MARCH, 1929 *PHYSICAL REVIEW* *VOLUME 33*

X-RAY STUDY OF THE SYSTEM PALLADIUM-HYDROGEN

By J. D. Hanawalt

Abstract

A unique *grating parameter* $a_0=4.017$A results when palladium is charged with hydrogen either electrolytically or from the gas phase, in disagreement with the results of Linde and Borelius. Larger values of a_0 are possible, but are not stable at 20°C. A difference in stability between some of the electrolytically charged specimens as compared to those charged from the gas phase is associated with the mechanical state of the micro-crystals in the two cases. The concentration Pd_2H is associated with the value $a_0=4.017$. *The* L_{III} *absorption limit* of palladium is changed by the presence of hydrogen which causes a shift of the main edge of 0.87 X.U toward shorter wavelengths, and the occurrence of a secondary absorption 10 X.U. toward shorter wavelengths. This is taken to indicate a chemical combination between palladium and hydrogen atoms. The molecule PdH is suggested. *Impurities* in the palladium affect very markedly its occlusion of hydrogen. The unique value $a_0=4.017$ does not appear but rather all distensions in the range 3.885 to 4.030 are observed. It is suggested that impurities in the palladium might account for the difference between the results of Yamada and those of McKeehan.

Introduction

EXPERIMENTAL studies of the system palladium-hydrogen have been made by various methods and by many observers, but there has been some disagreement and contradiction in the results obtained. The method of study in which pressure-concentration equilibria are measured at different temperatures seems to show quite definitely the existence of a hydrogen-rich phase with a concentration very closely in the neighborhood of 0.5 atomic weight of hydrogen per atomic weight of palladium; that is, a composition corresponding to the formula Pd_2H[1,2,3]. The isothermals of Lambert and Gates show 'breaks' at approximately the same composition (about 0.53 atom of hydrogen per atom of palladium) at temperatures of 75°, 103°, and 120°. (See Fig. 1) This phase may be supersaturated to concentrations as high as 0.7. There is, however, considerable difference in the equilibrium pressures obtained by different workers and even question as to whether it is possible to reach truly equilibrium pressures by operating isothermally. Gillespie and Hall consider that equilibrium can be obtained by a special heat treatment. They find 'breaks,' at 0°C at an excess of only 0.2 percent of hydrogen, while at higher temperatures the breaks occur at exactly the Pd_2H composition within the experimental error. In addition to this phase with a hydrogen

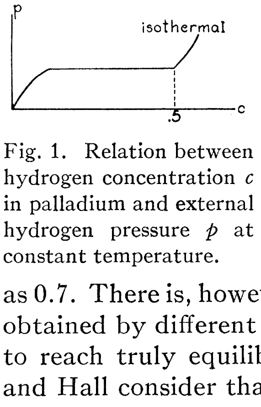

Fig. 1. Relation between hydrogen concentration c in palladium and external hydrogen pressure p at constant temperature.

---

[1] Troost and Hautefeuille, Ann. Chim. Phys. **2**, 279 (1874).

[2] Lambert and Gates, Proc. Roy. Soc. **A108**, 456 (1925).

[3] Gillespie and Hall, Journ. Amer. Chem. Soc. **48**, 1207 (1926).

concentration of 0.5, there have also been observed states in which the hydrogen concentration is *continuously* increased from zero up to a value greater than 0.5. However, this seems to be just chance behavior, and the causes of it are not understood. The presence of amorphous and crystalline varieties of palladium has been suggested.[4]

Another main line of attack on the problem has been to study the changes in the parameter a_0 of the crystal lattice of palladium when hydrogen is absorbed. Here Yamada[5] finds that hydrogen taken up by palladium from electrolysis of dilute H_2SO_4 may produce a distension of the pure palladium lattice of any amount up to 2.8 percent, and so concludes that the system may best be described as a solid solution of hydrogen in palladium with no indication of a chemical combination. It was found by McKeehan,[6] on the other hand, using either electrolysis of H_2SO_4 or absorption in the hydrogen furnace from the gas phase that palladium and hydrogen are *not* miscible in all proportions, but that two crystalline phases can coexist, one being practically pure palladium with $a_0=3.90$A and the other a saturated solution of hydrogen in palladium with a parameter varying between 4.000 and 4.039, 4.036 being suggested as corresponding to the composition Pd_2H. No suggestion as to the source of the discrepancy between these two investigations has been made as yet.

