High Pressure Research on Palladium-Hydrogen Systems

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High pressure studies involving hydrogen gas present considerable technological difficulties because of the embrittling effect of hydrogen on constructional materials. In recent work in Warsaw, however, it has been possible to study the absorption of hydrogen by palladium and by a series of palladium alloys at pressures of up to 25,000 atmospheres of hydrogen, and interesting results have been obtained.

The very great majority of results published for the palladium-hydrogen and palladium alloy-hydrogen systems have been obtained with low pressures of gaseous hydrogen or, in the case of electrochemical studies, at electrode potentials corresponding to relatively low pressures of hydrogen (1).

Of the studies with high pressures of gaseous hydrogen one must first mention the paper of Frumkin and co-workers (2) where isotherms of the palladium-hydrogen system have been measured at temperatures from -18.5 to $30°C$ up to 1700 atmospheres of gaseous hydrogen. An important finding of this study was that in purely β-phase ranges of hydrogen content a linear relationship exists between hydrogen content (expressed for example as the atomic ratio, H/Pd) and the logarithm of hydrogen pressure. A later study (3) by Levine and Weale, using pressures of up to 1000 atmospheres was carried out at temperatures adjacent to the critical region of the palladium-hydrogen system— for which T_c is $\approx 300°C$.

Experimental Arrangements for High Pressure Studies

The handling of gaseous hydrogen at high pressures is especially complicated because of its extremely damaging effect on steel vessels or components. Figure 1 shows a schematic diagram of a device designed to counteract this difficulty which is in current use in this laboratory (4), and which also represents an improvement in regard to this general problem over arrangements which we have employed earlier (5). The device described has allowed us to reach hydrogen pressures up to 25,000 atmospheres at room temperature.

Initiatives for High Pressure Research Studies

Interest or need for working with high pressures of hydrogen in metal-hydrogen systems can arise for different reasons:

(i) With clean surfaces the upper limit of hydrogen pressure which can be obtained at an electrode does not generally exceed the range 10 to 50 atmospheres (6). One can achieve much higher hydrogen activities (under irreversible kinetic conditions) at the electrode by adding promoting agents to the electrolyte (7) but this makes any equilibrium study impossible due to the non-reversible character of the electrode surface.

