Palladium Hydride. III. Thermodynamic Study of Pd₂D from 15 to 303°K. Evidence for the Tetrahedral PdH₄ Structure in Palladium Hydride[1]

BY DONALD M. NACE AND J. G. ASTON

The heat capacity of Pd₂D has been measured from 15 to 152°K. and 280 to 300°K. for comparison with that of Pd₂H to verify a theoretical conclusion based on the shape of the lambda transition in the latter. For completeness certain points in the isotherm and partial molal heats of absorption of deuterium in palladium have been measured. The heat capacities of Pd₂H have been analyzed. Reasonable barrier heights and frequencies have been calculated to fit for a model based on PdH₄·7Pd at low temperatures. To explain the heat capacities above 120°K., a dissociation process is postulated which involves a decrease in the average number of hydrogen bonds as the temperature is raised. Hydrogen diffusion through palladium is conceived as a movement of hydrogen atoms by a continuous combination of (1) rotation about a parent palladium atom and (2) bonding to, and subsequent rotation about, a neighboring palladium atom. A new theory has been developed to explain the phase separation and hysteresis in the absorption isotherm.

Introduction

This is a continuation of the work reported in the two previous papers.[2,3] A lambda transition was found in the heat capacity curve of Pd₂H which is reminiscent of the type found for solutions of methane in krypton and for ammonium compounds. The effect on the lambda transition of substituting all the hydrogen in methane by deuterium has been studied by Clusius, Popp and Frank.[4] Due to the smaller zero point energy of deuterium as compared to hydrogen, the temperature of the lambda transition for CD₄ is shifted to a higher temperature. It also is split into two peaks. A comparison of the heat capacity anomaly of palladium hydride and palladium deuteride to see whether the equivalent shift and splitting occur is thus desirable. The heat capacity of Pd₂D has therefore been studied from 15 to 152°K.

As will be seen presently, it was necessary to conclude from the results that Pd₂H was essentially PdH₄·7Pd at the low temperatures. It is necessary to assume that as the temperature is raised reactions of the type

$$PdH_{2x} + Pd = 2PdH_x \qquad (A)$$
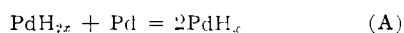
occur, giving a contribution to the heat capacity. Such reactions are essentially reactions of migrations. To substantiate this, the heat capacity of Pd₂D also was studied in the postulated temperature region of migration. In this paper, a calculation of the heat capacity curve for palladium hydride is made on the basis of this proposed PdH₄ model and correlated with the experimental data. The way in which the model explains other phenomena associated with the palladium–hydrogen system at high temperatures will be discussed.

Experimental

The adiabatic calorimeter and sample of palladium used for the heat capacity and calorimetric heat measurements is described in the preceding papers.[2,3] The deuterium used was obtained from the Cryogenic Laboratory at Boulder, Colorado (National Bureau of Standards), and reportedly contains 99.4 to 99.7% deuterium, the remaining fraction being HD.

(1) Aided in part by Contract N6onr-269, T. O. III of the Office of Naval Research. Reproduction in whole or in part is permitted for any purposes of the United States government.

(2) D. M. Nace and J. G. Aston, THIS JOURNAL, 79, 3619 (1957).

(3) D. M. Nace and J. G. Aston, ibid., 79, 3623 (1957).

(4) K. Clusius, L. Popp and A. Frank, Physica, 4, 1105 (1937).

Absorption of Deuterium by Palladium.—Seven increments of deuterium were absorbed at 30° in the palladium black sample, and the heat released by each increment was measured under adiabatic conditions. Deuterium was much slower than hydrogen in coming to pressure equilibrium during the heat of absorption measurements. In the case of hydrogen absorption, pressure equilibrium generally was reached in three to four hours, but, with deuterium, the pressure was decreasing at a rate of over 1 mm. per hour as much as seven hours after absorption. The heats, which are listed in Table I, were calculated on the basis of the temperature change after four hours of adiabatic conditions, at which time the rate of temperature change was never greater than 0.0003° per minute.

