of the lead(IV) ion in hydrochloric acid is $PbCl_6^-$, which would make the principal equilibrium in 0.10 *N* hydrochloric acid

$$PbCl^+ + Cl_2 + 2Cl^- \rightleftarrows PbCl_6^-$$

The decrease in $\bar{n}$ to 1.7 in 1.00 *N* hydrochloric acid probably is caused by an increased contribution of equilibria involving higher chloro complexes of lead(II), such as $PbCl_2$ and $PbCl_3^-$.

There is a comparatively small change in the absorption spectrum of lead(IV) between 1.00 and 0.10 *N* hydrochloric acid, and a large change between 0.10 *N* and zero hydrochloric acid. A simple explanation of these facts is that lead(IV) may exist as two forms in equilibrium

$$PbCl_4 + Cl^- \rightleftarrows PbCl_5^-$$

the equilibrium lying almost entirely to the right in 1.00 *N* hydrochloric acid, mainly to the right in 0.10 *N* hydrochloric acid, and mainly to the left in perchloric acid with no hydrochloric acid. More experimental work would be needed to show whether this suggestion is quantitatively reasonable.

The temperature coefficient of the rate of decomposition of lead(IV) in 1.00 *N* hydrochloric acid leads to an activation energy of 23 ± 5 kcal. per mole. This is consistent with a frequency factor of about 10^{13} per second, and a small entropy of activation.

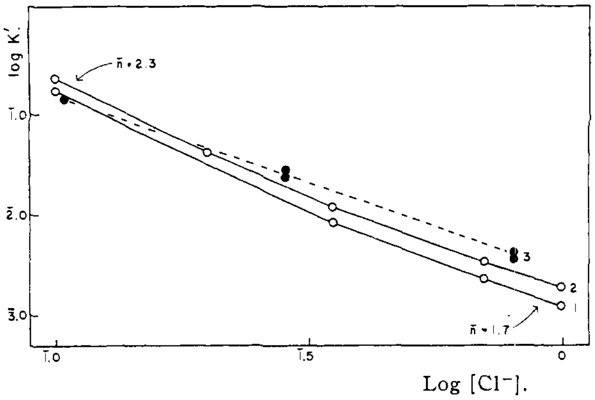

Fig. 4.—Variation of the equilibrium ratio K' with chloride ion concentration: (1) Our data at 19.5° (constant ionic strength = 1.00); (2) Our data at 25.0° (constant ionic strength = 1.00); (3) Calculated from Wescott's data (ionic strength varying, approximately equal to chloride ion concentration): temperature 25.0°. Concentrations in gram ions per liter. Slope = $\bar{n}$ = average number of chloride ions involved in conversion of lead(II) to lead(IV).

VANCOUVER 8, CANADA

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Surface Catalysis of the Ortho- to Para-Conversion in Liquid Hydrogen by Paramagnetic Oxides on Alumina

BY CLARENCE M. CUNNINGHAM[1] AND HERRICK L. JOHNSTON

RECEIVED OCTOBER 8, 1957

The influence of surface concentration and magnetic moments of paramagnetic ions on the rate of ortho- to para-conversion in liquid hydrogen was investigated for several catalysts supported on alumina. It was found that the rate of conversion increased directly with the surface concentration and as the square of the magnetic moment of the paramagnetic ions on the surface of the alumina carriers. It was assumed that (a) the reaction took place only within the first adsorbed layer, (b) there was preferential adsorption of the orthohydrogen within the first adsorbed layer and (c) the reaction was first order with respect to the orthohydrogen concentration in the first adsorbed layer. The experimental rate results were fitted to the equation $(s - 1)(0.75)x + \ln 1/(1 - x) = skt$, where x is the fraction of orthohydrogen converted at time t, s is the separation coefficient and k is the first-order rate constant. The separation coefficient was calculated from the rate equation and was found to be 16 ± 3. This large separation coefficient combined with a very low rate of conversion of ortho- to parahydrogen on pure alumina surfaces suggests that alumina could be used at liquid hydrogen temperature to prepare pure orthohydrogen.