(ii) There are several metals which exhibit hardly any solubility of hydrogen under low pressures of the gas. And this low solubility is generally accompanied by only rather uninterestingly small changes of physical parameters. In the case of nickel, however, it has already been shown (8) that at pressures of ≈ 8000 atmospheres a hydride phase
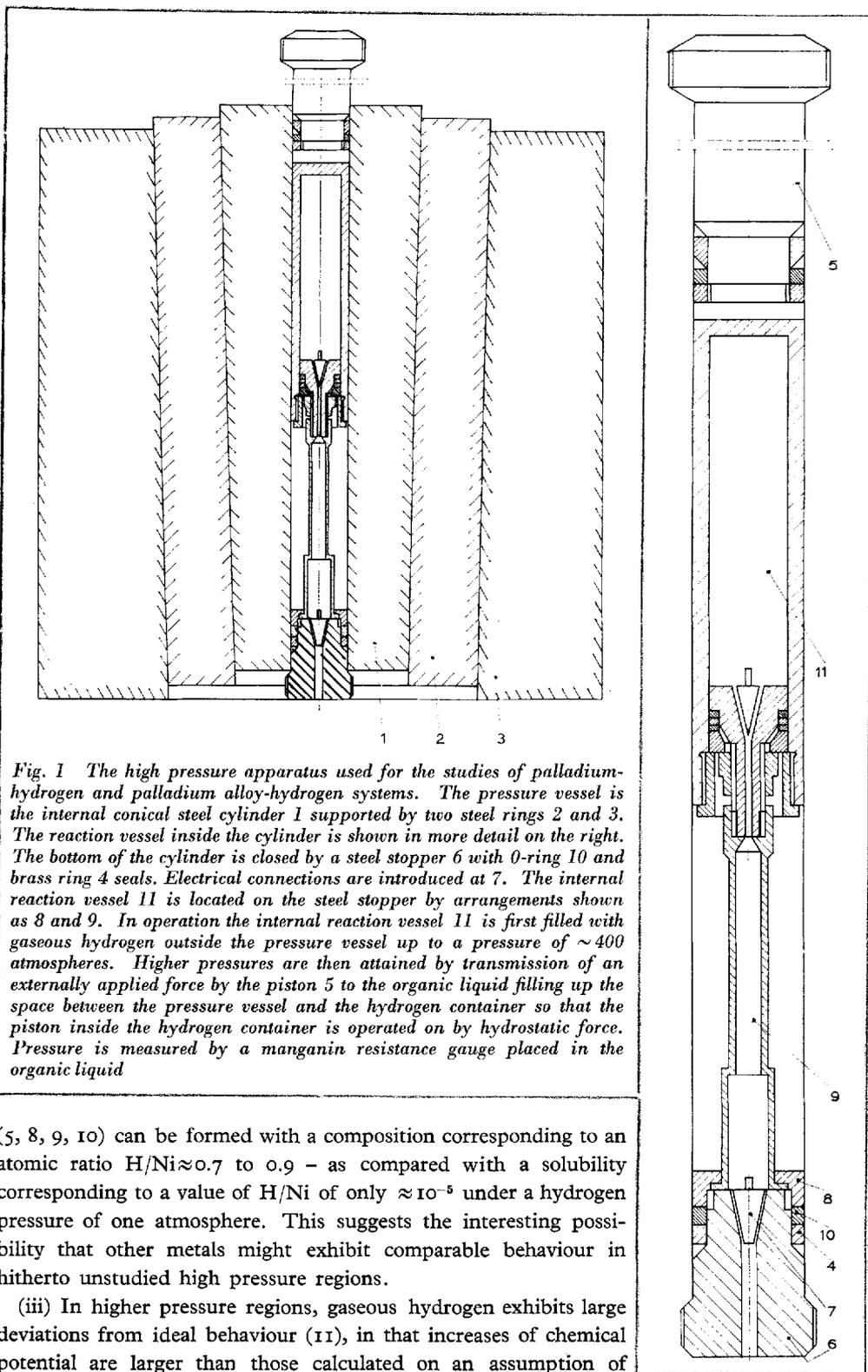
Fig. 1 The high pressure apparatus used for the studies of palladium-hydrogen and palladium alloy-hydrogen systems. The pressure vessel is the internal conical steel cylinder 1 supported by two steel rings 2 and 3. The reaction vessel inside the cylinder is shown in more detail on the right. The bottom of the cylinder is closed by a steel stopper 6 with 0-ring 10 and brass ring 4 seals. Electrical connections are introduced at 7. The internal reaction vessel 11 is located on the steel stopper by arrangements shown as 8 and 9. In operation the internal reaction vessel 11 is first filled with gaseous hydrogen outside the pressure vessel up to a pressure of ∼400 atmospheres. Higher pressures are then attained by transmission of an externally applied force by the piston 5 to the organic liquid filling up the space between the pressure vessel and the hydrogen container so that the piston inside the hydrogen container is operated on by hydrostatic force. Pressure is measured by a manganin resistance gauge placed in the organic liquid

(5, 8, 9, 10) can be formed with a composition corresponding to an atomic ratio $H/Ni \approx 0.7$ to 0.9 – as compared with a solubility corresponding to a value of H/Ni of only $\approx 10^{-5}$ under a hydrogen pressure of one atmosphere. This suggests the interesting possibility that other metals might exhibit comparable behaviour in hitherto unstudied high pressure regions.

