

platinum, as can be seen from Fig. 4. When the anodic polarisation was increased to +50 mV, the γ -spectra showed the presence of platinum in the solution, while the impurities were absent (see C).

The platinum cathode showed no γ -radiation, even after electrolysis for 180 h, including all three stages.

SUMMARY

1. Metallic platinum used as an anode without polarisation does not disintegrate or dissolve in 0.1 N HCl. This is also true of the impurities present in the platinum.
2. With anodic polarisation of the platinum equal to 24 mV, the impurities at or close to the electrode surface pass into solution.
3. The surface layer of an electrode previously purified from contaminants disintegrates or dissolves at 50 mV anodic polarisation. This shows that in the work cited above³, no contamination from the platinum took place. Disintegration of the platinum may take place, but not by the mechanism suggested by Frumkin. It is also clear that after preliminary electrolysis the solution should not be introduced into the cell without further distillation.

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THE FORMATION AND STABILITY OF THE β -PHASE SYSTEM OF PALLADIUM AND HYDROGEN IN AQUEOUS SOLUTION

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Schuldiner and his coworkers¹ came to the conclusion that palladium foil placed in a solution of an acid could not be saturated with molecular hydrogen to give the composition of the β -phase (this would be in equilibrium with molecular hydrogen at atmospheric pressure) and that the potential of this palladium electrode relative to a reversible hydrogen-platinum electrode in the same solution does not become zero. This statement contradicts the elementary

thermodynamic theory of the gaseous hydrogen electrode, and also results obtained by Frumkin, Aladzhanova, and Fedorova², who showed that the palladium electrode when saturated with hydrogen in an acid or alkali solution assumes the same potential as the reversible hydrogen-platinum electrode in the same solution.

Schuldiner and Hoare³ explained this discrepancy as being due to the use in the above-mentioned experiments of platinum contacts welded to the palladium electrodes. The presence of the Pd-Pt couple would contribute to the saturation of the electrode with hydrogen in the solution until the β -phase was attained. In the opinion of these authors a pure palladium electrode in the presence of platinum, immersed in a solution of an electrolyte, always assumes a stable potential 0.050 V more positive than the reversible hydrogen electrode in the same solution. They define this potential as the equilibrium potential of the α -phase.

Actually 0.050 V corresponds to the potential of the $\alpha \rightarrow \beta$ transition of the palladium electrode. A palladium electrode immersed in a solution through which hydrogen is being passed may maintain this potential for a greater or less time — from a few minutes to many months — depending on the dimensions of the electrode, on how well the cell is sealed, and, chiefly, on the activity of the electrode.

We have repeated the experiments on the saturation of a palladium electrode immersed in a solution with hydrogen. The electrodes were made of spectroscopically pure palladium foil 0.05 mm thick, and the contacts were made through palladium wires. Before the experiment the electrodes were degreased by heating to 60° in concentrated sulphuric acid*, carefully washed in twice-distilled water, anodically polarised for an hour in normal sulphuric acid, and then cathodically in a fresh solution of acid until the evolution of gas was noticed with the current at 0.002 A. The activity of the electrode was tested before and after the experiment by plotting charging curves as a function of the anode and cathode overvoltages, which did not exceed 0.12 to 0.04 V in the neighbourhood of the phase transition when the current was 0.002 A. The surface area of the electrode was about 1 cm². The cell was of glass, special care being taken to ensure that it was hermetically sealed, and also to ensure the cleanliness of the vessels in which the experiment was conducted and the purity of the reagents and the gas used.

The results of these experiments showed that a palladium electrode immersed in a normal sulphuric-acid solution in the presence of platinum is saturated with hydrogen molecules until the composition of the β -phase is reached, in equilibrium with hydrogen at atmospheric pressure. This state is stable if the solution is completely saturated with hydrogen, and the potential of the palladium electrode is zero**.

A comparison of the conditions of the work of Schuldiner and his collaborators with ours showed that the dimensions of their palladium electrode did not differ very much from ours. It is significant that in their work the activity of the

* The degreasing of the electrode can be done by heating it for a short time, but if an active electrode is to be obtained it must necessarily be subjected to prolonged cathodic polarisation before the experiment.

