

235. Pseudo-metallic Bonding of Hydrides.

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Experiments are described which show that the wetting of palladium by mercury is greatly facilitated if the palladium is first allowed to absorb hydrogen. After wetting, an amalgam of approximate composition $\text{PdH}_{0.6}\text{Hg}_4$ slowly liberates about three-quarters of the dissolved hydrogen at 1 atmosphere at 18°. Magnetic and X-ray evidence indicates that mercury combines with the palladium to form one or more intermetallic "compounds."

The observations are interpreted in terms of the hypothesis of pseudo-metallic bonding of hydrides, which permits a "chemical" approach to problems such as the wetting of metals by mercury, the solubility of hydrogen in transitional metals and their alloys, the possibility of preferred location of hydrogen at crystal boundaries in polycrystalline metals, and catalytic phenomena.

In an alternative formulation for hydrogen in metals, in which atomic hydrogen is considered as a compressed gas, hydrogen might be expected to show degeneracy phenomena different from those shown by deuterium.

Wetting of Metal Hydrides by Mercury.—The concept of metallic bonds as covalent bonds in a resonance system with a defect of electrons (Pauling and Ewing, *Rev. Mod. Physics*, 1948, **20**, 112) accords with the hypothesis that when metal atoms M are bonded with hydrogen, the grouping (M-H_n) behaves, with regard to further metallic bonding, approximately like the atom n places to the right of M in the Periodic System. For example, NH₄ or OH₃ should correspond to sodium and the grouping (Pd-H) to silver (cf. Ubbelohde, *Proc. Roy. Soc.*, 1937, *A*, **159**, 304). Earlier versions of this hypothesis are referred to by Rosenhall (*Ann. Physik*, 1935, **24**, 297; cf. especially Oxley, *Proc. Roy. Soc.*, 1922, *A*, **101**, 264).

The wetting of metals by mercury almost certainly involves the formation of "metallic" bonds between mercury atoms and the surface atoms of the metal. A number of observations on the action of mercury on transitional metals, in electrolysis and in hydrogenation catalysis at room temperature, may be interpreted on this basis.

Only a few examples are selected for discussion in the present paper. Experiments on palladium hydride amalgam are first described. There follow observations dealing with the effect of mercury on colloidal palladium and its effect on the overpotential of hydrogen on transitional metals.

When a strip of clean palladium, glowed by passage of a current to free it from hydrogen, was dipped into mercury under dilute sulphuric acid, the contact angle of wetting usually became \approx zero only after several hours. But as soon as the palladium was made cathodic the mercury wetted it with avidity.

A similar enhancement of wetting by mercury was observed with other transitional metals such as iron and platinum when these were dipped under mercury and then made cathodic (cf. also Casamajor, *Proc. Amer. Chem. Soc.*, 1877, **1**, 49; *Chem. News*, 1876, **34**, 34).

Experiments of this qualitative kind left it open to doubt whether the mercury was bonding

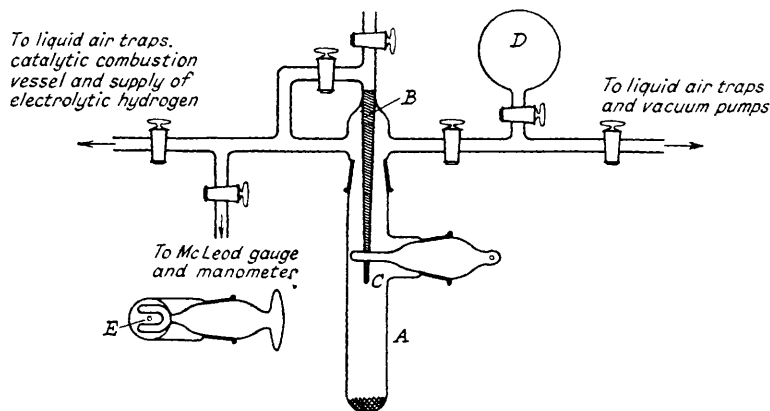
with the hydride groups MH_n or whether the function of the hydrogen was merely to reduce an oxide surface film which prevented the formation of metallic bonds between mercury and M.