(iii) In higher pressure regions, gaseous hydrogen exhibits large deviations from ideal behaviour (11), in that increases of chemical potential are larger than those calculated on an assumption of
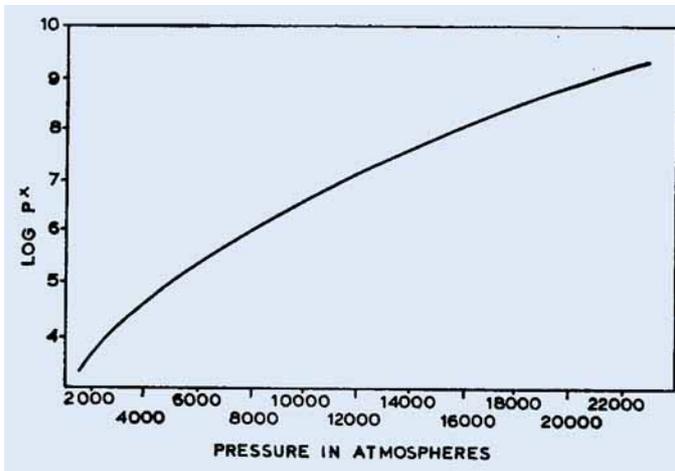
Fig. 2 Logarithm of hydrogen fugacity (Pˣ) plotted as a function of the pressure of hydrogen

ideality for complementary incremental increases of hydrostatic pressure. Although direct experimental evidence is only available up to ≈ 3000 atmospheres, Fig. 2 indicates that, if the constants used for extrapolation are pressure independent, a hydrogen pressure of 21,000 atmospheres should correspond to a fugacity of about 10^9 atmospheres.

Changes of Electrical Resistance and Other High Pressure Studies of the Palladium-Hydrogen System

It has been known for a long time that electrical resistance is quite a sensitive function of hydrogen content at compositions obtainable with relatively low pressures of hydrogen (1). (Changes of resistance are usually expressed for generality in terms of the relative resistance, R/R_{Pd}.) At room temperature R/R_{Pd} exhibits a gradual increase with increasing hydrogen content up to a fairly constant value at values of H/Pd of ≈ 0.7, which can be reached at equilibrium pressures only slightly above atmospheric. As illustrated in Fig. 3, recent results (12, 13) have shown that additional hydrogen introduced under high pressure causes a subsequent substantial lowering of resistance until it eventually decreases to slightly below the initial value of hydrogen-free palladium.
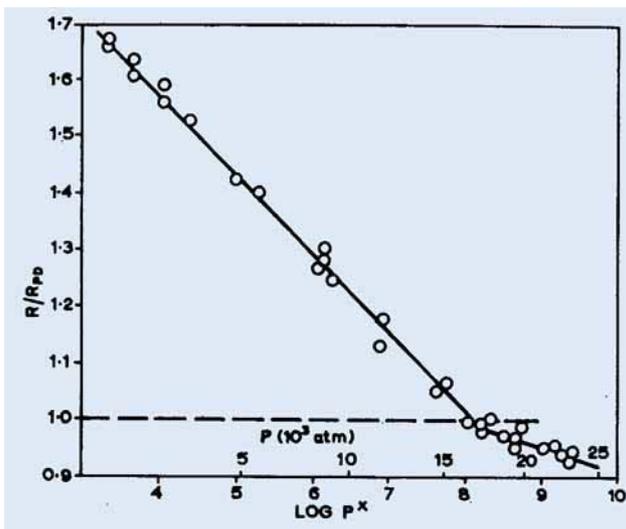

Fig. 3 Electrical resistance is a sensitive function of hydrogen content of palladium and its alloys. The relative resistance R/R_{Pd} of palladium hydride to palladium is plotted here as a function of hydrogen fugacity and the pressure scale is also indicated
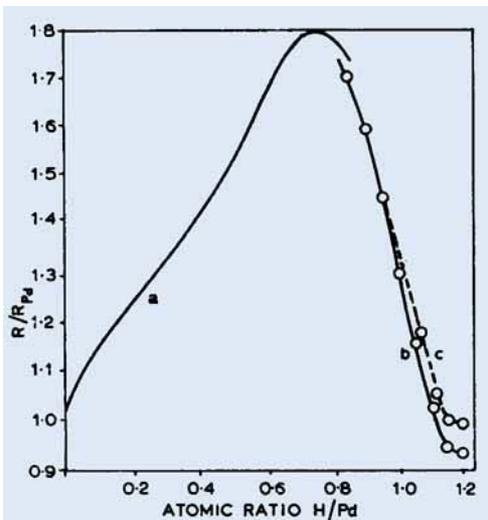
Fig. 4 *The relation of the relative resistance R/R_{Pd} of palladium hydride to the atomic ratio H/Pd as calculated from relationships derived by Wicke and Nernst (14)*

