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Hydrogen–Deuterium Equilibration and Parahydrogen and Orthodeuterium Conversion over Palladium: Kinetics and Mechanism

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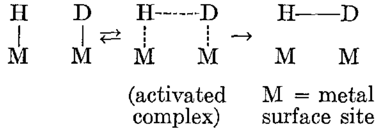
An extensive study is made of the kinetics and mechanisms of the hydrogen–deuterium equilibration and the parahydrogen and orthodeuterium conversion over palladium wires and sponge. The occurrence of two palladium-hydrogen phases at the surface influences the kinetic behavior. The kinetics over β samples are described by the general equation

$$v = Ap^{\sim 0.63} \exp(-12\,500/RT)$$

Primary and secondary isotope effects are discussed, and a reaction mechanism is proposed which is closely related to the Rideal mechanism and which accounts for the remarkable pressure dependence of the reaction.

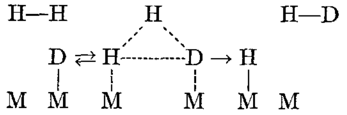
INTRODUCTION

In the past many attempts have been made to clarify the mechanisms of the reactions of hydrogen at the surface of metals. As to the parahydrogen and orthodeuterium conversion* we have the possibility of a nonchemical conversion by strong paramagnetic surface centers [Mechanism (I); Bonhoeffer, Farkas, and Rummel (*1*)]. In the case of a chemical conversion or equilibration it was obvious to suggest initially a mechanism comprising dissociative chemisorption and associative desorption of the hydrogen [Bonhoeffer and Farkas (*2*)].



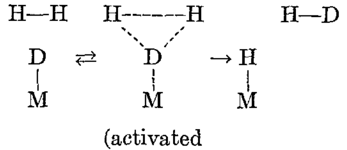
(II)

At a later stage alternative mechanisms were proposed to account for the occurrence of equilibration in cases where the rate of hydrogen desorption seemed to be lower than the equilibration rates observed. In the so-called Rideal mechanism (*3*) hydrogen molecules are thought to be adsorbed over a chemisorbed hydrogen atom next to a free site ("singleton").



(IIIa)

In the absence of free metal sites this mechanism is untenable, and in that case the Eley mechanism (*4*) may be operative.



(IIIb)

The study of the equilibration and exchange of hydrogen isotopes over platinum at temperatures below 100°K forced Boreskov and Vassilevitch (*5*) to introduce still

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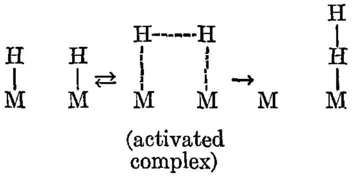
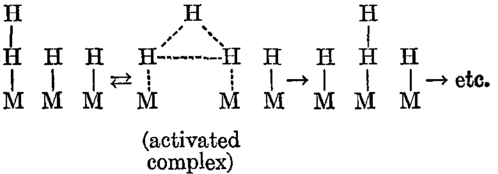
* Throughout this article we will use the following nomenclature: Equilibration: the heterogeneously catalyzed reaction between gas-phase hydrogen isotopes; Exchange: reaction between ad-(or ab-)sorbed hydrogen isotopes and isotopes in the gas phase; Conversion: the catalytic conversion of parahydrogen or orthodeuterium to an equilibrium mixture.

other mechanisms, which are modifications of (II) and (III). They concluded the rate-determining step in the low-temperature *exchange* to be the surface reaction



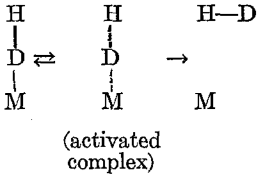
(IVa)

Hence they propose a reaction between two adsorbed hydrogen atoms, resulting in a molecularly chemisorbed group. This is followed by hydrogen transport over the surface to sites of low adsorption energy by a sequence of surface reaction steps



(IVb)

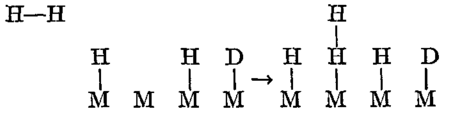
Steps (IVb), which are likely to proceed with a low activation energy, are closely related to the Rideal mechanism. Molecularly bound hydrogen that has arrived in a surface region of low adsorption energy can desorb in the following way:



(IVc)

Boreskov and Vassilevitch also proposed a mechanism for the *equilibration* reaction; this, however, is likely to hold only for the low-energy part of the surface:

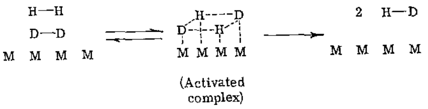
adsorption of H_2 (or D_2) on a free site



(Va)

(Vb), transport of H (or D) over the surface and desorption of HD from the weakest energy sites, according to (IVb) and (IVc).

Finally, a bimolecular exchange mechanism was proposed by Schwab and Killmann (*6*) according to the scheme



(VI)

From a literature review (*7*) it appears that mostly the Bonhoeffer-Farkas mechanism is adhered to for equilibration and exchange at high temperatures, whereas at lower temperatures (say below 150°K) there are often arguments in favor of Mechanisms (I) and (III)–(VI).

As to the metals studied, much of the work published is on nickel, platinum, iron, and tungsten catalysts, whereas relatively little is known on the behavior of palladium. The large hydrogen solubility in this metal forms a complication. This was first recognized by Farkas (*8*), who observed a difference in activation energy for the parahydrogen conversion processes at the inlet and outlet sides of a palladium disc through which hydrogen was diffusing. The activation energy was notably higher on the inlet side, where the concentration of dissolved hydrogen atoms is higher. This "self-poisoning" of the parahydrogen conversion over palladium was confirmed by a study of Couper and Eley (*9*); in a conversion experiment at 1.2 mm hydrogen pressure an activation energy of 4.3 kcal/mole was obtained, whereas at 6.1 mm, 6.3 kcal/mole was found. Finally, a palladium wire loaded with 8 atomic % hydrogen gave an activation energy of ~11 kcal/mole. Owing to this pressure sensitivity of the activation energy it was impossible to study the real pressure dependence of the reaction rate, and it is precisely a knowledge of this latter factor which can be helpful in the elucidation of the reaction mechanism.

The only attempt to determine the reaction *mechanism* of the hydrogen–deuterium equilibration over palladium was made by Kasansky and Wojewodsky (*10*), who showed that an increase of the hydrogen-atom concentration on a palladium surface hardly results in an acceleration of the reaction; from this they concluded that Mechanisms (IIIa) or (IIIb) are not operative (at temperatures above 150°C).

In view of the scanty information available from literature a closer study of the kinetics and mechanism seemed worthwhile. In previous studies the occurrence of two phases in the palladium-hydrogen system, the α and the β phase, has not been taken into account. The nearly constant hydrogen content of the β hydride makes this phase excellently suited for a study of the pressure dependence of the reaction rates.

THE PROPERTIES OF THE PALLADIUM HYDRIDES

Before we proceed to explain our experimental results it is necessary to give a short account of some properties of the palladium hydrides, together with a few complementary observations of our own.

