

Para-Ortho-Hydrogen Conversion and Adsorption of Hydrogen on Rhenium Powder

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The rates of *para-ortho*-hydrogen conversion, and the adsorption isotherms of hydrogen were investigated on rhenium powder at pressures of 10–180 mm Hg, and at temperatures of 77°–368°K, and 77°–293°K, respectively. The conversion rate was also measured on platinum powder at room temperature. The rate of conversion on rhenium was proved to be of the order of 10^{14} molecules $\text{cm}^{-2} \text{sec}^{-1}$, at room temperature it was about 70 times lower than that on platinum. At pressures below 70 mm the reaction order gradually increased from zero at 77°K to 0.32 at 368°K. At higher pressures, and at 77°K, the reaction order was close to unity, while at other temperatures a normal decrease of the reaction order with increasing pressure was observed. At 70 mm, and in the range of 77°–195°K, the rate was practically independent of temperature, while above 195°K it increased with temperature. In the range of 293°–368°K the apparent activation energy of 1.7 kcal mole^{-1} was obtained. Two forms of hydrogen adsorption were found. Their binding energies are not sharply defined but decrease considerably with coverage. A rather strongly bound hydrogen with saturation at about 7.0×10^{14} atoms cm^{-2} is partially reversibly chemisorbed at 293°K and 195°K, and probably at still lower temperatures. Weakly bound hydrogen, probably molecular, plays an important part at 77°K; its amount decreases considerably at 90°K and becomes negligible at higher temperatures. It is suggested that at all temperatures the Bonhoeffer-Farkas mechanism of conversion predominates; it consists of the recombination of hydrogen atoms held on the sites of low binding energy. At 77°K and high pressures the molecules adsorbed in the second layer seem to participate in the reaction. The low activity of rhenium as compared with that of platinum at room temperature is ascribed to the low activity for hydrogen chemisorption, and to the high initial adsorption heat of hydrogen, resulting in a low concentration of sites active in the reaction.

INTRODUCTION

The interest in rhenium catalysts has increased recently, in particular, in application to the reactions of hydrocarbons with hydrogen (1–3). Previous investigations have shown that the specific activity of silica- or γ -alumina supported rhenium for hydrogenation of benzene to cyclohexane is lower than that of ruthenium, platinum, palladium, and technetium (1). The low activity of rhenium as compared with that of the Group VIII metals could be ascribed to its low activity for hydrogen chemisorp-

tion which has been observed at room temperature when using metal powders, as well as to the rather high initial heat of hydrogen chemisorption (30.5 kcal mole^{-1}) reported recently by Poulter and Pryde (4).

In connection with the above results it is of interest to study the behaviour of rhenium in simple reactions involving hydrogen and to extend the measurements of hydrogen adsorption on this metal. Simple reactions of hydrogen on rhenium have not been studied so far, and only few data on

the chemisorption of hydrogen by this metal are available (4, 5).

In the present work, the conversion of *para-ortho*-hydrogen and the adsorption isotherms of hydrogen were investigated on rhenium powder at pressures of 10–180 mm, and in the temperature ranges of 77°–368°K and 77°–293°K, respectively. Comparative measurements of the conversion rate were also made at room temperature on platinum powder.

EXPERIMENTAL

The investigations were carried out in conventional vacuum systems with constant volumes of reaction and adsorption spaces which could be pumped to 10^{-6} mm or better.

The apparatus for the *para-ortho* conversion, shown schematically in Fig. 1, was essentially a simplified version of that described by Rossington *et al.* (6). It was adapted for the preparation and storage of pure normal hydrogen (*n*-H₂) and *para*-enriched hydrogen (*p*-H₂). Pure normal hydrogen was obtained by passage of electrolytic grade hydrogen through a heated Pd–Ag alloy thimble. *Para*-enriched hydrogen was prepared by adsorbing pure normal hydrogen at 77°K on charcoal, previously thoroughly outgassed at 450°C.

The equilibrium content of the *para*-modification in enriched hydrogen was assumed as 51%.