TABLE I

A. HEAT OF ABSORPTION OF DEUTERIUM AT 30°

Phase	Change in moles of D₂	Mean ratio D/Pd	Mean temp. T_{m}, °K.	ΔH
α	0.007436	0.023	302.434	−7497
α,α + β	.008436	.072	302.303	−8184
α + β	.013593	.141	303.263	−8336
α + β	.014085	.227	303.334	−8342
α + β	.015513	.319	303.274	−8406
α + β	.017687	.422	303.761	−8434

B. HEAT OF DESORPTION OF DEUTERIUM AT 30°

Phase	Change in moles of D₂	Mean ratio D/Pd	Mean temp. T_{m}, °K.	ΔH
α + β	0.005873	0.458	303.775	9536
α + β	.004874	.425	299.733	8873

The average heat of absorption of deuterium in the mixed phase region is −8379 cal. mole⁻¹ at an average temperature of 30.248°. These heats show a definite increase for each increment of gas added throughout the mixed phase region. The pressure over palladium deuteride also increased with each addition of deuterium. One month after the heats of absorption measurements were made, the equilibrium pressure over the final composition of palladium deuteride was measured, and at 35° was found to be 100 mm. instead of the value of 230 mm. observed several hours after addition. This amazingly slow equilibrium obviously has an effect on the accuracy of the heats of absorption for deuterium. The high heats of desorption compared to those of absorption shown in Table I correspond to a similar situation for palladium hydride.[3]

The temperature coefficient of the pressure of deuterium over palladium deuteride was measured

from 0 to 33° a month after the deuterium had been absorbed by the palladium. Figure 1 is a plot of log p versus $1/T$ at a D:Pd ratio of 0.479. The isosteric heat calculated from this straight line is 8635 cal. mole^{-1}.
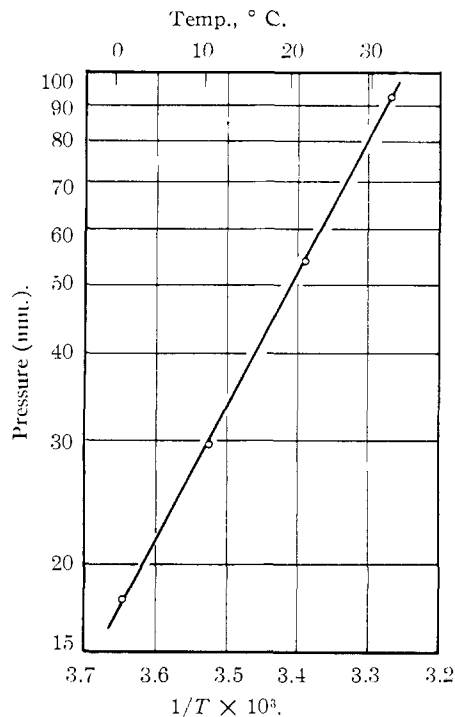

Fig. 1.—Pressure–temperature data Pd₂D.

Although calorimetric determinations of the heat of deuterium absorption in palladium never have been reported in the literature, isosteric heats above 200° have been determined before. The isosteric heat for deuterium desorption in the mixed phase region from the pressure–temperature relation of Gillespie and Downs[5] at an average temperature of 215° is 7760 cal. mole^{-1}. It is interesting to compare the isosteric heats obtained for palladium hydride and for palladium deuteride from this and the investigations of others.[5,6] The ratio of the isosteric heat, $\Delta H(\mathrm{Pd_2H})/\Delta H(\mathrm{Pd_2D})$, at 200° from the results of Gillespie and collaborators is 1.11. From this investigation, the same ratio at 30° is 1.12. The ratio of the equilibrium pressure over palladium deuteride to the pressure over palladium hydride shows an increase as the temperature is lowered. From the data of Gillespie the ratio is 2.1 at 270°, 2.4 at 250° and 2.9 at 200°. From this investigation the ratio is 4.6 at 30° and 4.8 at 20°.