Both from determinations of phase diagrams (*11, 12, 13*) and from X-ray diffraction studies (*13, 14*) it follows that there are at least two palladium-hydrogen phases (see Fig. 1). The α phase is formed by the absorption of small amounts of hydrogen;

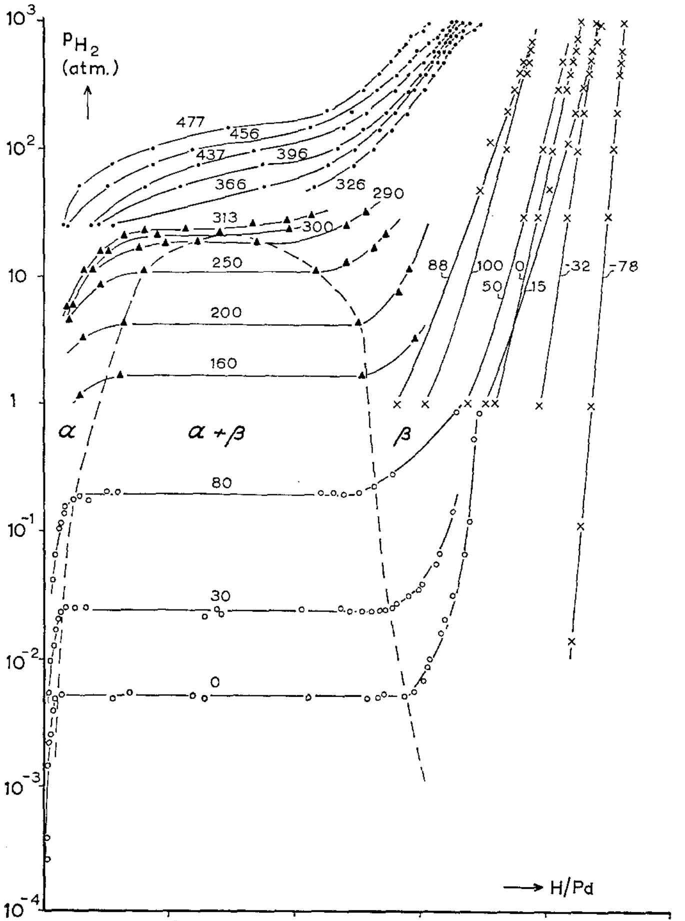


FIG. 1. Absorption isotherms of hydrogen in palladium, taken from different authors; pressure on a logarithmic scale. The dashed line encloses the area of coexistence of the α and β phases. The numbers in the graph indicate the temperature in °C. ●, 326–477°C, Levine and Weale (*12*); ▲, 160–313°C, Gillespie and Sieverts, quoted by Fowler and Guggenheim (*27*a); ○, 0–80°C, Gillespie and Hall, quoted by Smith (*11*); ×, −78–100°C (1–1000 atm), Perminov *et al.* (*13*).

the maximum composition is about $PdH_{0.03}$ at room temperature; at this temperature the lattice parameter is only slightly larger than that of pure palladium (3.889 Å). As hydrogen is further absorbed, the α phase becomes unstable and the lattice expands to about 4.018 Å ($PdH_{\sim 0.7}$) to form the β phase. Worsham *et al.* (*15*) have shown by neutron diffraction studies that the hydrogen atoms occupy about 70% of the octahedral interstices in the face-centered cubic palladium lattice, to give a NaCl-type structure with a hydrogen deficiency. They were unable to determine the hydrogen positions in the α phase because of the very small hydrogen concentration in this phase at room temperature.

TABLE 1

LATTICE STRETCH IN PALLADIUM ON UPTAKE OF HYDROGEN IN THE α AND β PHASES

	n_H/n_{Pd}[a]	Δd[b] (Å)	$\frac{\Delta d}{n_H/n_{Pd}}$
H_2 saturation at 100°C in α phase[c,d]	0.046	0.011	0.24
H_2 saturation at 200°C in β phase[e]	0.39	0.100	0.26
Undersaturation of β phase at 100°C[c]	—	—	0.22

[a] Number of hydrogen atoms taken up per palladium atom.

[b] Corresponding increase of lattice constant.

[c] Reference 17.

[d] Reference 18.

[e] References 14 and 16.

From a calculation of the lattice stretch per unit of hydrogen uptake (see Table 1) it appears, however, that the stretch is practically the same for the two phases, which indicates that there is no difference as to the hydrogen positions. Further PMR studies (*19*) point to the same *mode* of binding. The heats of solution of the hydrogen show only a small difference, being 8.95 and 9.61 kcal/mole for the α and β phase, respectively (*18*). Furthermore, the activation energy for the diffusion of hydrogen through α palladium hydride amounts to 4.1–4.4 kcal/mole [Farkas (*8*), Darling (*20*)], whereas for the transport in the β phase Norberg (*21*) found, from PMR studies, an activation energy of 3.7 (±1) kcal/mole, a value which is somewhat lower than that reported by Mitacek and Aston (*22*), who arrived at 5.5–6.4 kcal/mole from dynamic calorimetric determinations. Therefore, in the absence of pronounced differences between the properties of the two phases, the occurrence of the two-phase region can best be described as being due to a weak attraction between hydrogens in neighboring lattice positions in the β phase [Lacher (*16*), van Vucht (*23*)]. The energy gain thus obtained is accompanied by a lowering of the entropy, as the hydrogens tend to cluster in such a way that about four out of six of the octahedral interstices are filled. In the hydrogen-poor α phase, however, the hydrogens are randomly distributed over all octahedral interstices; this corresponds to a somewhat lower binding energy, but now the localization entropy is maximum.

Another question concerns the value of the H/Pd ratio in the β phase. From phase diagrams (see Fig. 1) it appears that, at that coexistence point of the α and β phases where the α phase disappears, this ratio is a function of temperature. At 200°C, for instance, $H/Pd \simeq 0.5$, but at room temperature it is $\simeq 0.6$ (this latter value was experimentally confirmed by the present authors).

When the pressure is raised more hydrogen may be taken up in the β phase, but the H/Pd ratio increases very slowly; at room temperature and 1 atm $H/Pd = 0.68$; the value of 0.70 is reached only at 10 atm, and $H/Pd = 0.85$ at 1000 atm. This means that in the atmospheric pressure region and around room temperature the composition $PdH_{0.68}$ figures as an apparently limiting composition.

Various authors connect the figure 0.68 with a number of about 0.6 4-*d*-electron holes available per palladium atom for the binding of hydrogen. This view is supported by the observation made by various authors (*24*) that the hydrogen or deuterium uptake at room temperature causes a linear decrease of the paramagnetism of palladium, which ends abruptly at 0.67 H (or D) per palladium atom. From the phase diagram (Fig. 1) it can be seen, however, that at other temperatures and pressures other limiting β compositions are found, and hence more susceptibility determinations, in a wider range of temperature and pressure, will have to be made before a clear statement can be given on this point.

Starting from normal palladium samples Perminov and co-workers (*13*) finally arrived at the composition $PdH_{0.92}$, at −78°C and 1000 atm. We have been able to show that it is even possible to arrive at the composition PdH_2, if hydrogen is absorbed in a sample of very finally divided palladium, *viz.* in a 0.5% Pd-on-alumina catalyst with a mean palladium crystallite size of about 15 Å. Analogous observations were made by Suhrmann *et al.* (*25*), for crystallites of ~85 Å, and by Turkevich (*26*).

In the research work presented in this paper the maximum hydrogen or deuterium uptake in the palladium sponge and wire samples was always found to correspond to the composition $PdH_{0.68}$. This is in accordance with what may be expected from the phase diagram (Fig. 1), as the lowest temperature used was −35°C and the highest pressure 265 mm Hg. As said before, deviations from this limiting composition can only be expected at much higher pressures (say 10 atm) and at temperatures of −50°C or lower.