The reaction space of about 200 cm³ effective volume consisted of a spherical reaction vessel with either 0.025 g or 0.05 g of rhenium powder, or 0.0025 g of platinum powder, and of a small cold-trap, connected via a pipette, another cold-trap and a burette to hydrogen reservoirs. Additional stopcocks connected the individual parts of the apparatus to the main vacuum line. The ionization gauge checked the vacuum in the reactor. The burette was used for determining the pressure and amount of hydrogen introduced into the reaction space. The pipette served to withdraw the samples of hydrogen from the reactor or from the burette for analysis. The analyses were performed by using a tungsten micro-Pirani gauge similar to that described by Bolland and Melville (7). The gauge and cold-traps were kept in liquid nitrogen. The gauge constituted one branch of a precise Wheatstone bridge, the latter being operated at constant voltage of 12 V. The same voltage was also applied for heating the wire of the gauge in hydrogen, and then under vacuum before each new experimental run. The difference in the resistance of the wire, when surrounded by samples

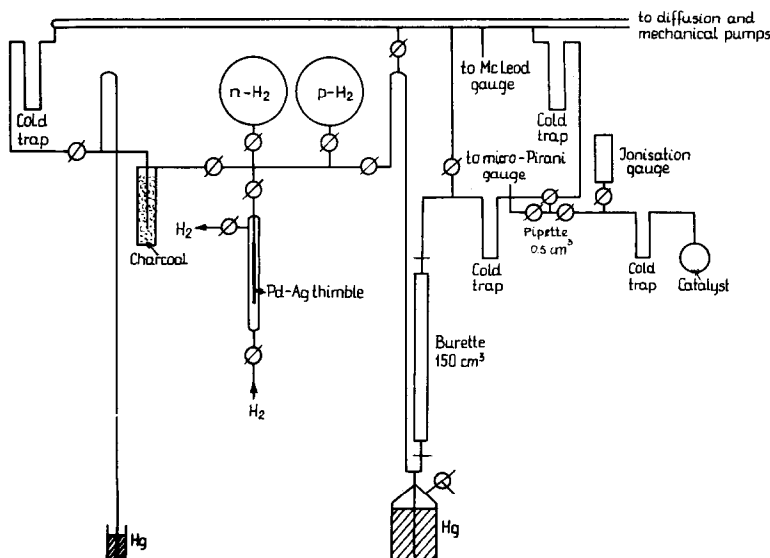


FIG. 1. Diagram of the apparatus for the *para-ortho*-hydrogen conversion.

of 51 to 25% *para*-hydrogen content at the standard pressure of 50 mm, was 2.50 Ω . The resistance was measured with an accuracy of 0.01 Ω . Thus, it was possible to estimate the *para*-hydrogen content to within 0.1%. At 77°K, the change of pure normal hydrogen to the corresponding equilibrium hydrogen was investigated, while at all other temperatures the reverse change was measured.

The adsorption measurements were performed on a rhenium sample weighing 9.75 g in an apparatus similar to that described by Emmett (8). Two liquid nitrogen cold-traps protected the sample against grease and mercury poisoning. The manometer and calibrated burette, the latter acting as a gas reservoir only, were thermostated at 20°C. The effective volume of the adsorption space, determined by using spectroscopically pure helium, was about 60 cm³. Pure normal hydrogen, and nitrogen obtained by thermal decomposition of sodium azide were used.

Temperatures of 77°, 90°, and 195°K were attained by immersing the reaction or adsorption vessel in liquid nitrogen, liquid oxygen, and a carbon dioxide-acetone mixture, respectively. Higher temperatures were obtained by using a thermostated water bath.

The investigations were carried out on rhenium and platinum powders (Johnson & Matthey) alternately treated with hydrogen and evacuated at 400°C. This procedure was repeated several times over a period of 20 hr. The surface areas derived from reversible adsorption of nitrogen at 77°K (1) were found to be 1.44 m² g⁻¹ and 2.00 m² g⁻¹, respectively. Magnetic mass susceptibilities at 77° and 293°K were 0.37×10^{-6} and 0.39×10^{-6} for rhenium, and 1.03×10^{-6} and 0.93×10^{-6} for platinum, both independent of the field strength. Prior to each measurement of the conversion rate at a given pressure, or of the adsorption isotherm, the sample was additionally treated with hydrogen and then evacuated at 400°C for 20 minutes. It was established that this additional heating did not influence the surface area of the sample.

