

**This Week's Citation Classic**<sup>®</sup>

Wicke E & Nernst G H. Zustandsdiagramm und thermodynamisches Verhalten der Systeme Pd/H<sub>2</sub> und Pd/D<sub>2</sub> bei normalen Temperaturen; H/D-Trenneffekte (Phase-diagram and thermodynamics of the Pd/H<sub>2</sub> and Pd/D<sub>2</sub> systems at normal temperatures; H/D separation effects). *Ber. Bunsen Ges. Phys. Chem.* 68:224-35, 1964. [Inst. Physikalische Chemie, Univ. Münster, Federal Republic of Germany]

Measurements of H<sub>2</sub>(D<sub>2</sub>) ab- and desorption on Pd clarified the thermodynamics of the phase diagram and the interaction effects between the H(D) atoms in the Pd lattice. The two-phase region was delineated and the desorption branch of the hysteresis loop shown to be the equilibrium isotherm. The H/D separation factor was found to be remarkably high. [The *SCI*<sup>®</sup> indicates that this paper has been cited in over 250 publications.]

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March 24, 1988

The detection of hydrogen transference catalysis of metal hydride formation at the end of the 1950s<sup>1</sup> enabled gas-solid investigations of transition metal/hydrogen systems at appreciably lower temperatures than before. G.H. Nernst—no relative, however, of the famous Walther Nernst—applied this method in his work for his diploma and doctoral thesis to the classical Pd/H<sub>2</sub>(D<sub>2</sub>) system, performing pressure-volume-temperature (P-V-T) measurements down to -78.5° C on bulk Pd (ribbons) in comparison to Pd black. His results revealed that, between the H atoms in the Pd lattice, attractive interaction prevails in the dilute  $\alpha$ -phase and repulsive interaction prevails in the highly concentrated  $\beta$ -phase. The hysteresis in the two-phase region was shown to originate from the mechanical strain pro-

duced by the volume expanding  $\alpha$ - $\beta$  phase transition, and the desorption branches were recognized as representing equilibrium, coincident for bulk Pd and Pd black.

Together with H. Brodowsky, a coworker of mine at that time, the attractive interaction was traced back<sup>2,3</sup> to a volume effect, i.e., the lattice expansion by the uptake of H atoms in the octahedral interstices, and the repulsive interaction was traced to an electronic effect, i.e., the filling up of the d band at the Fermi level of the Pd by electrons of the H atoms. Both effects could be confirmed by the influence of alloy components as first shown for the Pd-Ag/H<sub>2</sub>(D<sub>2</sub>) system.<sup>2,3</sup> Quite a number of investigations on Pd alloys in our own group and in other groups emerged from this beginning and continue to the present day. Brodowsky, H. Züchner, and I reviewed much of the earlier work.<sup>4</sup>

Developments in our own group subsequently followed two main lines, namely, P-V-T and magnetic measurements in the supercritical regions of the Pd/H<sub>2</sub>(D<sub>2</sub>) system up to 150 bar and 613 K<sup>5-7</sup> and the exploration of electronic properties of Pd alloys and their hydrides by the Mössbauer effect and magnetic investigations. From the results obtained in the supercritical region, the statement by G.H. Nernst that the desorption branches of the hysteresis loops represent equilibrium could be confirmed definitely,<sup>6,7</sup> and it could be shown that there is no electronic H/D isotope effect. The investigation of Pd alloys initiated the concept of a two-stage electronic screening model of the H atoms in the octahedral sites,<sup>8</sup> which led to a new interpretation of H-H repulsion and of the blocking effects of foreign metal atoms in the Pd lattice against H atoms.

Developments during the past 25 years have revealed that the Pd/H<sub>2</sub> system is not only the classical system, but also a most interesting test and directional system in the metal/hydrogen field.

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