ADSORPTION OF HYDROGEN ON TUNGSTEN IN A SOLUTION OF ALKALI

L. I. Krishtalik and B. B. Kuz'menko

UDC 541.13

As we have mentioned before [1], the considerable adsorptive capacity found in alkaline and acidic solutions at cathodic potentials [1,2] is at variance with data on the measurement of the adsorption of hydrogen from the gas phase on the surface of tungsten. The measurements made by Roberts on pure tungsten filament [3] showed that even with a hydrogen pressure of $3 \cdot 10^{-4}$ mm Hg the surface is completely covered with a monolayer of chemisorbed hydrogen atoms. Therefore, the formation of adsorptive capacity due to further deposition of hydrogen atoms on the surface with increase in the cathodic potential could only be explained by the following assumptions. 1) The W–H bond is largely weakened under the influence of the solvent, the hydrogen atoms are displaced by water molecules, and room is made for deposition of additional hydrogen atoms; such an assumption was earlier used to explain features of the behavior of metals in the iron group [4]; 2) the adsorption of hydrogen exceeds a monolayer in thickness; 3) the hydrogen dissolves in the metal.

To check the first of these possibilities, on the suggestion of A. N. Frumkin, we carried out the following experiment, the idea of which goes back to the work of Obrucheva [5]. It consists in measurement of the amount of hydrogen desorbed after the large surface of tungsten powder saturated with hydrogen has been wetted with the solution; the hydrogen should be released if significant weakening of the W–H bond does in fact occur in the solution.

Figure 1 shows a diagram of the apparatus. A 110-g portion of tungsten powder of grade VCh-3 was placed in the mixer 1, made from quartz. This powder was obtained by reduction of tungsten trioxide, and its impurity content was not greater than 0.06%, of which 0.04% was CaO and SiO_2. The specific surface area of the powder was measured by the BET method, and amounted to 0.95 m^2/g. * Before being filled the mixer was thoroughly washed and dried. The taps and joints were greased with high-temperature vacuum grease. The apparatus was flushed with hydrogen for several hours; the hydrogen was obtained electrolytically with standard purification and before introduction into the apparatus was in addition passed through two U tubes filled with purified activated charcoal and cooled with liquid nitrogen. The mixer was then heated and held at 750°C for 24 h. During this time the powder was in a stream of hydrogen. According to [6], this treatment of the powder secured complete reduction of its surface and saturation with a monolayer of chemisorbed hydrogen atoms. After the powder had cooled a 1 N potassium hydroxide solution was poured into vessel 3 and blown vigorously with hydrogen for 1 h. The hydrogen in the mixture was then pumped

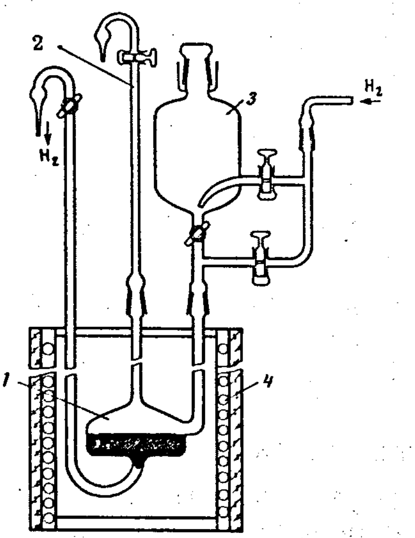

Fig. 1. Diagram of apparatus: 1) mixer; 2) buret; 3) vessel for solution; 4) furnace.

---

*The surface area was determined by F. Z. Sabirov and N. G. Bulavina, to whom we express our gratitude.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 9, No. 5, pp. 664-666, May, 1973. Original article submitted September 30, 1972.

out with a backing pump, and the solution from vessel 3 was admitted to the mixer, where it wetted the powder and filled the buret 2. An unfilled space of approximately 1 ml remained at the top of the buret, and this was due to the residual pressure of hydrogen in the mixture, the volume of which amounted to approximately 150 ml.

During the first minute after contact between the solution and the powder hydrogen bubbles were released; they broke away from the surface of the powder, floated up, and displaced the solution in the buret. The total volume of hydrogen released was 0.1-0.2 ml.