Considering the possibility of slow acti-

vated adsorption, the conversion rate was measured after the sample had been heated in hydrogen at about 200 mm at 150°C for 30 minutes; the hydrogen was then pumped from the reaction vessel at the temperature of the experiment. A similar heating procedure was applied before reading the first adsorption pressure, and was found to be adequate to obtain quite reversible adsorption isotherms in a short time. The adsorbed amounts were not increased within 1.5×10^{-6} moles by cycling the temperature of the powder between the temperature of the measurement and 150°C in the presence of hydrogen. Thus, it could be assumed that all the results obtained corresponded practically to adsorption equilibrium.

RESULTS

Conversion of para-ortho-hydrogen

The time course of the conversion at constant temperature and pressure followed the usual first order law with the experimental rate constant

$$k_e(\text{min}^{-1}) = \frac{1}{t} \ln \frac{C_0}{C_t}$$

where C_0 and C_t denote the concentration of *para(ortho)*-hydrogen in excess of its equilibrium value at time zero and t (6). The values of C_t were calculated assuming a linear decrease of the gauge resistance with the increase of the *para*-hydrogen concentration in the reaction mixture. Figure 2 shows typical plots of $\ln(C_0/C_t)$ against t obtained for rhenium at various pressures at 293°K. The reciprocals of the slopes of these lines give the values of k_e .

The absolute reaction rate was calculated as

$$k_m(\text{molecules cm}^{-2} \text{ sec}^{-1}) = \frac{Nk_e}{60S}$$

where N is the number of hydrogen molecules in the reaction space and S denotes the surface area of the sample in cm². The values of N , k_e , and k_m obtained for rhenium and platinum at 293°K are given in Table 1.

In Fig. 3 the pressure dependence of the

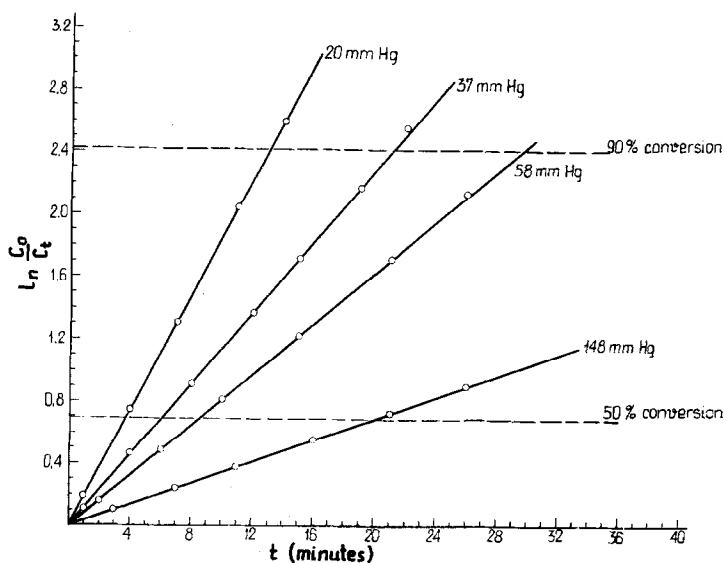


Fig. 2. Kinetic plots for the *para-ortho*-hydrogen conversion on rhenium at 293°K.

