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Ewald Wicke and his work on metal–hydrogen systems

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Abstract

Ewald Wicke born in Wuppertal, Germany, on August 17th 1914 died on March 7th 2000 in Münster, Germany after a fully scientific life. He was one of the pioneers in the field of metal hydrogen systems and he has formed the community of metal 'hydriders' by his manifold activities as an all-round physical chemist and scientist, as an organizer, a busy editor and a sound discussion partner.

Ewald Wicke

1. Introduction

It is not the intention of this paper to go into all details of Wicke's scientific achievements, but rather to highlight the breadth and depth of his scientific activities. Particularly, it is the aim to emphasize his fundamental contributions that have shaped the field of metal–hydrogen research forever.

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2. The all-round physical chemist Ewald Wicke

To understand the basis of Wicke's approach in studying metal–hydrogen systems one must know his principal attitude towards the natural sciences and especially to physical chemistry. His fields of interest covered a wide range from basic thermodynamics, kinetics and electrochemistry to technical chemistry and process engineering. But at any time it was the main challenge for him, to pay special attention to the applicability of physical chemistry in chemical engineering and to utilize complicated theories to evolve simple concepts that were understandable also for non-theorists.

Ewald Wicke was what one could call an all-round physical chemist. He determined the dissociation energy and heat conductivity of fluorine [1], he extended the Debye–Hückel theory for strong electrolytes to the high concentration region [2]. He investigated the structure of the hydronium ion [3] by applying IR and NMR methods and he suggested a structural model for water, that is still valid [4]. Nevertheless, his three main fields of interest were: (i) mass transport through porous systems [5], (ii) heterogeneous catalysis, especially oscillating reactions of gases at solid surfaces [6], and (iii) metal–hydrogen systems.

In view of this extraordinarily broad scientific interest one can imagine that Wicke applied a wide experimental spectrum of physical methods. The same holds for his measurements on diverse metal–hydrogen materials. It is worth emphasizing that he was very much ahead of his time in that also the study of fundamental properties of metal–hydrogen systems was always performed under the aspect of possible technical applications.

3. Search for a transfer catalyst for hydrogenation

Ewald Wicke was responsible for over a hundred PhD theses. One third of them dealt with metal–hydrogen systems, starting at the end of the 1950s and ending in 1990, after about 30 years of scientific research in this field. The motivating factor for the study of metal–hydrogen systems was his interest in heterogeneous catalysis, or more specifically, the search for a hydrogenating catalyst suitable especially for the hydrogenation of organic double bonds.

Wicke's student Otto [7] investigated in his thesis the kinetics of hydrogenation of uranium and the structure of the uranium-trihydride phases. He also determined *P–C*-isotherms and found a strong hysteresis between the formation and the decomposition curves of the hydride. Uranium trihydride has turned out to be an excellent hydrogen transfer catalyst. It has the property of strongly enhancing the hydride formation of metals such as palladium, titanium, tantalum and others when being in direct contact with them. However, uranium hydride fails as a catalyst for the hydrogenation of organic double bonds. Then Wicke's interest changed to investigating the hydrogenation of metals by transfer catalysts. Therefore, his next doctoral candidate Küssner [8] had to study the effect of various hydrogen transfer catalysts such as uranium hydride, UH_3, thorium hydride, ThH_3, cerium hydride, CeH_3, and titanium hydride, TiH_2, on the hydrogenation of palladium, tantalum and titanium. All these catalysts were suitable for the elimination of the kinetic inhibition of the establishment of equilibrium at the phase boundary. However, materials such as tantalum or titanium are characterized by strong surface oxide layers which had to be removed before use. The catalytic mechanism of these metallic hydrides is based on the hydrogen transfer occurring at direct contact of the materials.

