

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

(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.

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.

(17) R. P. Eishens and P. W. Selwood, *THIS JOURNAL*, **70**, 2271 (1948).

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

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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 Long³ 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.

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

(2) W. F. Giauque, *THIS JOURNAL*, **52**, 4819 (1930).

(3) H. L. Johnston and E. A. Long, *J. Chem. Phys.*, **2**, 390 (1934).

(4) H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 453 (1948).

Waldmann⁵ 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 Corte⁶ 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, Sandler⁷ found the separation coefficient of orthohydrogen on TiO₂ 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-

(5) L. Waldmann, *Z. Naturforsch.*, **1**, 483 (1946).

(6) K. Schafer and H. Corte, *Naturwissenschaften*, **33**, 92 (1946).

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

(8) C. M. Cunningham and H. L. Johnston, *THIS JOURNAL*, **80**, 2377 (1958).

shaw Chemical Company. This cylinder was then wound with an electric heating tape. The apparatus was immersed in a bath of liquid hydrogen, and normal hydrogen (or normal deuterium) was passed continuously into the center cylinder and out the annular space at a pressure of 50 mm. When the composition of the exit gas was constant, the flow of gas was stopped and the system was evacuated for one-half minute. The alumina was heated rapidly and nine samples of approximately 100 cc. S.T.P. each were collected at one-minute intervals. The ortho-para content was determined by the macro-thermal-conductivity method.⁹ Although direct calibration of this analytical method above 75% orthohydrogen was not feasible, the calibration curve between 0 and 75% orthohydrogen is very nearly a straight line. The extrapolation error was believed to be within one per cent.

The second apparatus consisted of three adsorption units of the type shown in Fig. 1. The inside chamber was filled with 296.6 g. of alumina. The outer chamber could be filled with helium during the adsorption cycle and evacuated during the de-adsorption cycle, so as to increase the rate of deadsorption by reducing the heat leak to the liquid hydrogen bath.

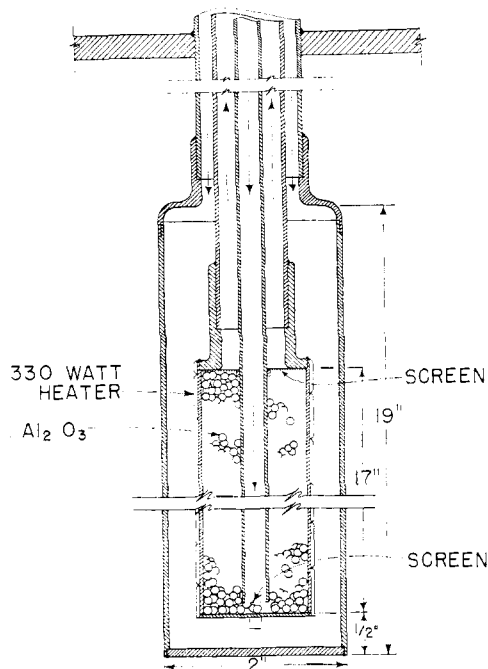


Fig. 1.—Orthohydrogen separator.

Each unit was independently connected to a mercury bubbler where a pressure of 50 mm. was maintained. Initially normal hydrogen (or deuterium) was adsorbed in all three units. When the composition of the exit gas became constant, the first and second units were evacuated for one-half minute. The first unit was then heated and the desorbed gas from this unit was passed through the second unit. After five minutes the second unit was heated and the desorbed gas from the second unit was passed through the third unit which had just been evacuated for one-half minute. At the end of five more minutes, unit three was again evacuated for one-half minute and then heated. The desorbed gas was collected in sample bulbs, each of which was filled for one-half to one minute. In the deuterium separation only two units were used.

Discussion and Results

The results of the initial experiments using the single-stage apparatus are given in Figs. 2 and 3. The results of the three-stage separation of hydrogen are given in Table I and Fig. 4, and the results of the two-stage separation of deuterium are given in Table II and Fig. 5. The decrease in con-

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

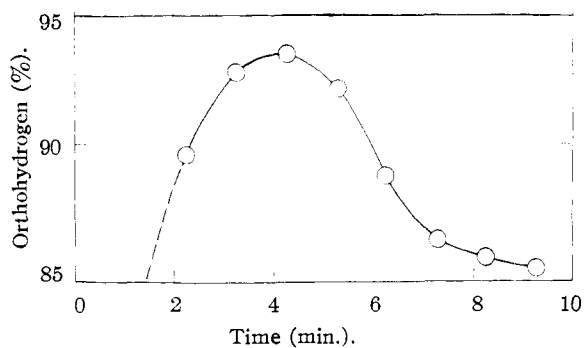


Fig. 2.—Single-stage separation of orthohydrogen on alumina.

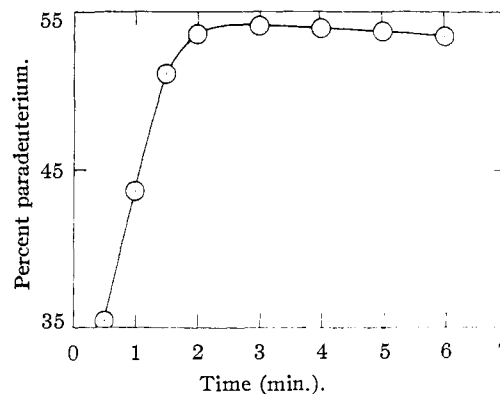


Fig. 3.—Single-stage separation of paradeuterium on alumina.

