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EXCHANGE OF HYDROGEN ISOTOPES ON PALLADIUM

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Using deuterium and tritium, the rate of hydrogen exchange between the adsorbed layer of hydrogen on a palladium cathode and the electrolyte was measured. The exchange proceeded according to the schemes:

$$\begin{array}{ll} \text{Experiments according to variant I} & \mathrm{Pd(H)}_n + \mathrm{D}_2^*\mathrm{O} \rightarrow \mathrm{Pd(H)}_{n-1}\mathrm{D}^* + \mathrm{HDO}. \\ \text{Experiments according to variant II} & \mathrm{Pd(H)}_{n-1}\mathrm{T}^* + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Pd(H)}_n + \mathrm{T}^*\mathrm{HO}. \end{array} \tag{1}$$

The process of hydrogen exchange is more complex than the process of exchange of metal ions studied on amalgams (^{1,2}). Theoretical consideration of the question from various points of view led the authors of papers ($^{3-5}$) to the conclusion that the true rate of exchange between the electrolyte and the adsorption layer on the surface need not coincide with the exchange rate calculated by extrapolating the overvoltage curves (i_{extr}).

The measurements carried out by us were intended to obtain experimental data that would make it possible to compare the true rates of hydrogen exchange on palladium with the exchange rates obtained by extrapolating the overvoltage and ionization curves to the value of the overvoltage corresponding to equilibrium. The extrapolated values of the exchange rates obtained on the basis of the measurements described in (^{6}) may be regarded as the rates of discharge and ionization at equilibrium, since the linear portions of the η— $\lg i$ curves on palladium in alkaline solutions at medium polarizations are determined by the rates of precisely these stages of the processes of hydrogen evolution and ionization.

The concept of a purely electrochemical mechanism of reaction (1) requires a decrease in isotope exchange when a cathodic or anodic overvoltage is imposed on the exchanging surface, corresponding to a decrease in the rate of the reverse ionic reaction.

The application of the isotope method made it possible to test the concept of the nature of reaction (1).

Fig. 1. Schematic of the polyethylene apparatus for measuring exchange currents. 1, 2—palladium membranes; 3—platinum anodes; 4—reference electrodes.

Figure 1: Fig. 1. Schematic of the polyethylene apparatus for measuring exchange currents. 1, 2—palladium membranes; 3—platinum anodes; 4—reference electrodes.

The apparatus in which the measurements were made consisted of three polyethylene sections, between which palladium membranes were clamped: the one under study between b and v, and the auxiliary one between a and b (Fig. 1). In sections a and b were placed solutions prepared with water of natural isotopic composition. In section v, in the experiments according to variant I, solutions of KOD or D_2SO_4 (90% D) were placed, and in the experiments according to variant II, an alkali solution enriched with tritium (0.2 Ci/cm^3). One of the surfaces of the membrane cathode under study served as the exchanging surface. Owing to cathodic polarization (0.05 A/cm^2) of the reverse side of the membrane, the exchanging surface was maintained in a state of stationary saturation with hydrogen—thereby ensuring the constancy of the hydrogen composition on it. Maintaining the saturation current during the experiment also caused continuous gas evolution, which occurred uniformly on both sides of the membrane. The stationary potential of the exchanging surface as a result of oversaturation by the polarizing current was always shifted by 0.04–0.02 V in···

to the cathodic side. The design of the apparatus made it possible, by anodic or cathodic polarization of the exchanging surface itself, to bring the overvoltage on it up to ±0.250 V. This was achieved with currents whose density did not exceed 1–5% of the saturation current density. Such a small opposing polarization could not change the composition of the adsorption layer on the exchanging surface, as was shown by separately performed measurements.

In experiments according to variant I, the heavy electrolyte of section exchanged with the adsorption layer of light hydrogen obtained on the right side of the surface of the membrane under study by saturating it with the light isotope from the side of section . As a result of the exchange that occurred, the volume of the membrane and the gases evolved on both its sides became enriched in deuterium. By measuring the rate of evolution and the isotopic composition of the gases, we could calculate the exchange rate with an accuracy of up to 25%.*

In experiments according to variant II, the heavy isotope—tritium—was used to label the adsorption layer of hydrogen that was created on the exchanging left side of the membrane under study by saturating it with enriched hydrogen from the side of section . As the exchange proceeded, tritium passed into solution. The activity of the solution, increasing with time, was measur—

Fig. 1. Schematic of the polyethylene apparatus for measuring exchange cur-

rents. 1, 2—palladium membranes; 3—platinum anodes; 4—reference electrodes.