The latest x-ray study to be published is that of Linde and Borelius,[7] who find quite different results depending upon the method used to occlude the hydrogen in the palladium. By letting the hydrogen furnace form the camera of the x-ray spectrograph, they were able to study the lattice parameter while the specimen was in the hydrogen atmosphere. The results of this experiment showed two coexisting phases, one hydrogen-poor with $a_0=3.89$ to 3.92, and the other hydrogen-rich with an average a_0 of 3.978A which they take to be Pd_2H. By charging the palladium with hydrogen by electrolysis of dilute H_2SO_4 they found a hydrogen-rich phase with a grating spacing larger than that obtained by absorption from the gas phase (4.034 at 20° and 4.023 at 90°). Continued electrolysis was found to produce supersaturation with a corresponding distension up to $a_0=4.07$A. The parameters 4.034 and 4.023 were determined by them to correspond to the hydrogen concentrations 0.70 and 0.65 respectively. Linde and Borelius emphasize the fact that these larger distensions could not be obtained in the hydrogen furnace at the temperatures and pressures at which they worked, nor could the lesser lattice constant 3.978 be obtained by electrolysis no matter how small the current density. Thus the hydrogen-rich phase from the electrolyte is considered by them to be entirely different from that of the hydrogen furnace and the composition $(PdH)_3Pd$ is suggested. This difference is apparently further borne out by the experimental result that the electrolytically charged specimens are more stable than the specimens charged in the hydrogen furnace.

[4] Holt, Edgar and Firth Zeits. f. Phys. Chem. **82,** 513 (1913).

[5] Yamada, Phil. Mag. **45,** 241 (1923).

[6] McKeehan, Phys. Rev. **21,** 334 (1923).

[7] Linde and Borelius, Ann. d. Physik **84,** 747 (1927).

While the work of Linde and Borelius seems fairly complete in itself, yet it is at variance with some earlier results and also with the results to be reported in this paper. The work performed in this laboratory consists of first, an x-ray study of the lattice parameter of palladium as influenced by hydrogen occluded in the palladium (a) by electrolysis; (b) from the gas phase, and (c) by sputtering in an atmosphere of hydrogen; second, a determination of the effect of the occlusion of hydrogen on the L_{III} x-ray absorption limit of palladium; third, a special investigation of the factors influencing the stability of the hydrogen-rich phase; and fourth, a study of the effects on the Pd-H system of impurities in the palladium.

II. EXPERIMENTAL PROCEDURE

For the purpose of measuring the parameter a_0 of the crystal lattice, an x-ray spectrograph of the usual type for working with powdered crystals was used. The tube itself was of the Siegbahn type. A copper anode was used, and the radiation was filtered through a thin nickel screen which also served as the window. The tube was operated at 25 ma and 28,000 volts, and exposures were usually for fifteen minutes. A calcite crystal was used to calibrate the camera, and when taking a diffraction picture, the palladium sheets were pressed against the face of this crystal. The radius of the film-holder was 8.570 cm, and a change in the palladium crystal parameter of about 0.003A could be measured.

The specimens used were from the American Platinum Company; some were 0.5 mm in thickness, while other specimens were rolled into sheets of various thicknesses from 0.05 mm to 0.001 mm. Hydrogen was forced into the palladium from the electrolyte by making it the cathode in dilute H_2SO_4 or HCl or NaOH, platinum being used as the anode. A second method of occluding the hydrogen was to heat the specimens for several hours at 200°C in a fore-pump vacuum, then admit hydrogen to a pressure of one atmosphere, and lower the temperature from 200°C to 80°C in a period of five hours; the temperature is then quickly dropped to 20°C and the specimen taken out and placed in the x-ray spectrograph.