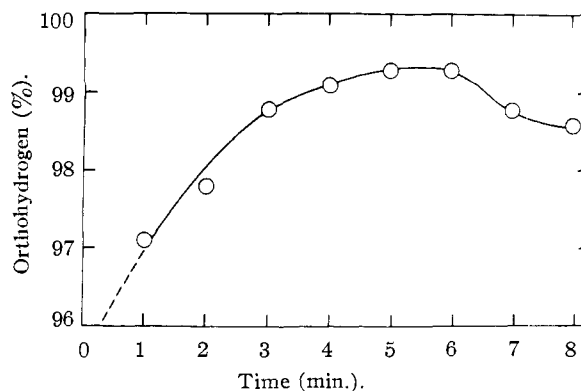


Fig. 4.—Triple-stage separation of orthohydrogen on alumina.

centration of orthohydrogen (or paradeuterium) after about four or five minutes probably was due to the ortho-para conversion taking place on the surface of the alumina.

According to calculation from the adsorption isotherm, the first adsorbed molecular layer forms at about 50 mm. pressure.³ A pressure of 50 mm. was used for these experiments, for it is likely that the separation is greatest in the first molecular layer. Higher pressures would result in considerable multi-layer adsorption which would increase the amount of gas that would have to be removed before the separated first layer could be desorbed. From the B.E.T. equation for the multi-molecular adsorption, it is calculated that the first adsorbed layer contained 1.67×10^{-3} mole of hydrogen per

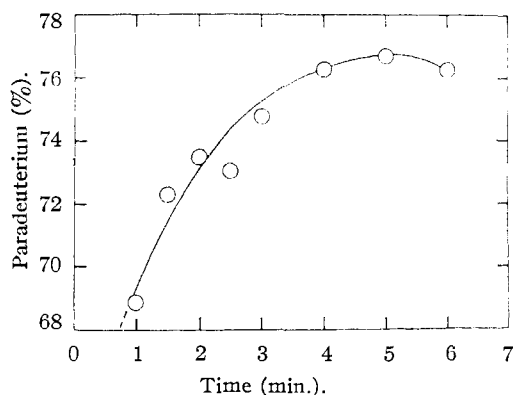


Fig. 5.—Double-stage separation of paradeuterium on alumina.

gram of alumina. The rate constant for the ortho-para conversion was found to be 3×10^{-7} mole per sec. per gram of alumina.⁸ From this rate constant it is calculated that approximately one hour would be required to convert a static monomolecular layer of 100% orthohydrogen to 50% orthohydrogen. This rate of conversion would give a decrease in the orthohydrogen concentration of about 1% per minute; however it must be remembered that these experiments were not conducted under static conditions. Gas was continuously removed, and the gas phase would be richer in parahydrogen than the adsorbed layer. This fact, combined with the fact that the rate of ortho-para conversion is not negligibly small, accounts for the observed rise in ortho concentration until a maximum of approximately 99% is reached and then the decrease as the rate of ortho-para conversion becomes effective.

Heating of alumina to bring about rapid desorption had no influence on the rate of ortho-para

Time, min.	Vol. removed, cc. S.T.P.	Concn. of orthohydrogen, %
1	500	97.1
2	330	97.8
3	300	98.8
4	250	99.1
5	200	99.3
6	150	99.3
7	120	98.8
8	80	98.6

Time, min.	Vol. removed, cc. S.T.P.	Concn. of paradeuterium, %
1	500	68.9
1.5	500	72.3
2	500	73.5
2.5	500	73.1
3	350	74.8
4	350	76.3
5	300	76.7
6	200	76.3

conversion, for it has been found that at these temperatures the rate of conversion is not temperature-dependent.¹⁰ By increasing the number of adsorption-desorption stages paradeuterium or orthohydrogen of very high purity could be prepared by this method.

Acknowledgments.—The authors are grateful to Professor E. N. Lassette for many helpful suggestions.

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

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Rate of Thermal Isomerization of *cis*-Butene-2

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RECEIVED NOVEMBER 9, 1957

The rates of isomerization of gaseous *cis*- and *trans*-butenes-2 were investigated using infrared absorption as the analytical technique. The ratio of the rate constants agrees well with the elsewhere determined value of the equilibrium constant. The first-order rate constants of the *cis*-butene isomerization, which was studied in more detail, show pressure dependence and fit reasonably well to straight lines in plots of $1/k$ against $1/P$. The derived limiting rate constants, k_{∞} , are represented very well by the equation $k_{\infty} = 10^{11} \exp(-52,000/RT)$ sec.⁻¹. The observed frequency factor is close to those reported elsewhere for several other *cis-trans* isomerization reactions. The discrepancy between the presently determined value of the frequency factor for butene-2 and an earlier measurement of it is traced to a concurrent heterogeneous reaction which distorted earlier work.

In 1936 Kistiakowsky and Smith¹ described experiments on the rate of thermal isomerization of *cis*-butene-2, analyzing by the melting point depressions. This work led to the surprising results that the first-order frequency factor A apparently equalled 2 sec.⁻¹ and the energy of activation $E = 18,000$ cal./mole in the Arrhenius equation $k = Ae^{-E/RT}$. Consequently *cis-trans* isomerizations

(1) G. B. Kistiakowsky and W. R. Smith, *THIS JOURNAL*, **58**, 766 (1936).

were divided into three classes, according to whether A and E were high, as expected from collision theory (*ca.* 10^{11} sec.⁻¹ and 45,000 cal., respectively), medium (10^5 and 26,000) or low, the last class being represented only by butene-2. The theoretical implications of this were discussed by Glasstone, Laidler and Eyring,² who offered an explanation for the middle group of isomerizations,

(2) S. Glasstone, K. L. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.