ON THE INFLUENCE OF ANION ADSORPTION ON THE PROCESS OF DISCHARGE OF HYDROGEN IONS ON PALLADIUM AND THE IONIZATION OF HYDROGEN DISSOLVED IN PALLADIUM

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ON THE INFLUENCE OF ANION ADSORPTION ON THE PROCESS OF DISCHARGE OF HYDROGEN IONS ON PALLADIUM AND THE IONIZATION OF HYDROGEN DISSOLVED IN PALLADIUM

(Presented by Academician A. N. Frumkin, March 9, 1960)

Adsorption of halide ions, especially Br^- and J^-, retards the process of ionization of molecular hydrogen on a Pt electrode (^{1}). Adsorption of these ions, although to a somewhat lesser extent, also affects the rate of ionization of hydrogen adsorbed on platinum (^{2}, ^{3}). Cl^- anions slightly lower the overvoltage of this reaction; Br^- anions, depending on the contact time, lower or raise it. The iodine ion sharply retards the exchange between adsorbed hydrogen and the hydrogen ion.

In the present work, by the method of recording anodic charging curves and polarization measurements on a palladized electrode, the influence of adsorption of Cl^-, Br^-, and J^- anions on the process of ionization of hydrogen dissolved in palladium was studied. Previously this process had been studied (^{4}, ^{5}); however, the question of the influence of anion adsorption on it had not yet been treated in the literature.

For the measurements, a procedure and apparatus analogous to those described earlier (^{6}, ^{7}) were used. The electrode was a platinum plate with an area of 1 cm^2, onto which a definite amount of palladium was deposited electrolytically; the electrolysis conditions were chosen so as to obtain electrodes with a certain standard activity. The temperature was maintained at 20 ± 1°.

Measurements were carried out in HCl, HBr, KJ + 1N H_2SO_4, and KJ + 1N NaOH. The charging curves recorded in HCl (0.1N, 0.5N, and 2N) (polarizing current density $5{\cdot}10^{-4}$ a/cm^2, amount of palladium black on the electrode 0.0053 g) practically do not differ from the charging curves recorded in 1N H_2SO_4 under the same conditions, and are close to equilibrium curves.*

In the presence of Br^-, a certain violation of the reversibility of the process is observed, which is the more strongly expressed the higher the anion concentration and the longer the electrode has been in contact with the electrolyte containing Br^-. On such electrodes, under cathodic polarization, the evolution of gaseous

Figure 1

Figure 1: Figure 1

hydrogen begins before saturation of the electrode with hydrogen occurs. On going from Br^- to J^-, the deviations from reversibility become still greater. The curves of the dependence of potential on the amount of electricity passed, recorded in KJ + 1N H_2SO_4 solutions, are given in Fig. 1. Curve 2, recorded in 0.01N KJ, still retains a form close to that of the curve in 1N H_2SO_4, although the overvoltage of the process of ionization of dissolved hydrogen in the β-phase is considerably increased, the plateau corresponding to the phase transition is deformed, and the width of the hysteresis loop reaches 60-70 mV. Curves 3 and 4, recorded in 0.1N and 1N KJ, already have a form completely different from the curve in 1N H_2SO_4. The overvoltage at the beginning of the ionization of dissolved hydrogen increases to 50-90 mV; the plateau corresponding to the phase transition disappears; and the width of the loop—hysteresis increased to 350 mV. It was not possible to obtain curves in $0.1N$ KJ and $1N$ KJ up to potentials more anodic than 200-300 mV, since dissolution of palladium occurred. Increasing the time for which the electrode remained in the solution containing KJ before the start of measurements leads to an intensification of the deformation of the charging curve (curves 2 and 5 in Fig. 1).

Fig. 1. Curves of the dependence of the potential of a palladium electrode on the quantity of electricity passed.
1 $-1N\ H_2SO_4$; 2 $-0.01N$ KJ $+\ 1N\ H_2SO_4$; 3 $-0.1N$ KJ $+\ 1N\ H_2SO_4$; 4 $-$ $1N$ KJ $+\ 1N\ H_2SO_4$; 5 $-0.01N$ KJ $+\ 1N\ H_2SO_4$ after an 18-hour stay of the electrode in this solution.