* The gas was analyzed with a mass spectrometer with an accuracy of up to 0.005%.

Table 1

Membrane no.	Solution	Deviation from η_{stat}	Equilibrium isotope exchange, $\frac{\text{A}}{\text{cm}^2} \cdot 10^{-4}$	Isotope exchange under polarization, $\frac{\text{A}}{\text{cm}^2} \cdot 10^{-4}$	$i_{\text{extr}}, \frac{\text{A}}{\text{cm}^2} \cdot 10^{-4}$
I variant					
1	KOD (90% D), 1N	0	0.6	–	0.25
1	KOD (90% D), 1N	+0.040	–	0.5-0.4	0.25
1	KOD (90% D), 1N	+0.084	–	0.39	0.25
1	KOD (90% D), 1N	+0.130	–	0.25	0.25
1	KOD (90% D), 1N	+0.130	–	0.31	0.25
1	KOD (90% D), 1N	+0.060	–	0.50	0.25
1	KOD (90% D), 1N	0	1.2	–	0.25
2	Same	0	0.4	–	
2	Same	+0.170	–	0.16	
II variant					
1	KOH, 1N	0	1.5	–	1.25
1	KOH, 1N	−0.240	–	1.9	
2	KOH, 1N	0	3.0	–	1.6
2	KOH, 1N	−0.160	–	3.0	

Membrane no.	Solution	Deviation from η_{stat}	Equilibrium isotope exchange, $\frac{A}{cm^2} \cdot 10^{-4}$	Isotope exchange under polarization, $\frac{A}{cm^2} \cdot 10^{-4}$	i_{extr}, $\frac{A}{cm^2} \cdot 10^{-4}$
3	KOH, $1N$	0	0.8	–	0.3
3	KOH, $1N$	−0.240	–	0.8	
4	KOH, $1N$	0	1.6	–	0.3
4	KOH, $1N$	−0.200	–	0.7	
5	KOH, $1N$	0	2.75	–	1.6
5	KOH, $1N$	−0.200	–	1.25	
6	H_2SO_4, $1N$*	0	22.5	–	–
6	H_2SO_4, $1N$*	−0.075	–	12	

* Similar results were obtained in a number of other experiments in acid solutions.

was carried out with an internal-filling Geiger–Müller counter with an accuracy of not less than $±$7%. The experimental procedure for this series, which will be described in more detail elsewhere, provided for the virtually complete exclusion of oxygen from entering the electrolyte being enriched.

Table 2

Influence of surface activation on the exchange rate according to variant I

Membrane No.	Solution	External saturation current, mA/cm^2	Isotope exchange, a/cm^2 $\cdot 10^{-4}$	i_{extr}, a/cm^2 $\cdot 10^{-4}$
1	D_2SO_4 (90% D), 1N	10	3.7	1.0
1	D_2SO_4 (90% D), 1N	40	4.0	1.0

Fig. 2. Course of enrichment of the electrolyte with tritium in the process of exchange with the adsorption layer. a —surface active toward exchange; b —less active surface. At the top—overvoltage curves on the same electrodes (a—$i_{\text{extr}} = 1.6 \cdot 10^{-4}$ a, $i_0 = 3 \cdot 10^{-4}$ a; b—$i_{\text{extr}} = 3 \cdot 10^{-5}$ a, $i_0 = 1 \cdot 10^{-4}$ a)

Figure 2: Fig. 2. Course of enrichment of the electrolyte with tritium in the process of exchange with the adsorption layer. a —surface active toward exchange; b —less active surface. At the top—overvoltage curves on the same electrodes (a—$i_{\text{extr}} = 1.6{\cdot}10^{-4}$ a, $i_0 = 3{\cdot}10^{-4}$ a; b—$i_{\text{extr}} = 3{\cdot}10^{-5}$ a, $i_0 = 1{\cdot}10^{-4}$ a)

Membrane No.	Solution	External saturation current, mA/cm^2	Isotope exchange, a/cm^2 $\cdot 10^{-4}$	i_{extr}, a/cm^2 $\cdot 10^{-4}$
2*	D_2SO_4 (90% D), 1N	30	150	100
2*	D_2SO_4 (90% D), 1N	60	150	100

* The exchanging surface was activated by anodic-cathodic polarization.