Accepting this limit, we can describe the solubility of hydrogen in the β phase by the absorption isotherm given by Fowler and Guggenheim (*27*a)

$$p_{\mathrm{H}_2}[(1-\theta_{\mathrm{H}})^2/\theta_{\mathrm{H}}^2] = (3.04 \times 10^7)\exp -(4078 + 9029\theta_{\mathrm{H}})/RT \quad \text{mm Hg} \quad (1)$$

where θ_{H} is the fraction of occupied holes in the bulk and $\theta_{\mathrm{H}} = 1$ for the composition $PdH_{0.68}$. The mutual interaction of the hydrogen atoms is reflected by the exponential term, which is a function of θ_{H}.

With the help of the deuterium isotherms given by Smith (*11*) we calculated an analogous equation for deuterium absorption

$$p_{\mathrm{D}_2}[(1-\theta_{\mathrm{D}})^2/\theta_{\mathrm{D}}^2] = (3.53 \times 10^7)\exp -(3483 + 8727\theta_{\mathrm{D}})/RT \quad \text{mm Hg} \quad (2)$$

In the discussion of this paper we need the fraction of free holes in the bulk as a function of the ratio D/(H + D) in the gas phase, in the region $\theta_{\mathrm{H(D)}} \simeq 1$ and at temperatures around T ≈ 300°K. For these conditions Eqs. (1) and (2) may be rewritten as

$$K_{\mathrm{H}} = \theta_{\mathrm{H}}^2/p_{\mathrm{H}_2}(1-\theta_{\mathrm{H}})^2 = 8.85 \times 10^4\ \mathrm{atm}^{-1} \quad (3)$$

and

$$K_{\mathrm{D}} = \theta_{\mathrm{D}}^2/p_{\mathrm{D}_2}(1-\theta_{\mathrm{D}})^2 = 1.69 \times 10^4\ \mathrm{atm}^{-1} \quad (4)$$

For equal hydrogen and deuterium pressures we find from (3) and (4)

$$(1-\theta_{\mathrm{D}})/(1-\theta_{\mathrm{H}}) = 2.29 \quad (5)$$

Hence, around room temperature and at the same pressure, the number of free holes in the deuteride is about twice the number in the hydride.

When dealing with a palladium sample in equilibrium with an equilibrium mixture of H_2, D_2, and HD, Eqs. (3) and (4) may be written as

$$K_{\mathrm{H}} \simeq \theta_{\mathrm{H}}^2/p_{\mathrm{H}_2}(1-\theta_{\mathrm{H}}-\theta_{\mathrm{D}})^2 \simeq 8.85 \times 10^4\ \mathrm{atm}^{-1} \quad (6)$$

and

$$K_{\mathrm{D}} \simeq \theta_{\mathrm{D}}^2/p_{\mathrm{D}_2}(1-\theta_{\mathrm{H}}-\theta_{\mathrm{D}})^2 \simeq 1.69 \times 10^4\ \mathrm{atm}^{-1} \quad (7)$$

where p_{H} and p_{D_2} are the partial hydrogen and deuterium pressures in the $H_2 - D_2 - HD$ mixture and $(1 - \theta_{\mathrm{H}} - \theta_{\mathrm{D}})$ is the fraction of free holes. Equations (6) and (7) are only approximations, since the change in mutual interaction, which is a function of the H/D ratio in the bulk, was not taken into account. Notwithstanding the neglect of the change in mutual interaction, the separation factor $\alpha = (p_{\mathrm{D}_2}/p_{\mathrm{H}_2})(\theta_{\mathrm{H}}/\theta_{\mathrm{D}})$, as calculated from Eqs. (6) and (7), is in good accord with the separation factor experimentally determined by Wicke and Nernst (*27*b). From Eqs. (6) and (7) it follows that

$$(1-\theta_{\mathrm{H}}-\theta_{\mathrm{D}}) = [1 + 100(8.85p_{\mathrm{H}_2})^{1/2} + 100(1.69p_{\mathrm{D}_2})^{1/2}]^{-1}. \quad (8)$$

With the aid of Eq. (8) we can calculate the fraction of free holes in the bulk as a function of the D/(H + D) ratio in the gas phase (see Fig. 7, dashed lines). The

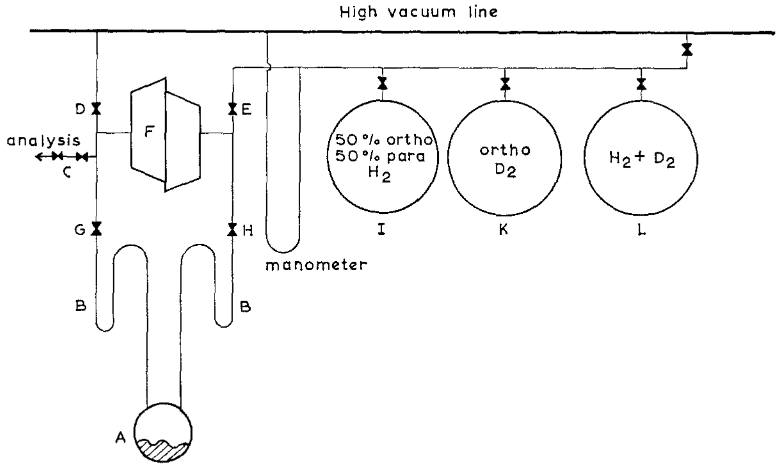


FIG. 2. Outline of the experimental setup. The meaning of the symbols is given in the text.

fraction of free holes does not change very much up to the gas-phase composition $D/(H + D) = 0.5$. Beyond this value it sharply rises to ~2.3 times the number for pure hydrogen.

EXPERIMENTAL

The apparatus is schematically represented in Fig. 2. The palladium sample is contained in vessel A. In experiments at high temperature (up to 320°C) it consisted of a piece of Johnson-Matthey spec. pure palladium wire with a geometrical surface area of 0.5 cm^2 and a roughness factor of about 2. In low-temperature experiments (from 40°C down to −40°C) a sample of Johnson-Matthey spec. pure palladium sponge was used, the total surface area of which was 1400 cm^2, as found from physical argon adsorption at −196°C. The catalyst was protected against water and mercury poisoning by two traps (B) cooled by liquid nitrogen. With the stopcocks C, D, and E closed the gases could rapidly be circulated over the catalyst by an all-glass magnetically operated piston pump F. I, K, and L are storage vessels for hydrogen and deuterium purified by diffusion through palladium thimbles. A mixture of 50% ortho- and 50% parahydrogen was prepared by equilibration of Pd-diffused hydrogen at 77°K over a cobalt-silica catalyst. A 98% ortho-, 2% paradeuterium mixture was prepared in the same way, but with equilibration at 20.4°K.

In the course of each experiment small gas samples for analysis were taken at point C at regular time intervals. The gas samples were analyzed by means of a thermal conductivity gauge according to Farkas; results with hydrogen-deuterium mixtures were checked mass-spectrometrically.

The reactor part of the apparatus with the catalyst was baked out at approximately 400°C in a high vacuum. Pretreatment of the sample was by oxidation at 400°C in 60 mm of oxygen for half an hour, followed by reduction for 2 hr at the same temperature. After this pretreatment hydrogen was rapidly taken up in the bulk of the catalyst, and the rate of parahydrogen conversion at 60°C and 6 mm Hg hydrogen pressure proved to be nearly equal to that reported by Couper and Eley (*9*).