The Heat Capacity Curve for Palladium Deuteride.—The heat capacities of the calorimeter containing palladium deuteride at a deuterium concentration corresponding to an atomic ratio D:Pd of 0.479 were measured from 15 to 152°K., and from 279 to 301°K. Because the time for this investigation was limited, it was not considered essential to cover the region from 152 to 279°K. The increase in heat capacity due to the deuterium

(5) L. J. Gillespie and W. R. Downs, THIS JOURNAL, **61**, 2496 (1939).

(6) L. J. Gillespie and L. S. Galstaun, ibid., **58**, 2565 (1936).

is listed for each temperature in Table II. The data are plotted in Fig. 2 and Fig. 3. Agreement among overlapping runs is again evident as it was in the case of palladium hydride. The anomalous hump is again present, the temperature corresponding to the maximum value at the peak having shifted from 55.0°K. for palladium hydride to 57.5°K. for palladium deuteride. This is a 4.6% increase, while the shift from 20.4°K. for CH₄ to 21.4°K. for the first peak of CD₄ represents a 4.9% temperature increase. Although a second peak is not immediately evident in the case of palladium deuteride, the heat capacity decreases only slightly after the peak, and the two peaks may be combined in the general shape of the curve. The peak of the palladium deuteride curve is higher than that of the palladium hydride curve.
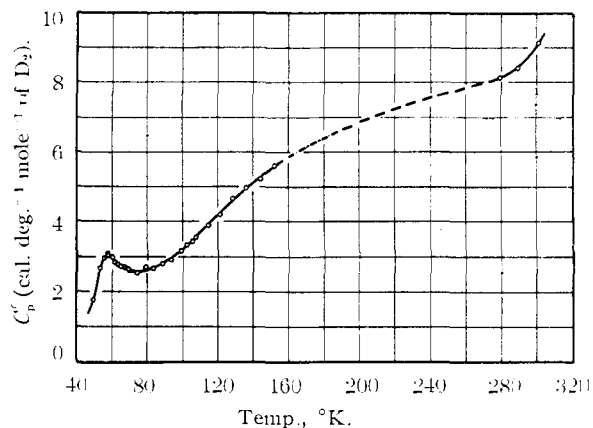

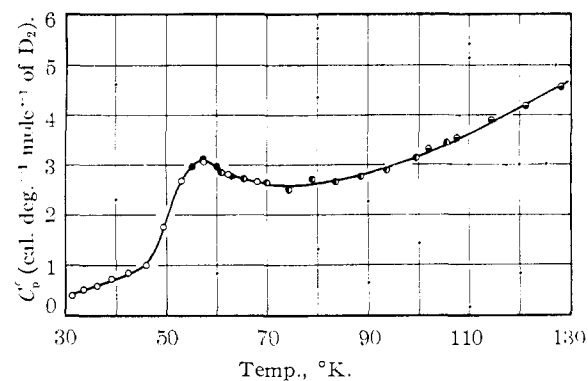Fig. 2.—Heat capacity increase of palladium due to one mole of deuterium.

Fig. 3.—Heat capacity increase of palladium due to one mole of deuterium: open circles, cooled to 15°K.; half-filled circles cooled to 59°K., only completely filled circles, cooled to 53°K.

The second rise in the heat capacity of palladium hydride above room temperature following a leveling off of the curve also finds its analogy in the palladium deuteride curve, the temperature of the rise being considerably lower.

Theoretical Heat Capacity Curve at Low Temperatures Based on PdH₄·7Pd and PdD₄·7Pd.— On the basis of the probable covalent bonding between palladium and hydrogen atoms, and the striking resemblance of the heat capacity anomaly to the coöperative rotational transition found in tet-

TABLE II

EXPERIMENTAL HEAT CAPACITY INCREASE DUE TO PRESENCE OF 0.07692 MOLE D_2

D/Pd = 0.4790; 1 cal. = 4.1833 int. joules; 0°C. = 273.16°K.