4. The $Pd/H_2(D_2)$ system

Küssner's results [8] on the kinetics of hydrogen transfer to palladium attracted special attention. He showed that the diffusion of hydrogen from the surface into the bulk, i.e. a bulk process, is rate determining in the absorption process. This particular result determined henceforth the direction of the research activity of Ewald Wicke in the field of metal–hydrogen systems towards bulk effects and palladium was to play an exceptional role in the further studies.

Küssner had already applied the fundamental results on the Pd–H system to the construction of a new palladium hydrogen diffusion electrode [8], and more important, he had developed a hydrogen (deuterium) generator. A tube of palladium or palladium/silver 77/23 (closed at one side) serves as a cathode in an electrolysis cell. Hydrogen is liberated at the outside of the tube, diffuses through the wall of the tube and is released at the inside of the wall into the interior of the tube. The inside of the tube wall is covered by a deposit of Pd black which acts as a hydrogen transfer catalyst. This cell which is shown schematically in Fig. 1 allows the production of hydrogen or deuterium, depending on the electrolyte solution, of highest purity up to pressures of more than 100 bar without any problems.

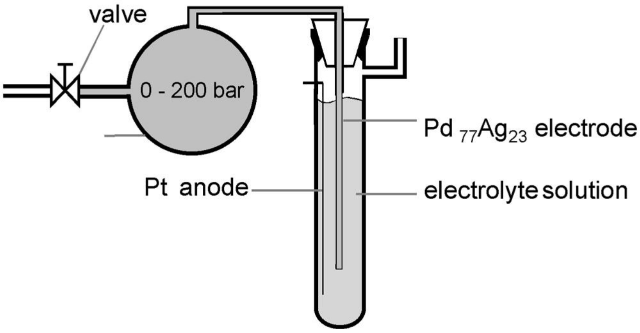

Fig. 1. Hydrogen (deuterium) generator.

Such cells for producing pure H_2 as well as pure D_2 have been working in our laboratory permanently for more than 30 years, but we never experienced anything that only remotely resembled the effect of cold fusion.

The discovery of the hydrogen transfer catalyst for metal hydride formation rendered it possible to study gas–solid reactions of transition metal/hydrogen systems at appreciably lower temperatures than was possible before. This effect was utilized by Nernst [9] in his diploma and PhD thesis. He used copper powder, uranium trihydride and trideuteride as transfer catalysts.

Nernst investigated the phase diagram and the thermodynamics of the Pd/H_2 and Pd/D_2 systems including H/D separation effects down to −78.5°C on palladium bulk samples. The hydrogen transfer catalyst itself was no longer the matter of interest but only a tool, the main interest and attention was directed to the bulk metal palladium and its behavior towards hydrogen/deuterium. The P–C–T-isotherms (cf. Fig. 2) were interpreted by Nernst and Wicke in terms of an attractive interaction between H atoms in the palladium host lattice in the dilute α-phase and a repulsive interaction in the highly concentrated β-phase. The hysteresis in the two-phase region was shown to originate from mechanical strain produced by the volume expansion that results from the α- to β-phase transition. The desorption branches have been found to be representative for the equilibrium between hydrogen in the metal and in the gas phase. The paper resulting from this thesis, published by Wicke and Nernst in the *Berichte Bunsengesellschaft Physikalische Chemie* (68, 224–235) in 1964 [9], was chosen 24 years later in August 1988 as a *Citation Classic*. The paper has been cited in over 250 publications. A rare event, that surely illustrates the international acceptance and appreciation of the work of the Wicke group.