It is difficult to assert that this amount of hydrogen was desorbed from the metal surface and was not the residual volume of gas trapped between the particles of powder during the rapid filling of the mixer with solution. In any case, this volume was extremely small compared with the total amount of adsorbed hydrogen. According to data in [7], the monolayer adsorption of hydrogen on tungsten amounts to $1.2 \cdot 10^{15}$ atom/cm^2, which converted to the conditions of our experiments (104.5 m^2) corresponds to 23 ml. Thus, the possible displacement of hydrogen during wetting of the powder does not exceed 1% of its initial amount. To explain the large values for the adsorptive capacity observed over a wide range of potentials [1] it is necessary to assume the possibility of additional adsorption of at least 0.3-0.4 monolayer. Consequently, the presented data show conclusively that the displacement of adsorbed hydrogen by water molecules does not play a significant part and cannot explain the observed adsorptive capacities.

The most likely explanation seems to us adsorption of hydrogen in a second monolayer. The saturation of a surface by hydrogen adsorbed from the gas phase, observed in adsorption experiments, may signify complete coverage of only one type of adsorption center. If there is another type of adsorption with a significantly lower bond energy, under the usual conditions of adsorption experiments these centers will be almost free, and adsorption on them will only begin with extremely significant increase in the chemical potential of hydrogen.*

In previous papers [1,2] it was shown that the most likely slow stage in the cathodic hydrogen evolution process is removal of adsorbed hydrogen atoms by their recombination. This means that on the surface of the electrode there must be a superequilibrium concentration of adsorbed hydrogen, i.e., its chemical potential must be significantly increased. In particular, if the discharge–ionization reaction is almost reversible here, the chemical potential of the hydrogen is increased by the quantity ηF, which under conditions of our experiments is equivalent to an enormous increase in pressure (by ten orders of magnitude or more). Therefore, the suggestion that the chemical potential of hydrogen is high enough for appreciable adsorption of hydrogen in a second monolayer is perfectly reasonable. The high energy level of the atomic hydrogen during cathodic polarization makes it possible, in principle, for it to dissolve appreciably in the volume of the metal, although at normal temperatures and pressures the solubility of hydrogen in tungsten is vanishingly small [8]. Unfortunately, the available data do not make it possible to distinguish between the contributions of adsorbed and dissolved hydrogen to the measured adsorptive capacity.

The arguments presented above can in principle apply not only to tungsten but also to other metals which readily adsorb hydrogen. It is known, for example, that with hydrogen at atmospheric pressure monolayer coverage is reached on platinum [9]. However, the cathodic behavior of activated platinum is best described by a slow recombination mechanism [4, 9] and is in all probability due to additional accumulation of hydrogen, i.e., adsorption of a second monolayer. It should be noted that recently Gokhshtein obtained arguments in favor of the idea that during monolayer coverage of platinum with hydrogen one of the two types of adsorption centers is only half filled [10].

LITERATURE CITED

1. B. B. Kuz'menko and L. I. Krishtalik, Élektrokhimiya, 9, 130 (1973).
2. B. B. Kuz'menko and L. I. Krishtalik, Élektrokhimiya, 9, 237 (1973).
3. I. K. Roberts, Proc. Roy. Soc., A152, 445 (1935).
4. L. I. Krishtalik, Advances in Electrochemistry and Electrochem. Engng., 7, 283 (1970).
5. A. D. Obrucheva, Zh. Fiz. Khim., 32, 2155 (1958).
6. W. Frankenburg, J. Am. Chem. Soc., 66, 1827 (1944).

---

*The metal atoms and interstices could, for example, serve as models of two such types of adsorption centers.

7. D. Hayward and B. Trapnell, Chemisorption, Plenum Press (1964).
8. A. A. Mazaev, R. G. Avarbé, and Yu. N. Vilk, Zh. Fiz. Khim., 42, 641 (1968).
9. A. N. Frumkin, Advances in Electrochemistry and Electrochem. Engng., 3, 287 (1963).
10. A. Ya. Gokhshtein, Élektrokhimiya, 7, 594 (1971).