To avoid changes in the hydrogen concentration or in the hydrogen-deuterium ratio in the palladium during the equilibration experiments, the samples were always equilibrated for 20 hr with hydrogen, deuterium, or the appropriate hydrogen-deuterium mixtures, at the temperature and pressure at which the equilibration experiment was finally performed.

A difference in behavior between wire and sponge was observed in the absorption of larger amounts of hydrogen up to the β-phase composition. Owing to the difference in lattice parameter the crystallization of the β phase in an α-phase environment may result in high internal strain. In the case of *sponge* this caused a strong X-ray line-broadening. From a $\beta \cos \theta$ vs. $\sin \theta$ plot for six diffraction lines (θ is the Bragg angle and β the integral breadth of the line) it was found that this broadening was due on the one hand to a decrease of the mean crystallite diameter from ~10^4 Å to ~450 Å and on the other to a distortion of the lattice. This grain-boundary cracking [or "transition rifting" (*11*)] could be avoided by passing around the area of coexistence of the α and β phases (see Fig. 1) during the preparation of the β hydride; this was done by preparing the β hydride in an autoclave at 300°C and 35 atm hydrogen pressure. From X-ray analysis it appeared that now, indeed, line-broadening did not occur.

When wires were used, grain-boundary cracking was never observed. This can be understood from the fact that, owing to cold-working and annealing, the orientation and crystallization in wires is much better than it is in the sponge material. In this case rifts in the material are absent and the β phase can only grow from the outside to the inside of the wire, which is attended with less internal strain.

General Kinetics

The gas in the closed reaction system was circulated so rapidly that "the half-life time of homogenization" was very small as compared with the half-life time of the reaction ("quasi-homogeneous" reaction). Furthermore, the total pressure in the system was constant during an experiment, it being hardly influenced by the removal of the small gas samples for analysis. Under these conditions the rate of the conversion

$$H_2(p) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2(o)$$

is given by

$$dx/dt = k_f(a - x)^n - k_b(b + x)^n \qquad (9)$$

where a and b are the initial para- and orthohydrogen pressures, respectively, and $(a - x)$ and $(b + x)$ are the pressures after time t; k_f and k_b will for the present be called *apparent* rate constants, as they may prove to be a function of the total hydrogen pressure at which the reaction is performed.

The power n is in the first instance unknown and depends on the mechanism; if *one* gas-phase molecule is involved in the formation of the activated surface complex, $n = 1$, whereas if *two* are needed $n = 2$ [Schuit and van Reyen (*28*)].

Integration of Eq. (9) for $n = 1$ results in

$$-\ln(1 - \eta) = (k_f + k_b)t \qquad (10)$$

where $\eta = x/x_\infty$ and x_∞ is the equilibrium maximum value of x reached at infinite time.

Integration of Eq. (9) for $n = 2$ and $b = 0$ leads, according to Harris (*29*), to

$$-\ln(1 - \eta) + \ln\left[1 - \eta\left(\frac{\epsilon - \sqrt{\epsilon}}{\epsilon + \sqrt{\epsilon}}\right)\right] = \frac{2ak_f}{\sqrt{\epsilon}}t \qquad (11)$$

where $\epsilon = k_f/k_b = K^n$. K is the equilibrium constant of the parahydrogen conversion ($K = 3$ at 44°C). For $b \neq 0$, we arrive at

$$-\ln(1 - \eta) + \ln\left[1 - \eta\left(\frac{\epsilon - \sqrt{\epsilon}}{\epsilon + \sqrt{\epsilon}}\right)\left(\frac{a\sqrt{\epsilon} - b}{a\sqrt{\epsilon} + b}\right)\right] = \frac{2(a + b)k_f}{\sqrt{\epsilon}}t \qquad (11a)$$

In all our experiments it appeared that plotting $-\ln(1 - \eta)$ as a function of t according to Eq. (10), resulted in a perfect straight-line relationship, whereas a plot of the left-hand side of Eq. (11a) as a function of time did *not*. For one of our experiments this is demonstrated in Fig. 3. Values of $n > 2$ or $n < 1$ can practically be excluded, and hence all experiments were analyzed according to Eq. (10).

For hydrogen–deuterium equilibration

$$H_2 + D_2 \rightleftharpoons 2HD$$

the rate equation reads

$$dx/dt = k_f(a - x)^n(b - x)^n - k_b(c + 2x)^{2n} \qquad (12)$$

a is the initial hydrogen pressure, b the initial deuterium pressure, and c the initial HD pressure. Again we point out that k_f and k_b are apparent constants, as the values may later prove to be a function of the total hydrogen pressure and of the H/D ratio in the gas phase.

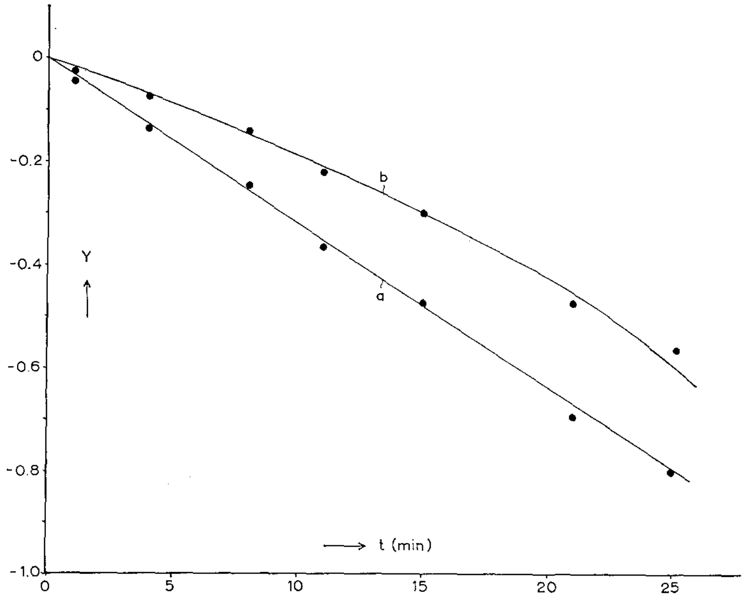


FIG. 3. Parahydrogen conversion over β palladium hydride at $p_{\text{tot}} = 50$ mm Hg and 44°C. Experimental results plotted according to (a) Eq. (10), with $Y = -\ln(1-\eta)$; (b) Eq. (11a), with $Y = -\ln(1-\eta) + \ln\{1 - \eta(\epsilon - \sqrt{\epsilon}/\epsilon + \sqrt{\epsilon})(a\sqrt{\epsilon} - b/a\sqrt{\epsilon} + b)\}$.

For equimolecular hydrogen-deuterium mixtures a is equal to b, and integration of Eq. (12) for $n = 0.5$ results in

$$-\ln(1-\eta) = (k_f/2 + k_b)t \qquad (13)$$

For $n = 1$ an equation analogous to Eq. (11) is found. By the same method as demonstrated in Fig. 3 it was found that our experiments only obeyed Eq. 13, so that in Eq. (12) $n = 0.5$.

The general solution of Eq. (12) for $a \neq b$ is very complicated. Therefore, this equation was numerically integrated by means of a digital computer from $x = 0$ up to $x = \frac{1}{2}x_\infty$, for chosen values of a and b.