Introduction

Until the present time few investigations have been conducted of the heterogeneous ortho- to para-conversion in liquid hydrogen. Cremer and Polanyi[2] investigated the homogeneous conversion in liquid and solid hydrogen in the absence of a catalyst and found that the conversion was second order with respect to the concentration of orthohydrogen. In both liquid- and solid-phase reactions the rate constant was found to be independent of the temperature. Swenson[3] investigated the heterogeneous ortho- to para-conversion in liquid hydrogen on charcoal and silica gel and reported that the rate was first order with respect to the concentration of orthohydrogen.

The low temperature, or magnetic, mechanism for the ortho–para conversion in the gas phase has been understood for some time. A theoretical equation for the transition probability for conversion by collision with a paramagnetic substance was developed by Wigner.[4] Farkas and Sassche[5] found that both the homogeneous gas-phase conversion catalyzed by oxygen and other paramagnetic gases and the conversion catalyzed by paramagnetic ions in aqueous solution could be explained by the Wigner theory. Harrison and McDowell[6] modified the Wigner theory and applied it to the surface catalysis of the ortho- to para-conversion in hydrogen adsorbed on a paramagnetic surface at low pressures and liquid nitrogen tem-

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(1) Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma.

(2) E. Cremer and M. Polanyi, *Z. physik. Chem.*, **B21**, 459 (1933).

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

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

(5) L. Farkas and H. Sassche, *ibid.*, **B23**, 1, 19 (1933).

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

peratures. Recently Chapin and Johnston[7] found that the Harrison and McDowell equation applies at pressures as high as 100 atmospheres at liquid nitrogen temperatures. These gas-phase investigations suggest that the magnetic mechanism may apply also to the paramagnetic surface catalysis of the ortho- to para- conversion in liquid hydrogen. The present experiments were conducted to determine the influence of the magnetic moment and concentration of paramagnetic ions adsorbed on the surface of alumina on the rate of the conversion in liquid hydrogen.

Experimental

Apparatus.—The rate of conversion was determined by the static method. 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 areas. The hydrogen used was purified by the method described by Chapin and Johnston.[7] After the last distillation the purified hydrogen was condensed in the upper chamber of the reaction apparatus.

The reaction apparatus consisted of an upper and a lower chamber separated by a needle valve. The catalyst was placed in the lower chamber and conditioned for 16 hr. at 200° under high vacuum. The reaction apparatus was submerged in liquid hydrogen, and 25 cc. of purified liquid hydrogen was collected in the upper chamber. At time zero the needle valve was opened and the purified liquid in the upper chamber was forced into the lower chamber with helium at one and one-third atmospheres absolute pressure. Twelve samples were extracted on a time schedule by means of a stainless steel capillary tube extending into the liquid phase of the lower chamber. In order to remove the stagnant liquid from the capillary tube, a purge was taken before each sample. The error in the rate constant resulting from the removal of some of the reacting liquid was calculated to be less than 5%. The samples were placed in glass storage bulbs and analyzed at a later time.

The ortho–parahydrogen content of the samples was determined by the macro-thermal-conductivity method as described by Bonhoeffer and Harteck[8] and modified by Geib and Harteck[9] and Grilly.[10] A further modification was made by replacing the microammeter used by Grilly with a Rubicon portable potentiometer to measure the unbalance of the bridge. The analytical cells were calibrated with known mixtures of ortho- and parahydrogen.

The conventional gas-adsorption apparatus was used to determine adsorption isotherms for the catalysts used in these investigations. Adsorption isotherms were determined up to one atmosphere absolute pressure by adsorbing hydrogen at liquid hydrogen temperature and nitrogen at liquid nitrogen temperature.

Catalysts.—One series of catalysts used in these investigations consisted of solid solutions of ferric oxide or chromic oxide in solid solutions with γ-alumina. The other series consisted of γ-alumina impregnated with chromic oxide or ferric oxide.

1. **Solid Solution Catalysts.**—Stock solutions of ferric nitrate, chromic nitrate and aluminum nitrate were prepared and standardized by standard methods. A measured quantity of the 0.1 *M* ferric nitrate or chromic nitrate solution was added to 400 ml. of 0.1 *M* aluminum nitrate and diluted to four liters. These solutions were constantly stirred while five liters of 0.3 *N* ammonium hydroxide was added at the rate of 60 to 100 drops per minute. The precipitates were allowed to settle, separated from supernatant liquid by decantation and washed until the ammonium nitrate concentration was less than 0.04% by weight. The final separation was made by centrifuging for 30 minutes at 2500 r.p.m. The precipitates were dried in air, first for three days at 90°, then for one day at 130° and finally for 2 hr. at 400°. An alumina blank was prepared in the same manner, without the addition of ferric or chromic nitrate.