III. GRATING SPACING OF ELECTROLYTICALLY CHARGED PD

Immediately after electrolysis the specimens showed the face-centered cubic lattice with an a_0 varying in the different specimens from 4.017 up to as great as 4.045 (a_0 for pure Pd was determined as 3.885) depending upon the conditions of electrolysis. All specimens with an initial a_0 greater than 4.017 were found to lose hydrogen when kept in air at 20°C until in the course of ten days or less the lattice had shrunk to the value 4.017. In no case was a specimen found to drop below this value, nor did any specimen stop shrinking until it had reached the value 4.017. Specimens with $a_0 = 4.017$ kept this value unchanged as long as they were under observation (several months). In most specimens this hydrogen-rich phase alone was present, though in some cases the pure Pd, 3.885 or slightly greater, coexisted with this phase. In order to determine whether this particular lattice spacing 4.017 was simply an equilibrium concentration corresponding to a temperature of 20°C, other specimens were held at temperatures of 50°, 70° and 90°C. As a result of these experiments it was found that the 4.017 lattice would not shrink to smaller values, but that if the temperature was too high, the 4.017 phase would break down completely to the pure palladium lattice. In this process of breaking down, no distension intermediate between 4.017 and 3.885 was observed, the lines of the 3.885 spacing simply appeared and grew stronger and those of the 4.017 phase grew weaker and finally disappeared.

IV. Grating Spacing of Pd Charged from the Gas Phase

The procedure in studying the specimens charged with hydrogen from the gas phase was the same as that described above for the electrolytic specimens. Immediately upon being removed from the hydrogen furnace, the palladium was found to have a face-centered lattice with a_0 equal to 4.017 or very slightly larger (though never reaching the highest values obtained in the electrolyte.) In those cases in which it was larger, it quickly dropped to the value 4.017. In this respect the behavior was exactly like that of electrolytically charged specimens. The behavior was also the same in that no specimens dropped to an a_0 smaller than 4.017. The difference in distension between electrolytically charged Pd and Pd charged from the gas phase as observed by Linde and Borelius did not appear in this work. However, there did appear to be, under certain circumstances a difference in the stabilities of the hydrogen-rich phase at 20°C depending on whether they had been charged electrolytically or from the gas phase. The 4.017 hydrogen-rich phase charged with hydrogen from the furnace was not stable at 20°C, breaking down to the 3.885 of pure Pd in from three to seven days. In this process, no values of a_0 between 4.017 and that of practically pure Pd were observed.

V. Pd Sputtered in Hydrogen

The specimens of palladium which were sputtered in hydrogen were very thin films, probably of the order of 10^{-4}cm thick. Immediately after sputtering the different films showed various distensions of the lattice above 3.885, though none was very large. The lattice constants were all in the range 3.885 and 3.920. By heating a given specimen a few minutes at 300°C in a vacuum, the lattice could be shrunk to a slightly smaller value, and by this means apparently all values of a_0 between 3.920 and 3.885 could be obtained. One specimen produced broad bands instead of lines on the x-ray film, indicating that micro-crystals with a_0's, differing by about 0.01A were existing very close together. After two years in air at 20°C three of these specimens with small distensions showed no observable shrinkage to still smaller values of a_0.

Bredig and Allolio[8] report for palladium sputtered in hydrogen an a_0 of 3.991Å. This large difference may likely be because of a difference in temperature of the cathode in their work and in this.

---

[8] Bredig and Allolio, Zeits. f. phys. Chem. **126,** 41 (1927).

