	21.1	4.51	11.13	14.64

Table X

The Ortho-Para Conversion of Liquid Hydrogen by Catalyst 20 Cr

Run L-VI-1

Fraction Converted x	Time in Minutes t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75)x	$\frac{\ln 1/(1-x)}{x}$	t*/x
0.112	1.0	1.4	0.118	1.27	1.39	1.05	12.5
0.227	1.5	1.9	0.257	2.55	2.81	1.13	8.4
0.307	2.0	2.4	0.366	3.45	3.82	1.19	7.8
0.382	2.5	2.9	0.479	4.29	4.77	1.25	7.6
0.448	3.0	3.4	0.594	5.05	5.64	1.33	7.6
0.542	4.0	4.4	0.779	6.10	6.88	1.44	8.1
0.661	5.0	5.4	1.081	7.43	8.51	1.64	8.2
0.764	6.0	6.4	1.442	8.59	10.03	1.89	8.4
0.867	7.0	7.4	2.018	9.76	11.78	2.33	8.6
0.939	8.0	8.4	2.795	10.58	13.38	2.98	9.0
0.977	9.0	9.4	3.770	11.00	14.77	3.86	9.7
0.995	10.0	10.4	5.29	11.21	16.50	5.32	10.5

Table XI

The Ortho-Para Conversion of Liquid Hydrogen by Catalyst 2 Fe

Run L-VI-2

Fraction Converted x	Time in Minutes t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75)x	$\frac{\ln 1/(1-x)}{x}$	t*/x
0.116	1.0	0.5	0.123	1.31	1.43	1.06	4.3
0.104	1.5	1.0	0.111	1.25	1.36	1.07	9.6
0.129	2.0	1.5	0.137	1.45	1.59	1.06	11.6
0.161	2.5	2.0	0.175	1.81	1.99	1.09	12.4
0.197	3.0	2.5	0.217	2.22	2.44	1.10	12.7
0.246	4.0	3.5	0.281	2.77	3.05	1.14	14.2
0.328	5.0	4.5	0.398	3.69	4.09	1.21	13.7
0.391	6.0	5.5	0.494	4.40	4.89	1.26	14.1
0.467	7.0	6.5	0.627	5.25	5.88	1.34	13.9
0.537	8.0	7.5	0.767	6.04	6.81	1.43	13.9
0.659	10.0	9.5	1.074	7.41	8.48	1.63	14.6
0.782	12.0	11.5	1.521	8.80	10.32	1.95	14.7
0.911	15.0	14.5	2.415	10.25	12.66	2.65	15.9
0.977	18.0	17.5	3.77	10.99	14.76	3.86	17.9

Table XII

The Ortho-Para Conversion of Liquid

Hydrogen by Catalyst 2 Fe*

(16 hours ignition at 600° C)

Frac- tion Con- verted x	Time in Min. t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75):
0.0303	1	1.8	0.032	0.340	0.372
0.0343	2	2.8	0.035	0.386	0.421
0.0480	3	3.8	0.049	0.539	0.588
0.0598	4	4.8	0.062	0.673	0.735
0.0680	5	5.8	0.070	0.764	0.834
0.0838	6	6.8	0.088	0.943	1.031
0.0960	7	7.8	0.1009	1.080	1.181
0.1086	8	8.8	0.1149	1.222	1.397
0.1208	9	9.8	0.1287	1.360	1.489
0.1344	10	10.8	0.1443	1.513	1.657
0.1555	12	12.8	0.1689	1.750	1.919
0.1830	14	14.8	0.2005	2.058	2.259

Table XIII

The Ortho-Para Conversion of Liquid

Hydrogen by Catalyst Al_2O_3 -Blank

Run L-VII-2

Frac- tion Con- verted x	Time in Min. t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75)x
0.0232	1	51	0.023	0.261	0.284
0.0261	3	53	0.026	0.294	0.320
0.0306	6	56	0.031	0.345	0.376
0.0668	60	110	0.068	0.752	0.820
0.1022	121	171	0.106	1.150	1.256
0.1387	180	230	0.150	1.560	1.710
0.1754	241.5	291.5	0.192	1.974	2.166
0.2094	300	350	0.234	2.36	2.59

Table XIV

The Ortho-Para Conversion of Liquid Hydrogen by Catalyst Fe_2O_3 (25)