X-Ray diffraction photographs indicated that these substances were homogeneous. The principal lines were those of γ-alumina.

2. **Impregnated Catalysts.**—A series of catalysts in several concentrations was prepared by impregnating alumina pellets with solutions of chromium or iron. The preparation of the alumina catalyst carrier and the chromic oxide impregnated catalysts was described by Chapin and Johnston.[7]

The ferric oxide impregnated catalyst (2Fe) 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-porosity 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 solution from coming in contact with air.

In the meantime the support was prepared by passing dry nitrogen over the leached carrier for 16 hr. at 300°. A 500-ml. bottle was evacuated and filled with nitrogen and the carrier was poured directly into the bottle from a U-tube with a slow stream of nitrogen still flowing through the tube. The ferrous ammonium nitrate solution was diluted to 200 ml. with 100 ml. of 1 *N* nitric acid and added to the bottle with the carrier. The bottle was closed quickly, and the catalyst was rolled, washed and dried in the same manner as the chromium catalyst. Finally the catalyst was placed in a U-tube and heated for 5 hr. at 300° 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 were adsorbed on the carrier. It was found that adsorbed oxygen on the carrier oxidized the ferrous ions forming brown colloidal ferric hydroxide. This colloid was adsorbed on the outer surfaces 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 hydrochloric acid and the iron was estimated colorimetrically.[11]

Development of the Rate Equation

In developing the rate law for the surface catalysis of the ortho- to para-conversion in liquid hydrogen, the following assumptions were made.

(1) The ortho-parahydrogen conversion takes place only in the first adsorbed layer on the surface of the catalyst. The homogeneous conversion in liquid hydrogen is slow and can be neglected.[2]

(2) There is a preferential adsorption of orthohydrogen by the surface. All liquid hydrogen in the chamber except the first adsorbed layer is at the same ortho–parahydrogen concentration.

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

From these assumptions the topochemical equation

$$\mathrm{H_2(ortho)} + \text{(paramagnetic ion)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{H_2(para)} + \text{(paramagnetic ion)} \quad (1)$$

and the differential equation

$$-\mathrm{d}O_b/\mathrm{d}t = O_s k_1 - (1 - O_s)k_2 \quad (2)$$

can be written, wherein k_1 is the forward reaction rate constant, k_2 is the reverse rate constant, O_b is the mole fraction of orthohydrogen in the body of

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[7] D. S. Chapin and H. L. Johnston, THIS JOURNAL, **79**, 2406 (1957).

[8] K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

[9] K. H. Geib and P. Harteck, *ibid.*, Bodensteinband, 849 (1931).

[10] E. R. Grilly, *Rev. Sci. Instr.*, **24**, 72 (1953).

[11] W. M. MacNevin and T. R. Sweet, "Quantitative Analysis," Harper and Brothers, New York, N. Y., 1952, p. 169.

TABLE I

SUMMARY OF RESULTS

1 Catalyst	2 Wt. of catalyst, g.	3 Separation coefficient s	4 H_2 surface area, m.²/g.	5 N_2 surface area, m.²/g.	6 Paramagnetic oxide, moles, $M \times 10^6$	7 Paramagnetic oxide on surface, moles, $M^* \times 10^5$	8 k_1, sec.⁻¹ × 10⁵	9 k_1/μ^2, sec.⁻¹ × 10⁵
Acid leached carrier	27.88	..	142	87.4	2.8	0.32	1.01 ± 0.03	0.029 ± 0.001
19 Cr Al	27.83	14	..	87.6	8.90	4.00	6.73 ± 0.04	0.450 ± .003
21 Cr Al	27.88	22	..	...	43.5	38.6	57 ± 1	3.80 ± .09
25 Cr A	28.02	..	..	99.3[a]	52.7	47.8	72 ± 2	4.8 ± .1
20 Cr Al	28.01	16	138	...	116	111	168 ± 2	11.2 ± .1
2 Fe	28.02	12	..	88.1	41.8	....	85.9 ± 0.9	2.45 ± .03
2 Fe*[b]	27.95	..	..	84.2	41.7	....	14.5 ± 2	0.414 ± .005
Fe_2O_3 (25)	10.18	12	482	...	506 × 10²	209	175 ± 2	4.98 ± .06
Fe_2O_3 (10)	10.64	16	525	...	222 × 10²	98.3	96.2 ± 0.4	2.75 ± .01
Cr_2O_3 (25)	11.22	..	511	...	637 × 10²	280	89.6 ± 0.9	5.99 ± .06
Cr_2O_3 (10)	9.32	..	559	...	221 × 10²	105	33.2 ± 0.2	2.22 ± .02
Al_2O_3 (blank)	13.48	..	518	381	....	....	0.829 ± 0.007	0.0236 ± .0002