rate at various temperatures is presented in terms of $\log k_m$ vs $\log p$. The slopes of these plots give the values of the apparent

reaction order n based on the Freundlich isotherm

$$k_m = \text{const.} \times p^n.$$

In Fig. 4, the temperature dependence of the rate at pressures of 20, 70, and 130 mm is shown, according to the Arrhenius equation

$$k_m = B_m e^{-E/RT},$$

from which the apparent activation ener-

TABLE I
NUMBER OF HYDROGEN MOLECULES IN THE REACTION SPACE N , EXPERIMENTAL RATE CONSTANTS k_e , AND RATES k_m OF THE *para-ortho*-HYDROGEN CONVERSION ON RHENIUM AND PLATINUM AT 293°K

p (mm)	N (molecules)	k_e (min^{-1})	k_m (molecules $\text{cm}^{-2} \text{sec}^{-1}$)
Rhenium powder; $m = 0.025 \text{ g}$, $S = 360 \text{ cm}^2$			
15.0	0.92×10^{20}	23.5×10^{-2}	1.00×10^{15}
20.0	1.25×10^{20}	18.5×10^{-2}	1.08×10^{15}
30.5	1.90×10^{20}	13.5×10^{-2}	1.19×10^{15}
37.0	2.30×10^{20}	11.5×10^{-2}	1.22×10^{15}
39.5	2.51×10^{20}	10.5×10^{-2}	1.25×10^{15}
46.5	2.97×10^{20}	9.55×10^{-2}	1.29×10^{15}
51.0	3.19×10^{20}	8.85×10^{-2}	1.30×10^{15}
54.0	3.41×10^{20}	8.30×10^{-2}	1.31×10^{15}
58.0	3.58×10^{20}	8.15×10^{-2}	1.35×10^{15}
74.0	4.62×10^{20}	6.35×10^{-2}	1.36×10^{15}
79.0	4.95×10^{20}	5.95×10^{-2}	1.37×10^{15}
98.5	6.21×10^{20}	4.95×10^{-2}	1.42×10^{15}
115.0	7.20×10^{20}	4.25×10^{-2}	1.42×10^{15}
129.0	8.07×10^{20}	3.85×10^{-2}	1.43×10^{15}
148.0	9.30×10^{20}	3.45×10^{-2}	1.48×10^{15}
Platinum powder; $m = 0.0025 \text{ g}$, $S = 50 \text{ cm}^2$			
102.0	6.47×10^{20}	43.5×10^{-2}	0.97×10^{17}
166.0	10.5×10^{20}	30.5×10^{-2}	1.08×10^{17}

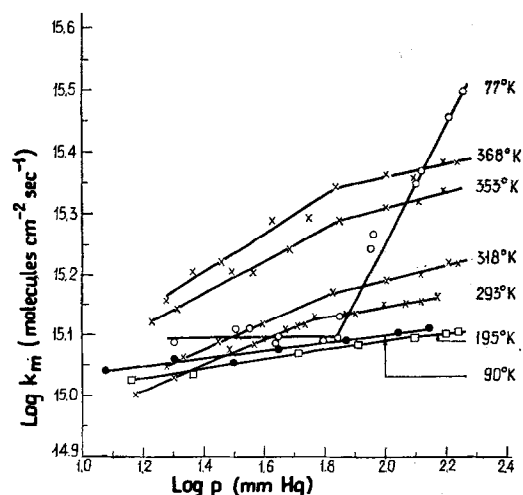


Fig. 3. Pressure dependence as Freundlich isotherms for the *para-ortho*-hydrogen conversion on rhenium.

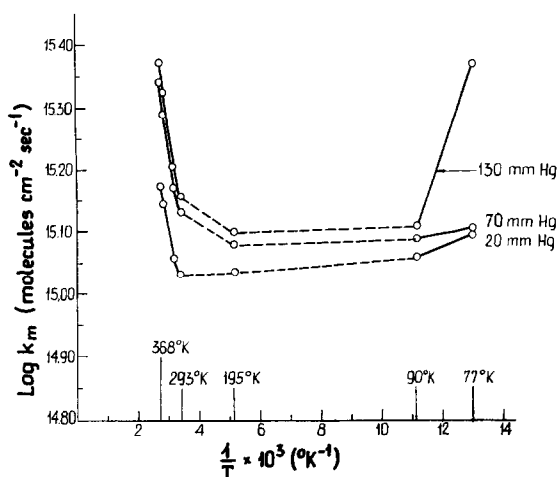


FIG. 4. Arrhenius plots for the *para-ortho*-hydrogen conversion on rhenium at 20, 70, and 130 mm.

gies, *E*, were derived. The values of *k_m* and *E* at 70 mm, and those of *n*, are listed in Table 2. The frequency factors *B_m* corresponding to positive values of *E* are also given in the table.