TABLE 2
THE PRODUCTS OF RATE CONSTANT AND HALF-LIFE TIME (THE TIME AT WHICH $x = \frac{1}{2}x_\infty$) FOR DIFFERENT VALUES OF a AND b IN EQ. (12)
$k_f/k_b = \epsilon = 1.776$ (at −10°C)
$n = 0.5$; $c = 0$

a	b	$k_f \times t_{1/2}$	$k_b \times t_{1/2}$
0.1	0.9	0.381	0.215
0.2	0.8	0.519	0.292
0.5	0.5	0.652	0.367
0.8	0.2	0.519	0.292
0.9	0.1	0.381	0.215

The products of k_f and the half-life time and of k_b and the half-life time are given in Table 2. The result for $a = b = 0.5$ corresponds to the well-known relation

$$k_f/2 + k_b = k_{\text{exptl}} = 0.69/t_{1/2} \qquad (14)$$

The reaction rate v, in molecules per cm^2 and per sec, is found by multiplication by the total number of molecules in the gas phase, N, and division by the total catalyst surface S (in cm^2).

$$v = k(N/S) \text{ molecules cm}^{-2}\text{ sec}^{-1} \qquad (15)$$

RESULTS AND DISCUSSION

I. *α phase*

The kinetics of the parahydrogen conversion over the α-phase samples are represented by the points to the left of the crosses in Fig. 4. No difference in activity between wire and sponge samples was found. The observed activation energies are dependent on pressure and temperature. Table 3 shows the good correspondence with Couper and Eley's observations (*9*).

In Fig. 4 it is seen that the kinetics at 265 mm Hg show a sudden activity decrease

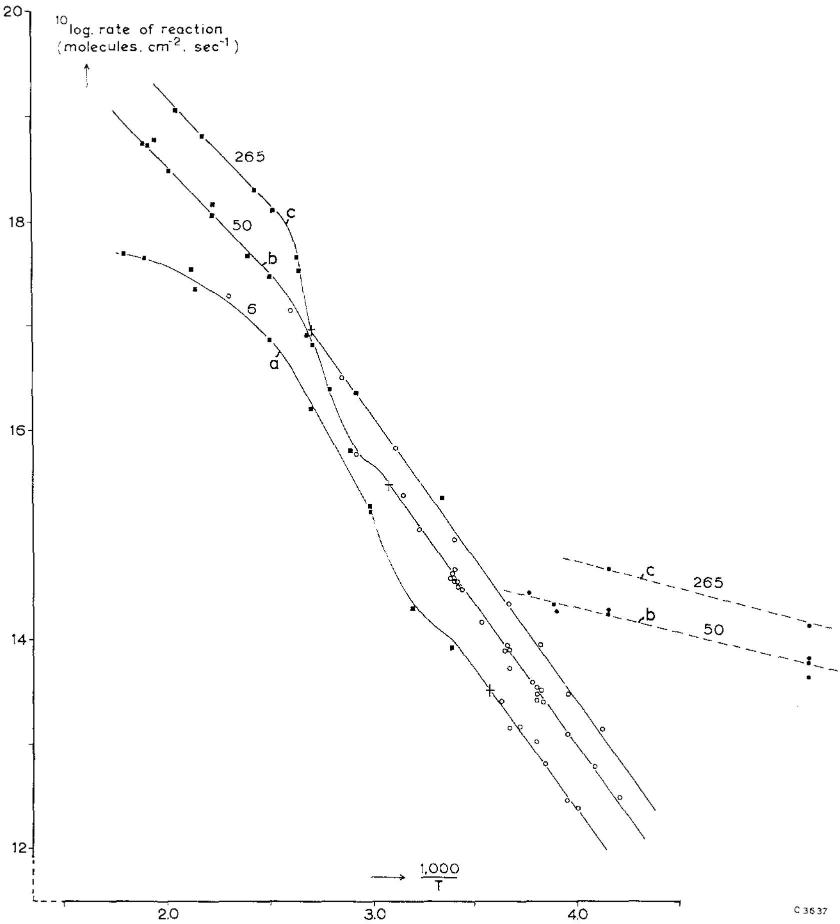


FIG. 4. Parahydrogen conversion over α and β palladium hydride: +, transition points $\alpha \rightarrow \beta$ hydride, calculated from an extrapolation of Gillespie's and Galstaun's results, quoted by Smith (*11*); ■, Pd wire; ○, Pd sponge; a, p_{H_2} = 6 mm Hg; b, p_{H_2} = 50 mm Hg; c, p_{H_2} = 265 mm Hg; dashed curves, conversion over β phase; after grain-boundary cracking.

TABLE 3
PARAHYDROGEN CONVERSION OVER α PALLADIUM HYDRIDE AT 450 °K

Pressure (mm Hg)	Activation energy (kcal/mole)	Pre-exponential factor (molecules cm⁻² sec⁻¹)
265	9.5	2.9×10^{23}
50	9.3	1.4×10^{23}
6	6.3(6.3[a])	$\sim 1.5 \times 10^{22}(1.5 \times 10^{22})$[a]
1.2	4.3[a]	5×10^{20}[a]

[a] Observations of Couper and Eley (*9*).

by a factor of the order of 10 just before the β phase in the bulk is formed (indicated by a cross). Analogous activity decreases are found at 50 and 6 mm Hg pressure, where, again, the decrease starts *before* the bulk transition to the β phase, and is accompanied by an activity decrease of a factor of between 10 and 100. Furthermore it appears that at the points which indicate the $\alpha \rightarrow \beta$ transition in the *bulk* no change in the catalytic surface activity of the samples is observed; hence, there are no indications from this work that an influence of the hydrogen *bulk* concentration on the kinetics should exist.

The decrease in activity occurring before the bulk $\alpha \rightarrow \beta$ transition may be interpreted by assuming an $\alpha \rightarrow \beta$ transition at the *surface* starting before the bulk transition, owing to the heat of *ad*sorption being higher than the heat of *ab*sorption. This transition will be accompanied by a strong increase in

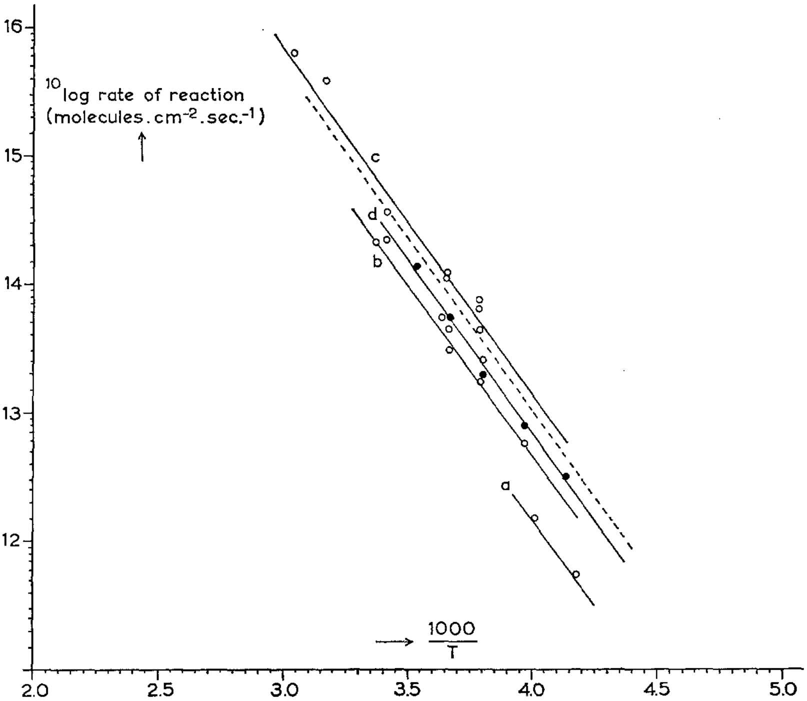


FIG. 5. Hydrogen–deuterium equilibration and orthodeuterium conversion over β palladium hydride (sponge). H_2–D_2 equilibration: curve a, $p_{tot} = 6$ mm Hg; curve b, $p_{tot} = 50$ mm Hg; curve c, $p_{tot} = 265$ mm Hg. Ortho-D_2 conversion: curve d, $p_{tot} = 50$ mm Hg. Dashed curve, parahydrogen conversion at $p_{tot} = 50$ mm Hg, taken from Fig. 4.

hydrogen coverage, and hence by a strong decrease in the number of free active sites and of the activity ("hydrogen self-poisoning").