[a] Determined on unimpregnated unleached carrier. [b] Heated for 16 hr. at 600° after impregnation.

the liquid at time t and O_s is the mole fraction of orthohydrogen on the surface at time t.

By defining the separation coefficient as

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

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

$$k_2 = k_1 O_s^\infty/(1 - O_s^\infty) = k_1 s O_b^\infty/(1 - O_b^\infty) \qquad (4)$$

where the superscript, ∞, denotes the mole fraction of orthohydrogen at infinite time. Substituting the values for s and k_2 from equations 3 and 4 into equation 2 gives an equation which on integration and substitution of the limits $t = 0$ and t becomes

$$[1 + (s - 1)O_b^\infty] \ln \frac{O_b^\infty - O_b^\circ}{O_b^\infty - O_b} + (s - 1)(O_b^\circ - O_b) = \frac{sk_1t}{1 - O_b^\infty} \qquad (5)$$

where O_b° is the mole fraction of orthohydrogen in the liquid at time zero. It should be noted that as $s \rightarrow 1$ the second term of equation 5 approaches zero giving the expected first-order reaction. As the reaction nears completion the second term becomes small and the reaction becomes first order. At small extent of reaction the first term is insignificant and the reaction approaches zero order. This equation can be made more general by substituting for k_1 the term k/M where $k = k_1$ (0.87) and M is the number of moles of hydrogen in the reaction chamber. (In all of these experiments 0.87 mole of hydrogen was used.)

For the purpose of graphical determination of k_1 and s, equation 5 was simplified by expressing the extent of conversion of orthohydrogen as the fraction converted x, where $x = (O_b^\circ - O_b)/(O_b^\circ - O_b^\infty)$. At the temperature of these experiments, 20.3°K., O_b^∞ is 0.002 and O_b° is 0.75. In practice, experimentally observed times were corrected by extrapolating so as to make O_b equal to 0.75 at zero time. With these substitutions equation 5 becomes

$$[1 + (s - 1)O_b^\infty] \ln 1/(1 - x) + (s - 1)(0.748)x = sk_1t/0.998 \qquad (6)$$

This equation is solved graphically for s (for an example see Fig. 1) and k_1 is calculated by the method of "least squares" using the average value for s and experimentally observed t and x. The error in k_1 shown in Table I is the calculated probable error.

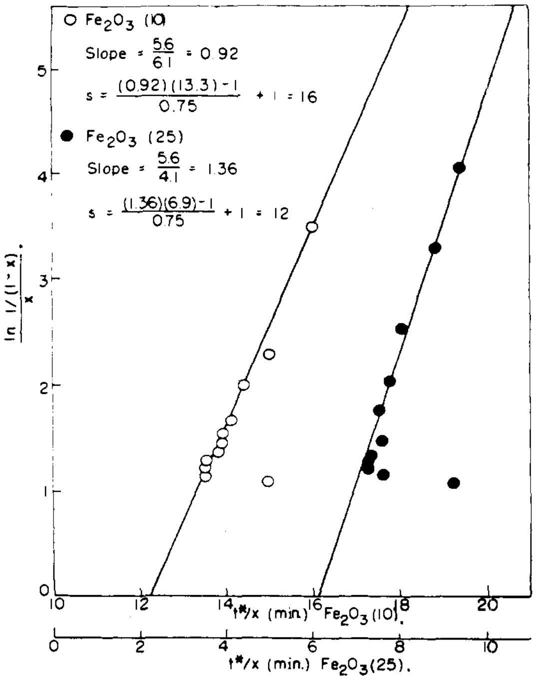

Fig. 1.—Determination of separation coefficients on catalyst Fe_2O_3 (10) and Fe_2O_3 (25).