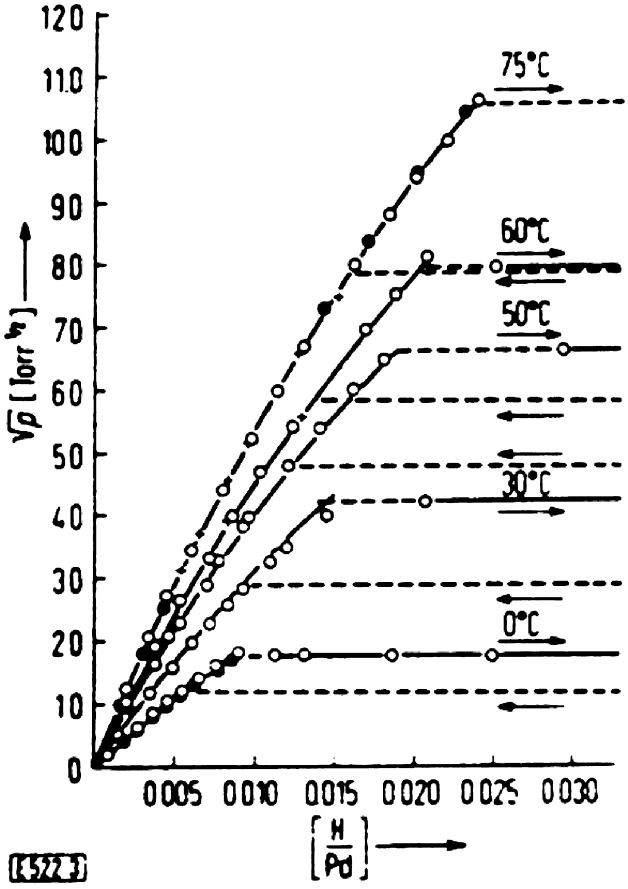

Fig. 2. P–C–T isotherms for Pd/H_2 [9].

This special public recognition of Wicke's scientific activities only highlights one side of his character: he was always fascinated by the results obtained on the classical $Pd/H_2(D_2)$ system and this motivated him strongly and therefore he paid special attention to this system in his further scientific life.

Together with his coworker Brodowsky, Wicke interpreted the attractive interaction between H atoms at small concentrations as a volume effect, while the repulsive interaction was explained by an electronic effect. The d-band of the palladium at the Fermi level is filled up by electrons of H atoms. This explanation has been confirmed by investigations of the system $Pd–Ag/H_2(D_2)$ in the doctoral thesis of Poeschel [10]. The main result of this thesis and the following publication was the finding of a competition between silver and hydrogen as electron donors to the palladium host lattice.

Based on these fundamental investigations Wicke subsequently followed three main lines of research: (i) P–C–T and magnetic measurements up to pressures of about 150 bar and temperatures of about 600 K, (ii) studies of hydrogen isotope diffusion and permeation behavior in palladium and palladium alloys, and (iii) the exploration of electron properties of palladium and related alloys and their hydrides.

5. The phase diagram and thermodynamics of the $Pd/H_2(D_2)$ system at high pressures

In 1972 Wicke and his students extended the measurements on the Pd/H_2 phase diagram up to the critical region by means of a high pressure gravimetric method. Frieske [11] measured simultaneously P–C–T isotherms and magnetic susceptibilities, that is χ–C–T isotherms between 20 and 300°C at hydrogen pressures between 0.01 and 140 bar (Fig. 3). From the combination of these methods he could determine precisely the coexistence curves of the α- and β-phases as well as the critical data of this system.

A couple of years later Blaurock [12] carried out new measurements on both the Pd/D_2 and the Pd/H_2 system. He also applied the method of synchronous determination of P–C–T and χ–C–T isotherms by gravimetric techniques. However, he increased the upper pressure to 151 bar and extended the temperature range to 340°C. Thereby