Evidence for the existence of $\alpha \rightarrow \beta$ transitions at metal surfaces may be found from the work of Mignolet (*30*) and Geus (*31*).

On α-phase samples at low hydrogen coverage the reaction was about first order in pressure. Only a few hydrogen–deuterium exchange experiments were performed at 430°K and $p = 50$ mm Hg. A kinetic isotope effect of ~0.63 was found with respect to the parahydrogen conversion.

The value of n [in Eq. (9)] was equal to unity in all experiments (in the case of H_2–D_2 exchange n was 0.5).

II. β phase

a. Kinetics on Noncracked Samples

Once the hydrogen content in the bulk is constant in the β phase a normal Arrhenius behavior is found (see Fig. 4, to the right of the crosses).

The kinetics of the parahydrogen conversion are described by the equation

$$v = (5.8 \times 10^{22}) p_{tot}^{0.62} \exp(-12\,400/RT) \text{ molecules cm}^{-2}\text{ sec}^{-1} \quad (16)$$

where p_{tot} is the total pressure in mm Hg. Analogous results were arrived at for the orthodeuterium conversion (see Fig. 5)

$$v = (6.7 \times 10^{22}) p_{tot}^{0.64} \exp(-12\,670/RT) \text{ molecules cm}^{-2}\text{ sec}^{-1} \quad (17)$$

and for the hydrogen–deuterium equilibration (1:1 mixture) (Fig. 5)

$$v = (3.5 \times 10^{22}) p_{tot}^{0.64} \exp(-12\,540/RT) \text{ molecules cm}^{-2}\text{ sec}^{-1} \quad (18)$$

The correctness of the value ~0.63 for the power m was checked once more by separate experiments at constant temperature and at five different pressures between 5 and 256 mm Hg (see Fig. 6); m was found to be 0.62 ± 0.03 in the case of parahydrogen conversion, and 0.64 ± 0.04 in the case of

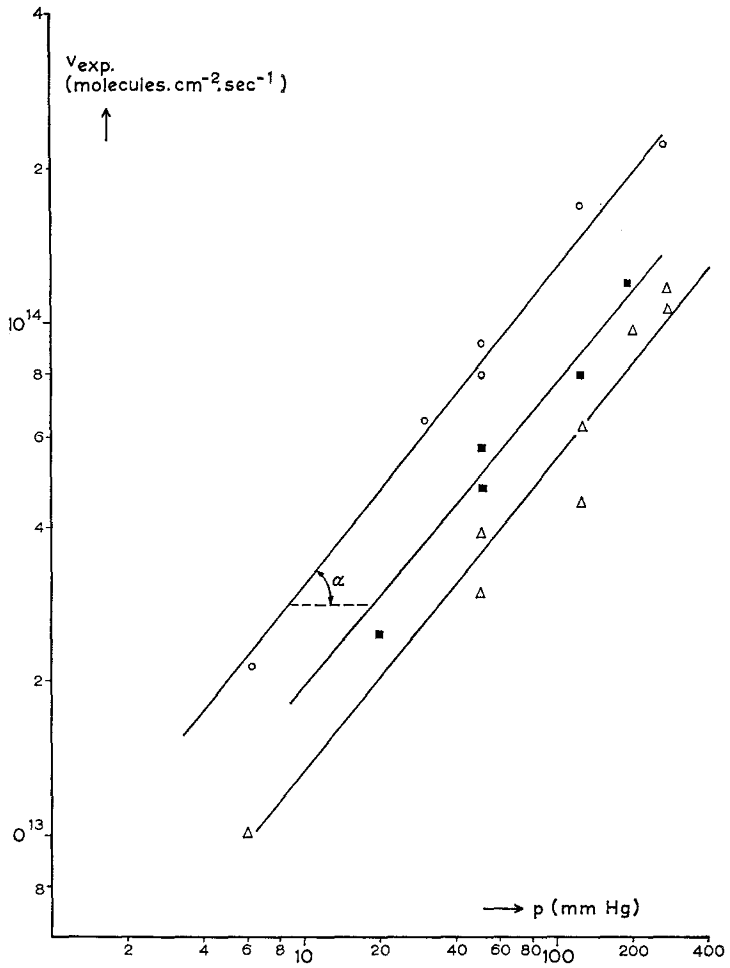


Fig. 6. The rate of reaction as a function of the total pressure, on a logarithmic scale: Catalyst, β palladium hydride; temperature, 273°K; ○, parahydrogen conversion $\tan \alpha = m = 0.62$; ■, orthodeuterium conversion $\tan \alpha = m = 0.64$; Δ, hydrogen-deuterium equilibration $\tan \alpha = m = 0.64$.

orthodeuterium conversion and of hydrogen-deuterium equilibration.

Though a full discussion of these results is not yet given in this section, a number of direct conclusions are obvious at once. The rate constants k [proportional to v according to Eq. (15)] indeed seem to be apparent constants, as they are functions of the total pressure. The exponent of p_{tot}, m, appears to be *independent of pressure and temperature* within the experimental limits where the β phase was studied, i.e., between $p_{\text{tot}} = 5$ and 265 mm Hg and between -40°C and 90°C. This means that it is impossible to interpret the fractional order of the reaction simply by saying that the reaction rate is proportional to a hydrogen coverage θ_{H_2} given by a Langmuir isotherm

$$\theta_{H_2} = K(T)p_{H_2}/[1 + K(T)p_{H_2}] \qquad (19)$$

as in this case the reaction order must be dependent on pressure and temperature.

The observed pressure- and temperature-independent order of the reaction seems to be quite unique for β palladium hydride. For nickel samples, for instance, Eley and Shooter (*32*) recently reported a zero order parahydrogen conversion in the same pressure and temperature range as applied here, whereas for platinum the rate dependence on pressure takes the form of a Langmuir isotherm (*33*). Therefore we will propose, in the final discussion, a mechanism which is closely related to the special structure of the β hydride.

The observed activation energy of 12.5 kcal/mole is in good accordance with the value reported by Kasansky and Wojewodsky (*10*), who arrived at 13 kcal/mole for hydrogen-saturated palladium, and close to Couper and Eley's result (*9*) for a less-saturated sample (~11 kcal/mole). Since the reaction is not zero order it is likely that we have to do with an apparent activation energy; this idea will be further developed in the final discussion.

b. *Kinetics on Cracked Samples*

The results indicated in Fig. 4 by the *dashed* lines represent measurements with β-phase sponge samples in which grain-boundary cracking occurred. (About this phenomenon see the "Experimental" section.) The equation describing the kinetics for this sample reads

$$v = (8 \times 10^{15}) p_{\mathrm{tot}}^{\sim 0.6} \exp(-2200/RT) \text{ molecules cm}^{-2}\,\text{sec}^{-1} \quad (20)$$

In the calculation of Eq. (20) use is made of the fact (observation by X-ray line-broadening) that the crystallite diameter changed from ~10^4 Å to ~450 Å, which corresponds to a surface area increase by a factor of ~22.