T (°K.)	ΔC_p (cal./deg.)	T (°K.)	ΔC_p (cal./deg.)
15.389	0.015	74.360	0.194
17.358	.022	78.928	.211
18.928	.024	83.527	.206
20.546	.024	88.409	.215
22.183	.020	93.664	.224
23.915	.026	99.390	.243
25.981	.019	105.535	.268
28.118	.014	55.209[b]	.229
30.979	.031	57.464	.243
33.388	.041	60.017	.231
36.009	.047	63.044	.216
38.957	.057	101.951	.258
42.153	.067	107.659	.274
45.759	.079	114.204	.301
49.299	.138	121.053	.324
53.004	.207	128.179	.359
57.402	.237	136.022	.383
62.363	.217	144.119	.403
67.838	.208	152.485	.432
61.061[a]	.220	278.895	.624
65.268	.211	289.324	.643
69.810	.206	300.514	.701

[a] Cooled to 59.0°K.   [b] Cooled to 53.3°K.

rahedral NH_4^+ ions and CH_4 molecules, a starting hypothesis for the molecular unit is PdH_4.

In comparing the experimental data with those calculated from any model, the former must be expressed on the basis used in the theoretical calculations. Accordingly, the experimental heat capacities from Fig. 1 of the preceding paper[2] must be calculated on the basis of one mole of PdH_4, and this can be done simply by adding the known molar heat capacity of one gram atom of pure palladium[7] to the experimental heat capacity contribution of four hydrogen atoms in palladium hydride in units of cal. per mole of PdH_4, if the theoretical calculation also neglects the excess palladium.

It now remains to define the details of the model more precisely. At the over-all composition of Pd_2H, one out of every eight palladium atoms would have four hydrogen atoms covalently bound to it according to the PdH_4 model. Also, in order to have the hydrogen atoms present in Pd_2H uniformly distributed throughout the lattices of the metal, two hydrogen atoms must be present in each palladium lattice cube since each face centered cubic palladium lattice contains the equivalent of four palladium atoms. The hydrogen atoms can satisfy both these requirements if PdH_4 molecules replaced palladium atom on four corners of each palladium lattice. If the hydrogen atoms of each PdH_4 molecule are tetrahedrally arranged about their central palladium atom, they can be directed toward the center of four different palladium lattice cubes. The two hydrogen atoms which are oriented toward the center of each cube lie at a point at which each hydrogen atom is equidistant from four tetrahedrally surrounding palladium atoms. The coöperative

(7) K. Clusius and L. Schachinger, Z. Naturforsch., 2a, 90 (1947).

aspect of rotation of hydrogen atoms around adjacent corner palladium atoms is obvious. Rotation must be in phase so that only two hydrogen atoms occupy a minimum energy position in a cube at the same time. Figure 4 shows one possible arrange-
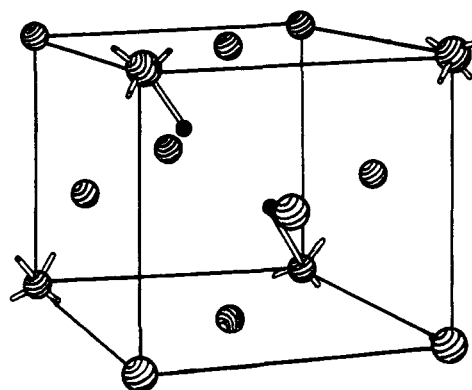

Fig. 4.—One possible arrangement of PdH_4 molecules in the palladium lattice: open circles, Pd atoms; black circles, H atoms.

ment of four PdH_4 molecule on corners of a palladium lattice cube. At the composition Pd_2H, each cube has attained this capacity of two hydrogen atoms. Based on this model and the crystallographic dimensions of the expanded palladium lattice in the β-phase, the Pd–H bond distance is 1.72 Å. and the moment of inertia of the spherical top molecule PdH_4 is 13.0 × 10^{-40} g. cm.^{2}.

