mm. Thus an error of 1 mm. in measurement leads to an inaccuracy of only 0·05 per cent of the bridge signal.

This device was demonstrated by applying fixed signals from the katharometer bridge and noting that for each mV. applied from the test-box the expected decrease in recorder response was obtained. The device was then incorporated into new chromatographic units under construction and has since been used in the analysis of more than 200 gaseous mixtures containing hydrogen as a major component.

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Heat Capacity and Resistivity Anomalies in Palladium Hydride

A RECENT paper on the electrical resistivity (ρ) of solutions of hydrogen in palladium[1] records maxima at 43° K. and 52° K. for the compositions (hydrogen/palladium) 0·60 and 0·54 respectively, whereas there is a linear fall of ρ when the hydrogen/palladium ratio is 0·48. A reproduction of the curves of ρ versus T by Schindler *et al.* is shown in Fig. 1. The maximum is evident in the graphs for the composition 0·60, but not for the composition 0·54; however, the authors state that for this composition there is a definite maximum in the points at the lower temperatures.

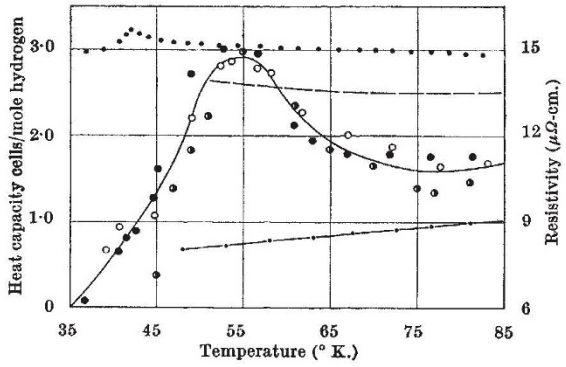

Fig. 1. Electrical resistivity and heat capacity per mole of hydrogen in certain solutions of hydrogen in palladium. ○, Cp H/Pd = 0·50 (Nace and Aston); ◑, Cp H/Pd = 0·25; ●, H/Pd = 0·125; ●●, ρH/Pd = 0·6; — —, ρH/Pd = 0·54; ●—●, ρH/Pd = 0·48

While the neutron diffraction work in ref. 2 leaves little doubt that there is hydrogen (hydrogen/palladium ~0·05) in the α-phase at room temperature, it is not unlikely that all the hydrogen is in the β-phase at lower temperatures.

Recent thermal studies in this laboratory have revealed slow exothermal processes on cooling solutions of hydrogen in polycrystalline palladium occurring near 150° K. and above 200° K. From the thermal drifts of the adiabatic calorimeter after various degrees of annealing, energies of activation of 6,400 and 2,900 calories were found for the upper and lower temperature processes respectively. In both cases graphs of the log of the rate of energy emission against $1/T$ gave good straight lines, except where annealing produced a state near equilibrium. This is in accord with anomalies in the heat capacity of hydrogen in palladium black (hydrogen/palladium = 0·50)[3] and one or both of these two processes may perhaps be thought of as connected with migration of hydrogens from the α- to the β-phase.

In view of the work on the resistivity[1] and of recent speculations concerning hysteresis in palladium hydride[4], heat capacity measurements for hydrogen in polycrystalline palladium with hydrogen/palladium ratios of 0·25 and 0·125 are of interest though perhaps not unexpected. The results, based on 1 mole of hydrogen in each solution, are given in Fig. 1 along with the earlier values for hydrogen/palladium equal to 0·50. The method used and the accuracy of the results are as given in ref. 3. Thus at hydrogen/palladium ratios of 0·125 and 0·25 the accuracy is respectively 2 per cent and 1 per cent of the heat capacity due to the hydrogen.

The heat-capacity maximum at 55° K. previously reported for a hydrogen/palladium ratio of 0·50 is not shifted at either composition and the results for both solutions lie on the same curve. The slow process occurring below 50° K. reported in ref. 3 was noted again. This is not connected with the two processes mentioned. By cooling the sample slowly through a temperature-range 30° above maximum, the slow process was 'annealed out' and all measurements were taken after this annealing.

The fact that the maximum is unchanged by composition at compositions of hydrogen/palladium below 0·50 might be taken to mean that all the hydrogen is in a phase of constant composition below room temperature. This would require migration of hydrogen from the α- to β-phase at low temperatures. However, if the hydrogen atoms are bound to palladium in such a way that there is little or no interaction between the protons, the heat capacities would not be affected very much by composition. This situation is unlikely. If the composition of the β-phase is constant, in view of the slow process occurring at the higher temperatures, it would seem that any process of ordering would most likely be one resulting in removal of some sort of rotational or librational process.

A comparison between the resistivity and heat-capacity data leaves little doubt that the maxima are connected. The results of Schindler *et al.*[1] indicate that the maximum in the resistivity curve may well be at 55° K. for a hydrogen/palladium ratio of 0·50. It is also not unlikely that the maximum in the heat-capacity curve would be shifted at higher concentrations of hydrogen. Heat capacities in this temperature-range at higher hydrogen concentrations will be studied.

Schindler *et al.*[1] suggest an anti-ferromagnetic transition as a possible cause of the maximum. The onset of rotational or re-orientation process used to explain the heat capacity maximum[3] would also produce an anomaly in $g(\nu)$ for the phonons and it is possible that the resistivity results might be explained on this basis. For compositions above Pd_2H it is not possible to connect the palladium atoms without bound hydrogen in endless chains[3].

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