From a calculation of the Thiele modulus (*34*), both for the catalyst particles and the bulk, it was found that the effectiveness factor was unity, which means that there was no diffusion retardation.* We are therefore confronted here with the fact that for the cracked samples the frequency factor and the activation energy are appreciably lower than for the noncracked samples, whereas the reactions are practically of the same order (0.6 ± 0.1).

Several interpretations of this remarkable result may be given: One might think that the results found for the noncracked samples [Eqs. (16), (17), and (18)] are valid only for a partly poisoned surface, and that they do not hold for the surface of the freshly cracked sample, which is of greater purity, as it is about 20 times larger and difficult of access to poisons, owing to the small size of the rifts. If this is true, Eq. (20) represents the "real kinetics." However, a number of arguments can be advanced against this.

(*i*) The "residual gases" which may be left in a high vacuum in a glass apparatus are water, carbon dioxide, and nitrogen. Of these gases, carbon dioxide and nitrogen are not chemisorbed by palladium (*35*). Water can, indeed, poison the reaction, as we found by intentional addition of some water vapor to the gas. However, it could be rapidly desorbed from the catalyst by heating in dry hydrogen at only 80°C, after which procedure the activity appeared to be restored to exactly the original value. Since water is much more strongly bound to the glass wall (from which it desorbs only at 350°C), it is unlikely that the samples were water-poisoned.

(*ii*) Moreover, the catalyst was protected at the inlet and outlet sides of the reactor by cold traps around which the liquid nitrogen was automatically kept at a constant level, and the wall of the reactor was baked out at ~400°C. Further arguments against water-poisoning are the good correspondence between our wire (low-area) and sponge (high-area) results.

Another, and we think better, interpretation is that owing to cracking new planes and distorted surface sites are exposed on which the reaction can proceed with a much lower activation energy, and that these planes and strained sites are not very stable, this being the reason that they are not present on the noncracked samples (which were heated up to 400°C). The frequency factor for the cracked samples is 10^7 times lower than that for the noncracked ones, and this points to the presence of a *very small* amount of the more active planes. Indeed, the difference in activation energy is great—of the order of 10 kcal/mole—but differences of such magnitude are often recorded in catalysis. Here we may mention the specificity of crystal planes as reported by

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* For the particle size of the spongy Pd ~ 1.6 μ was taken, which value was found by electron microscopy. The diameter of the rifts was calculated from the rift volume given by Smith (*11*); it is of the order of 10 Å.

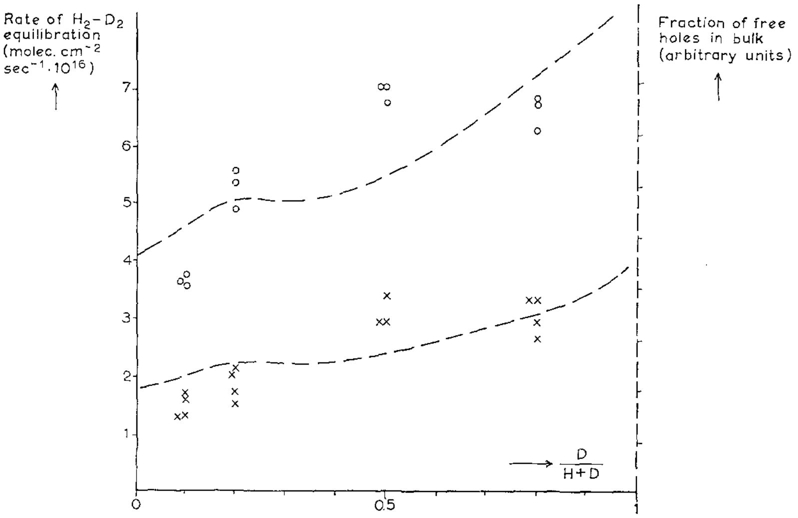


FIG. 7. The rate of H_2–D_2 equilibration, as influenced by the D/(H + D) ratio in the gas phase. The reaction rates are calculated by means of the relations given in Table 2. $p_{tot} = 50$ mm Hg; ○, T = 0°C; ×, T = −10°C. Dashed lines: The change in the fraction of free holes in the bulk, as calculated from Eq. (8).

Sosnovsky (*36*); in the decomposition of formic acid on silver she found a variation ranging from 12 kcal/mole (111 planes) to 35 kcal/mole (100 planes).

c. *Kinetic Isotope Effects*

A study of the kinetic isotope effects was performed with the aid of the noncracked β-phase samples. From Figs. 5 and 6 it can be seen that the hydrogen–deuterium equilibration is 2.3 ± 0.5 times slower than the parahydrogen conversion and 1.7 ± 0.5 times slower than the orthodeuterium conversion. The magnitude of these effects is of the same order as found with platinum, for para-H_2 conversion compared with H_2–D_2 equilibration (*37*). A direct interpretation of the sequence

$$v_{p\text{-}H_2} > v_{o\text{-}D_2} \geq v_{H_2\text{-}D_2} \qquad (\alpha)$$

is difficult. Besides the primary isotope effects, which are due to energetic differences between the potential energy curves of the rate-determining steps of the reactions, secondary isotope effects may play a part.

To check this, a number of hydrogen–deuterium equilibration experiments were performed in which the D/(H + D) ratio in the gas phase was varied (see Fig. 7). It is seen that the rate increases accordingly as more of the heavy isotope is in the gas phase. Finally, at D/(H + D) ~ 1, the rate is about two times faster than at D/(H + D) ~ 0. A primary kinetic isotope effect is not operative here, as we have to do with one and the same reaction (transition state) at all D/(H + D) ratios investigated.

Hence, the results plotted in Fig. 7 demonstrate that a secondary isotope effect indeed plays a role. This effect may be interpreted as caused by the fact that the number of free (catalytically active) sites increases with an increase of the amount of deuterium in the gas phase. It is of interest that the number of free holes *in the bulk* also increases with an increase of the deuterium concentration in the gas phase (see the dashed line in Fig. 7). This last effect, however, though of the same magnitude, is not fully in line with the first.

Further evidence for the occurrence of a secondary isotope effect emerged from a number of exchange experiments, carried out around room temperature, between β palladium deuteride and hydrogen in the gas phase, and, *vice versa*, between β palladium hydride and deuterium in the gas phase. The exchange rates could be described by equations analogous to Eqs. (16), (17), and (18).

At the start of the exchange reaction between the deuteride and hydrogen, when the surface is still highly covered with deuterium, the rate is ~1.5 times faster than that of the parahydrogen conversion over the hydride. The reverse is found for the exchange between the hydride and deuterium; here the initial exchange rate was ~1.4 times slower than that of the orthodeuterium conversion over the deuteride. Both effects may be accounted for by saying that the deuteride offers more reactive sites than the hydride.

After exchange for 1 min both HD and D_2 (respectively, HD and H_2) desorb in about equal amounts, though calculation showed that the catalyst was still fully deuterated (hydrogenated). This means that on the surface the exchange is somewhat more rapid than in the bulk.

