INVESTIGATION OF THE EVOLUTION OF HYDROGEN ON TUNGSTEN IN ALKALINE SOLUTIONS

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

UDC 541.13

The study of the evolution of hydrogen on tungsten is of interest from the standpoint of the general theory of the hydrogen overvoltage, since tungsten is one of the strong adsorbents of hydrogen. The literature data on the overvoltage of hydrogen on tungsten, especially in alkaline solutions, are extremely scanty. In addition to the study [1], which does not correspond to the modern requirements, we know only of the work of Bockris and Srinivasan [2], who measured the overvoltage and coefficient of separation of isotopes in 0.5-N NaOH. On the basis of the latter quantity, the authors arrived at a mechanism of decelerated discharging with subsequent rapid recombination; however, this conclusion cannot be considered unambigious. The purpose of this work was an investigation of the basic kinetic characteristics of the process.

EXPERIMENTAL

The Pyrex glass cell for polarization measurements is shown in Fig. 1. The working surface of the investigated electrode was the end of a tungsten wire 1 mm in diameter, embedded flush in glass, turned upward. During the preparation of the electrode, the wire was sealed into a Pyrex tube and cut on a diamond disc. To prevent leakage of the electrolyte, special attention was paid to the quality of the seal. The tungsten used contained no more than 0.01% impurities. The reference electrode was a hydrogen electrode in the same solution. Solutions of KOH were prepared from the analytical grade reagent, while solutions of LiOH, CsOH, $Ba(OH)_2$, and tetrabutylammonium were prepared from cp reagents.

Concentrated solutions of alkali were purified by electrolysis on smooth platinum electrodes with a current of 0.5 A/cm^2 in an individual cell for 12 h; the electrodes were periodically removed and etched. Then the solution of set concentration was treated in one of the auxiliary compartments of the cell on a platinized grid with visible surface 48 cm^2 with a current of 1 mA with intensive mixing with a magnetic mixer and purging with hydrogen for 10-12 h. The solutions were prepared in double-distilled water. K_2SO_4 was recrystallized twice and calcined at 700°.

The vessels and cell were washed with sulfuric acid in a mixture with perhydrol, then with double-distilled water, and steam treated. The investigated electrode was washed in hot alkali, then in double-distilled water, and set up in the cell. The measurements and change of solutions were performed in an atmosphere of hydrogen, which was produced electrolytically, followed by standard purification, and, moreover, was passed through purified activated charcoal, cooled with liquid nitrogen. The cell was placed in an air thermostat, and the temperature maintained with an accuracy within ±0.2°. The overvoltage was measured with an LP-5 tube potentiometer. A PO-5122 oscillographic polarograph was used to determine the adsorption capacity.

A peculiarity of the method we used is the possibility of simultaneous treatment of two different solutions on auxiliary electrodes 2 and 2'. The solutions were mixed in the required concentrations in the cathode compartment; mixing was ensured by intensive purging with hydrogen. Part of the solution prepared in the cathodic compartment was delivered to the compartment of the reference electrode, which was preliminarily washed twice with the same solution. The solution was replaced without disconnection from the polarization source. This method permitted measurements in a series of solutions of varying concentrations on the same electrode in a short period of time, which is especially important on account of the poor reproducibility of the data on different electrodes and the possible change in the state of the

---

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 9, No. 1, pp. 130-135, January, 1973. Original article submitted June 5, 1972.

