

# Symposium on Hydrogen in Metals

## A SELECTIVE REVIEW OF THE PLATINIFEROUS PAPERS

By Paul A. Sermon

Department of Chemistry, Brunel University, Uxbridge, England

*Over one hundred and fifty participants met at The Queen's University of Belfast, Northern Ireland, on March 26th to 29th of this year to attend an international conference sponsored by the Institute of Physics, the Society of Chemical Industry, the Royal Society of Chemistry, the Bunsengesellschaft für Physikalische Chemie, the International Association for Hydrogen Energy, and the International Union of Pure and Applied Chemistry, to consider metal hydrides. Some of the papers concerned the platinum metals.*

Non-stoichiometric hydrides may become of considerable importance for heat pumps, fuel cells, batteries, energy conversion and storage, and in hydrogen purification-storage-compression. Transition metals play a prominent role in each area as metal and alloy hydrides and to activate bulk metals by providing a ready source of dissociated hydrogen.

### Single Metal Hydrides

Several papers considered newer techniques of analysis of equilibrium states of sorbed hydrogen. Thus, for example, J. W. Hanneken of Memphis State University, Tennessee, reported non-destructive methods of determining local hydrogen concentrations in  $\text{PdH}_x$ , while Y. Andersson, Professor S. Rundqvist and R. Tellgren, University of Uppsala, and Professor T. B. Flanagan, University of Vermont, found that D atoms dissolved in  $\text{Pd}_{15}\text{P}_2\text{D}_{0.46}$  at 296K and 500kPa occupied distorted interstices.

Professor H. Brodowsky and J. Fleischauer (Universität Kiel, F.R.G.) considered the internal friction spectrum of  $\text{PdH}_x$  and polycrystalline  $\alpha$ -phase  $\text{PdB}_y\text{H}_x$ . Hydrogen sorption isotherms, measured gravimetrically at 423 to 573K and up to 30 bar for  $\text{PdB}_y\text{H}_x$ , were evaluated in terms of the contribution of the rise in the Fermi level and lattice distortions to deviations from ideality. Bearing in mind the ease of carbon inclusion in palladium in

catalysts during hydrocarbon and carbon monoxide reactions, it was interesting that Ted Flanagan, and S. Kishimoto of Kobe University, Japan reported that small amounts of interstitial carbon increased the solubility of hydrogen and lowered the plateau hydrogen pressure for hydride formation, but did not greatly affect the extent of hysteresis. The exothermic solubility of hydrogen in amorphous  $\text{Pd}_{0.80}\text{Si}_{0.20}$  was reported by R. Fromageau, CNRS, France.

The novel use of catastrophe theory to explain some structural and phase relationships in the extent of sorption of hydrogen by palladium was described by F. A. Lewis of the Queen's University, Belfast. While the presence of subsurface and surface hydride phase-transitions in  $\text{PdH}_x$  on palladium was suggested by S. G. McKee and F. A. Kelly also of the Queen's University. R. C. Johnston and F. A. Lewis (Queen's University) described results on the overpotential of hydrogen on electrode surfaces during electrolysis in hydrogen-saturated catholytes. Interestingly, M. W. Lee, J. Villalobos and R. Glosser of the University of Texas at Dallas reported that the absorption properties of sapphire-supported palladium films with a thickness of 30 to 100nm were different from those of bulk palladium (in a similar manner to the results of P. Newbatt, P. A. Sermon and M. Luengo) and involved a