Though the presence of a secondary isotope effect is established both by the equilibration experiments with varying D/(H + D) ratio and by the exchange experiments, an interpretation of the sequence (α) remains difficult. After correction for the secondary isotope effect one would expect to find

$$v_{pH_2} > v_{H_2-D_2} > v_{oD_2}$$

However, this is not the case, and the reason for this is not clear.

d. Discussion of the Mechanism

In Table 4 we confront our kinetic findings with what may be expected for mechanisms proposed earlier for various metal catalysts. In this table n gives the number of gas-phase molecules used in the formation of the activated complex. The values of m given in this table are derived from the scheme of the mechanism, on the supposition that the chemisorption isotherm of H_2 is given by

$$k'p_{H_2}(1 - \theta_H)^2 = k''\theta_H^2 \qquad (23)$$

Then, at low coverage,

$$\theta_H = [(k'/k'')p_{H_2}]^{1/2}$$

and

$$1 - \theta_H \simeq 1 \qquad (24)$$

whereas at high coverage

$$1 - \theta_H = (k''/k'p_{H_2})^{1/2}$$

and

$$\theta_H \simeq 1$$

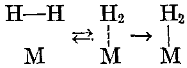
Taking into account the pressure p_{H_2} and the values of $(1 - \theta_H)$ and θ_H just calculated for each particular case, the values of m given in the table can easily be derived.

i. α-Phase results. Within the range studied a nonchemical conversion by paramagnetic centers can be excluded, since equilibration and conversion follow the same kinetics. The observed values of n exclude Mechanism(VI). At the highest temperatures used, when the surface coverage was low, m was found to be ~1, and this points to the Bonhoeffer-Farkas mechanism being operative [Mechanism(II)].

ii. β-Phase results. For the same reason as given for the α-phase samples, a nonchemical conversion is excluded. As we have to do here with a nearly fully covered surface the experimental m values have to be compared with the m values expected for high coverage (Table 4). We then see that only Mechanisms(IIIa) and (Vb) with $n = 1$ (respectively, 0.5) and $m = 0.5$ are about in accordance with our observation $n = 1$ (resp., 0.5) and $m \simeq 0.63$.

Mechanism(Vb) calls for a rate-determining surface diffusion. The observed activation energy of ~12.5 kcal/mole seems difficult to reconcile with this mechanism; the activation energy of the diffusion of hydrogen through the bulk of β-Pd hydride is only ~4 kcal/mole, and on platinum the activation energy of surface diffusion was found to be only ~5 kcal/mole (*5*).

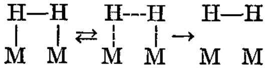
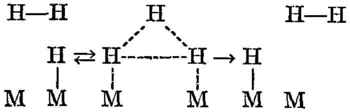
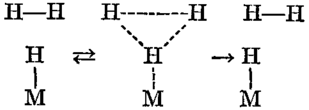
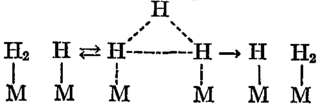
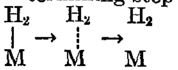
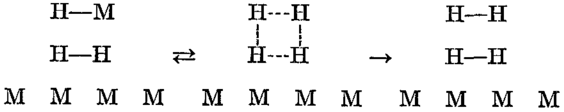
Therefore, Mechanism(IIIa), which calls for the encounter of a gas-phase hydrogen molecule with the combination of a covered and an uncovered site, seems very likely. At high coverage the chance of an encounter with this combination is equal to the chance of an encounter with *one* free site only. Therefore, the mechanism



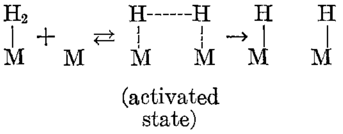
$$\begin{array}{ccccc} H{-}H & & H_2 & & H_2 \\ & \rightleftarrows & \vdots & \rightarrow & | \\ M & & M & & M \end{array} \qquad (25)$$

is equally probable. The fact that a secondary isotope effect was found which was associated with the number of free sites is in accordance with (25). The next step may be diffusion of the adsorbed H_2 molecule over the surface in the "sea of mobile H atoms,"

TABLE 4
VALUES OF n AND m TO BE EXPECTED FOR DIFFERENT CONVERSION AND EQUILIBRATION MECHANISMS

Mechanism	Scheme of the mechanism	n in Eq. (9)	n in Eq. (12)	m (exponent of p_{tot})
(II) Bonhoeffer-Farkas		1	0.5	1 at low coverage 0 at high coverage
(IIIa) Rideal		1	0.5	1.5 at low coverage 0.5 at high coverage
(IIIb) Eley		1	0.5	1.5 at low coverage 0 at high coverage
(V) Boreskov-Vassilevitch	(Vb) surface transport rate-determining 	1	0.5	1.5 at low coverage 0.5 at high coverage
	(Vc) desorption from sites of low adsorption energy is rate-determining step 	1	0.5	0 at high coverage
(VI) Schwab-Killmann		2	1	2 at low coverage 0 at high coverage
(VII) Found experimentally On β-phase palladium hydride	—	1	0.5	0.63 ($\pm$0.04) at high coverage
On α-phase hydride	—	1	0.5	1 at low coverage

till this molecule encounters a second free site



$$\begin{array}{cccccc} H_2 & & H\text{-----}H & & H & H \\ | \ + & \rightleftarrows & \vdots \quad\ \ \vdots & \rightarrow & | & | \\ M & M & M \quad\ M & & M & M \end{array} \qquad (26)$$

(activated state)

Finally, in a region of low adsorption energy, desorption can take place according to the backward reactions (26) and (25).

One of the basic observations in this work is that the pressure dependence of the reaction is $p^{\sim 0.64}$. The reproducibility of this observation is such that the deviation from $p^{0.5}$ (this last value is to be expected on the basis of the mechanism just proposed) is significant. Perhaps the observed pressure dependence can be made understandable by the following explanation. It is assumed that the composition of the β phase at the surface is Pd_3H_2 (which corresponds to about $PdH_{0.68}$). Furthermore, hydrogen is adsorbed in the holes between the surface palladium atoms. For the dissociation of Pd_3H_2 at the surface we then have

$$2\,\boxed{H}_s \rightleftarrows 2\,\boxed{}_s + H_2 \qquad (27)$$

where $\boxed{}_s$ stands for a surface hole. As we are dealing with the composition Pd_3H_2 it follows that two surface holes correspond to three surface palladium atoms, and hence (27) may be written

$$2\,\boxed{H}_s \rightleftarrows 3\,Pd_{surf} + H_2 \qquad (28)$$

The equilibrium constant of (28) is:

$$K = [\boxed{H}_s]^2/[Pd]^3_{surf}\,pH_2 \qquad (29)$$

and hence the concentration of free Pd atoms at the surface is

$$[Pd]_{surf} = (\boxed{H}_s^{2/3}/K^{1/3}) \times p_{H_2}^{-1/3} \qquad (30)$$

According to the mechanism proposed, the rate of reaction, v, is given by the number of H_2 collisions with the surface, multiplied by the chance that a free Pd atom will be encountered. Hence

$$v = c(T)p_{H_2}[Pd]_{surf}$$

or

$$v \simeq c'(T)p_{H_2}p_{H_2}^{-1/3} = c'(T)p_{H_2}^{0.66} \qquad (31)$$

The pressure dependence thus derived is in quite good accord with the experimental value. This derivation is only valid, however, when the adsorbing hydrogen molecules initially contact a surface palladium atom and not a surface hole.

Our formulation points to the occurrence of a thermodynamic isotope effect besides a kinetic isotope effect, as $c'(T)$ comprises $c(T)$ and K. This means that we are dealing with an apparent activation energy. Our ignorance about K prohibits further calculation of the real activation energy and of the kinetic isotope effect.

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