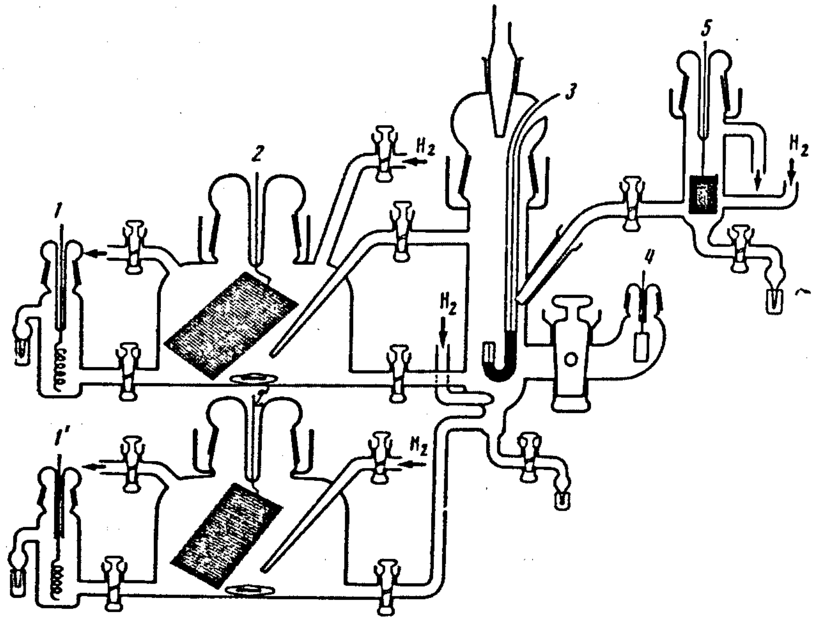

Fig. 1. Cell for polarization measurements: 1, 1', 4) anodes; 2,2') auxiliary cathodes; 3) investigated electrode; 5) reference electrode.

surface with time. Although the absolute values of the overvoltages on different electrodes showed extremely substantial discrepancies, the nature of the concentration dependences taken on the same electrode proved the same in all cases.

EXPERIMENTAL RESULTS

After immersion of the electrode in the solution, the state of the surface varied with time, and the change in the overvoltage was ±50 mV. However, after 2-3 days there was a stabilization of the state of the surface, as a result of which the polarization curve was shifted by no more than 7-8 mV per day. All the results cited were obtained on a stabilized surface. The polarization curves were taken as rapidly as possible (in 4-5 min), and also slowly (1-2 h), from the top down and from the bottom up; the results practically coincide, and hysteresis did not exceed 7 mV. The surface of the electrode was apparently freed of phase oxides, since they are readily soluble in alkalies [3, 4]. This is confirmed by the fact that the cathodic reduction of the surface at a current density of 10^{-2} A/cm^2 for several hours did not influence the results of the measurements.

Figure 2a presents a typical series of polarization curves in KOH solutions of various concentrations. The upper part of curve 3 is apparently somewhat distorted by ohmic losses. The lack of coincidence of curves 1 and 5 within 20-40 mV is evidence that the state of the surface was changed to some degree when the solution was diluted. The polarization curve 1 has a monotonically varying slope, which is equal to 206 mV at a current density of $10^{-1.5}$ A/cm^2, 118 mV at $10^{-3.5}$ A/cm^2, and 56 mV at $10^{-4.5}$ A/cm^2. The substantial decrease in the slope in the region of the lowest overvoltages may be due to the current of self-dissolution of tungsten.

Self-dissolution may occur as a result of the reaction: $W + 4H_2O = WO_4^{-2} + 8H^+ + 6e$, for which the equilibrium potential [5] in 1-N KOH relative to a hydrogen electrode in the same solution lies in the range from 227 to -286 mV when the WO_4^{2-} concentration is varied from 10^{-6} to 1 M. However, the reaction does not reach equilibrium, probably on account of its limited rate [6].

Figure 2b presents the polarization curves in a mixture of KOH and K_2SO_4. When curve 4 was recorded, a sensitivity of the overvoltage to mixing of the solution was detected, which is an indication of a possible superposition of concentration polarization in such a dilute solution. The state of the surface changes to a lesser degree than in the case of solutions of pure alkalies when the OH^- concentration is reduced, which is evidenced by the discrepancy of curves 1-5 within 20 mV. The influence of the nature of the cation on the polarization curves is shown in Fig. 3. The polarization curves were also taken in 0.5-N $Ba(OH)_2$. The

