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Abstract

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Electrochemical Determination of the Heat of Adsorption of Hydrogen on a Disperse Palladium Electrode

(Presented by Academician A. N. Frumkin, April 19, 1961)

The study of the absorption of hydrogen by palladium from the gas phase did not make it possible to distinguish between the adsorption and dissolution processes occurring in this case. This was accomplished only in the presence of an electrolyte, using the charging-curve method (1).

Adsorption of hydrogen on palladium takes place in the pressure range $10^{-10} \div 10^{-2}$ atm, and the specific adsorption of solution anions on the electrode leaves its mark on the form of the corresponding isotherms. In acid solutions the effect of anion adsorption on the strength of the bond between hydrogen and the metal decreases in the series $Br^- > Cl^- > SO_4^{2-}$. As experiments with a platinum electrode have shown (2), the specific adsorption of the SO_4^{2-} ion is insignificant; therefore it may be expected that determining the heat of adsorption of hydrogen on palladium in the presence of sulfuric acid will apparently give results close to the data for adsorption from the gas phase.

Preparation for the experiment and a description of the apparatus for recording charging curves are given in (1). The experimental procedure was altered somewhat: ionization of the hydrogen dissolved in palladium was carried out with a current of 0.6 mA, and when the adsorption portion of the charging curve was investigated the current was reduced to 0.1 mA. Palladium black (0.006–0.012 g) was deposited on a platinum electrode from a hydrochloric-acid solution of $PdCl_2$ at a current density of 70 mA/cm^2. In order to avoid errors associated with a decrease in the surface area of the samples under study upon heating, the experiment at the highest temperature was always carried out first—in our experiments, at 43°. Charging curves measured in different electrolytes make it possible to separate the regions of absorption and adsorption, since ionization of dissolved hydrogen does not depend on the nature of the electrolyte.

Fig. 1. Adsorption portions of charging curves for a Pd electrode in 1 N H_2SO_4 (1) and 1 N HCl (2); $t = 18°$.

The general form of the adsorption portions of the charging curves of a palladium electrode in hydrochloric and sulfuric acids is shown in Fig. 1. Owing to the

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Fig. 2

Figure 2: Fig. 2

considerable adsorption of the Cl^- ion, the bond strength of the adsorbed H atom with the metal is weakened; therefore its ionization requires a smaller expenditure of energy, and the charging curve in HCl lies in the region of lower anodic potentials than the corresponding curve in H_2SO_4.

For the charging curves of a palladium electrode in sulfuric acid, a plateau at $\varphi = 250$ mV* is characteristic, also observed on a number of Pd—Ag alloys (^{3}). This section is present both on the anodic and on the cathodic charging curves and changes its shape only slightly with temperature. In HCl the plateau is located at lower values of φ and is not so sharply expressed. The point of divergence of the charging curves of one and the same electrode, measured in different electrolytes, determines the potential and, correspondingly, the pressure at the onset of hydrogen dissolution. Without great error it may be assumed that at this value of the potential hydrogen adsorption on Pd ends and the metal surface is completely filled with hydrogen.

At 43°, the samples of palladium black studied by us adsorbed 0.09 g-at H/g-at Pd. A decrease in temperature was accompanied by a slight decrease in adsorption.

Fig. 2. Effect of filling of the Pd surface with hydrogen on the electrode potential.
H_2SO_4: 1 –0°; 2 –18°; 3 –23°; 4 –43°;
HCl: 5 –43°.

Fig. 3. Dependence of $(\lg P_{H_2})_{\theta=\text{const}}$ on temperature (Pd in H_2SO_4).

The experiments were carried out at 43, 23, 18, and 0° on one and the same electrode; the apparatus was not dismantled, only the temperature of the thermostat was changed. Since the duration of the whole cycle was from 2 to 4 days, the surface of the palladium black decreased somewhat, and the adsorption sections of the charging curves at 43°, recorded at the beginning and at the end of the cycle, differed noticeably in length.

Fig. 3

Figure 3: Fig. 3

In processing the results of individual measurements, the beginning of adsorption (filling $\theta = 0$) was determined from the transition of the slightly sloping section of the charging curve into the steeply rising linear section of double-layer charging ($\varphi = 40 \div 70$ mV), and the beginning of dissolution ($\theta = 1$), as indicated, from the point of divergence of the charging curves of one and the same electrode, measured in electrolytes (H_2SO_4 and HCl). The principal error in determining the point of onset of adsorption falls on the value of the potential; the error along the time axis (amount of electricity) is small.