different activation process. Fortunately, M. W. McKergow, P. W. Gilberd, D. J. Picton and D. K. Ross of the University of Birmingham together with P. Fratzl and O. Blaschko of Universität Wien, Austria and I. S. Anderson and M. Hagen of Grenoble, France confirmed palladium-deuterium interactions to be attractive in  $\beta$ -PdD<sub>0.8</sub>. P. Newbatt, P. A. Sermon and M. Luengo (Brunel University and CSIC, Madrid) found that hydrogen sorption by oxide-supported palladium at 303K produced distorted isothermal hysteresis of a form seen previously by P. C. Aben, but different from those shown by a medium surface area palladium black. The rate of hydrogen sorption under flow conditions at 303K and 101kPa passed through a maximum at intermediate values of  $x$  in PdH <sub>$x$</sub> , and at low and high  $x$  showed orders of 0.0 to 0.2 and 0.9 at  $x$  and  $(1-x)$ , respectively. This the authors believed did not suggest that the dissociation of molecular hydrogen was the rate determining step on such high surface samples. The effect of surface roughness, contamination and electrolyte concentration upon the rate of permeation of hydrogen through palladium membranes were studied by R. V. Bucur of the Institute of Isotopic and Molecular Technology, Romania using transient electrochemical methods with either constant entrance flux or concentration conditions. Hydrogen and deuterium diffusion coefficients determined at 278 to 323K ( $2.48 \times 10^{-3}$  cm<sup>2</sup>/s and  $1.67 \times 10^{-3}$  cm<sup>2</sup>/s) were in good agreement with non-electrochemically derived values. Interestingly, R. V. Bucur and V. Mecea also used stripping potentiostatic methods to study diffusion and permeation rates through a palladium film 80 to 140nm thick on a polyethylene-terephthalate substrate. Professor H. Züchner, H.-G. Schöneich and U. Bilitewski of Institut für Physikalische Chemie, Münster, F.R.G. also used electrochemical methods to consider the influence of dislocations in palladium on the diffusivity and mobility of hydrogen therein. E. S. Carnell and S. P. Wach of the City of London Polytechnic determined mass transport coefficients of hydrogen in palladium membranes in the  $\alpha$ -phase region, and found that

these were strongly influenced by deformation. E. Fromm of the Max-Planck-Institut für Metallforschung, Stuttgart found that oxide layers retarded the rate of hydrogen sorption below 673K but that palladium overlayers could accelerate the process.

## Alloy Hydrides

Much recent work has concentrated on the study of alloy hydrides, and this was a significant component of the Belfast meeting. Professor H. Kronmüller, G. Higelin, P. Vargas of the Max-Planck-Institut für Metallforschung and R. Lässer of Kernforschungsanlage Jülich, F.R.G. have studied low temperature diffusion of hydrogen isotopes in nickel-iron- and palladium-alloys using magnetic relaxation techniques.

In addition Lässer studied tritium in PdT <sub>$x$</sub>  and Pd <sub>$1-y$</sub> Ag <sub>$y$</sub> T <sub>$x$</sub>  systems and obtained p-c-temperature data. While Professor Y. Sakamoto of Nagasaki University, Japan and Ted Flanagan studied hydrogen sorption by palladium-cerium alloys. A. W. Szafranski and S. M. Filipek of the Polish Academy of Science, Warsaw reported hydrogen sorption by palladium- and nickel-based amorphous alloys at 373K and up to 10kbar. D. A. Smith, J. Braithwaite, J. P. G. Farr and I. R. Harris of the University of Birmingham measured the electrical resistance of PdYH <sub>$x$</sub>  solid solution alloys (where Y is silver, cerium and yttrium) with increasing values of  $x$ ; increases in resistance with  $x$  were related to electronic states. Professor Y. Sakamoto and K. Baba measured hydrogen diffusion in Pt-Cu ordered alloys in specific crystallographic directions. J. Hauck of K.F.A., Jülich described results obtained on the structure and stability of ternary hydrides including PdNi <sub>$x$</sub> H <sub>$x$</sub>  and PdAu <sub>$y$</sub> H <sub>$x$</sub>  where the site preference energy is stronger than other structural parameters.

Recently obtained data on crystal structure and superconducting properties of high pressure phases in R-M-H <sub>$x$</sub>  systems, where M is molybdenum, tungsten, titanium, niobium or tantalum and R is ruthenium or rhenium were reported by V. E. Antonov, L. T. Belash, V. Yu.