A theoretical heat capacity curve can now be drawn for the hypothetical molecule PdH_4. This curve is drawn in Fig. 5 as the solid curve and super-
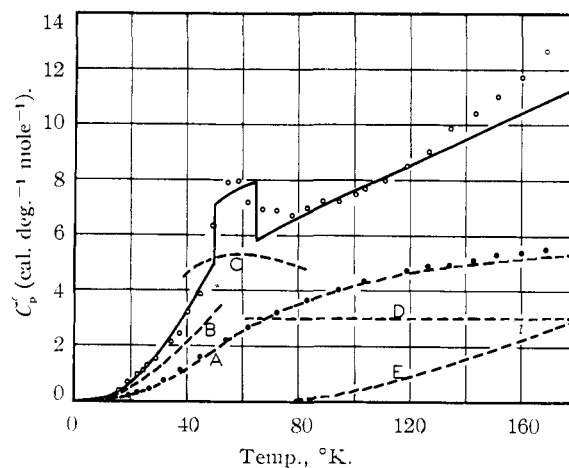

Fig. 5.—Theoretical contribution to the heat capacity of PdH_4: curve A, Debye translation; curve B, Debye torsional modes; curves C and D, rotation; curve E, Einstein modes; solid curve, A + (B, C, or D) + E; open circles, experiment for PdH_4; filled circles, experimental atomic heat capacities of palladium.

imposed on the experimental heat capacity data (open circles) expressed on the basis of PdH_4. The theoretical curve is composed of five contributions to the heat capacity. Curve A is the contribution of three translational degrees of freedom in the crystal based on a Debye $\theta(\theta_t)$ of 275°, the value for

pure Pd. The filled circles are the experimental value for pure palladium.[7] Curve B represents the contribution of the additional three rotational degrees of freedom which would be present in the PdH_4 molecule, representing oscillations of the hydrogen atoms in the potential energy barrier restricting full rotation. The curve is based on a Debye $\theta(\theta_r)$ of 200° chosen to fit the heat capacity in excess of that calculated from the above-mentioned translational Debye lattice. This value of θ_r corresponds to a cut-off frequency (ν_m) which is associated, by the standard formula, with an oscillation in a potential well of a sinusoidal potential function.

$$V = V_0 (1 - \cos 3\varphi)/2 \qquad (1)$$

with V_0 equal to 1600 cal. mole^{-1} barrier in the region 35 to 45°K. Near the heat capacity maximum coöperative effects would lower this barrier. At the maximum the barrier can be calculated from the heat capacity using the tables for the thermodynamic functions for molecules with restricted internal rotation. Curve C then represents the heat capacity curve due to a restricted rotor with V_0 equal to 390 cal. calculated from these tables. By considering that rotation becomes essentially free of hindering effects above the transition peak, the heat capacity contribution from the three rotational degrees of freedom must approach the classical limit of $3/2 R$, represented in Fig. 5 as line D. Since the experimental heat capacity curve for PdH_4 increases sharply above 90°K., additional contributions must come from the nine remaining vibrational degrees of freedom in the molecule. Curve E is the vibrational contribution based on five bending frequencies, empirically set equal to 500 cm.$^{-1}$ to get the best fit with the experimental data. The assumption is made that the four stretching frequencies are too high to make a contribution. The bending frequencies are lower than the corresponding ones in methane. This is easily accounted for by lower force constants as well as the higher moments of inertia. The decreased bending frequencies of CCl_4 compared with those of methane constitute an example of the operation of both effects. The experimental curve is still increasing rather rapidly above 120°K., but the contribution of the four remaining stretching frequencies would not be expected to be the cause since they could hardly make an appreciable contribution until above room temperature. The cause of the rapid rise in the experimental curve must therefore be due to another factor. This will be discussed presently.