In order to compare the solid solution catalysts with the impregnated catalysts, the amount of paramagnetic oxide on the surface was determined. It was assumed that practically all the paramagnetic ions in the impregnated catalysts were on the surface. The paramagnetic oxide concentration on the surface of the solid solution catalysts was determined in the following manner.

The area covered by a "molecule" of alumina can be calculated from the size of the unit cell for γ-Al_2O_3, which is composed of 32 oxygen atoms in cubic close pack with a = 7.895 Å. By considering the surface to be composed of a plane of closely packed oxygen atoms, the area covered by a "molecule" of alumina is 20.3×10^{-20} m.²/molecule.

Next it was 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 on the surface is equal to the mole fraction of paramagnetic ions in the bulk of the solid. From these considerations it follows that the moles of paramagnetic oxide on the surface, M^*, can be calculated from the equation

$$M^* = \frac{A_s W M_F}{A N_A} \qquad (7)$$

where A_s is the surface area per gram, W is the weight of catalyst in the cell in grams, M_F is the mole fraction of paramagnetic oxide in the catalyst, A is the area per "molecule" and N_A is Avogadro's number.

Discussion and Results

A summary of all experimental results is given in Table I and Figs. 2 and 3. The number of moles of paramagnetic substance on the surface, column 7, was calculated in the case of the solid solutions by equation 7. A plot of M (column 6) *vs.* k_1/μ^2 (Fig. 3) for the three chromia catalysts on leached carrier gives a straight line, but this line does not pass through the origin. This suggests that possibly some of the adsorbed paramagnetic ions have diffused from the surface into the body of the catalyst. For these catalysts the intercept of this line with the y-axis is subtracted from column 6, and the difference is given in column 7. In column 9, k_1 is divided by the square of the effective magnetic moment for the various ions. The values μ (Cr^{+3}) = 3.87 and μ (Fe^{+3}) = 5.92 Bohr magnetons used in this work are those given by Van Vleck.[12]

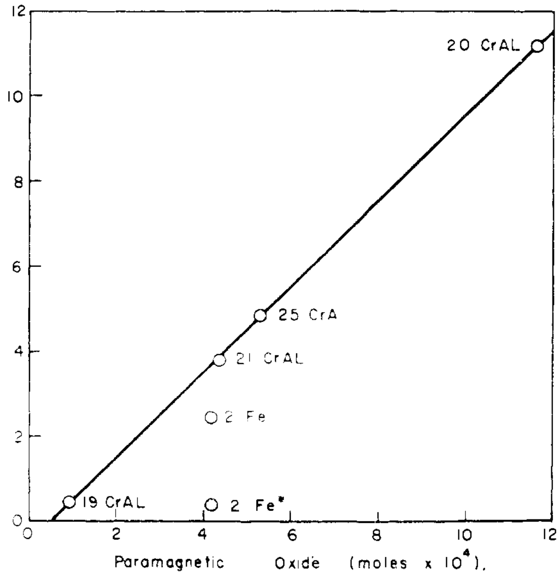

Fig. 2.—Rate of ortho- to para-conversion in liquid hydrogen per unit of magnetic moment as a function of the amount of paramagnetic oxide on alumina pellets.

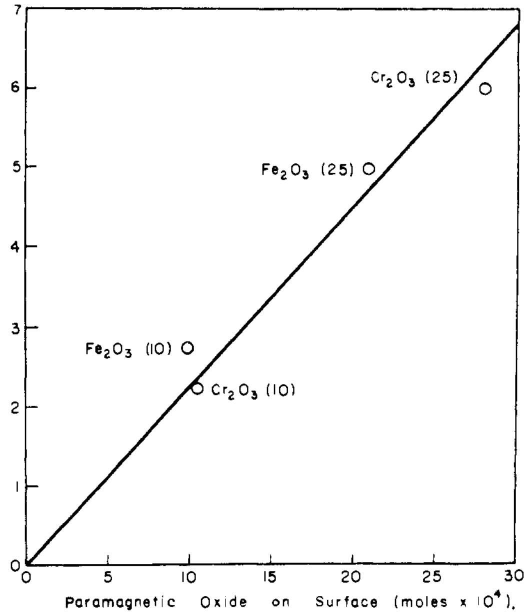

Fig. 3.—Rate of ortho- to para-conversion in liquid hydrogen per unit of magnetic moment as a function of the amount of paramagnetic oxide on the surface of alumina solid solutions.