Malyshev and Professor E. G. Ponyatovskii, U.S.S.R. Academy of Sciences.

### Catalytic Applications

First, the work of E. L. Fromm, who used platinum group metals to catalyse absorption on hydrogen by single metals, has already been mentioned. Secondly, I. Manninger, Z. Paál and P. Tétényi, Institute of Isotopes of the Hungarian Academy of Sciences, reported the effect of hydrogen on the rate and mode of recrystallisation of platinum black as measured by X-ray methods, and the role the adsorbed-adsorbed hydrogen might have. Thirdly, the catalytic activity of palladium alloy tubes charged with hydrogen electrolytically was considered by S. E. J. Bell, T. J. McBride, S. G. McKee, J. P. Magennis and F. A. Lewis (Queen's University). Professor V. M. Gryaznov of the U.S.S.R. Academy of Sciences also reported on the catalytic activity of palladium alloy membranes in selective hydrogenation and dehydrogenation reactions, such as the conversion of acetylenic alcohol into ethylenic alcohols and conversion of butane to butadiene. As a result of the palladium shifting the equilibrium or oxygen removing extracted hydrogen the reactions may proceed to extents exceeding thermodynamic equilibrium. The hydrogenation

activity of alumina-supported palladium was shown to depend upon the previous treatment in hydrogen in the abstract of O. Leonte, M. Birjega, D. Macovei, P. Pausescu, N. Popescu-Pogriion and M. Georgescu of Romania. In addition P. Newbatt, P. A. Sermon and M. Luengo reported continuing work on the use of supported Pd<sub>2</sub> for selective catalysis of hydrocarbon reactions.

### Future Developments

Professor E. Wicke, University of Münster, F.R.G. outlined future prospects for metal-hydrogen systems and how these will be achieved with controlled expansion, rearrangement and reconstruction. To enable these hydrides to find their full potential in applications as diverse as heterogeneous catalysis, heat pumps and hydrogen purification the rate and extent of hydrogen adsorption-desorption and heat transfer must be optimised. Platinum metals are making, and will continue to make a significant contribution. This and other symposia show the international and interdisciplinary work which will allow these goals to be achieved.

The proceedings of this symposium will be published in *Zeitschrift für Physikalische Chemie Neue Folge* in the Spring of 1986.

## The Thermodynamics of Ruthenium Systems

After the publication last year of Seddon and Seddon's massive monograph "The Chemistry of Ruthenium", it might be supposed that little remains to be said on the chemistry of ruthenium (for a review of this book see *Platinum Metals Rev.*, 1984, 28, (4), 177). However, a new review paper, "The Chemistry and Thermodynamics of Ruthenium and Some of its Inorganic Compounds and Aqueous Species", by Joseph A. Rard of the Lawrence Livermore National Laboratory, succeeds in covering somewhat different ground, and contains much of value. (*Chem. Rev.*, 1985, 85, (1), 1-39).

The present paper provides a critical review of the literature, from 1910 up to mid-1984, of the inorganic chemistry of some ruthenium compounds and aqueous species with special emphasis on their thermodynamic properties.

Thus Seddon and Seddon quote thermodynamic values for RuO<sub>4</sub>, for instance, from a number of sources, while Rard provides a critically assessed table of self-consistent values.

Included in the review are ruthenium metal, hydrides, chalcogenides, oxides, hydroxides, halides, oxyhalides (except fluorides), complex sulphates, sulphites, nitrates and nitrites. Aqueous systems considered are aquo ions, hydrolysed cations, oxyanions and halide and sulphate complexes. The oxide, halide, oxyhalide and aqueous systems are described in considerable detail and an effort is made to resolve some of the conflicting claims and values in the literature. The thermodynamic properties of some intermetallic compounds are considered, together with a brief look at phase diagrams for ruthenium-metal and some ruthenium-non metal systems. J.R.T.