THE SOLUBILITY OF HYDROGEN IN THE PLATINUM METALS UNDER HIGH PRESSURE*

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Abstract—The technique for compressing macroscopic volumes of hydrogen to record pressures of tens of kilobars, developed in the Institute of Solid State Physics of the USSR Academy of Sciences, has permitted the first syntheses of the hydrides of a number of metals namely: manganese, iron, cobalt, molybdenum, technetium, rhenium and gold. This paper presents the results of the application of the technique for the hydrogenation of the platinum metals. The data obtained on hydrogen solubility at high pressures are used to estimate its equilibrium solubility at atmospheric pressure.

INTRODUCTION

The first metal hydride investigated was that of palladium [1], but more than 120 years passed before the synthesis of a hydride of a second platinum metal, rhodium, occurred [2]. To date hydrides of all the transition metals have been synthesised except those of the remaining four platinum metals and tungsten [3–5].

As far as the platinum metals are concerned, this situation has not resulted from any lack of attempts to synthesise platinum, iridium, osmium and ruthenium hydrides, but is due to their low levels of acceptability of hydrogen into their lattices. This inertness or resistance to hydrogen absorption is characterised by the fact that as the chemical potential of hydrogen dissolved in the metal is very high, solubilities of hydrogen corresponding to equivalent high external pressures of hydrogen gas, are generally very low.

Even the development of very high chemical potentials within the above metals by traditional non-equilibrium methods (for example, by electrolysis) has not previously been successful in introducing very high hydrogen contents.

The most direct way to increase the chemical potential of the hydrogen is to compress the hydrogen to high pressures. By this means we have synthesised rhodium hydride [2] by using molecular hydrogen compressed to $P_{H_2} \gtrsim 50$ kbar, and recently the range of investigation has been extended to $P_{H_2} \approx 90$ kbar. In this paper we will summarise observations made on platinum metals under such record hydrogen pressures.

The specimens were of 99.99% purity. Palladium, rhodium, iridium and platinum specimens were cut from polycrystalline foils approximately 0.1 mm thick, while the ruthenium and osmium specimens with a thickness of about 0.15 mm were cut from single crystals. Hydrogen compression was carried out by a method which has been outlined [6] and later described in detail [4].
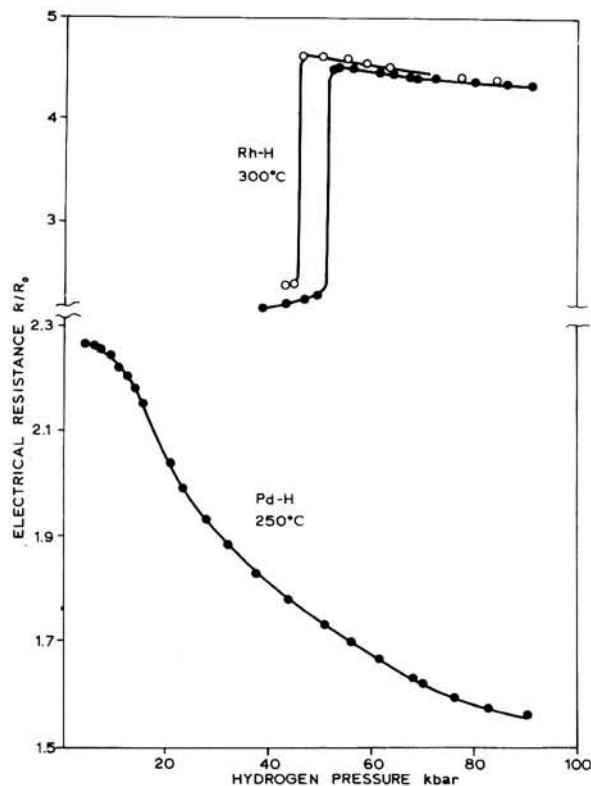

Fig. 1. Isotherms of electrical resistance of palladium and rhodium in a hydrogen atmosphere: ● with increase in pressure; ○ with decrease in pressure; R_o is the resistance of a specimen at atmospheric pressure and room temperature.