VI. Influence of the Presence of Hydrogen on the L_{111} Absorption Limit of Pd

In the quest for some property of the Pd-H system which might indicate the nature of the combination, it was decided to determine whether the energy of the L_{111} absorption limit of Pd was influenced in any way by the presence of the hydrogen. A Siegbahn vacuum spectrograph was used for this work, and the $K\alpha_1$ and $K\alpha_2$ (1932.30 and 1936.51) lines of iron reflected in the second order from calcite were used as reference lines from which to determine the wave-length of the edges. The dispersion at this position was 20.11X.U. per mm, the crystal-plate distance being 124.4 mm. It was necessary to roll all of the specimens used to a thickness of 0.001 mm in order to secure very distinct edges, and to bring out their character. With absorbing screens of this thickness, the most dense part of the absorption was confined to a narrow band, thus giving the appearance of a white line adjacent to the main edge. Exposures were of the order of 100 ma. hours.

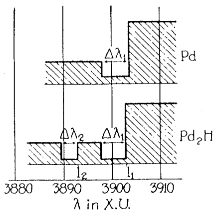

Fig. 2. Diagram of the L_{111} absorption spectra of Pd and of Pd in Pd_2H.

The results of these experiments are shown in Table I, and by the diagram Fig. 2. It is seen that the wave-length of the main L_{111} absorption edge (l_1 in the table) is shifted in the 4.017 phase by 0.87 X.U. (0.6 volts) toward shorter wave-lengths, and that there is in addition a second absorption edge, l_2, which is 10. X.U. (8.0 volts) less in wave-length than the pure Pd edge. The l_1 edge was measured on a comparator reading to 0.001 mm, but the l_2 edge was not dense enough to be measured on the comparator, and the accuracy of these measurements corresponds to about 0.6 volts. The absorption edges of electrolytically charged specimens and of specimens charged from the gas phase were identical in appearance. Microphotograms of the edges are shown in a preliminary report.[9]

Table I. L_{111} *x-ray absorption limits.*

Screen	a_0	l_1	l_2	$\Delta\lambda_1$(volts)	$\Delta\lambda_2$(volts)	l_2-l_1 (volts)
Pd	3.885	3903.90	•	4.4		
Pd_2H	4.017	3903.03	3893.9	3.8	2.4	7.4

VII. Stability of the Pd-H System

Since the hydrogen-rich phases from the electrolyte and from the hydrogen gas furnace are identical in their lattice constants of 4.017, and also in the character of their L_{111} absorption edges, it seemed probable that the difference in stability might be due to physical causes rather than to an inherent difference in the phases. This is also suggested by the fact that there is only a general agreement among the more than thirty specimens

---

[9] J. D. Hanawalt, Proc. Nat. Acad. Sci., Dec. 1928.

studied in the length of time necessary for the dissociation or break-down of the 4.017 phase at 20°C in air. After the usual conditions of occlusion, the specimens from the hydrogen furnace were found to go completely from the 4.017 phase to the 3.885 phase in some cases in as short a time as ten hours, and in others as long as six days. The specimens from the electrolyte on the other hand after the usual conditions of electrolysis (one hour at 0.1 to 0.4 ampere per sq. cm), were apparently stable at 20°C in air, though in a month or forty-five days a small part might be found to have dropped to 3.885. About ten days at 70°C is usually sufficient for complete dissociation of the whole specimen, and a temperature of about 200°C is necessary to drive the hydrogen out in a few hours.

The possibility that a sulphide of palladium or any other chemical compound was forming a protecting layer on the surface of the specimens from the electrolyte seems precluded by the fact that electrolysis in H_2SO_4, HCl, and NaOH all gave the same results.

