# COMPARISON OF THE AMOUNTS OF HYDROGEN ADSORBED ON PLATINUM IN KOH SOLUTION WHICH WERE DETERMINED BY THERMODESORPTION AND BY CHARGING CURVES

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A direct method for the determination of hydrogen adsorption on disperse electrodes at any potential has been suggested in [1]. This method was quantitatively verified on platinum in hydrochloric acid in [2]. Difficulties met when applying the method to other systems have also been detected and described there [2]. In the present communication we suggest an updated version of this method in which it can be extended to hydrogen adsorption on platinum in other solutions: Polarization must be performed in the test electrolyte, then the platinum must be washed free of this electrolyte, which must be replaced by sufficiently concentrated hydrochloric acid (about 3 M); but this must be done so that no hydrogen is lost.

The updated version of thermodesorption in the presence of electrolyte was used by us with platinum in KOH solution. In the cell shown in Fig. 1 in [1], the stopcock of the reference electrode was made of large volume (30 ml). Potentiostatic polarization was conducted in 0.25 N KOH (this concentration was chosen for purely technical reasons: the solution is sufficiently conducting, but does not corrode quartz too strongly). After attainment of equilibrium at $\varphi_r = 0.7$ V, the potentiostat was detached, and the cell was connected to a buret for gas collection. Without opening the system the KOH solution was drained from the reference electrode, replaced by twice distilled water, and purged with argon. Then this water was passed through the capillary of the reference electrode to wash the platinum black 5 to 6 times while heating the lower part of the cell to the boiling point of water (for better washing of the platinum). Then the water in the stopcock of the reference electrode was replaced by 3 N HCl, purged with argon, and another 4-5 washings were performed. The washing concluded, we heated the lower part of the cell with the platinum to 600°C, and analyzed the collected gas for the hydrogen content.

At potentials of 0.6-0.7 V, usually only traces of hydrogen were found. This served as a control operation in working out the washing procedure. When this was worked out, experiments were done at less positive

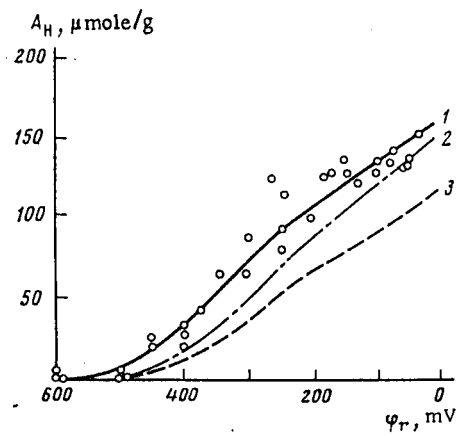



Fig. 1. Hydrogen adsorption on platinum in 0.25 N KOH (explanations in the text).

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potentials. The results obtained on platinum black in 0.25 N KOH at room temperature are presented in Fig. 1. Points show the amounts of hydrogen found at different potentials after its thermodesorption from the platinum. These points were used to draw the averaged curve 1. Curve 2 was calculated from the charging curve using the distances from the curve to a vertical line drawn at 500 mV. Curve 3 was constructed similarly, but using the distances from the charging curve to the tangent drawn at 500 mV. One can see first of all from the figure that hydrogen adsorption is close to zero at $\varphi_r$ of around 500 mV (in the present method we shall only talk about hydrogen adsorption in excess over oxygen adsorption, since equivalent amounts of hydrogen and oxygen can react with each other during heating). In absolute value, the hydrogen adsorption $A_H$ is higher at all potentials (0-500 mV) than the change in total charge, $\Delta Q$, represented by curve 2. This means, according to the well-known equation [3]

$$\Delta\varepsilon=\Delta Q+\Delta A_H,$$

that the free charge ($\Delta\varepsilon$) is negative in the same potential region. The low accuracy attained so far in the thermodesorption measurements prevents us from quantitatively estimating $\Delta\varepsilon$ from the difference between curves 1 and 2. However, it is completely obvious that in alkaline solutions one cannot calculate hydrogen adsorption from the charging curve by subtracting double-layer charge using the device of a tangent. Curve 3, which has been constructed in this way, gives results which are much too low. If in alkaline solution one does not know the true potential dependence of double-layer capacity, then it is best to disregard this, and assume that hydrogen adsorption is approximately equal to the change in total charge, i.e., to estimate it from curve 2.

The method described can be used to examine hydrogen adsorption on platinum in any electrolyte, provided that after polarization it can be replaced completely by hydrochloric acid. There are no principal difficulties in the way of raising the accuracy of this method. It will only be necessary to design the equipment as a single vessel with rigorous control. Then the accuracy with which the amount of adsorbed gas can be measured will not be less than that of ordinary chromatographic analysis.

## LITERATURE CITED


1. V. Sh. Palanker and E. N. Baibatyrov, Élektrokhimiya, 11, 308 (1975).
2. V. Sh. Palanker, B. B. Dyusenbina, and E. N. Baibatyrov, Élektrokhimiya, 13, 121 (1977).
3. A. N. Frumkin and A. I. Shlygin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 773 (1936).