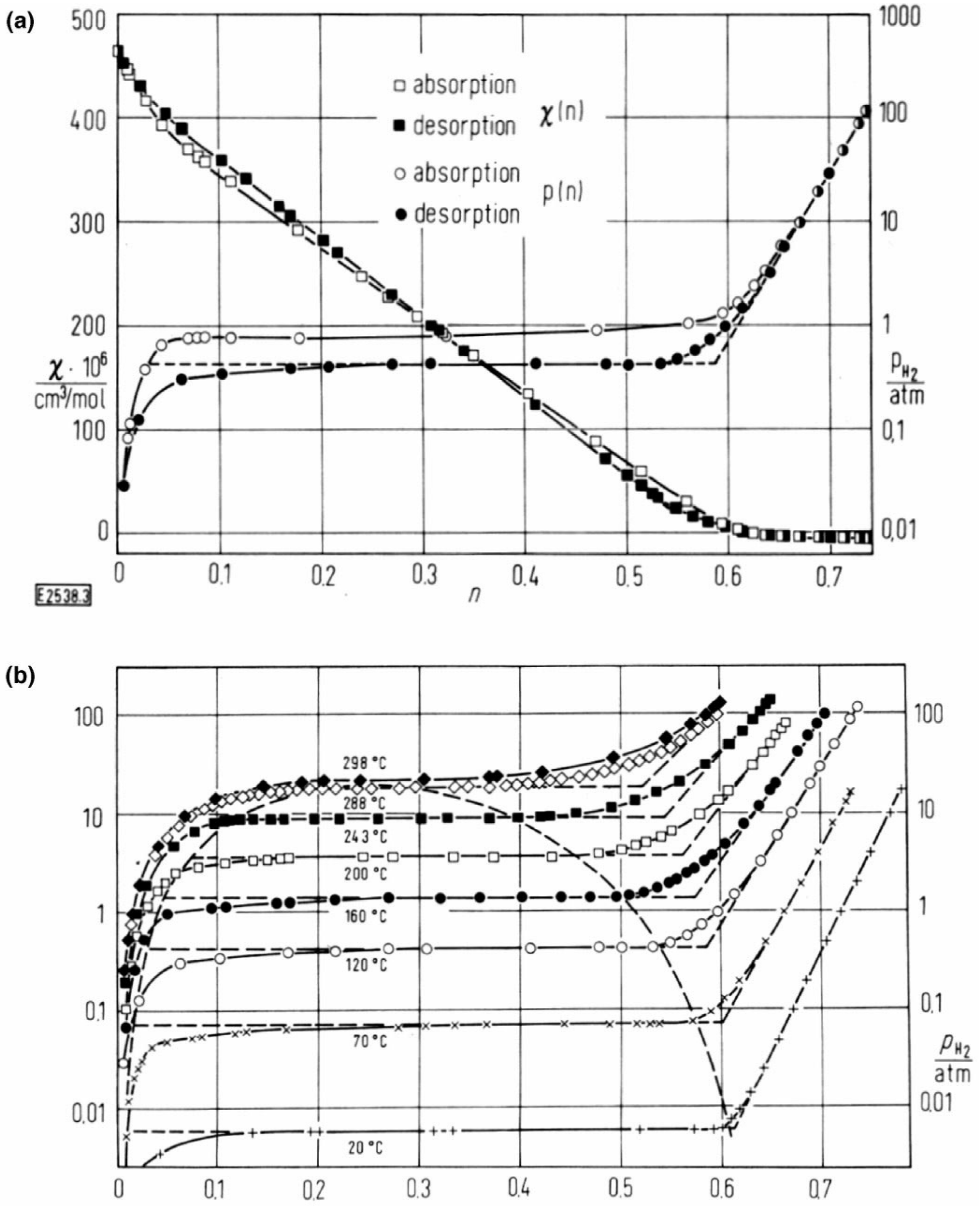

Fig. 3. (a) P–C–T and χ–C–T isotherms and (b) desorption isotherms and two-phase region for Pd/H_2 [11].

he could measure isotherms also in the supercritical region (Fig. 4). These measurements yielded precise thermodynamic and critical data and allowed an exact determination of the miscibility gap. It could be demonstrated, that no electronic H/D isotope effect exists and that the desorption branch represents the equilibrium isotherm. However, the problem of the origin of the hysteresis remained unsolved. Blaurock also confirmed the results obtained by other investigations in the Wicke group dealing with the electronic properties of metal hydrides. It was shown that the idea of short range attraction has to be replaced by a concept of long range attraction. Additionally, his experiments also shed some doubt on the applicability of the rigid band model.