A corresponding treatment of the results with deuterium can be made in the same way. The results are shown in Fig. 6 which corresponds exactly to Fig. 4. The barrier to give the best fit at the peak is 475 cal. mole^{-1}, whereas the θ_r value for the torsional vibration to obtain the best fit below the peak is 235° corresponding to a ν_m of 164 cm.$^{-1}$. The value of V_0 calculated from the value of ν_m is 4480 cal. mole^{-1}. The agreement between this frequency and the 139 cm.$^{-1}$ value for ν_m for palladium hydride is illusory since the reduced mass is greatly increased with deuterium. The contribution of the five internal bending modes cannot be

arbitrarily made because once the average frequency has been set at 500 cm.$^{-1}$ for PdH_4 the value of PdD_4 is determined. The Teller–Redlich rule states that for a heavy central atom replacement of all the hydrogen by deuterium changes the frequencies inversely as the square root of two. This rule predicts quite closely the results of replacing the four hydrogens of methane by deuterium.[8]

On this basis the frequency for PdD_4 is 355 cm.$^{-1}$, and this was used in calculating the theoretical curve in Fig. 6. Inspection of Fig. 8 shows that the experimental points deviate considerably from the calculated curve on the high temperature side of the peak in a manner quite different from that of methane. The palladium hydride fits because the average frequency of the bending modes was chosen to obtain a fit, but obviously no reasonable frequency could be chosen to fit the deuterium results. The contribution for the vibration frequencies is negligible at temperatures immediately above that of the peak for any physically real frequency.

There are two a priori factors which would predict a higher heat capacity contribution. One of them is the possibility of a second peak in the rotational heat capacity on the high temperature side of the anomaly as has been mentioned above (as with deuteromethane); the other is that the dissociation process causing the deviation of the measured curve from the theoretical curve for palladium hydride above 120°K. is shifted to a much lower temperature. The higher barrier for palladium deuteride is most naturally attributed to its lower zero point energy.

High Temperature Model of Palladium Hydride.

The only previous heat capacity study of a transition metal hydride at low temperatures was made on tantalum containing small amounts of hydrogen.[9] The tantalum hydrides (in the α-phase) have about the same heat capacity as pure tantalum up to 100°K.; then the heat capacity rises considerably and reaches a peak at a temperature that is determined by the concentration of hydrogen. After the peak is reached, the heat capacity rapidly falls to the heat capacity of pure tantalum. The height of each peak is the same regardless of the concentration of hydrogen present if the heat capacity is expressed on a molar basis for the hydrogen. The peak occurs at 220°K., for an atomic H:Ta ratio of 0.0284; at 255°K., for a ratio of 0.0676; and at 265°K., for a ratio of 0.0958. The peaks form an envelope which is the heat capacity curve for the highest H:Ta ratio.
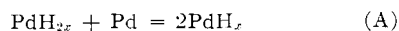
The rapid rise in heat capacity of palladium hydride up to room temperature in place of an expected leveling out above 150°K. may be analogous to Kelly's broad heat capacity peak. Kelly believes this anomaly is due to ordering of the dissolved hydrogen atoms (which are assumed to be free protons) as the temperature is lowered. Recent X-ray diffraction studies[10] on tantalum hydrides at low temperatures indicate that Ta_2H begins to pre-

(8) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y. (1945), pp. 235 and 307.

(9) K. K. Kelly, J. Chem. Phys., 8, 316 (1940).