Hydrogen significantly alters the electrical resistance of a metal in which it is dissolved. Thus changes in the electrical resistance of specimens can serve as conveniently measurable indicator of processes occurring in metal-hydrogen systems at high pressures. Some forms of electrical resistance-pressure isotherms measured in the present work are shown in Figs. 1 and
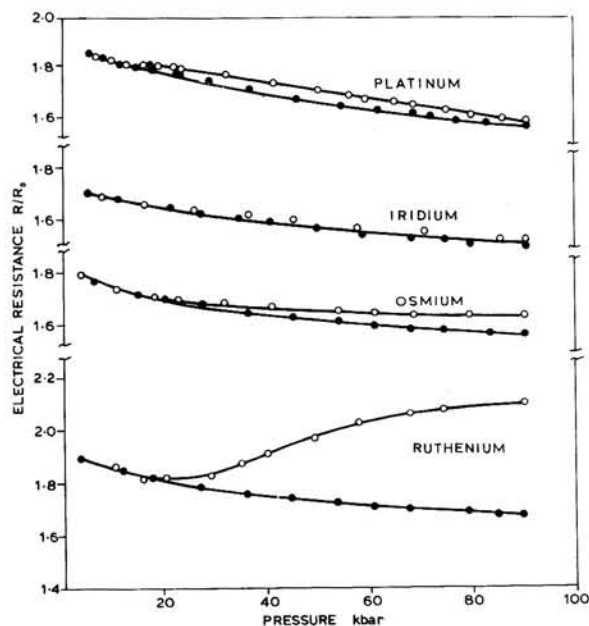

Fig. 2. Isotherms of electrical resistance of ruthenium, osmium, iridium and platinum at a temperature of 250°C measured with increase in pressure: ● in an inert medium; ○ in hydrogen; R_o as defined in Fig. 1.

2. The measurements were obtained as the pressure was altered in steps, each pressure being maintained until any observed drift in resistance had stopped. It should be noted that when the measurements were performed in an inert medium (hexane) no such drifts were observed.

The observations of the drifts in a hydrogen atmosphere are consistent with alterations of the hydrogen content of the specimen. A change of hydrogen concentration in a metal-hydrogen solid solution is a diffusion process, and the duration of the resistance drift characterises the kinetics of the specimen attaining the hydrogen content corresponding to the new magnitude of P_{H_2}. In order that the hydrogenation of the specimens to equilibrium concentrations would occur in a reasonable time, the greater part of the investigations was conducted at elevated temperatures ($\gtrsim 250°C$).

For the determination of hydrogen solubility in platinum metals, samples were equilibrated for 24 h at fixed values of temperature and hydrogen pressure. The high-pressure chamber was then rapidly cooled down to approximately $-180°C$; the pressure was next reduced to atmospheric and the specimens were removed from the chamber and stored in liquid nitrogen until their hydrogen contents were determined; this was carried out by a method which has been described elsewhere [5]. Testing has shown that at the temperature of liquid nitrogen, no detectable loss of the hydrogen takes place from the samples prepared in this way for at least one year.

PALLADIUM

The palladium-hydrogen system is one of the most important and interesting metal-hydrogen systems, and much attention has been paid to its thorough investigation. A detailed review and analysis of the available data on this system can be found elsewhere [7, 8].

As far as the phase composition of the palladium-hydrogen system is concerned, hydrogen and palladium form wide regions of interstitial solid solutions with essential retention of the f.c.c. structure of the lattice of the metal atoms. The T-n diagram (where n is the ratio of hydrogen to metal atoms) of the palladium-hydrogen system exhibits a discontinuity corresponding to co-existence of the isomorphic phases γ_1 and γ_2 (in other literature [7, 8] designated α and β or α and α'), depleted and enriched with hydrogen, respectively. On the T-P_{H_2} diagram, this is reflected by lines corresponding to the $\gamma_1 \rightarrow \gamma_2$ and $\gamma_2 \rightarrow \gamma_1$, isomorphic transformations terminating at a critical point, with parameters of $T_{cr} = 292°C$, $(P_{H_2})_{cr} = 19.7$ bar and $n_{cr} = 0.25$ (7).