In studies at very high pressures it is not, however, easy to make direct concurrent measurements of changes of hydrogen content. Estimates of H/Pd can nevertheless be obtained by using extrapolations of relationships between pressure and content derived (14) over lower ranges of pressure. Figure 4 indicates that if these relationships were reasonably correct, then the decrease of R/R_{Pd} with increasing H/Pd would remain of the same form up to values of the atomic ratio H/Pd of close to a stoichiometry of 1:1. It seems from Fig. 3, however, that the linear dependence between relative resistance and the logarithm of hydrogen fugacity only holds up to $\approx 16,000$ atmospheres.

At higher pressures there is a change of slope to a further linear relationship which seems to extend up to $\approx 25,000$ atmospheres, which represents the upper limit of pressure so far attained. At the highest pressures the extrapolated relationships would suggest that H/Pd had reached values of ≈ 1.2 as indicated in Fig. 4. Attempts have been made to estimate directly the maximum contents of hydrogen which can be absorbed, by outgassing specimens in vacuo after their removal

from the high pressure apparatus following a cooling to $-40°C$ (mass spectrometry was used for the quantitative analysis of hydrogen). Indications are, however, that some loss of hydrogen always occurs from such specimens as compared to the volume which had been absorbed under very high pressure. Nevertheless, specimens with compositions approaching H/Pd=1 have been isolated; and values of the lattice constant of such specimens have been shown to be consistent with general relationships between lattice constant and hydrogen content which have recently been discerned (15) for the palladium-hydrogen and a number of palladium alloy-hydrogen systems.

Specimens containing the larger contents of hydrogen introduced under high pressure have also recently been employed in studies (16) of the anomaly in relationship between electrical resistance and temperature in the region of 60 K.

Thus, as illustrated in Fig. 5, the interesting information has been found that a sample with H/Pd≈ 0.89 showed little evidence of an anomaly whilst effects of a maximum degree
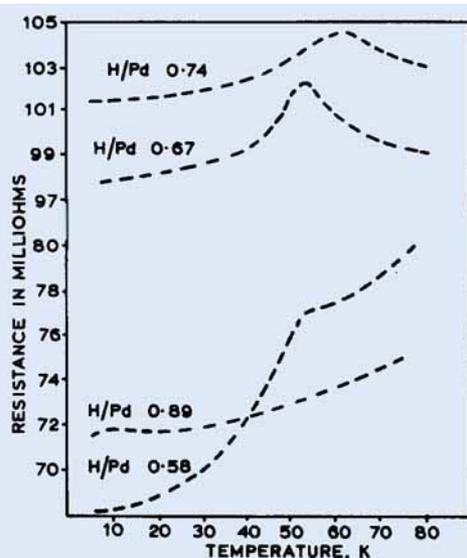

Fig. 5 *The electrical resistance of various palladium hydride samples as a function of temperature*

are obtained for specimens for which $H/Pd \approx 0.7$. The relevance of these findings to alternative explanations of the anomaly in terms either of transitions of hydrogen between octahedral and tetrahedral interstices (17) or the existence of islands of stoichiometric PdH (18) has been discussed. At present it seems that additional experimental information is still necessary to resolve this problem, such as determinations of the lattice structures of samples with high contents of hydrogen, at higher temperatures than it has been convenient to use so far.

High Pressure Research on Various Palladium Alloys

An initial study (13) with a single Pd-Au alloy (≈ 35 atom per cent Au) at 25°C showed that electrical resistance continued to increase linearly as a function of logarithm of hydrogen fugacity up to 24,000 atmospheres after passing through a minimum below 300 atmospheres.

Recently systematic investigations have been in progress for comprehensive series of Pd-Ag, Pd-Pt and Pd-Rh alloys. It has again been found that a substantial proportion of hydrogen introduced at high pressure can be retained after removal from the high pressure apparatus by using a similar cooling procedure to that discussed above for the Pd-H system. It has therefore been possible to show that values of lattice parameters derived at these high hydrogen contents also correspond with the general relationships for the palladium and other palladium alloy-hydrogen systems (15) to which attention has recently been drawn, as mentioned earlier above.