The rate data fit equation 6 very satisfactorily (see Fig. 4 and column 8, Table I). The solid lines of Fig. 4 were calculated by equation 6.

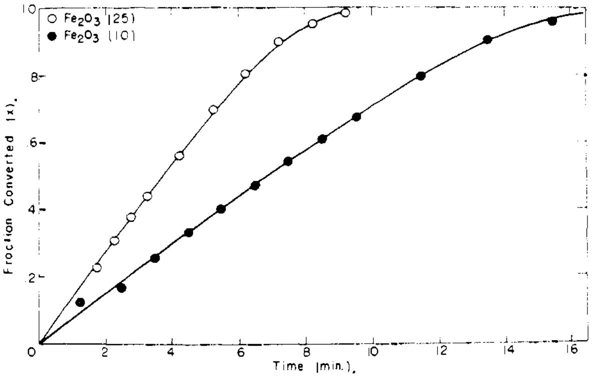

Fig. 4.—Ortho–para conversion of liquid hydrogen on solid solutions of Fe_2O_3 and Al_2O_3.

In the six runs in which the rate data were complete enough to permit calculation of a value for s the average value was found to be 16 ± 3. An error of ± 5 in s causes less than 5% error in the determination of the first-order rate constant.

Sandler[13] suggested that the preferential adsorption of orthohydrogen on a surface is due to hindered rotation. By assuming that the molecules of hydrogen are restricted to rotation in a plane, he gives the separation coefficient

$$s = 2/3e^{\epsilon/2RT} \qquad (8)$$

where ϵ = 338 cal./mole, the molar heat of conversion of ortho- to parahydrogen. Although this equation was developed for the separation by adsorption from the gas phase, it may be applicable to adsorption from the liquid phase provided the

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

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

proper value of ϵ is used. An equation for calculating the heats of vaporization of ortho–para-hydrogen mixtures was given by Wolley, Scott and Brickwedde.[14] From their equation it was calculated that the heat of vaporization for orthohydrogen is 4.3 cal./mole higher than that for parahydrogen. Thus for the liquid ortho- to parahydrogen conversion ϵ is taken to be 334 cal./mole. Substituting this value into equation 8 yields s = 41 at 20.3°K. If this treatment is valid, it would appear that the first adsorbed layer is not entirely restricted to planar rotation.

Wigner[3] has obtained an equation for the over-all collision efficiency of the homogeneous para- to orthohydrogen conversion induced by paramagnetic molecules. Although this equation 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 Table I and Fig. 3 will show that 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 produced a much lower rate than was expected (Table I and Fig. 2). A portion of this catalyst was heated for 16 hr. at 600° and the rate again determined. The rate decreased to approximately one-fifth of its original value. These experiments indicate that the ferric oxide diffused into the solid carrier. The decrease in rate could not possibly have been due to a change in surface area, for this change was less than 5%. As further evidence for diffusion, the rate *vs.* concentration curve for the leached chromia catalysts (Fig. 2) does not pass through the origin. Apparently chromic oxide also diffuses into alumina but not so rapidly as ferric oxide. The rapid diffusion of the ferric oxide is probably due to the fact that γ-Fe_2O_3 and γ-Al_2O_3 have identical crystal structures.

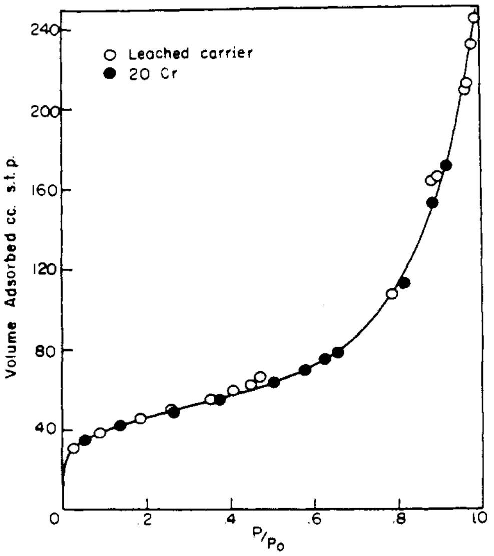

Fig. 5.—Hydrogen adsorption isotherm on leached carrier and catalyst 20 Cr at 20.3°K.

