

INVESTIGATION OF THE INFLUENCE OF THE STATE OF THE DIFFUSION SIDE OF AN IRON MEMBRANE ON THE RATE OF DIFFUSION OF ELECTROLYTIC HYDROGEN

![Figure 1](figure)

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Abstract

Full Text

PHYSICAL CHEMISTRY

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**INVESTIGATION OF THE INFLUENCE OF
THE STATE OF THE DIFFUSION SIDE OF
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(Presented by Academician A. N. Frumkin, March 17, 1960)

In the present work we investigated the influence of the state of the surface of the diffusion side of an iron membrane on the rate of diffusion of electrolytic hydrogen v_d , while keeping the polarization conditions on the polarization side constant. In the literature there apparently are no indications that this question has been studied in the case of an iron electrode. The measurement procedure, the preparation of the membranes, and the apparatus in which the measurements were carried out have been described by us previously ⁽¹⁾. Hydrogen diffusion was produced by cathodic polarization of the polarization side in a solution of distilled HCl containing traces of $\text{Pb}(\text{NO}_3)_2$, or twice-distilled 2N H_2SO_4 , containing traces of $\text{Pb}(\text{NO}_3)_2$ and Na_2S , with a current of $50 \cdot 10^{-3}$ A/cm².* On the diffusion side the electrode was in contact with a 1N NaOH solution prepared from chemically pure alkali, or with alkali obtained by decomposing sodium amalgam in twice-distilled water, followed by purification from traces of mercury by prolonged cathodic polarization on a large Pt electrode. By the volumetric method described earlier, the rate of diffusion of hydrogen v_d was determined under cathodic polarization of the diffusion side with currents of $4 \cdot 10^{-6}$ and $2 \cdot 10^{-3}$ A/cm². Since, even when the experimental conditions on the polarization and diffusion sides were kept constant, the magnitude of v_d nevertheless changed somewhat with time, the measurements were carried out as follows. Low and high polarization of the diffusion side were alternated successively every 6 min, and the amount of hydrogen diffusing in 5 min at the given cathodic polarization of the diffusion side was measured. v_d was determined as the difference between the total amount of hydrogen liberated from the diffusion side v , and the amount of hydrogen liberated from the diffusion side according to Faraday's law v_ϕ as a result of its cathodic polarization: $v_d = v - v_\phi$ (v_d was expressed in cm³/min). In the case where the diffusion side had a clean iron surface—a surface activated by deposition of platinum or covered with galvanic deposits of nickel and copper—we found no influence of cathodic polarization of the diffusion side on v_d . However, after etching the diffusion side with mercury

Figure 1

Figure 1: Figure 1

or lead at a current density from the diffusion side

Fig. 1. Dependence of the diffusion rate on cathodic polarization of the diffusion side of an iron membrane at different fluxes of diffusing hydrogen: light points— $i_d = 2.5 \cdot 10^{-3}$ A/cm²; black points— $i_d = 4 \cdot 10^{-6}$ A/cm². *a*—pure iron, *b*—iron etched with mercury.

* Pb(NO₃)₂ and Na₂S were added in order to increase and stabilize over time the flux of diffusing hydrogen.

$i = 2 \cdot 10^{-3}$ A/cm², v_d proves to be higher than at $i_d = 4 \cdot 10^{-6}$ A/cm² (Fig. 1). In the case of iron poisoned with mercury, this effect may reach 25% with respect to v_d at $i_d = 4 \cdot 10^{-6}$ A/cm² and, as is evident from Fig. 1, does not depend on the absolute magnitude of the flux of diffusing hydrogen. The observed picture—at first glance paradoxical—of acceleration of the passage of hydrogen through the membrane under cathodic polarization of the diffusion side,

Fig. 2. Dependence of the diffusion rate on cathodic polarization of the diffusion side on iron poisoned with lead;

a— $i_d = 2 \cdot 10^{-3}$ A/cm², $\Delta\eta = -6$ mV; *b*— $i_d = 4 \cdot 10^{-6}$ A/cm²; *c*— $i_d = 2 \cdot 10^{-4}$ A/cm², $\Delta\eta = -3$ mV; *d*— $i_d = 2 \cdot 10^{-5}$ A/cm², $\Delta\eta = 10$ mV

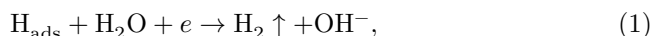
which, it would seem, should have slowed the passage of hydrogen, admits of two explanations.

It may be assumed that on the diffusion side, in the alkaline solution, there is an oxide film that impedes the diffusion of hydrogen; at $i_d = 2 \cdot 10^{-3}$ A/cm² it is reduced and the diffusion of hydrogen increases, whereas when the cathodic polarization of the diffusion side is decreased the oxide film reappears owing to traces of oxygen present in the solution, and the diffusion of hydrogen decreases. Probably, on pure iron the action of the oxide film should be more pronounced than in the case of iron poisoned with mercury or lead. We subjected this consideration to experimental verification by studying the influence of anodic polarization of the diffusion side with currents of $2 \cdot 10^{-6}$ – $2 \cdot 10^{-4}$ A/cm² on v_d in the case of pure iron and of iron poisoned with mercury and lead. The measurements were carried out in such a way that anodic polarization of a specified current density was alternated every 6 min with cathodic polarization by a current of $2 \cdot 10^{-3}$ A/cm². It turned out that on pure iron, under anodic polarization by a current $i_d = 2 \cdot 10^{-6}$ A/cm², the rate of hydrogen diffusion is the same as under cathodic polarization by currents $i_d = 2 \cdot 10^{-3}$ A/cm² and $4 \cdot 10^{-6}$ A/cm², and only a further increase in anodic polarization leads to a slowing of hydrogen diffusion (under anodic polarization by a current of $2 \cdot 10^{-4}$ A/cm² by $\sim 20\%$). An analogous phenomenon is also observed in the case of iron poisoned with mercury and lead; however, the retarding action of