The data for rhenium powder refer to the 0.025 g sample. It was established that a nearly two-fold increase of the rate constant *k_e* occurred when the weight of the sample was doubled. This indicates that practically the whole catalytic activity was due to the catalyst surface. Indeed, the conversion rate in the reaction space without catalyst was found to be at least 100 times lower than that in the presence of the catalyst, so that it could be neglected. On the other hand, the diffusion-

controlled rate constants calculated according to Wheeler (9) both for catalyst particles and the bulk, were found to be much higher than the experimental ones *k_e*. This means that there was probably no diffusion retardation. In the calculations, particle size of 1.8 μ, bulk density of 16 g cm⁻³ (10), and pore volume of 0.13 cm³ g⁻¹, yielding a mean pore radius of 2000 Å (9), were assumed. A platinum sample of only 0.0025 g was used because larger amounts gave conversion rates too high to be measured.

The conversion rate on rhenium is of the order of magnitude of 10¹⁵ molecules cm⁻² sec⁻¹, at room temperature it is roughly 70 times lower than that on platinum. At pressures below 70 mm, the order of the pressure dependence of the rate gradually increases from zero at 77°K to 0.20 at room temperature, and to 0.32 at 368°K. At 77°K and 70 mm, the zero reaction order is followed by one of unity. At other temperatures, a normal decrease of the reaction order with increasing pressure is observed, characteristic of Langmuir adsorption. Indeed, as shown in Fig. 5, the plots of (1/*k_e*) against *p* according to the Langmuir isotherms

$$\frac{1}{k_e} = \frac{1}{kb} + \frac{1}{k}p$$

where *k* is the rate constant, and *b* the adsorption coefficient, are straight lines at all temperatures above 77°K. At low temperatures, and at 77°K when pressure is less than 70 mm, they pass through or

TABLE 2
RATES *k_m*, ARRHENIUS PARAMETERS *E* AND *B_m* AT 70 mm, AND REACTION ORDERS *n* FOR THE *para-ortho*-HYDROGEN CONVERSION ON RHENIUM AT 77°-368°K

<i>T</i> (°K)	<i>k_m</i> (molecules cm ⁻² sec ⁻¹)	<i>E</i> (kcal mole ⁻¹)	<i>B_m</i> (molecules cm ⁻² sec ⁻¹)	<i>n</i>	
				<70 mm	>70 mm
77	1.27 × 10 ¹⁵	-0.03		0	0.97
90	1.23 × 10 ¹⁵			0.06	0.06
195	1.20 × 10 ¹⁵	-0.01		0.08	0.06
293	1.36 × 10 ¹⁵			0.20	0.09
318	1.48 × 10 ¹⁵	0.15	1.7 × 10 ¹⁵	0.22	0.12
353	1.95 × 10 ¹⁵			0.27	0.12
368	2.20 × 10 ¹⁵			0.32	0.10