Our measurements have shown that at temperatures above 200°C and hydrogen pressures up to 90 kbar, no other transformations occur in the palladium-hydrogen system, and hydrogen solubility in the γ_2 phase increases monotonically with pressure up to $n \approx 1$ at $P_{H_2} = 90$ kbar. Figure 1 shows a typical isothermal plot showing changes with pressure of the electrical resistance of the γ_2 phase of the palladium-hydrogen system at high pressures. Resistance drifts taking place after alterations of pressure continued for several minutes.

RHODIUM

The hydriding of rhodium, like that of palladium, is structurally describable in terms of γ_1 and γ_2 interstitial hydrogen solid solution phases, developed from an initial f.c.c. metal lattice whose lattice parameter only finally increases by $\approx 6\%$ (2). At atmospheric pressure and $T = -190°C$ the lattice spacing of the rhodium hydride with $n = 1.02 \pm 0.03$ is $a = 4.020$Å.

The onset of the $\gamma_1 \rightarrow \gamma_2$ transition in the rhodium-hydrogen system at high hydrogen pressures, is indicated by an abrupt increase in the electrical resistance of the specimen, and the γ_2 hydride decomposition ($\gamma_2 \rightarrow \gamma_1$ transition) by an abrupt decrease in the resistance, see Fig. 1. The T-P_{H_2} diagram of the rhodium-hydrogen system constructed on the basis of a study of the resistance behaviour [9], is shown in Fig. 3. As is seen from Fig. 3, the temperature dependence of the pressure of the $\gamma_2 \rightarrow \gamma_1$ transition can be interpolated by a straight line with a slope $dT/dP_{H_2} \approx 27°Ckbar^{-1}$. At $T \gtrsim 275°C$ the extent of the hysteresis of the $\gamma_1 \rightleftharpoons \gamma_2$ transformation is difficult to ascertain in view of the experimental scatter. At $T < 275°C$, the experimental pressures required for the $\gamma_1 \rightarrow \gamma_2$ transition have been found to increase rapidly, and at 200°C it has not been found possible to form the γ_2 hydride phase, even at pressures up to $P_{H_2} = 90$ kbar.
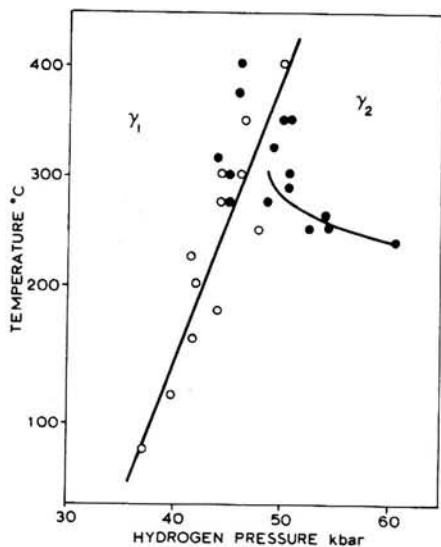
Fig. 3. Temperature-hydrogen pressure phase diagram of the rhodium-hydrogen system: ● pressure of the hydride formation transition $\gamma_1 \rightarrow \gamma_2$; ○ pressure of the hydride decomposition transition $\gamma_2 \rightarrow \gamma_1$.

The observed behaviour of the $\gamma_1 \rightarrow \gamma_2$ and $\gamma_2 \rightarrow \gamma_1$ transition curves in Fig. 3 agrees with the assumption of [10, 11] that in the metal-hydrogen systems relationships corresponding to true thermodynamic equilibrium are more closely represented by plots of the $\gamma_2 \rightarrow \gamma_1$ hydride decomposition transition rather than plots corresponding to the $\gamma_1 \rightarrow \gamma_2$ hydride formation transition.