The point of onset of hydrogen dissolution was determined in separate experiments and for the temperatures studied, 43, 23, 18, and 0°, was respectively equal to 54, 65, 70, and 82 mV. In determining the length of the charging curves, a correction was introduced for the amount of electricity corresponding to double-layer charging in the potential interval from the beginning of dissolution to the beginning of adsorption, analogously to how this was done by A. N. Frumkin and A. N. Shlygin in studying the platinum electrode (^{4}).

* All potential values are reckoned from the potential of the hydrogen electrode in the same solution.

The adsorption portions of the charging curves in coverage—potential coordinates for one and the same temperature coincided within 2-3 mV, both in experiments on a single electrode and for different loadings of palladium black. The results of experiments in H_2SO_4 for the four temperatures studied are shown in Fig. 2. Since the electrode potential is related to the pressure by the Nernst equation, the curves obtained correspond to adsorption isotherms in the coordinates $\lg P_{\mathrm{H2}}, \theta$. Immediately after the arrest at φ = 240—260 mV there is a linear section of the charging curve, corresponding to the semi-logarithmic adsorption isotherm (^{5}). The next, gently sloping section corresponds to the region of high coverages. Similar experiments were carried out in HCl solution. Fig. 2 shows the adsorption portion of the corresponding charging curve, measured at 43°. In this case the arrest preceding the linear section is expressed less clearly than in H_2SO_4, but extends to higher values of θ.

The experimental material obtained makes it possible to calculate the heat of adsorption of hydrogen on palladium at a constant value of θ, using the Clausius—Clapeyron equation.

As is seen from Fig. 3, which gives data for several coverages, the dependence of $(\lg P)_{\theta=\mathrm{const}}$ on reciprocal temperature is linear.

The slight scatter of points for small θ at 0° is due to the fact that, as the temperature is lowered, the first arrest on the charging curve (Fig. 2) extends over a large region of coverages. The calculated values of the heat of adsorption Q are given in Fig. 4. The data obtained in the presence of SO_4^{2-} ions are characterized by constancy of the heat of adsorption in the interval $0 < \theta < 0.5$, just as was the case in studies of hydrogen adsorption on platinum in the works of Mexted and Hassid (^{6}) and Kwan (^{7}). The independence of the heat of ad-

Fig. 4

Figure 4: Fig. 4

sorption from coverage includes almost the entire region of the semi-logarithmic isotherm. The heat of adsorption of hydrogen on palladium in this region of θ proved to be 27.5 kcal/mole, which is very close to the value obtained by Bick ([8]) for adsorption from the gas phase; further filling of the metal surface is accompanied by a decrease in Q. The general form of the heat-of-adsorption—coverage curve resembles the dependence of Q on θ calculated for mobile layers formed in the dissociation of diatomic molecules into atoms ([9]).

Fig. 4. Effect of coverage on the heat of adsorption of hydrogen on Pd (1) and on an alloy of 42% Ag, 58% Pd (2) in H_2SO_4, and on Pd in HCl (3)

The lower values of Q at $\theta = 0.05$—0.15 may be connected with the fact that we are dealing with different forms of bonding of hydrogen to the metal.

The heat of adsorption of hydrogen on palladium in HCl solution, as was to be expected, is considerably lower (Fig. 4). The region of constant values of Q in this case is almost completely distorted.

The character of the change in the heat of adsorption of hydrogen on palladium with coverage resembles the corresponding curve for the heat of dissolution ([10]).

In addition to palladium, measurements of the heat of adsorption in $1\,N$ H_2SO_4 were carried out on several Pd—Ag alloys. The dependence Q, θ for an alloy containing 8 at.% silver is the same as on Pd. On the charging curves of alloys containing $> 32\%$ Ag, there was no arrest in the region $\varphi = 240 \div 260$ mV; correspondingly, on the curve for the alloy with 42% Ag (Fig. 4) no distortions were observed in the region of small θ.

Our results on Pd resemble the data of Böld and Breiter ([11]), who used a somewhat different electrochemical method to determine the dependence of the heat of adsorption of hydrogen on θ for Rh. In the case of Pt, according to the same data, the heat of adsorption changed only slightly with cov—

only in the interval $0.5 \leq \theta \leq 0.75$. In all cases, no linear variation of Q with θ was observed in the semilogarithmic portion of the isotherm.

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