To distinguish between these possibilities, more rigorously controlled experiments have been carried out on the comparative ease of wetting of palladium by mercury, before and after the palladium has absorbed hydrogen. These showed that palladium (sponge), carefully cleaned *in vacuo*, absorbed mercury only slowly over a period of days, to form one or more amalgam phases. If the palladium was first saturated with hydrogen, to form approximately $PdH_{0.6}$, the mercury wetted it very rapidly and with considerable evolution of heat. When the product was kept for several days, some of the hydrogen was evolved, but the remainder was retained for comparatively long periods. The palladium hydride amalgam and the palladium amalgam were diamagnetic. Preliminary X-ray spectrography indicated that complex phase systems were formed [Mellor ("Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1936, Vol. XV, p. 592) states that Pd-Hg occurs as an ore].

EXPERIMENTAL.

The essential portions of the vacuum apparatus are illustrated.

The palladium sponge (Johnson and Matthey, Ltd.; 99.9%-pure) was weighed into the bottom of the Pyrex tube *A*, which was joined to the vacuum apparatus by a ground joint waxed with "Picein" and specially designed to minimise contamination of the apparatus. The required quantity of triple-distilled mercury was stored in the tube *B*. When required, the sealed tip *C* of this tube could be broken *in vacuo* by turning the Pyrex key which carried a stout horseshoe of Pyrex *E*, as shown. A fresh tip was sealed on for each experiment. Hydrogen, prepared by electrolysis of aqueous potassium hydroxide-barium hydroxide, was purified by passage over platinised asbestos at 450° and was taken into the apparatus through a liquid-air trap as required. The container *D* was calibrated for volume, which facilitated the estimation of volumes of gas absorbed and desorbed, with the aid of a McLeod gauge and mercury manometer.



Preparation of "Clean" Palladium Sponge and Action of Mercury.—After the walls of the apparatus, whilst it contained hydrogen, had been washed and flamed, the apparatus was evacuated, air was let in, and 0.5–1.5 g. of palladium sponge was weighed into *A*. The tube *A* was heated to about 400° *in vacuo* ($<10^{-4}$ mm. Hg.), and the taps to all exposed mercury surfaces were shut. Hydrogen was then passed in to a pressure of 1 atmosphere, and the palladium allowed to cool in hydrogen. The hydrogen was then removed again, by evacuation at 400° , and after cooling of the palladium in a high vacuum the tip *C* was broken. By this means pure dry mercury came into contact with palladium freshly reduced and activated by sorption and desorption of hydrogen.

Although there was some appearance of wetting, the palladium sponge normally tended to "float" on the mercury, and only gradually absorbed it over a period of many hours. According to the relative amounts of mercury and palladium used, the amalgams eventually formed had overall compositions ranging from $PdHg_3$ to $PdHg_{34}$. It is not finally established in these experiments under what conditions more than one amalgam phase was formed, but the systems of high mercury content were obviously not homogeneous and contained liquid mercury.

Preparation of Palladium Hydride Amalgams.—Palladium sponge, prepared and cleaned as above was saturated with hydrogen at room temperature and atmosphere, and, whilst hydrogen was left in the apparatus, arbitrary amounts of mercury stored above *C* were brought into contact with the Pd-H as above.

Vigorous wetting was observed with the evolution of substantial amounts of heat. The mercury was at once absorbed to form a silvery-white amalgam, without change in pressure in the apparatus. A typical freshly formed amalgam had the composition $PdH_{0.6}Hg_4$. When kept for several hours, the amalgam changed in colour, to a dark grey, and part of the hydrogen was re-evolved so that the pressure of hydrogen in the apparatus rose above 1 atmosphere, and the residual composition was approx. $PdH_{0.15}Hg_4$.

After they had lost part of their hydrogen in this way, the amalgams were transferred to stoppered weighing-bottles. They retained their residual hydrogen for many days, as was verified by freezing a quantity of amalgam in *A* by surrounding the vessel with liquid air, evacuating it to a low pressure, and then warming it in an oven to 400°; the residual hydrogen was evolved at approx. 100–120°.

