

**Remarkable Interstitial Hydrogen Contents  
Observed in Rhodium-Palladium Alloys  
at High Pressures**

*Sir:* There has been considerable recent interest in the absorption of hydrogen by palladium alloys because these systems provide valuable tests for theories of hydrogen absorption. With the exception of the nickel-palladium system,<sup>1</sup> these investigations have been limited to palladium alloys in which the added metal is generally considered to absorb only insignificant amounts of hydrogen, e.g., silver-palladium,<sup>2-5</sup> gold-palladium,<sup>6,7</sup> platinum-palladium,<sup>8,9</sup> rhodium-palladium,<sup>10,11</sup> copper-palladium,<sup>12,13</sup> tin-palladium.<sup>14</sup> In none of these studies have hydrogen-to-palladium atomic ratios in excess of 1 been reported; *i.e.*, there is no evidence that the added metal absorbs hydrogen when located within the palladium matrix.

**Table I:** Hydrogen Contents Observed in Rhodium-Palladium Alloys after Removal from the High-Pressure Vessel

Alloy % Rh	Hydrogen-to- palladium	Hydrogen-to- metal	Max. H <sub>2</sub> pressure used, atm
5	0.90 ± 0.02	0.86 ± 0.02	2,300
5	0.86	0.82	5,100
5	0.95	0.91	23,200
10	0.99	0.89	2,300
10	1.02	0.92	21,300
15	1.07	0.91	21,300
20	1.15	0.91	2,300
20	1.26	1.01	5,100
20	1.22	0.97	23,200
30	1.34	0.93	2,300
30	1.44	1.00	5,100
30	1.46	1.01	23,200
40	1.52	0.90	2,300
40	1.61	0.96	5,100

In this research we wish to report for the first time hydrogen-to-palladium ratios well in excess of 1 (Table I) for an alloy system, rhodium-palladium, where the added metal is believed to be, itself, a nonabsorber of hydrogen. Evidence that pure, bulk rhodium absorbs appreciable amounts of hydrogen has never been presented.<sup>15,16</sup>

The hydrogen was introduced into a high-pressure vessel (25°) described elsewhere.<sup>17</sup> The samples were in the form of thin foil. The pressure was applied to the samples in stages over a period of many hours. The final pressures (Table I) were applied for a period of at least 1 hr. The vessel was cooled (~-60°), the samples were removed and stored in liquid nitrogen prior to their examination with X-ray diffraction and

(1) F. A. Lewis, "The Palladium Hydrogen System," Academic Press, London and New York, N. Y. 1967.

(2) G. Rosenhall, *Ann. Phys. Leipzig*, **24**, [5] 297 (1935).

(3) Z. L. Vert and I. P. Tverdovskii, *Zh. Fiz. Khim.*, **28**, 317 (1954).

(4) E. Poeschel and H. Brodowsky, *Z. Phys. Chem. (Frankfurt am Main)*, **44**, 143 (1965).

(5) A. Carson and F. A. Lewis, *Trans. Faraday Soc.*, **63**, 1447, 1453 (1967).

(6) A. Maeland and T. B. Flanagan, *J. Phys. Chem.*, **69**, 3575 (1965).

(7) K. Allard, A. Maeland, J. W. Simons, and T. B. Flanagan, *ibid.*, **72**, 136 (1968).

(8) A. I. Stetsenko and I. P. Tverdovskii, *Zh. Fiz. Khim.*, **26**, 647 (1952).

(9) A. Carson, T. B. Flanagan, and F. A. Lewis, *Trans. Faraday Soc.*, **56**, 371, 1311 (1960).

(10) I. P. Tverdovskii and A. I. Stetsenko, *Dokl. Akad. Nauk SSSR*, **84**, 997 (1952).

(11) J. C. Barton, J. A. Green, and F. A. Lewis, *Trans. Faraday Soc.*, **62**, 960 (1966).

(12) R. A. Karpova and I. P. Tverdovskii, *Zh. Fiz. Khim.* **33**, 1393 (1959).

(13) D. Chisdes and T. B. Flanagan, results to be published.

(14) H. Husemann, PhD Dissertation, Munster, 1968.

(15) E. Müller and K. Schwabe, *Z. Phys. Chem. Abt. A*, **154**, 143 (1931).

(16) A. Sieverts and E. Jurisch, *Ber.*, **45**, 228 (1912).

(17) B. Baranowski and W. Butjnowski, *Roczn. Chem.*, in press.



the analysis of their hydrogen contents mass spectrometrically.

The hydrogen-free alloys were fcc with lattice spacings corresponding quite well with those reported by Raub.<sup>18</sup> Upon absorption of hydrogen the alloys remained fcc with a single lattice spacing indicative of an increased lattice parameter. The observed parameters were consistent with the large hydrogen contents observed. For example, the 20% rhodium-palladium alloy's lattice parameter increased from 3.87 to 4.08 Å when the alloy's hydrogen content increased from 0 to hydrogen-to-metal =  $1.01 \pm 0.02$ . The consistency of this increase, 0.21 Å, with the observed hydrogen content can be more fully appreciated when compared to the increase of parameter of 0.151 Å for the palladium-hydrogen system when palladium absorbs hydrogen to form H-to-Pd = 0.7 at an equilibrium pressure of 1 atm (25°).<sup>19</sup>

At pressures between 2300 and 5100 atm stoichiometric 1:1 hydrides have been obtained for the 20 and 30% rhodium-palladium alloys. Concomitant measurements of the electrical resistance of the samples supports the view that these are limiting hydrogen contents, at least for the investigated pressure range, because significant resistance changes did not occur between 5100 and 23,200 atm, *i.e.*, changes which could not be attributed to purely hydrostatic effects. Such a limiting stoichiometry has not been obtained as yet even in the pure palladium-hydrogen system.<sup>1,19</sup> It can be noted from Table I that there is not always an

increase of hydrogen content with pressure. This is because hydrogen may be lost from the sample upon cooling, reduction of the pressure, and removal from the vessel.

These results suggest that either rhodium itself can absorb hydrogen, but in a higher pressure range than palladium, or that rhodium can function as an absorber of hydrogen only when situated within the palladium matrix. So far we have not been successful in obtaining hydrogen absorption by pure, bulk rhodium but efforts are continuing in this attempt.

*Acknowledgments.* T. B. F. is grateful for his appointment as a participant in the exchange program between the National (U. S.) and Polish Academies of Sciences and for the hospitality of the Polish Academy of Sciences (Warsaw). The authors wish to thank Mr. M. Krukowski for valuable experimental aid. We are grateful to Professor E. Wicke for the 15% rhodium-palladium alloy.

(18) E. Raub, *Z. Metallk.*, **50**, 428 (1959).

(19) P. C. Abens and W. G. Burgers, *Trans. Faraday Soc.*, **58**, 1989 (1962).

\* Chemistry Department, University of Vermont, Burlington, Vt. 05401.

THE INSTITUTE OF PHYSICAL CHEMISTRY      TED B. FLANAGAN\*  
POLISH ACADEMY OF SCIENCE                      B. BARANOWSKI  
WARSAW, POLAND                                      S. MAJCHRZAK

RECEIVED JULY 22, 1970