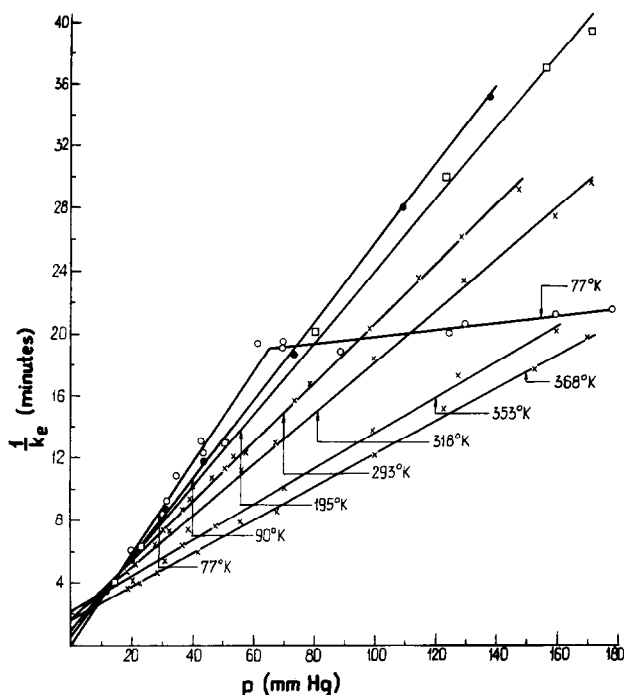


FIG. 5. Pressure dependence as Langmuir isotherms for the *para-ortho*-hydrogen conversion on rhenium.

near the origin, confirming the zero or near-zero reaction order.

The observed activation energies are dependent on pressure and temperature. The rather sharp decrease of the rate between 77° and 90°K at 130 mm corresponds to the onset of the first-order reaction at the temperature of liquid nitrogen. The rate decreases at first slightly with increasing temperature (at 20 mm), or it is practically independent of temperature (above 70 mm). Above 293° or 195°K, a positive temperature coefficient of the rate is observed. At 293°–368°K the apparent activation energy of 1.7 kcal mole⁻¹ was obtained; it is practically independent of the pressure.

Adsorption of Hydrogen

Hydrogen adsorption isotherms are shown in Fig. 6, N_{ads} is the amount of hydrogen adsorbed in molecules cm⁻², and θ_1 or θ_2 expresses the ratio of hydrogen atoms adsorbed to the number of metal surface atoms. In calculating the values of θ_1 or θ_2 , it was assumed that the most closely packed 001, or equal parts of 001

and 110 planes are exposed on the surface with 15.3×10^{14} or 12.5×10^{14} sites per cm² respectively. Curves (1) correspond to the total adsorption. Curves (2) represent its reversible part: This was measured after adsorption (1) by first pumping off hydrogen from the adsorption vessel for 15 min to a pressure below 1×10^{-5} mm. In Fig. 7 the data of curves (1) are re-plotted as Freundlich isotherms, $\log N_{ads}$ vs $\log p$.

It is evident that at each temperature irreversible, as well as pressure-dependent adsorption of hydrogen occurs. At 77°K the hydrogen uptake increases considerably with increasing pressure, while at 90°K the pressure dependence of adsorption decreases at high pressures. At still higher temperatures, the isotherms have a rather saturated character, at 195°K in the whole pressure range, and at 293°K most particularly at high pressures. At sufficiently high pressures, and at temperatures increasing from 77° to 195°K, the amount of hydrogen adsorbed decreases sharply, while only a small decrease in adsorption occurs when the temperature rises from 195° to 293°K. At