On the basis of the data obtained on the influence of KJ adsorption on the shape of the charging curves, it could be assumed that the amount of hydrogen dissolved in Pd decreases when J^- is introduced into the solution. In order to test this assumption, the shift of the electrode potential upon adsorption of J^- was studied. When a KJ solution was introduced into the system, the electrode potential, equal to the potential at the beginning of the phase transition (60-70 mV), shifted in the cathodic direction by 10-15 mV, but then rapidly returned to its initial value. If the total amount of hydrogen dissolved in Pd decreased upon adsorption of J^-, the observed potential shift would be stable.

Since this does not occur, apparently the total amount of hydrogen dissolved

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* In the region of the β α transition of the Pd—H system, as is known, there are always certain deviations from equilibrium, which lead to the appearance of a hysteresis loop when charging curves are recorded in the forward and reverse directions. This phenomenon is also observed in 1N H_2SO_4 (see Fig. 1).

Figure 2

Figure 2: Figure 2

Fig. 3

Figure 3: Fig. 3

in Pd remains constant. A small shift of the potential in the cathodic direction is associated with adsorption of iodide ions; as a result of the restoration of equilibrium between hydrogen in Pd and hydrogen ions in the solution, the initial value of the potential is restored.

Fig. 2. a —curves of the dependence of potential on the quantity of electricity passed in the region of the β-phase (forward (2) and reverse (3) run), obtained in a solution of $5 \cdot 10^{-3}$ KJ $+ 1N\ H_2SO_4$ at a current density $I = 5.5 \cdot 10^{-5}$ A/cm^2, and potential values measured at open circuit (4, 5). 1 $-1N\ H_2SO_4$; $I = 5 \cdot 10^{-4}$ A/cm^2; b —curves of the dependence of overvoltage on the logarithm of the current density.

We also carried out measurements of the dependence of the potential of a palladized electrode on the quantity of electricity passed in sol—

solution of 0.005 N KJ + N H_2SO_4 at different densities of the polarizing current for hydrogen-saturated β-phases. Figure 2a shows curves obtained under anodic polarization, under cathodic polarization following the anodic polarization, and also gives the values of potentials measured after the current was switched off. As is seen from Fig. 2, the sections of the forward and reverse paths of the polarization curves do not coincide; neither do the curves expressing the dependence of the potential values, measured at open circuit, on the amount of hydrogen in palladium after cathodic and anodic polarization, whereas in 1 N H_2SO_4 in this case their complete coincidence was observed. With an increase in the density of the polarizing current the discrepancies increase more and more. The dependence of the magnitude of the deviation of the potential of the palladized electrode from the equilibrium potential of the β-phase of the same composition on $\lg I$ is linear, with a proportionality coefficient of 180 mV (Fig. 2b).

Measurements carried out in alkaline solutions with additions of KJ at various concentrations showed (Fig. 3) that the effect of J^- on the ionization process of dissolved hydrogen on palladium is very small. The small effect observed has the opposite sign.

Fig. 3. Charging curves in 1 N NaOH in the presence of KJ (forward and reverse paths). Density of the polarizing current $I = 5 \cdot 10^{-4}$ a/cm^2. Dashed line—values of the potential measured after switching off the current.
1—1 N NaOH; 2—1 N NaOH + $5 \cdot 10^{-3}$ N KJ; 3—1 N NaOH + $5 \cdot 10^{-2}$ N KJ; 4 —1 N NaOH + $5 \cdot 10^{-1}$ N KJ.

The dependence of the overvoltage in the region of the β-phases on $\lg i$ at sufficiently high current densities in alkaline solutions is linear, with a proportionality coefficient of 0.09–0.1 V. The same dependence, determined in the region of the phase transition, is also linear.

The small magnitude of the effects caused by J^- in alkaline solutions is evidently connected with the fact that the shift of the electrode potential to the negative side on going from acidic to alkaline solutions leads to a sharp decrease in the adsorption energy of J^-. The action of the relatively weakly adsorbed J^- ions is determined no longer by their influence on the bond energy of adsorbed hydrogen with palladium, but, as in the case of adsorption of J^- on mercury, by a change in the structure of the double layer. The slight decrease in overvoltage in alkaline solutions in the presence of J^- can be explained by facilitation of the orientation of dipole water molecules with the positive (i.e., hydrogen) end toward the electrode, which facilitates their discharge.

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