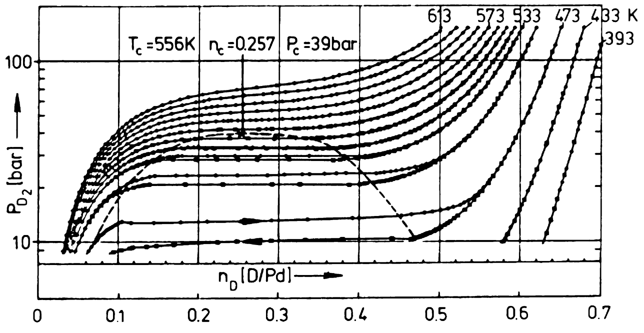

Fig. 4. P–C–T-isotherms around the critical point for Pd/D_2 [12].

6. Hydrogen(deuterium) diffusion and permeation in Pd-based alloys

The observation of Küssner [8], that the diffusion from the surface into the bulk of palladium is the rate determining step, caused Wicke and Küssner [13] to study the diffusion behavior of hydrogen and its isotopes in palladium and some special Pd-based alloys. A deposit of palladium black on foils of palladium and palladium alloys had turned out to be an excellent hydrogen transfer catalyst. Thus the transfer resistance at the gas–metal interface could practically be neglected in permeation measurements. Therefore, diffusion data could be obtained directly from permeation measurements. This was the basis of the diffusion measurements by Bohmholdt [14] who applied a stationary gasometric permeation method at normal temperatures and hydrogen/deuterium pressures between 1 and 20 bar. Simultaneously with Bohmholdt, Holleck [15] worked with electrochemical methods on the same system at comparable temperatures but with pressures up to only 1 bar. Both these Wicke students yielded identical, reliable values for the individual hydrogen isotope diffusion coefficients, activation energies and preexponential factors and observed for the first time the inverse H/D diffusion isotope effect, i.e. deuterium diffuses faster in palladium and its silver alloys than hydrogen.

A series of hydrogen isotope diffusion measurements in metals and alloys were performed in the Wicke group in the period that followed. I was one of these students involved in the diffusion studies starting in 1967. I have measured in detail — applying electrochemical time-lag techniques — not only the hydrogen and deuterium diffusion as a function of the hydrogen/deuterium concentration and silver concentration (up to 60% silver content) at normal temperatures [16] (Fig. 5). I also determined the hydrogen and deuterium diffusion coefficients in tantalum by an X-ray method via the lattice expansion during a long range diffusion process [17]. The results from the measurements on the palladium and palladium–silver alloys could partially be interpreted on the basis of thermodynamic results on these systems from Nernst [9], Brodowsky and Poeschel [10]. The inverse isotope effect could also be confirmed by these experiments, while the diffusion isotope effect in tantalum showed a normal behavior. Later, Sicking together with his coworker Glugla [18] made tracer diffusion measurements on palladium and palladium alloys. They applied a special time-lag technique and were able to show, that also tritium exhibits unusual isotope behavior, it diffuses faster than deuterium.

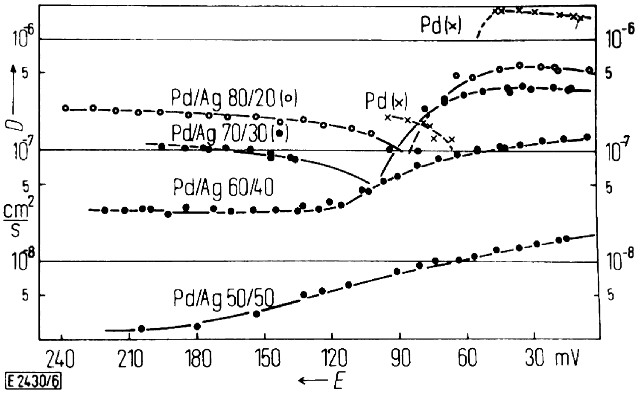

Fig. 5. Hydrogen diffusion coefficients in Pd/Ag alloys as a function of hydrogen concentration [16].