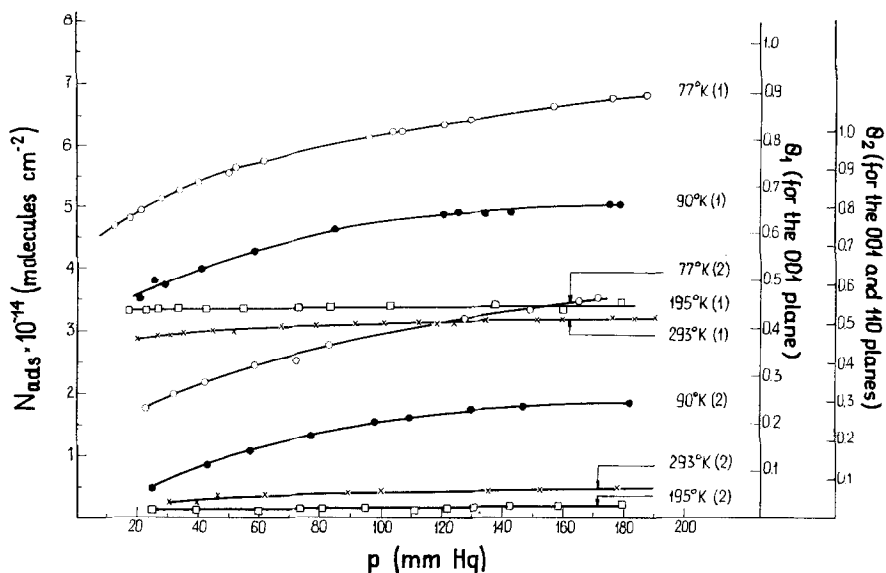


FIG. 6. Adsorption isotherms of hydrogen on rhenium; (1) total adsorption, (2) reversible part of adsorption.

180 mm the surface coverage of 3.4×10^{14} and 3.25×10^{14} molecules cm^{-2} , or 6.8×10^{14} and 6.5×10^{14} atoms cm^{-2} is attained at the latter temperatures, the difference being only 4%.

As indicated by the differences between curves (1) and the corresponding curves (2), the amount of hydrogen irreversibly bound decreases from 6.6×10^{14} atoms cm^{-2} at 77°K to 6.4×10^{14} atoms cm^{-2} at 195°K, and to 5.5×10^{14} atoms cm^{-2} at

293°K. The reversible part of adsorption at the highest pressure used decreases from about 50% at 77°K to 6% at 195°K, and then increases to 15% at 293°K.

The 77° and 90°K isotherms yield a value of 2.2 kcal mole⁻¹ for the isosteric heat of adsorption at a coverage of 9.0×10^{14} atoms cm^{-2} . Higher coverages at 77°K correspond to a large extent to a very weak, probably physical, adsorption in the second layer ($\theta_2 \approx$ or > 1), which does not occur at higher temperatures. If the extrapolation of the logarithmic isotherms is permissible, the isosteric heat of adsorption derived from the 195° and 293°K isotherms at a concentration of 6.5×10^{14} atoms cm^{-2} is approximately 7 kcal mole⁻¹. The logarithmic 77° and 90°K isotherms extrapolated to this coverage give an adsorption heat of about 2.7 kcal mole⁻¹.

The adsorption values obtained at 293°K are about 20% higher than those reported previously (1). This may be due to the improved method of measurement, and in particular to the saturation of the rhenium surface with hydrogen at elevated temperature. The figure of 6.1×10^{14} atoms cm^{-2} for the coverage at 100 mm (at this temperature) is lower than that of 9.1×10^{14} atoms cm^{-2} obtained previously for

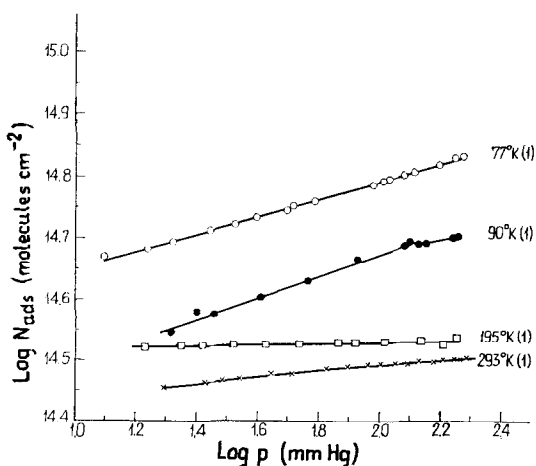


FIG. 7. Freundlich isotherms for the adsorption of hydrogen by rhenium.

platinum powder (1). The difference may in fact be still larger, since the value given previously for platinum may, like that for rhenium, be too low.

DISCUSSION

The mechanism which determines the activity pattern of metal surfaces in the conversion of the *para-ortho*-hydrogen is largely dependent on the nature of the adsorbed layer of hydrogen (11).