(10) T. R. Waite, W. E. Wallace and R. S. Craig, ibid., 24, 634 (1956).

cipitate from a homogeneous α-phase hydride when the temperature is lowered below room temperature. In view of this discovery, the energy taken up by palladium hydride as the temperature is raised probably is due to heat of dissociation. The dissociation process involves a disordering migration of hydrogen atoms from the low energy position in PdH₄·7Pd to more random arrangements throughout the lattice. Such reactions can be symbolized by

$$PdH_{2x} + Pd = 2PdH_x \qquad (A)$$

In the case of palladium hydride, the second rise in heat capacity occurring at about 290°K. may well be the stage in which reaction (A) becomes

$$PdH_2 + Pd = 2PdH \qquad (B)$$

Evidently the second rise in heat capacity near room temperature due to this cause is shifted down the temperature scale on replacement of hydrogen by deuterium. Therefore a corresponding effect would be expected for the abnormal rise just above 120°K. It is apparently this effect which is at least in part responsible for the different behavior of palladium deuteride in the high temperature side of the peak.

The Diffusion Mechanism of Hydrogen through Palladium.—The disordering process that occurs when PdH₄·7Pd is heated is thus taken to involve a redistribution of hydrogen bonds among various palladium atoms in each lattice cube. The stability of the hydrogen bond itself most likely is due to resonance forms involving hydrogen atoms which lie midway between two or more palladium atoms. The bonds themselves may be similar to the "half bonds" which Rundle proposed[11] for electronically deficient compounds. He predicted that in the case of great electron deficiency, such as occurs in transition metals, four or more atomic orbitals may be combined to give a single bond orbital of lower energy than the single atomic orbital. After it has settled into a hydride configuration, the rotating PdH₄ molecule (or lower hydrides such as PdH₂) may be thought of as being in a higher energy state with the hydrogens bonded to only one palladium atom. If rotation of the hydrogen atoms in a PdH₄ molecule (or a lower hydride) occurs, it is feasible for a hydrogen atom bridging two palladium atoms to be rotated about the second palladium atom with which it shares a common orbital. The availability of rotational energy allows a translation of hydrogen atoms from one palladium lattice to another by a combination of hydrogen atoms being first shared with and then rotated about neighboring palladium atoms.

This concept of hydrogen transfer through the metal differs from previous theories in which inexplicably free protons drift at random in the metal. The proposed mechanism is supported by two recently published discoveries. Results of a neutron diffraction study of palladium hydride at room temperature show that the most probable positions for the hydrogen atoms are on the edges of the palladium lattice cube, mid-way between the corner palladium atoms, and at the center of the cube (coördinator ½a,0,0; 0,½b,0; 0,0,½c; and ½a,½b,½c, re-

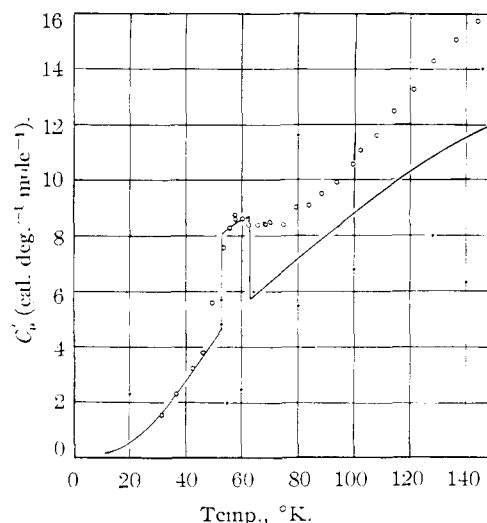(11) R. E. Rundle, *J. Chem. Phys.*, **17**, 671 (1919).

Fig. 6.—Theoretical heat capacity of PdD₄: open circles, experimental PdD₄ points; solid line, total of Debye translation, Debye torsion, rotation and Einstein modes.

spectively).[12] In the model of palladium hydride proposed in this paper, each palladium atom in the lattice is a revolving sphere with a high hydrogen probability on the surface. Four of these spheres nearly intersect at the center of the cube and at points on the edges midway between the corners; therefore, maximum intensity should be found at these positions in the neutron diffraction patterns. The nuclear magnetic resonance studies[13] of palladium hydride at room temperature by Norberg have revealed line widths which indicate rapid proton motion within the lattice. The activation energy for diffusion necessary to explain his result in terms of the free proton theory led Norberg to propose a "short circuit" diffusion mechanism consisting of diffusion along lattice imperfections. According to the present theory, the "short circuit" is formed by the resonance-rotation mechanism which arises in a natural fashion.