Figure 3

Figure 2: Figure 3

anodic polarization in this case proves to be smaller than on pure iron. These experiments thus did not confirm the assumption made concerning the role of the oxide film. Another cause of the increase in v_d with cathodic polarization could be sought in the reaction of electrochemical desorption



which proceeds readily at high cathodic polarizations on iron poisoned with mercury and lead, as was shown previously ⁽¹⁾. To test this assumption, we determined the magnitude of the increase in v_d in the case of iron poisoned with lead, with a successive increase in the cathodic polarization of the diffusion side up to $2 \cdot 10^{-3}$ A/cm², comparing it with v_d at $i_d = 4 \cdot 10^{-6}$ A/cm², and compared it with the action of the diffusing hydrogen on the overvoltage on the diffusion side η at the corresponding cathodic polarizations from the diffusion side. As is evident from Fig. 2, an increase in the rate of hydrogen diffusion begins to be observed only at

at a cathodic polarization of the diffusion side ($2 \cdot 10^{-4}$ A/cm²), at which the diffusing hydrogen lowers η , i.e., at which removal of hydrogen from the electrode surface by the reaction of electrochemical desorption appears; a negative value of $\Delta\eta$ corresponds to a decrease in η under the influence of the diffusing hydrogen, and the increase in v_d grows as the decrease in η increases. These data confirm the assumption concerning the role of the electrochemical-desorption reaction in accelerating hydrogen diffusion under cathodic polarization of the diffusion side. If the existence of an equilibrium between dissolved hydrogen near the electrode surface and adsorbed hydrogen is assumed, then, since the rate of hydrogen diffusion is proportional to the difference in the concentration of hydrogen dissolved in the metal near the diffusion and polarization sides, it would follow from the above that, on electrodes poisoned with lead and mercury, the surface coverage by adsorbed hydrogen θ decreases with increasing cathodic polarization. In that case one would expect a decrease in the rate of hydrogen diffusion from an alkali solution through an iron membrane whose polarization side is poisoned with mercury as its cathodic polarization increases. The method we used made it possible to determine v_d volumetrically only within the range of variation of i_n from $40 \cdot 10^{-3}$ to $2.5 \cdot 10^{-3}$ A/cm²,*

Fig. 3. η on side *B* of an iron membrane under cathodic polarization with a current of $5 \cdot 10^{-5}$ A/cm² as a function of the cathodic polarization current of the opposite side *A* by currents: $b-i = 0$, $a-i = 3.5 \cdot 10^{-3}$ A/cm², $v-i = 4 \cdot 10^{-4}$ A/cm², $g-i = 1 \times 10^{-4}$ A/cm²

whereas the increase of v_d with increasing i_d was observed by us in the range of variation of i_d from $4 \cdot 10^{-6}$ to $2 \cdot 10^{-3}$ A/cm², i.e., at lower current densities.

In order to determine at least the direction of the change in v_d with i_n at low current densities, we carried out a series of measurements based on measuring the decrease in overvoltage η of an iron electrode poisoned with mercury in 1N NaOH solution, with increasing flux of diffusing hydrogen (2). One side (side *A*) of an iron membrane, poisoned with mercury in 1N NaOH solution, was successively subjected to cathodic polarization by currents $i = 0$; $3.5 \cdot 10^{-3}$; $4 \cdot 10^{-4}$, and $1 \cdot 10^{-4}$ A/cm²; at the same time the potential was measured of the opposite side *B*, also consisting of iron poisoned with mercury in 1N NaOH, maintained under constant cathodic polarization by a current $i = 5 \cdot 10^{-5}$ A/cm². It was shown (Fig. 3) that when cathodic polarization was applied to side *A* with a current of $3.5 \cdot 10^{-3}$ A/cm², η on side *B* decreased. Subsequent decreases in the cathodic polarization of side *A* of the membrane lead to an increase in η , which corresponds to a decrease in the flux of diffusing hydrogen. From the experimental material presented it follows that, on an iron electrode poisoned with mercury in alkali solution, the increase of v_d with i_d at $i_n = \text{const}$ cannot be explained by a decrease in θ with increasing cathodic polarization of the electrode on which atomic hydrogen is removed by the reaction of electrochemical desorption (1). Apparently, the accelerating effect of cathodic polarization on the process of diffusion of atomic hydrogen in the presence of electrochemical desorption is connected with the fact that hydrogen atoms located near the surface enter into the reaction

* In this range of variation of i_n we observed a linear increase of v_d with $\sqrt{i_n}$ (i_n is the current density of cathodic polarization of the polarization side).

dissolved hydrogen atoms, without passing through the "normal" equilibrium state of the adsorbed atom. In other words, the exit of atomic hydrogen from the metal into the solution occurs in a single elementary act of the electrochemical desorption reaction. This result requires some modification of the formulations in work (3).

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