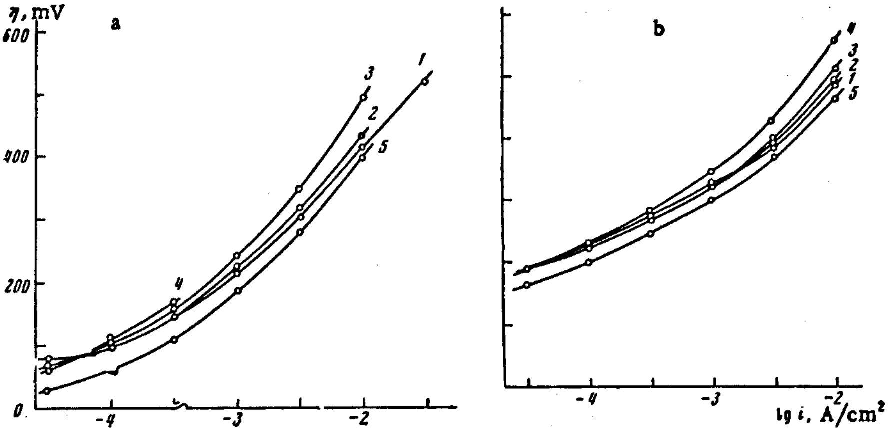

Fig. 2. Polarization curves in solutions of KOH; a) pure KOH with concentration 1–1; 2–0.097; 3–0.026; 4–0.0075; 5–1 N, b) mixture of KOH and K_2SO_4 with constant total concentration of ions K^+. KOH concentration equal to: 1–1,1; 2–0.0078; 3–0.037; 4–0.008; 5–1.1 N. The curves, just as in Fig. 3, were taken during a day in the sequence indicated by their numbers. The temperature in all the experiments was -30°.

measurements showed a negligible ($\lesssim$ 20 mV) increase in the overvoltage in $Ba(OH)_2$ in comparison with KOH. Figure 4 is one of the typical potentiodynamic curves; the total current i_t, which is equal to the sum of the current of evolution of molecular hydrogen i_{H_2}, which depends on the overvoltage, and the capacitance current i_{cap}, which depends on the rate of development, is plotted along the Y axis. When V = 0.0125 V/sec, $i_{cap} \ll i_{H_2}$, and the total current is equal to i_{H_2}. If we assume that at large V, i_{H_2} is practically the same as at V = 0.0125 V/sec, then in this case the difference between the values of the ordinates of curves 2, 3, 4, and 1 at a given η is equal to the value of the capacitance current, from which we can estimate the value of the capacitance. For example, when η = 300 mV and V = 20 V/sec, C = 500 $\mu F/cm^2$ is a quantity known to be greater than the double-layer capacitance, and, consequently, is of the nature of adsorption capacitance.

This value should be considered only as an approximate estimate. The areas included between curves 2 and 1, 3 and 1, and 4 and 1, bounded by straight lines parallel to the Y axis, give us the amount of electricity consumed for the deposition of hydrogen when η is varied from 180 to 430 mV, with the corresponding rate of development. At rates of development 10, 20, and 40 V/sec, these amounts ensure liberation of $9.31 \cdot 10^{14}$, $8.3 \cdot 10^{14}$, and $7.25 \cdot 10^{14}$ atoms per unit visible surface, respectively. Assuming a roughness factor equal to 2, and a number of tungsten atoms per cm^2 of surface equal to $12.15 \cdot 10^{14}$ [7], we find that this is equivalent to a coverage of 0.38, 0.34, and 0.30 monolayer.

For a determination of the actual activation energy A, we took the polarization curves in 1-N KOH at various temperatures in the range from 10 to 50°C. The quantity $A = A_0 - \alpha \eta F$ was determined from the slope of the linear dependence of i on 1/T at constant η. Measurements performed on three different electrodes gave value of A equal to 5.8, 5.5, and 7.8 kcal/mole at η = 480, 400, and 350 mV, respectively. The transport coefficients α were calculated from the slopes of the polarization curves at the same η. The calculated values of A_0 proved equal to 10.2, 9.2, and 11.0 kcal/mole. From this the average value for the activation energy A_0 at η = 0 is 10.1 kcal/mole.

DISCUSSION OF RESULTS

The substantial value of the adsorption capacity contradicts the data on the practically complete coverage of the surface at normal pressure, which occurs in the case of adsorption of H_2 from the gas phase [7]. This may be explained either by a great weakening of the W-H bond in solution and displacement of hydrogen atoms by water molecules, or by the formation of multilayer coverage, or by partial dissolution of hydrogen in the metal. The deposition of a substantial amount of hydrogen on the surface with increasing η indicates a substantial irreversibility of the step of removal of H atoms.