X-Ray Structure and Magnetic Susceptibility of the Amalgams.—X-Ray powder photographs of the amalgams showed that the structures were very much more complex than that of the original palladium. Palladium amalgams and palladium hydride amalgams gave rather similar X-ray spectra, with lattice spacings which suggested distorted cubic structures. A detailed X-ray analysis of what appeared to be a complex phase diagram would be necessary to sort out the phases present. This has not yet been attempted. Recently published preliminary X-ray analyses of UHg_n are suggestive in this connection (n can be 2, 3, or 4; cf. Rundle and Wilson, *Acta Crystall.*, 1949, 2, 148). Measurements of magnetic susceptibilities showed that, whereas palladium is paramagnetic, the palladium amalgams and palladium hydride amalgams described above were diamagnetic, approx. susceptibilities per g. being -0.13×10^{-6} for the amalgam $\text{PdHg}_{5.2}$ and -0.19×10^{-6} for the amalgam $\text{PdH}_{0.15}\text{Hg}_4$. This diamagnetism suggests some form of intermetallic bonding which saturates all the *d* orbitals of the palladium.

DISCUSSION.

Action of Mercury on Colloidal Palladium-Hydrogen Sols.—Paal and Steyer (*Ber.*, 1918, 51, 1743) described experiments which showed that liquid or colloidal mercury gradually interacted with aqueous colloidal palladium hydride with the displacement of hydrogen. They claimed that all the hydrogen was evolved as a result of the action of the mercury, but their evidence was indirect and inconclusive.

Poisoning of Palladium by Mercury in the Absorption of Hydrogen.—Ramsay (*Phil. Mag.*, 1894, 38, 206) claimed that palladium was poisoned by mercury, so that absorption of hydrogen did not occur. The present work indicates that fairly prolonged action would be required to obtain amalgamation. Mercury should act as a poison only if it reaches the palladium before the hydrogen can enter the lattice (cf. Hoitsema, *Z. Physik. Chem.*, 1895, 17, 1, and Lambert and Gates, *Proc. Roy. Soc.*, 1925, A, 108, 456 for the use of mercury manometers in measuring palladium-hydrogen absorption isotherms).

Increased Overpotential of Transitional Metals after Poisoning of the Surface by Mercury.—Observations on septum diffusion through iron (Aten and Zieren, *Rec. Trav. chim.*, 1930, 49, 641) indicate that mercury is adsorbed on the surface of metals such as iron after the surface has been made cathodic. This adsorption promotes higher pressures on the gas side of the septum. According to the arguments advanced by Ubbelohde (*J.*, 1949, 2008), this indicates that the overpotential of hydrogen is increased by adsorption of mercury on the iron-plus-hydrogen. On the basis of the "pseudo-metallic hydride" hypothesis, the mercury atoms form metallic bonds with surface hydride groups, and thereby delay transfer of hydrogen atoms required to permit pairing off as molecules of hydrogen. Reactive groups for hydrogen transfer are thereby blocked.

Alternative Formulations of Hydrogen in Transitional Metals.—Some consequences of the chemical formulation of the grouping (Pd-H) as a unit which forms pseudometallic bonds with other atoms, in a way similar to silver, may be briefly examined.

Critical Solubility of hydrogen in alloys. (a) At room temperature, the alloy of approximate composition $\text{PdH}_{0.65}$ marks a system such that further addition of hydrogen leads to a steep rise in the dissociation pressure, as may be shown, *e.g.*, by extrapolating the compositions found by Lambert and Gates at 75° to room temperature. This alloy may be written $\text{Pd}_{0.35}(\text{PdH})_{0.65}$ or $\text{Pd}(\text{PdH})_{1.9}$. By analogy, ternary alloys of compositions $\text{Pd}(\text{PdH})_m\text{Ag}_n$ would be expected to show a steep rise in dissociation pressure of hydrogen when $n + m \gg 1.9$, *i.e.*, the solubility of hydrogen should sink to zero approximately when $n \gg 1.9$ and $m = 0$, at room temperature. This corresponds with 65 atoms-% of silver, which is very near to the critical value actually found by various authors (cf. Rosenhall, *loc. cit.*).