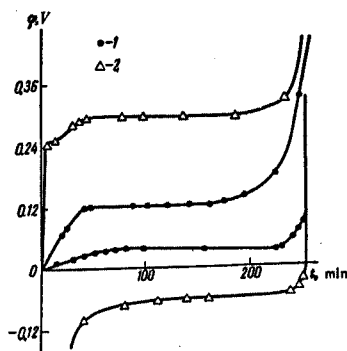
** In this work the potential was always measured in relation to the reversible hydrogen platinum electrode in the same electrolyte solution.

palladium electrodes investigated was not checked, although the method of treating them before the experiments suggests that inactive electrodes were made.

We conducted the following experiments with the object of testing this. The electrode made from the same palladium foil was treated by the method used by Schuldiner and his coworkers before it was investigated. This consisted in washing it in hot concentrated nitric acid, then washing it in twice-distilled water, and then heating it to white heat in air. After this the electrode was immersed in a normal solution of sulphuric acid, anodically polarised at 0.0002 A until its potential with the current flowing assumed a value of about 1 V, and then saturated with hydrogen, the potential and the time being measured.

This method of preliminary treatment of the electrode, with the complete exclusion of cathodic polarisation, gives an electrode of low activity, the deactivation of the electrode being variable according to the duration and intensity of the heating. Charging curves may be used to compare the activities of electrodes, and the results are shown in the diagram. It is noticeable that the diminution in the activity of the electrode is progressive if the anodic polarisation is repeated a few times and the electrode is then saturated with molecular hydrogen, without cathodic polarisation.

The time required to saturate the electrode with hydrogen increases with this loss of activity. We observed instances when the electrode potential maintained the value for the phase transition for a fortnight and did not shift towards negative values when the solution was saturated with hydrogen. That the electrode was not completely saturated is evidenced by the fact that when it is subsequently anodically polarised much less time is required at the same current density for the removal of all its hydrogen than when the electrode is active*.



1) Charging curve for a smooth palladium electrode previously treated by the authors' method, $i = 2.10^{-3}$ A; 2) charging curve for the same electrode previously treated by Schuldiner's method, $i = 2.10^{-3}$ A.

* Hoare shows in his recent work⁵ that the time for the saturation of palladium with hydrogen depends on the ratio of the surface area of the electrode to its volume; but even in this paper no account is taken of the part played by the activity of the surface of the electrode.

We noticed in previous work⁴ that when a palladium electrode saturated with hydrogen is treated with nitrogen at a high temperature it loses its activity in respect of the evolution of hydrogen. This loss of activity was indicated by a break in the potential-time curve, due to an interruption in the evolution of hydrogen from within the electrode itself to its surface. It was then observed also that after prolonged treatment with nitrogen, alternating with saturation with hydrogen, the electrode also became inactive with respect to the absorption of hydrogen. Apparently palladium electrodes sufficiently active in respect of the absorption and evolution of hydrogen can be made only by alternate anodic and cathodic polarisation.

Schuldiner, Castellan, and Hoare⁶ affirm that there is a difference between the physicochemical properties of the Pd-H alloy with the atomic ratio H: Pd ≈ 0.6 obtained by direct saturation of palladium with gaseous hydrogen (β -phase) and those of the same alloy obtained by the electrolytic saturation of palladium with hydrogen in solution (β' -phase)*. This difference is that, after the interruption of the current, the latter spontaneously loses hydrogen until the potential of the electrode becomes 0.050 V. This led the authors to think that the β -phase has a higher free energy than the β' -phase.

It must be said in this context that if a palladium electrode is saturated with hydrogen under conditions approaching equilibrium, that is, with a low current density and with a weight of metal such that it can be completely saturated, the electrode in the electrolyte solution, saturated with hydrogen, does not lose its hydrogen when the current is interrupted, and the potential of the electrode remains almost zero. If the electrode is saturated under non-equilibrium conditions, with a high current density, gaseous hydrogen may be evolved from the surface of the electrode even though deeper layers of the electrode have not been saturated with hydrogen. Under these circumstances the potential of the electrode may assume a higher positive value after the current is cut off, owing to the redistribution of the hydrogen. However, this does not give any grounds for concluding that the electrolytically prepared β -phase is unstable.

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* Symbolism of Schuldiner, Castellan, and Hoare.