The average value for k_1/μ^2 per mole of paramagnetic oxide on the surface of the catalyst (the slopes of the curves in Figs. 2 and 3) is 10.1 and 2.3, respectively. Equation 7 is used in calculating the number of moles of paramagnetic oxide on the surface of the solid solution catalyst. The surface areas were determined by adsorbing hydrogen on the surface at 20.3°K. If the surface areas obtained with nitrogen at 77.8°K. are used in this calculation, the value for k_1/μ^2 mole of paramagnetic oxide for the solid solutions is approximately one-third that for the impregnated catalyst. In an effort to find an explanation for the lower rate for the solid solution, the hydrogen and nitrogen adsorption isotherms were determined for some of these catalysts (see Figs. 5, 6 and 7).

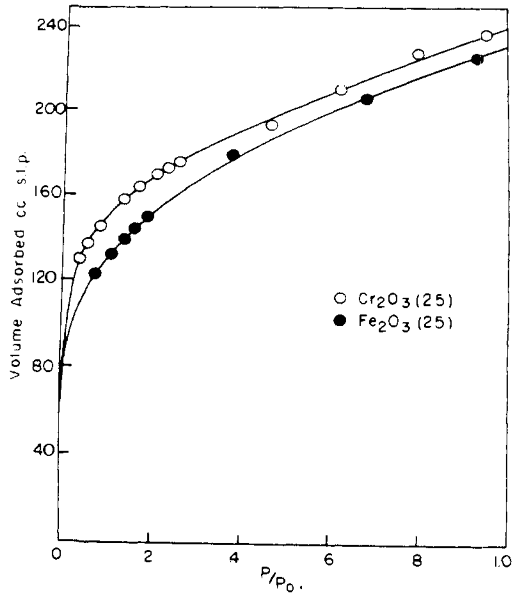

Fig. 6.—Hydrogen adsorption isotherm on solid solution catalysts Cr_2O_3 (25) and Fe_2O_3 (25) at 20.3°K.

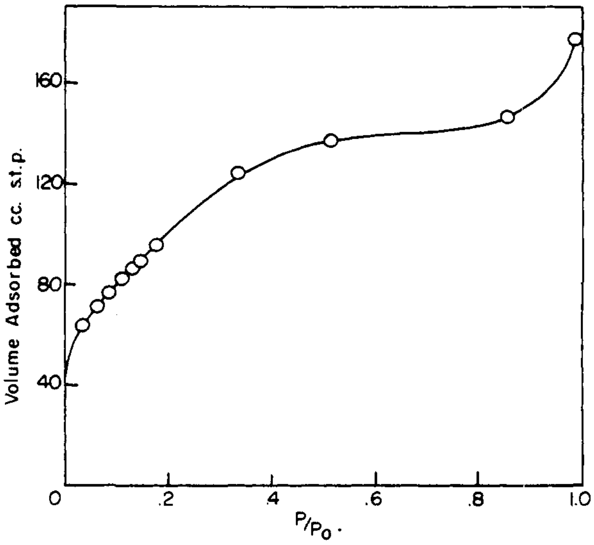

Fig. 7.—Nitrogen adsorption isotherm on Al_2O_3 blank at 77.8°K.

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[14] H. Wolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 466 (1948).

The impregnated carriers gave a Type II adsorption isotherm which is characteristic of surfaces of wide pores.[15] Such a surface would be favorable for a rapid exchange between the surface layer and the body of the liquid. Also it must be noted that these catalysts were prepared by the adsorption of chromic acid from water solution. The large chromate ions would not penetrate the smaller pores. Most of the adsorption probably took place in the wider pores, thus making practically all the paramagnetic ions available on a surface where the exchange reaction would be rapid.