This critical value differs from that calculated on the electron-band formulation (Vogt, *Ann. Physik*, 1932, 14, 1; Mott, *Proc. Physical Soc.*, 1935, 47, 571). From the observation that the paramagnetism of palladium sinks to zero when it is alloyed to form $\text{PdM}_{0.6}$ where M is a monovalent "metal" (Ag, Au, H, etc.), it has been argued that the peculiar solubility of hydrogen is associated with the vacant levels in the *d* band of palladium. If this were a complete theory, the solubility of hydrogen might be expected to sink to zero at the composition $\text{PdAg}_{0.6}$, but this is not observed experimentally. The discrepancy is probably due to the fact that when the palladium lattice expands, *e.g.*, by alloying with hydrogen, or thermally, the change in overlap of the orbitals changes the energetics of the solution process (cf. Ubbelohde, *loc. cit.*).

(b) At higher temperatures, palladium-silver alloys actually show an enhanced solubility for hydrogen (Sieverts, Jurisch, and Metz, *Z. anorg. Chem.*, 1915, 92, 329). Though the

observations are too confusing to permit elucidation of the whole effect, it seems significant that the alloy which shows *maximum* solvent power has the approximate stoichiometric composition $\text{PdAg}_{0.67}$. On the "chemical" view the palladium appears to be able to free additional bonding orbitals when the palladium atoms are separated by silver, and when the rise in temperature reduces the overlap of the bonding orbitals in the palladium.

Migration of Hydrogen to the Crystal Boundaries in Polycrystalline Metals.—On the Pauling concept of metallic binding, boundaries between crystals in a polycrystalline metal must be regions where the bond system is distorted owing to imperfect matching of the planes of atoms. Some of the bonding orbitals may actually be unused at the separation of two crystal grains. This would correspond on the "chemical" formulation to the development of partial free valencies at the crystal boundaries. When only small amounts of hydrogen are dissolved in a metal it would be expected that the hydrogen atoms would migrate to the regions of partial free valency, where the units M-H should be formed with greater stability than within the crystal lattice. This possibility of preferred location at internal discontinuities has important metallographic implications, of which the most familiar to chemists is the liberation, in ingots of steel, of hydrogen gas at very high pressures, with the formation of hair-line cracks.

Pseudo-metallic Units in Catalysis.—There is nothing new in the concept that (MH_n) on the surface of a metal may play an important part in catalysis. It is, however, important to emphasise that if (MH_n) has an external electronic system capable of forming further *metallic* bonds, this may help to explain phenomena of poisoning of hydrogenation catalysts at low temperatures by metals such as mercury (cf. Vanhaeren and Jungers, *Bull. Soc. chim. Belg.*, 1945, 54, 236). No simple alternative explanation of poisoning by mercury can be suggested, unlike poisoning by electronegative atoms such as sulphur.

NOTE ON DEGENERACY OF THE PROTON GAS IN METALLIC SOLID SOLUTIONS.

As has been indicated above, the "chemical" formulation of hydrides such as (PdH) seems the most convenient in certain cases. Alternative formulations, such as the electron-band theory, have powerful mathematical advantages, but are less amenable for consideration of the behaviour of individual atoms. Finally, if hydrogen is considered as a metal formed on compression of H_2 molecules to about 10^5 atmospheres (cf. Ubbelohde, *loc. cit.*, 1937), it is worth noting that the degeneracy parameter,

$$C = (v/Nh^3)(2\pi mkT)^{3/2} = 3.074 \times 10^{-4} M^{3/2} T^{3/2} / n$$

where M = mol. wt., and n = concentration in moles/litre, takes on a value in so-called interstitial hydrides which indicates that substantial degeneracy of the "proton gas" could be attained experimentally. Writing $n \approx 10^{-1}$, $T = 300^\circ \text{K.}$, and $M = 1$ gives $C = 16$. Deuterium with $M = 2$ should have $C = 45$ and should furthermore have different statistics from hydrogen.

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