In the case of the $\gamma_2 \rightarrow \gamma_1$ transition, a linear extrapolation of the slope of the line in Fig. 3 yields $P_{H_2} \approx$ 25 kbar for the pressure of the $\gamma_2 \rightarrow \gamma_1$ transition at 0K. From this it would seem reasonable to conclude that the pressure corresponding to thermodynamic equilibrium between γ_1 and γ_2 phases will not be less than 25 kbar at any temperature above 0K.

The essential thermodynamic instability of rhodium hydride shows itself in its strong tendency to decompose back into rhodium and molecular hydrogen. Release of hydrogen from specimens becomes noticeable, even at $T \approx -100°C$, and at room temperature the hydride is decomposed in a few minutes. At high hydrogen pressures, the rates of the processes of hydrogen absorption and desorption are quite different, depending on initial and final compositions of the solid. When the pressure is changed in regions of uniformity of either the γ_1 or γ_2 phases, the periods of resistance drift extend only to times $\Delta\tau \approx 10$ to 30 min at all temperatures in the range $50 < T \le 400°C$. However, when $\gamma_1 \rightarrow \gamma_2$ transitions occur, $\Delta\tau \approx 1.5$ h at $T \ge 275°C$ and this increases to approximately 10 h at 225°C. The times of resistance drift when $\gamma_2 \rightarrow \gamma_1$ transitions occur are somewhat less temperature dependent: $\Delta\tau \approx 2.5$ h at $T \ge 250°C$, approximately 1 day at 100°C and approximately 10 days at 50°C.

At $250 \le T \le 400°C$, maximum solubilities of hydrogen in the γ_1 phase initial range of solid solution of hydrogen in rhodium correspond to $n \le 0.01$. However, hydrogen contents in the γ_2 phase are much higher, corresponding to $n \approx 1$, and are almost independent of pressure and temperature.

RUTHENIUM AND OSMIUM

Both metals have an h.c.p. lattice. At $T = 250°C$, the hydrogen solubility in ruthenium and osmium increases continuously with pressure, reaching $n = 0.03 \pm 0.01$ and $n = 0.003 \pm 0.0015$, respectively, at $P_{H_2} = 90$ kbar. An increase in the hydrogen concentration in ruthenium and osmium leads to a deviation of the electrical resistance isotherms for these metals when in a hydrogen atmosphere, compared to those in an inert medium, see Fig. 2. In a hydrogen atmosphere a pressure change resulted in a drift in the samples' resistance, lasting for about 2 h in the case of ruthenium and about 30 min for osmium.

The ruthenium-hydrogen and osmium-hydrogen solutions obtained were unstable at room conditions and decomposed into metal and molecular hydrogen in about 1 day and 10 min, respectively.

IRIDIUM AND PLATINUM

The metals have a f.c.c. lattice. The hydrogen content of samples obtained by treatment at $T = 250°C$ and $P_{H_2} = 90$ kbar reached $n \approx 0.005$. At atmospheric pressure and room temperature, the hydrogen completely escaped from the samples in less than a minute. It is to be noted, however, that the behaviour of the electrical resistance of iridium and platinum in a hydrogen atmosphere did not differ significantly from that in an inert medium, see Fig. 2. No resistance drift was observed after changes in the hydrogen pressure. In this connection, it remains obscure whether, under the experimental conditions, the hydrogen dissolved in the bulk of the metals or if, for example, adsorption took place only on macrodefects.

In view of such low hydrogen solubility in ruthenium, osmium, iridium and platinum even at $P_{H_2} = 90$ kbar, it would be interesting to estimate what solubility should be observed in these metals under hydrogen pressures of the order of 1 bar, which are usually employed for hydrogenation. This might be done by assuming that these hydrogen in metal solutions are ideal.