From the polarization curves of Fig. 2, it follows that the dependence of η on the pH is extremely weakly expressed. In a solution of pure alkali a weak increase in η is observed with increasing pH, and

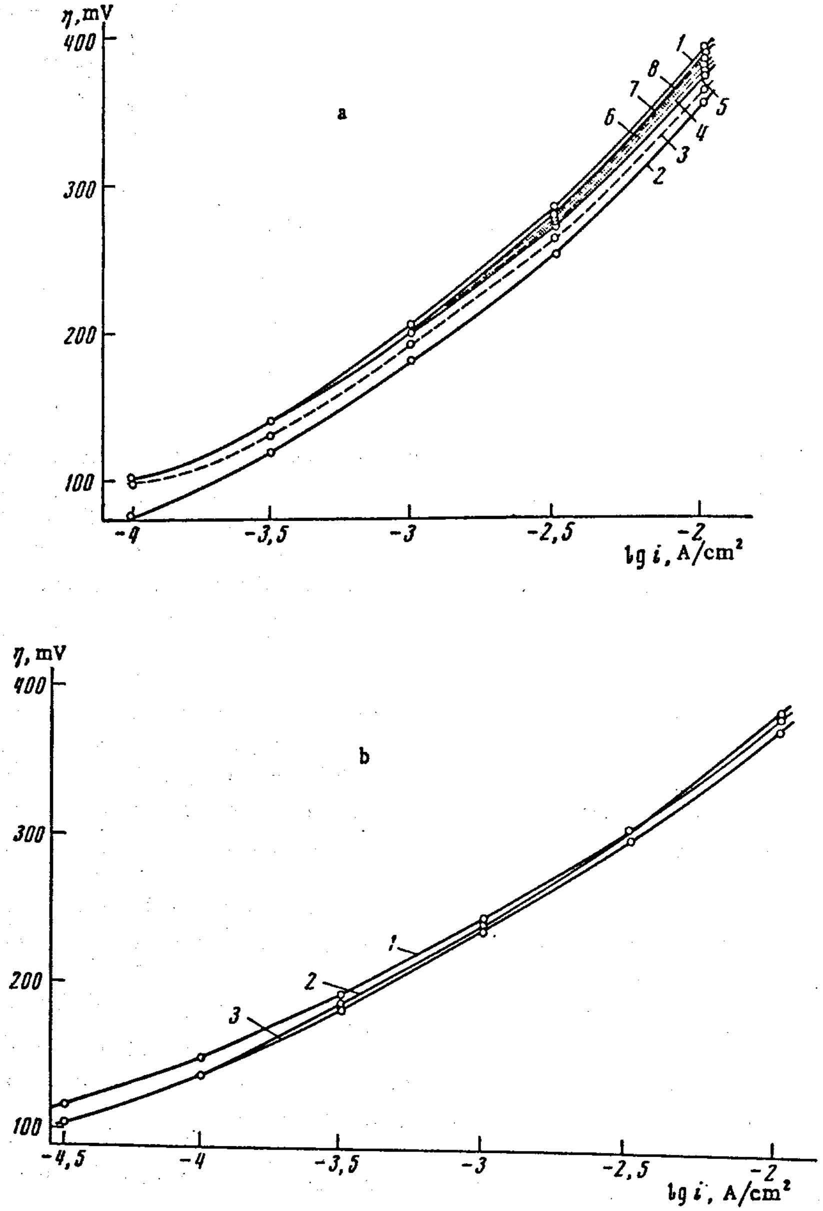

Fig. 3. Polarization curves in solutions of various alkalies. a) 1, 3, 4, - 0.5 N KOH; 2 - 0.5 N NaOH (curve 4 was taken 5 h after curve 3, and in the interim η = 150 mV was maintained); 5 - 0.5 N CsOH; 6 - 0.5 N KOH; 7 - 0.5 N LiOH; 8 - 0.5 N KOH. b) 1, 3 - 0.5 N KOH; 2 - 0.5 N $N(C_4H_9)_{11}OH$.