Most of the specimens used were thin sheets of palladium which had been cold-rolled, and in many of them there were evidences of orientation of the micro-crystals as indicated by the extra intensity of some of the diffracted lines on the photographic film. Following this lead, the following experiments were performed. One sheet of palladium which showed orientation was divided into five pieces, two were put into the hydrogen furnace and three into the electrolyte. The two from the furnace showed the same orientation still strongly marked in the expanded lattice, while in the three from the electrolyte, no indication of orientation remained. Those from the electrolyte were stable as usual, while the two from the hydrogen furnace dissociated in four days at 20°C. Further experiments with specimens cold-rolled to 0.001 mm indicated that the instability of the specimens from the hydrogen furnace increased with the amount of cold-rolling. Evidences of orientation were not always present in these cold-rolled specimens, but the instability was just as decided whether the orientation existed or not. If these thin sheets were put in the electrolyte, the 4.017 phase appeared stable as usual. Apparently the process of occluding hydrogen from the electrolyte differs from that of the hydrogen furnace in that the micro-crystals are broken up and the mechanical strains induced by the rolling process are relieved. If mechanical strains are introduced into an electrolytic specimen, it proves to be as unstable as specimens from the hydrogen furnace. Hydrogen was put into a specimen by electrolysis, and it was then cold-rolled from .01 mm down to .003 mm. Immediately after the rolling process, the 4.017 phase still existed alone showing that the hydrogen was not forced out in the process of rolling. Two days later there was a good percentage of the 3.885 phase present, and in eight days the 4.017 phase had completely disappeared, and only the 3.885 phase was present. The control piece which was not rolled, showed no signs of dissociation of the 4.017 phase at the end of thirteen days.

The breaking up of the micro-crystals was observable directly in the x-ray diffraction patterns. By heating the palladium to 1000°C for various intervals of time, micro-crystals of various sizes could be grown, and three distinct sizes of micro-crystals could easily be distinguished by the appearance of the x-ray picture. Large enough crystals cause separate individual spots on the film, somewhat smaller crystals will give a line, but will be large enough to resolve the Cu $K\alpha$ doublet, while still smaller crystals will not resolve the α doublet. By observing these indications of crystal size, it was seen that the micro-crystals were broken up when the hydrogen was absorbed, but to a greater extent by electrolytic charging than by charging from the gas phase. This difference is probably due to two factors: first, the more rapid occlusion from the electrolyte causing differential strain, and second, the fact that the initial a_0 of the electrolytically charged specimens is considerably in excess of 4.017Å while the a_0 produced in the furnace is always just 4.017Å or only slightly greater. The mechanical strain in the electrolytically charged specimens is diminished to some extent when the hydrogen in excess of the 4.017 phase has escaped. This view is further borne out by the fact that if the electrolytic charging is done with a current density of 0.0001 amp./sq. cm instead of 0.1 amp./sq. cm, so that the initial a_0 does not exceed 4.017, then the specimen exhibits the same degree of instability as the specimens charged from the gas phase.

VIII. EFFECT ON THE PD-H SYSTEM OF IMPURITIES IN THE PD

In the early part of the investigation, two specimens of palladium were used whose origin is unknown. They had evidently been used for work in the laboratory some years previously. The behavior of these two specimens, as concerns their absorption of hydrogen was distinctly different from the behavior of all of the specimens of pure palladium (99.66% pure) obtained from the American Platinum Co. It was not found possible either by annealing or mechanical working, or removal of the surface layer, to influence the behavior of these two specimens in any way, so an analysis of the material was made. A spectroscopic analysis of one (A) of the specimens of pure palladium and one (B) of the specimens of unknown origin was carried out by Baker & Co., Inc., of Newark, N.J. This analysis showed that the specimen B was distinctly inferior in purity to specimen A. Specimen A was found to contain the usual small amounts of impurities; namely, calcium, magnesium, platinum, copper, iron and silicon. Specimen B contained the usual small amounts of calcium and magnesium, but *considerably* more than usual of copper, iron and silicon. The percentage excess of copper iron and silicon in specimen B above that in specimen A is not known.

The behavior of this, what we may call 'impure' palladium, stands in sharp contrast to that of the pure palladium as described in the preceding pages. Instead of observing the definite distension $a_0=4.017$Å or somewhat larger but no values of a_0 in the range between 4.017 and about 3.885, it was found that the impure palladium specimens could have apparently *any* distension within the region $a_0=3.885$ up to above 4.017, and that there was no stable distension which was characteristic of the system.