The course of changes of electrical resistance in the high regions shows a rich variety of behaviour for these alloy systems. The palladium-platinum series of alloys (19) exhibits a gradual modification of the behaviour of the Pd-H system in that, for rising overall platinum content, electrical resistance still increases as a function of pressure to a maximum value, which, how-ever, is attained at progressively higher pressures. Furthermore, in the regions of decreasing resistance following the maximum, the relationship between relative resistance and the logarithm of fugacity finally again becomes linear for those alloys (containing < about 35 per cent platinum) where the pressure range has been sufficient for this to be revealed.

For the palladium-silver series of alloys (20) the patterns of change of relative resistance with pressure are slightly more difficult to summarise. However, one generalised finding is that alloys in the lower range of silver contents again exhibit a final decrease of electrical resistance which becomes a linear function of log{fugacity} over the highest ranges of pressure employed. With regard to findings at higher contents of silver, it was already known from low pressure measurements (1) that alloys containing ≈ 55 per cent silver exhibited a steep initial increase of resistance with increasing hydrogen content. In high pressure studies (20) we have now observed increase of relative resistance up to ≈ 1.8 at pressure of ≈ 8000 atmospheres for an alloy containing 70 atom per cent silver. The inference that alloys containing >70 per cent silver might absorb significant amounts of hydrogen was not paralleled in the Pd-Pt series; for example, up to pressures as high as 24,000 atmospheres an alloy with 70 atom per cent platinum exhibited virtually no changes of electrical resistance – which seems reasonably indicative of a correspondingly very low hydrogen solubility.

Despite the indications of significant solubility of hydrogen in alloys with >70 per cent silver, the overall indications from the changing form of the relationships between relative resistance and pressure are that making comparisons at any given pressure over the whole range of higher pressures, the solubilities of hydrogen in both the Pd-Pt and Pd-Ag series of alloy decreased continuously as a function of either platinum or silver contents at 25°C. This did not seem to indicate a very active participation of the

platinum or silver atoms in hydride formation. A considerably contrasting behaviour has, however, been found in the case of the Pd-Rh series of alloys. Here alloys with contents of rhodium extending up to 40 per cent have been found to exhibit solubilities corresponding to ratios of hydrogen to palladium atoms greater than one (21). These high contents have been measured directly by outgassing specimens removed from the high pressure apparatus after cooling and pressure reduction; the contents are also in keeping with measurement of changes of lattice parameters (15). Data are as yet incomplete over the whole range of alloy compositions but the results available seem to indicate either supplementation by rhodium in certain concentration ranges of the ability of palladium to form distinct hydride phases or the possibility of rhodium itself being able to form a hydride phase.

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Platinum Compounds in Cancer Research

Professor B. Rosenberg of Michigan State University has reported previously that certain platinum compounds are very potent anti-tumour agents against a wide variety of tumours (Platinum Metals Rev., 1971, 15, (2), 42–51). Tests were carried out initially on laboratory mice but trials of cis-dichloro-diamminoplatinum(II) have now been extended to human patients at six hospitals and institutes in the U.S.A. and at one in London.

B. J. Leonard and co-workers of I.C.I. Pharmaceuticals and Dyestuffs Divisions, Macclesfield, Cheshire have also now reported that cis-dichlorodiamminoplatinum(II) and cis-tetrachlorodiamminoplatinum(IV) have strong antileukaemic effects in rats on myeloid and lymphatic leukaemias (Nature, 1971, 234, (Nov. 5), 43–45). Although the effects are accompanied by uraemia, these two compounds seem to be superior to those in clinical use as they have no undesirable side effects on the normal cells of the marrow, gonads and intestine. These antileukaemic and nephrotoxic properties seem to be related to the molecular configuration of the platinum compounds because the corresponding trans compounds had no effect on either type of rat leukaemia or on the kidneys of mice, rats and marmosets. The I.C.I. team suggest that it is not clear whether the antileukaemic effect of the compounds is direct and selective on the tumour cells or indirect and perhaps mediated through the immunological system but they believe that clinical trials on human tumours and leukaemias would be justified.