the most probable effect is from zero to 20 mV per pH unit (compare curves 1 and 2 of Fig. 2). At a constant concentration of cations, the influence of the pH is even smaller in absolute magnitude and has opposite signs at high and low current densities—from +16 to -5 mV per pH unit, respectively. The polarization curves, taken in various alkalies, show a very weak dependence of the overvoltage on the nature of the cation, including the very large tetrabutylammonium cation and the doubly charged Ba^{2+} ion. Within the limits of the observable small variations (maximum deviations of η from the value for K^+ do not exceed 20 mV), the cations can be arranged in the following series: $Ba^{2+} > Li^+ \geq K^+ \approx N(C_4H_9)_4^+ \geq Cs^+ > Na^+$, moreover, with the exception of Ba^{2+} and Na, for the remaining cations the differences lie within several millivolts, i.e., there are practically no differences. It is difficult to see a pattern in this series. We should especially emphasize that in all the thus far investigated cases of a slow electrochemical step with the participation of water molecules on Hg, Sb, Sn, Ga, and indium amalgam, distinct decreases in the overvoltage were observed after the addition of Cs^+ (by 30-40 mV) and Ba^{2+} (by 50-90 mV) [8], and a large increase in η, no less than 300 mV against a background of tetrabutylammonium [9].

Taken together, the data cited agree best with a mechanism of decelerated recombination, although it is possible that to some degree, especially at large current densities, the removal of hydrogen also occurs by electrochemical desorption. Possibly the substantial change in the slope of the polarization curves is associated with the complex nature of the dependence of the heat of adsorption, and, consequently, the activation energy of recombination, on the degree of coverage. Such a form of the polarization curves also exists in the case when removal occurs by barrierless, and then by the usual electrochemical desorption. The possibility of such a mechanism on tungsten is indicated in [10]. However, the data obtained show that this mechanism is relatively improbable, since in alkaline solutions, in the case of barrierless electrochemical desorption, the overvoltage should depend on the pH and the ψ_1-potential, just as in the case of the usual electrochemical desorption, which does not occur.

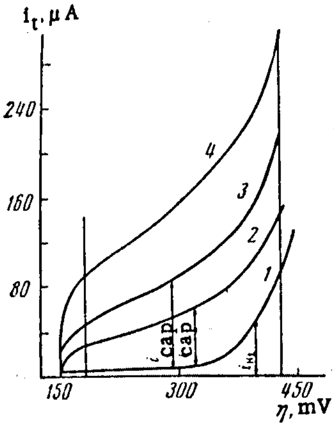

Fig. 4. Potentiodynamic curves at rate of development: 1 - 0.0125; 2 - 10; 3 - 20; 4 - 40 V/sec.

LITERATURE CITED

1. M. de Kay Thompson and C. W. Rice, Trans. Amer. Electrochem. Soc., 67, 71 (1935).
2. J. O'M. Bockris and S. Srinivasan, Electrochim. Acta, 9, 31 (1964).
3. B. V. Nekrasov, Course in General Chemistry [in Russian], Goskhimizdat, Moscow–Leningrad (1948), p. 339.
4. E. Deltombe, N. De Zoubov, and M. Pourbaix, Internat. Committee Electrochem., Thermodyn. and Kinetics (8th Meet, Madrid, 1956), London, Butterworths (1958), p. 250.
5. The Chemist's Handbook [in Russian], Vol. 3, Khimiya, Moscow–Leningrad (1964) p. 771.
6. A. Ya. Shatalov and I. A. Marshakov, Zh. Fiz. Khimii, 29, 42 (1954).
7. B. Trapnell, Chemisorption [Russian translation], Izd-vo Inostr. Lit., Moscow (1958), p. 1762.
8. V. É. Past, M. É., Khaga, Élektrokhimiya, 5, 319 (1969); Yu. A. Kukk, V. É. Past, Élektrokhimiya, 12, 1860 (1971); I. A. Bagotskaya, N. M. Genkina, and V. G. Boitsov, Élektrokhimiya, 5, 132 (1969); I. A. Bagotskaya and E. N. Potapova, Élektrokhimiya, 5, 1465 (1969); I. A. Bagotskaya and E. N. Potapova, Élektrokhimiya, 6, 855 (1970); V. N. Korshunov, A. N. Frumkin, and T. V. Ivanova, Élektrokhimiya, 4, 1120 (1968); I. P. Gladkikh and V. N. Korshunov, Élektrokhimiya, 5, 1102 (1969).
9. Z. A. Iofa, A. N. Frumkin, and É. A. Maznichenko, Zh. Fiz. Khimii, 31, 2042 (1957).
10. L. I. Krishtalik, Zh. Fiz. Khimii, 34, 117 (1960).