Figure 2 presents the course of the experiments on two membranes differing in activity with respect to the exchange reaction. To express the exchange rate (in a/cm^2), the rate of enrichment of the electrolyte with tritium was measured under anodic polarization of the exchanging surface by a current of specified magnitude.

Fig. 2. Course of enrichment of the electrolyte with tritium in the process of exchange with the adsorption layer. *a* —surface active toward exchange; *b* —less active surface. At the top—overvoltage curves on the same electrodes (a—$i_{\text{extr}} = 1.6 \cdot 10^{-4}$ a, $i_0 = 3 \cdot 10^{-4}$ a; b—$i_{\text{extr}} = 3 \cdot 10^{-5}$ a, $i_0 = 1 \cdot 10^{-4}$ a)

The results of the experiments are summarized in Tables 1 and 2. From the data in these tables it is evident that the rates of isotopic exchange on all our electrode surfaces were 2-3 times greater than the exchange currents calculated from extrapolation of the overvoltage curves. In order of magnitude, the values of both rates are close to one another*.

When the activity of the exchanging surface is changed and when the composition of the electrolyte is changed (Tables 1 and 2), the values of the true

* In the experiments according to variant I (Table 1), the overvoltage curves of hydrogen ionization were recorded on electrodes saturated with light hydrogen, whereas in the experiments according to variant II the overvoltage curves

of hydrogen evolution were recorded upon polarization of the electrodes in a light electrolyte; thus, the values of i_{extr} refer to reactions of the light isotope. Accordingly, the difference between the rates of true exchanges and the values of i_{extr} is actually somewhat larger than that indicated in Table 1.

the exchange rates and extrapolated exchange currents change in the same way. The rate of enrichment of the gas with the heavy isotope decreases somewhat when an anodic overvoltage is applied to the exchanging surface. However, even at an overvoltage of +0.130 V, the enrichment rate decreases by only a factor of 2–3, whereas extrapolation of the overvoltage curve indicates that the rate of the hydrogen discharge reaction at +0.130 V decreases by more than a factor of 10. It follows from this that, on the exchanging surface, along with the discharge-ionization reaction, a reaction proceeds by another mechanism, which may be called the reaction of catalytic exchange.

The rate of enrichment of the electrolyte in alkaline solutions, when a cathodic overvoltage is applied to the exchanging surface, in most experiments does not change at all (Table 2). In those cases where some decrease is noticeable (this applies especially to acidic solutions), it is also 5–6 times smaller than the decrease in the rate of the hydrogen ionization reaction calculated from extrapolation of the ionization curve. Thus, cathodic polarization not only does not inhibit, but, on the contrary, somewhat increases the rate of "catalytic" exchange.

On the basis of the data presented, the following picture may be proposed for the mechanism of exchange on the hydrogen electrode*. A water molecule (or hydroxide ion) is adsorbed on the surface of palladium saturated with hydrogen in such a way that one of its hydrogen atoms is located directly on the metal surface. In such an arrangement, detachment of the hydrogen atom from the water molecule may occur with simultaneous replacement by an atom of the adsorption layer, i.e., an exchange chemical reaction that is not directly dependent on the potential drop at the metal-solution interface. According to this scheme, the rate of isotopic exchange is determined by the ability of the surface to adsorb and deform water molecules. Since adsorption and deformation of the adsorbed molecules change substantially, during polarization cases may be observed in which, with increasing cathodic potential, true isotopic exchange by the "catalytic" pathway is accelerated to such an extent that the inhibition of the ionic reaction becomes imperceptible.

We emphasize that the increase in the rate of isotopic exchange with increasing cathodic potential cannot be associated with an increase in the activity of hydrogen on the exchanging surface, since the activity, owing to saturation of the membrane from the outer side, was maintained constant.

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* In a private communication, A. N. Frumkin suggested the possibility of explaining the results obtained without resorting to the assumption that catalytic exchange exists, by imagining exchange according to the mechanism of so-called electrochemical desorption. In this case it is necessary to assume that the exchange current of the desorption stage considerably exceeds the exchange current of the discharge stage.

Note: Figure translations are in progress. See original paper for figures.

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