Employing the usual expression for the thermodynamic potential of the solution [12] and representing the chemical potential of molecular hydrogen as $\mu_{H_2} = \mu_0(T) + kT\ln f$, the pressure dependence of the concentration of an ideal dilute solution of hydrogen in the metals can be obtained as an expression for the anticipated ratio n/n_0 of the solubility (hydrogen content) n at pressure P to the solubility n_0 at a pressure

Table 1. The dependences of the quantities entering into equation (i) on hydrogen pressure P for $T = 250°C$, $\beta = 2.5$ Å^{3}atom^{-1} hydrogen and $P_0 = f_0 = 1$ bar

P(kbar)	f(kbar)	$\sqrt{f/f_0}$	$\exp\left\{-\dfrac{\beta}{kT}\cdot(P-P_0)\right\}$	n/n_0
1	1.443	38.0	0.97	37
10	253.6	504	0.71	360
20	6477	2545	0.50	1.3×10^3
50	5.96×10^6	7.72×10^4	0.18	1.4×10^4
90	4.4×10^9	2.1×10^6	0.044	9.2×10^4

P_0 of 1 bar:

$$\frac{n}{n_0} \approx \sqrt{\frac{f}{f_0}} \cdot \exp\left\{-\frac{\beta}{kT}(P - P_0)\right\} \qquad \text{(i)}$$

where k is Boltzmann's constant, f is the fugacity of hydrogen at temperature T and pressure P, β is the partial volume of hydrogen in the solution. The exponential factor accounts for an increase in the chemical potential of the hydrogen dissolved in a metal with increasing pressure, due to an increase in the sample volume resulting from the dissolved hydrogen.

For all the metal-hydrogen solutions of Group VI–VIII transition metals and their alloys studied, $\beta \approx 2.5$ Å^{3}atom^{-1} hydrogen [7, 4, 5]. The pressure dependences of the quantities entering into equation (i) are illustrated in Table 1. With $P_0 = 1$ bar and $T = 250°C$, hydrogen is practically an ideal gas, and $f_0 \approx P_0$. The magnitudes of f for high values of P are estimated by means of the extrapolation formulae [13] using the value of μ_0 $(250°C) = -14783$ cal mol^{-1} molecular hydrogen [14].

As shown in Table 1, the equilibrium concentration of hydrogen in an ideal metal-hydrogen solution at $P_{H_2} = 1$ bar has to be approximately 10^5 times lower than that at $P_{H_2} = 90$ kbar. For the platinum metals, this yields the magnitudes of hydrogen concentration at $P_{H_2} = 1$ bar listed in Table 2.

The obtained values of the equilibrium hydrogen concentration in a perfect defect-free lattice of ruthenium, osmium, iridium and platinum at atmospheric pressure are small compared with the concentration of hydrogen which could be trapped by various micro- and macrodefects and open surfaces [15]. For this reason, the effective values of hydrogen solubility in

these metals determined from direct experiments on hydrogen absorption at pressures of the order of 1 bar may be significantly higher than those of the "true" solubility. For instance, the available experimental data show [3] that at $P_{H_2} = 1$ atm and $T = 250°C$, the concentration of hydrogen in platinum should correspond to $n \approx 10^{-5}$ which is approximately 200 times higher than follows from our estimates.

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Table 2. Hydrogen solubility in ruthenium, osmium, iridium and platinum at 250°C. The values of n_{cal} are estimated from the experimental values n_{exp} using equation (i)

Metal	Ruthenium	Osmium	Iridium	Platinum
n_{exp} ($P_{H_2} = 90$ kbar)	0.03	0.003	$\leqslant 0.005$	$\leqslant 0.005$
n_{cal} ($P_{H_2} = 1$ bar)	3×10^{-7}	3×10^{-8}	$\leqslant 5 \times 10^{-8}$	$\leqslant 5 \times 10^{-8}$

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