When fresh from the electrolyte, this impure palladium had distensions varying, in the nine separate experiments carried out, from $a_0=3.950$ to as high as $a_0=4.030$. Also different distensions existed in different parts of the same specimen at the same time. The following description of one experiment brings out the essential points shown by all of them. The specimen was 3 cm long, 1 cm wide and 0.007 cm thick. It was so supported in the electrolyte that about 1 cm of the length was below the surface. After one hour at 1.5 amp., the distensions ranged from $a_0=4.030$ at the lower end to $a_0=4.000$ at one cm from the end. Measurements taken at intervals throughout a period of 106 days showed that at all points there was a *continuous* shrinkage to smaller values of a_0 down to 3.888. Raising the temperature simply increased the rate at which the shrinkage took place.

The effect of mechanical strain on these impure palladium specimens was the same as that on the pure palladium; namely, to increase the rapidity of the dissociation of the Pd-H system. A specimen was cold-rolled from 0.07 mm to 0.001 mm; after the rolling it still contained hydrogen, a_0 being 3.940. A picture taken eight hours later contained broad diffraction lines, showing that micro-crystals with a_0 from 3.930 to 3.885 existed close together. This may be due to the more rapid dissociation of the micro-crystals with the greater strain. Three days later the specimen had completely dropped to 3.885, while the part of the specimen which was not rolled showed no detectable dissociation in three days.

IX. Discussion of Experimental Results

The results of this study indicate that in the range between $a_0=3.885$Å and 4.045A there exists just one outstanding stable lattice parameter of the Pd-H system; namely 4.017Å, regardless of the method used to occlude the hydrogen. And since pressure-concentration equilibrium studies show 'breaks' only at the concentration 0.5, it seems certain that the value 4.017 corresponds to the composition Pd_2H. The source of the discrepancy between this work and that of Linde and Borelius is not clear. As has been stated in the introduction to this paper, Linde and Borelius find different distensions of the Pd lattice depending on the method of occluding the hydrogen. The absorption of hydrogen from the gas phase, in the present work, was carried on under the conditions described by them so that their value 3.978 should have been observed. On the other hand, the phase 4.017 occurred every time the experiment was performed by us, and should have been observed by them. There is a possibility that the difficulty lies in the fact that Linde and Borelius used a different x-ray spectrograph for their electrolytically charged specimens than for their hydrogen furnace specimens, and that the latter had a film radius of only 2.5 cm.

It is well known that x-ray absorption limits of elements are changed by the valency or state of chemical combination of the element, and that in chemical compounds in addition to the principal edge, there may also be secondary edges or 'fine structure.' On this basis the results of the x-ray absorption work on the Pd-H systems indicate that the hydrogen is in chemical combination with the palladium. There seem to be at least two possible interpretations of the complex absorption edge exhibited by Pd_2H.

Since there are twice as many Pd atoms as H atoms present, the complex edge might correspond to a Pd atom which shares an H atom with one other Pd atom, or secondly, it might correspond to the superposition of two simple edges, one, l_1 due to Pd atoms alone, and the other, l_2, due to Pd atoms with which are combined H atoms. If we accept the first point of view, then it should be remarked that it seems unusual to find fine structure caused by chemical combination, and yet the main edge remaining almost unchanged as it is in this case. If, on the other hand, we accept the second hypothesis, then we have the result that combination with the hydrogen atom causes the L_{111} absorption limit of the Pd atom to shift 10. X.U. toward shorter wave-lengths, and that the L_{111} limit of the remaining Pd atoms which are not in intimate association with H atoms has been shifted by 0.87 X.U., perhaps due to the effect of the greater isolation of the atoms in the expanded lattice.