Run L-III-2

Fraction Converted x	Time in Minutes t	Corrected Time in Minutes t^*	$\ln 1/(1-x)$	$(s-1)(.75)x$ $s=16$	$\ln 1/(1-x)$ $+(s-1)(.75)x$	$\frac{\ln 1/(1-x)}{x}$	t^*/x
0.126	0.0	1.25	0.133	1.42	1.55	1.06	9.92
0.230	0.5	1.75	0.262	2.59	2.85	1.14	7.61
0.309	1.0	2.25	0.370	3.48	3.85	1.20	7.28
0.378	1.5	2.75	0.476	4.25	4.73	1.26	7.28
0.443	2.0	3.25	0.584	4.98	5.56	1.32	7.34
0.560	3.0	4.25	0.820	6.30	7.12	1.46	7.59
0.699	4.0	5.25	1.228	7.86	9.09	1.76	7.51
0.802	5.0	6.25	1.614	9.02	10.63	2.01	7.79
0.897	6.0	7.25	2.265	10.09	12.36	2.53	8.08
0.953	7.0	8.25	3.055	10.46	13.52	3.28	8.87
0.981	8.0	9.25	3.975	11.04	15.02	4.05	9.43

Table XV

The Ortho-Para Conversion of Liquid Hydrogen by Catalyst Fe_2O_3 (10)

Run L-III-1

Fraction Converted x	Time in Minutes t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75)x	$\frac{\ln 1/(1-x)}{x}$	t*/x
0.166	0	2.5	0.181	1.87	2.05	1.09	15.0
0.259	1	3.5	0.300	2.91	3.21	1.16	13.5
0.332	2	4.5	0.403	3.74	4.14	1.21	13.5
0.406	3	5.5	0.519	4.57	5.09	1.28	13.5
0.470	4	6.5	0.634	5.29	5.92	1.35	13.8
0.541	5	7.5	0.781	6.09	6.87	1.44	13.9
0.610	6	8.5	0.941	6.86	7.80	1.54	13.9
0.674	7	9.5	1.121	7.58	8.70	1.66	14.1
0.796	9	11.5	1.589	8.96	10.55	2.00	14.4
0.903	11	13.5	2.330	10.16	12.49	2.28	15.0
0.966	13	15.5	3.365	10.87	14.24	3.48	16.0

Table XVI

The Ortho-Para Conversion of Liquid

Hydrogen by Catalyst Cr_2O_3 (25)

Run L-II-4

Frac- tion Con- verted x	Time in Min. t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75)x
0.137	0.2	2.0	0.145	1.54	1.68
0.198	1.0	2.8	0.222	2.23	2.45
0.287	2.1	3.9	0.338	3.23	3.56
0.363	3.0	4.8	0.451	4.08	4.53
0.422	4.0	5.8	0.547	4.74	5.29
0.473	5.0	6.8	0.639	5.32	5.96
0.529	6.0	7.8	0.736	5.95	6.68
0.598	7.0	8.8	0.907	6.72	7.63
0.669	8.0	9.8	1.101	7.52	8.62
0.734	9.2	11.0	1.324	8.26	9.57
0.790	10.0	11.8	1.559	8.89	10.45

Table XVII

The Ortho-Para Conversion of Liquid

Hydrogen by Catalyst $\text{Cr}_2\text{O}_3(10)$

Run L-III-4

Frac- tion Con- verted x	Time in Min. t	Corrected Time in Minutes t*	$\ln 1/(1-x)$	$(s-1)(.75)x$ s=16	$\ln 1/(1-x)$ + (s-1)(.75)x
0.083	0.0	2.4	0.088	0.94	1.02
0.120	2.0	4.4	0.128	1.36	1.58
0.179	4.3	6.7	0.198	2.01	2.21
0.230	6.3	8.7	0.262	2.58	2.85
0.287	8.5	10.9	0.337	3.23	3.57
0.345	10.8	13.2	0.422	3.88	4.30
0.404	13.0	15.4	0.517	4.55	5.07
0.455	15.0	17.4	0.606	5.12	5.72
0.512	17.0	19.4	0.716	5.77	6.48
0.580	20.0	22.4	0.866	6.53	7.39
0.655	23.0	25.4	1.063	7.37	8.43

AUTOBIOGRAPHY

I, Clarence Marion Cunningham, was born in Delta County, Texas, on July 24, 1920. My secondary school education was received in the public schools of the city of Pampa, Texas, from which I received my high school diploma in 1938. In 1942 I received the degree Bachelor of Science in Chemical Engineering from the Agricultural and Mechanical College of Texas. From 1942 to 1946 I served in the Armed Forces of the United States. I received the degree Master of Science from the University of California in 1948. While at the University of California I held a teaching assistantship. The year 1948-1949 I taught chemistry and physics at the California State Polytechnic College. In 1949 I received a research fellowship at The Ohio State University to work on the degree Doctor of Philosophy. My studies at the University were interrupted in 1952 while I was on a leave of absence for one year to work on an Atomic Energy project at Eniwetok Atoll. In 1953 I returned to The Ohio State University to complete work for the degree Doctor of Philosophy.