In contrast with this, the solid solutions with hydrogen gave what appears to be a Type I adsorption isotherm, which is characteristic of surfaces composed of pores of less than two molecular diameters in width.[16] The nitrogen isotherm is not quite so definite, especially if the last point ($P/P_0 = 0.988$) is considered. Nevertheless, much of the surface of the solid solution catalysts must be located in pores of small widths. No doubt diffusion in and out of the smallest of these pores becomes a rate-determining factor.

It should also be noted that if the so-called "solid solutions" are not truly solid solutions then the surface concentration of paramagnetic oxide calculated by equation 7 is too large. Clustering of paramagnetic oxide would reduce the number of paramagnetic ions available on the surface.

In the case of the chromia-impregnated catalysts, Fig. 2, the linear dependence of k_1 on the concentration of chromia indicates that the adsorbed chromia is evenly distributed over the surface and not adsorbed in piles. Had the ortho- to parahydrogen conversion experiments been extended to higher-chromia catalysts, evidence of piling, such as found by Eishens and Selwood,[17] might have been obtained.

Columbus, Ohio

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[15] S. Brunauer, "The Adsorption of Gases and Vapors, Physical Adsorption," Vol. I, Princeton University Press, Princeton, 1945, p. 155.

[16] S. Brunauer, ref. 15, p. 166.

[17] R. P. Eischens and P. W. Selwood, This Journal, **70**, 2271 (1948).

[Contribution from the Cryogenic Laboratory and the Department of Chemistry, The Ohio State University]

Separation of Orthohydrogen from Parahydrogen and of Paradeuterium from Orthodeuterium by Preferential Adsorption

By Clarence M. Cunningham,[1] Douglas S. Chapin and Herrick L. Johnston

Received October 8, 1957

A method for the preparation of orthohydrogen and paradeuterium is described. Hydrogen containing more than 99% orthohydrogen was prepared by a three-stage adsorption–desorption of normal hydrogen (75% ortho) on alumina at 20.4°K. and at a pressure of 50 mm. of Hg. By a two-stage adsorption–desorption under the same conditions, deuterium containing 76% paradeuterium was prepared from normal deuterium (33.33% para).

Introduction

The thermodynamic equilibrium composition of ortho–parahydrogen at various temperatures was calculated by Giauque.[2] The composition is 99.814% para at 20°K., 25.141% para at 273.1°K. and 25% para at infinite temperature. Johnston and Long[3] calculated the composition of ortho-paradeuterium in thermodynamic equilibrium to be 97.973% ortho at 20°K. and 66.667% ortho at 220°K. and higher temperatures. Thus it is apparent that the concentrations of orthohydrogen in ortho–parahydrogen or paradeuterium in ortho–paradeuterium cannot be increased above 75% or 33.333%, respectively, by equilibrating at higher temperatures.

At 20.39°K. the vapor pressure of parahydrogen is 786.9 mm. and the vapor pressure of orthohydrogen at this temperature is 745.7 mm.[4] Thus it is theoretically possible to separate the two forms by distillation. In order to produce 99% orthohydrogen by distillation, a column of at least 100 theoretical plates operating between the temperatures of 20.273 and 20.454°K. and at a pressure of 760 mm. would be required.

Waldmann[5] from thermodynamic-statistical considerations calculated the diffusion constants for ortho- and parahydrogen and predicted that some separation of normal hydrogen could be obtained by thermal diffusion. By using this method Schafer and Corte[6] were able to obtain a 4.8% separation between the top and the bottom of a thermal diffusion tube 1 m. long by cooling the walls to 80°K.

From kinetic studies of the ortho- to para- conversion in liquid hydrogen, Sandler[7] found the separation coefficient of orthohydrogen on TiO_2 and charcoal to be 1.6 at 90.2°K. A separation coefficient of 16 ± 3 was determined in this Laboratory for orthohydrogen on alumina at 20.4°K.[8] This large separation coefficient combined with the very low rate of ortho- to parahydrogen conversion on the alumina suggested that alumina could be used at liquid hydrogen temperature to separate orthohydrogen from parahydrogen.

Experimental Apparatus

The first apparatus used for the separation of orthohydrogen or paradeuterium consisted essentially of two concentric copper cylinders. The inside cylinder was filled with 38 g. of $^1/_8''$ pelleted γ-alumina, which was supplied by the Har-

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