The hydrogen diffusion measurements have also been extended to highly heat-resistant steels. The behavior of these materials against hydrogen and tritium were of great technical interest, because these steels were discussed as materials for tubes which should be used in the process of coal gasification by waste heat utilization from nuclear reactors [19]. Here again the openness of Wicke's research for technical applications becomes obvious.

7. Electronic structures and properties of alloys and their hydrides

In the last 15 years of his active time in the institute, Wicke was particularly interested in the electronic properties of hydride-forming metals and alloys. Motivated by the manifold and promising results obtained from P–C–T and χ–C–T isotherm measurements on palladium and palladium–silver alloys as well as on their hydrides, Wicke and his students started to investigate the influence of alloying elements other than silver on the width of the miscibility gap, on the critical data and on the plateau pressures. Silver was substituted by well-selected metals such as Cu, Fe, Ru, Mo, Nb, V and others [20,21]. Consequently, Wicke also extended the spectrum of experimental techniques. Electronic specific heat and Mößbauer measurements [20,22–24] were performed and the results of these studies supplemented and supported the results and the interpretation of the magnetic measurements.

Wicke discussed the influence of alloying on the phase diagram in terms of 4d-band filling and depletion of host transition metals by electrons of the alloying metals and of hydrogen. Wicke assumed that the transferred electrons remain localized in the d-holes of the adjacent palladium atoms and thereby built up a second screening shell around the impurity ion. This two-stage screening model permits the interpretation of the influence of all the diverse alloying components consistently. But it turned out to be even more general. Wicke could show, that it is also suited for interpretation of the behavior of the analogous 3d-metal series V/Cr/Ti and their hydrides [24], as well as to various other systems [20,22]. These have been thoroughly investigated by the Wicke group over the years applying the complete spectrum of methods mentioned before.

The two-stage screening model [25] explains both, the short-range H–H repulsion (electronic H–H blocking effect) and the repulsion between hydrogen atoms and foreign metal atoms that compete with hydrogen for the empty states in the host lattice.

At this point again the technical orientation of Wicke should be emphasized. In all these investigations he never forgot to ask to what extent the electronic effect of alloying components could be made useful for the construction of effective hydrogen storage alloys [23].

8. The organizer, editor, referee and discussion partner Ewald Wicke

It would be incomplete to limit Wicke's efforts and commitments in the metal–hydrogen community only to his extensive scientific work. He had other important responsibilities. As (chief) editor of the *Zeitschrift für Physikalische Chemie* he was responsible for the publication of the proceedings of the international metal hydrogen conferences in Münster (1979), Stuttgart (1988), Belfast (1989), Uppsala (1992). However, besides his editorial activities, he also was the 'chief referee'. Furthermore, he was organizer and co-organizer of metal hydrogen conferences, 1968 in Münster, 1972 in Jülich and 1979 again in Münster, but he also was a normal participant and a normal referee at many metal–hydrogen conferences. He was famous for being an active and sound discussion partner. His contributions were always fair, well-founded and precisely formulated.

He was definitely principally an experimentalist, no theorist. Nevertheless, he applied the theories and concepts developed by pure theorists, such as Friedel, Switendick or Gupta and developed plausible and simple models which allowed him frequently to explain the experimental results graphically.

He showed also great respect to all his colleagues. Especially his long-standing companions Ted B. Flanagan, Fred Lewis and Bogdan Baranowski were highly appreciated and their scientific work gave him consistent impetus and new ideas.

Wicke's ideas, his respectful approach to science and his quest to scientific truth will leave a permanent impression on people who had the opportunity to know him.

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