On this basis the crystal lattice of Pd_2H would be a face-centered cubic lattice in which alternate grating points are occupied by Pd atoms. Then higher concentrations of hydrogen than 0.5, (Pd_2H), would correspond to more of the grating points being occupied by PdH molecules than by Pd atoms. Whereas, if the hydrogen atoms in Pd_2H were shared between two palladium atoms, then for concentrations higher than 0.5 the excess hydrogen atoms would have to be associated in some different manner. The recent results of Coehn[7] showing that at least some of the hydrogen is in the ionic state may be of importance in this connection.

That the Pd-H system is composed of the units Pd and PdH has been suggested by Linde and Borelius on the basis of experiments on the behavior of the electrical resistance. Oxley[8] has also suggested on the basis of susceptibility measurements that the hydrogen is in intimate association with the palladium.

Since the effect of impurities in the palladium was to give results identical with those of Yamada, while the results with pure palladium agreed with McKeehan's work, this would seem to be the source of the difference in their results. Yamada's interpretation of his results to mean a solid solution of hydrogen in palladium, and not a chemical combination is not a necessary one since his results may also be explained on the assumption that the hydrogen atom is combined with a palladium atom, but that the symmetrical and stable arrangement Pd_2H with $a_0=4.017$ cannot be attained because of the presence of foreign atoms (which do not combine with hydrogen atoms) in place of palladium atoms at some of the grating points.

The fact that the distensions in the range between $a_0=3.885$ and 3.920 in the sputtered Pd specimens remained unchanged over a period of two years at 20°C might be explained on the assumption that these specimens were free from mechanical strain. The process of 'building up' the material in the presence of atomic hydrogen being different in this respect from the

---

[7] Coehn, Naturwissenschaften **11,** 183 (1928).

[8] Oxley, Roy. Soc. Proc. **A101,** 264 (1922)

process of occluding hydrogen in palladium which is already in the crystalline state.

X. SUMMARY AND CONCLUSIONS

1. X-ray investigation of the crystal lattice of the Pd-H system showed that after electrolyzing in dilute H_2SO_4 specimens might have various distensions with a_0 in the range 4.017 to 4.045, but that in the course of ten days or less at 20°C those with a_0 greater than 4.017 would shrink down to this value, but not below it.

2. This value 4.017 is independent of the temperature at which the specimen is held in a range up to about 80°C. If the temperature is raised higher than this, the phase with $a_0 = 4.017$ dissociates completely, and a_0 becomes 3.885, (pure palladium).

3. Palladium which absorbs hydrogen from the gas phase shows the identical value $a_0 = 4.017$ and behaves in the same way as the electrolytically charged specimens. The difference reported by Linde and Borelius was not observed in this work.

4. A greater stability of this 4.017 phase in some electrolytically charged specimens as compared with the specimens from the hydrogen furnace is associated with a difference in the mechanical state of the micro-crystals in the two cases.

5. The existence of the unique value $a_0 = 4.017$ and the results of other observers on the pressure-concentration equilibrium of the Pd-H system lead to the association of the lattice parameter 4.017 with the concentration Pd_2H.

6. X-ray absorption pictures of the L_{111} limit of palladium show that the presence of the hydrogen causes a shift of the main edge of 0.87 X.U. toward shorter wave-lengths, and the occurrence of a secondary absorption 10 X.U. toward shorter wave-lengths. This is taken to mean that the hydrogen is in chemical combination with the palladium. The appearance of the edge may be explained on the hypothesis that it is the superposition of two absorption edges, one due to the molecule PdH and the other due to the atom Pd.

7. A study of palladium containing certain impurities showed that *any* value of a_0 between 3.885 and 4.017 was possible, and that these phases showed a continuous shrinkage with time to smaller values of a_0. This agrees with Yamada's work on palladium, while the results with pure palladium correspond with those of McKeehan, indicating that the source of the discrepancy between those two investigations may be impurities in the palladium.

In conclusion, the writer wishes to express his appreciation to Dr. C. E. Mendenhall for many valuable suggestions, and to Dr. L. R. Ingersoll for his kindness in making the sputtered Pd specimens.

UNIVERSITY OF WISCONSIN.
November 22, 1928.