From the results presented, it is concluded that two adsorption states of hydrogen occur on rhenium powder. Their binding energies are not strictly defined, but decrease considerably with coverage. The rather strongly bound hydrogen, with saturation at about 7×10^{14} atoms cm^{-2} , is partially reversible at 293° and 195°K, and probably at still lower temperatures. About 80% of this hydrogen (5.5×10^{14} atoms cm^{-2}), which was found to be irreversible at room temperature, must be adsorbed with a heat exceeding ~ 20 kcal mole^{-1} . The adsorption heat of the less tightly bound part of this hydrogen is only ~ 7 kcal mole^{-1} when the coverage of 6.5×10^{14} atoms cm^{-2} is attained. The much more weakly held hydrogen plays an important part at 77°K, but the quantity present decreases considerably at 90°K, and is negligible at higher temperatures. The maximum adsorption energy of this hydrogen does not appreciably exceed the value of 2 kcal mole^{-1} which is probably an upper limit for the heat of physical adsorption (12).

The strong and weak adsorption of hydrogen on rhenium powder can be roughly compared to the β - and α -binding states of Hickmott who restricted the term α to the state of adsorption occurring for the H_2/W wire system below 195°K (13). It is believed that the β -hydrogen is atomic. A chemisorbed part of α -hydrogen may be molecular, as for instance on tungsten (13, 14), or atomic, as on iridium and rhodium (14).

The simplest explanation of the dependence of the conversion rate on pressure and temperature seems to be similar to that discussed by Eley and Shooter for

evaporated films of some first row metals (15). It may be based on the assumption that both at elevated and low temperatures, the Bonhoeffer-Farkas mechanism predominates. This consists of the recombination of hydrogen atoms with a rate-determining activation energy related probably to the heat of desorption of hydrogen. As has been shown by other authors (11, 15), the obedience of the reaction kinetics to the Langmuir isotherm, does not exclude the possibility of the Bonhoeffer-Farkas mechanism.

The near-zero or zero reaction order at room temperature and below, characteristic of metals strongly adsorbing hydrogen, indicates that the reaction is proceeding at almost complete or complete coverage. This may be safely assumed for the strongly bound hydrogen, designated β . The reaction orders equal to 0.20 at 293°K and 0.08 at 195°K correspond to coverages of 0.80 and 0.92 respectively. These values are in agreement with the adsorption results under the assumption that complete coverage by chemisorbed atoms amounts to 7.0×10^{14} cm^{-2} . The near-zero reaction order at low temperatures and pressures at which the surface coverage is found to be far from saturation may be explained by assuming that the main part of reversibly adsorbed hydrogen at these temperatures is molecular, and does not participate appreciably in the reaction.

The low or almost zero, apparent activation energies are reconcilable with coverage, near saturation, at which reversible adsorption begins. They indicate that the reaction proceeds only on sites with low adsorption heat, probably decreasing with decreasing temperature (16).

The change of reaction order from zero to unity at 70 mm and 77°K indicates that another mechanism begins to operate here. It is possible that at sufficiently high pressure, the weak adsorption of hydrogen molecules in the second layer becomes important, as indicated by the adsorption isotherm obtained at this temperature. These molecules can react with atoms of the first adsorbed layer according to the Eley mechanism (15), or be converted by

the magnetic mechanism which seems to be of more frequent occurrence on transition metals than was previously believed (17).

The low activity of rhenium as compared with platinum in the *para-ortho* conversion of hydrogen is consistent with that found in the hydrogenation of benzene. It may be related to the low activity for hydrogen chemisorption (at 293°K it is probably mainly dissociative on rhenium as well as on platinum (18)), and to the high initial heat of chemisorption of hydrogen. In the case of hydrogen conversion these correlations may be associated with the mechanism of recombination of hydrogen atoms which are held on sites with low binding energy. The investigations have shown that at low temperatures an almost monolayer coverage of the rhenium surface is attained, but this is due to the very weakly bound, probably molecular hydrogen, the main part of which does not participate in the conversion. On the other hand, the high initial chemisorption heat of hydrogen may result in high proportion of the strongly bound nonreactive hydrogen atoms. Indeed, it seems remarkable that the reversible part of hydrogen chemisorbed by rhenium at room temperature appears to be much lower than that of about 60% given by some authors for platinum (19). Further studies of the interaction of hydrogen and rhenium are in progress.

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