Phase Separation Hysteresis.—It has been pointed out that, because the lattice is face centered cubic, for the composition Pd₂H the maximum number of hydrogen atoms that can be present in a palladium lattice cube is two. This presupposes that each hydrogen atom lies at a position equidistant from four different palladium atoms. At high temperatures where absorption isotherms are measured, PdH₄ molecules have reacted with palladium neighbors to share their hydrogen or form lower hydrides. The same number of hydrogen atoms per unit cell, on an average, are demanded by the configuration. The average is maintained by the rotation (*not necessarily free*) of each hydrogen atom around a parent palladium atom in phase with the other hydrogen atoms. At low temperatures the hydrogen atoms cluster as PdH₄ molecules on corners of the palladium lattice. This leads to the prediction of the first break in the absorption isotherm at a composition Pd₈H (H:

(12) J. E. Worsham, Jr., C. G. Shull and M. K. Wilkinson, Paper No. 46, 13th Annual Pittsburgh Diffraction Conference, Pittsburgh, Pa., 1955.

(13) R. E. Norberg, *Phys. Rev.*, **86**, 745 (1952).

Pd = 0.125). At this composition each lattice has a PdH$_4$ molecule on one, and only one, corner site. A square block of eight lattice cubes contains a PdH$_4$ molecule situated on the corner position which is common to all eight cubes. This PdH$_4$ molecule, on rotating, can orient its four tetrahedrally arranged hydrogen atoms at any instant into four of the eight lattice cubes to which it belongs. No cube could have more than one hydrogen atom in it unless the atomic ratio H:Pd exceeded 0.125. Thus the increase in lattice dimension (β-phase) has its *raison d'etre* in the accommodation of two interacting hydrogen atoms in the same lattice cube. While it is only at low temperatures that there is one PdH$_4$ at this one of the eight corners of the palladium lattice, it seems reasonable to believe that there would be a related situation near room temperature. Thus the break is not sharp but gradual, moving to higher H:Pd ratios as the temperature increases as observed experimentally.

From the evidence given in the first paper[2] in this series, the absorption isotherm (as distinct from the desorption process) for hydrogen in palladium black is convincingly an equilibrium isotherm. Hydrogen must be able to penetrate into all the lattices of the palladium sample, and the β-phase which is formed must be uniformly distributed. This is not true for many isotherms which have been published, such as is shown in Fig. 7
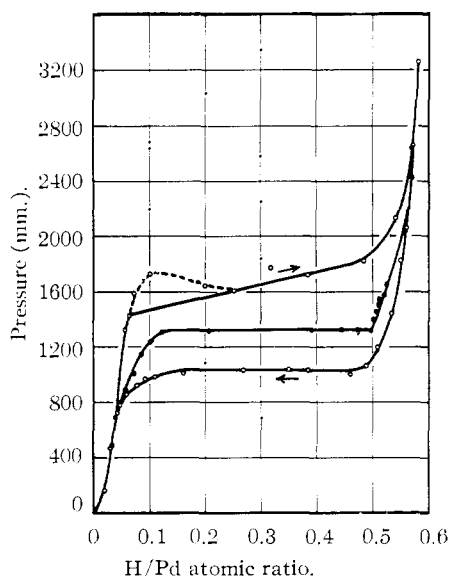

Fig. 7.—Absorption, desorption and equilibrium isotherms at 160° for hydrogen on palladium: open circles, absorption and desorption; filled circles, equilibrium.

where the hysteresis involved in a 160° isotherm[14] is contrasted with the isotherm of Gillespie and Hall at 160°.[15] The diffusion of hydrogen into palladium proceeds rapidly and without hysteresis to a composition approximately Pd$_8$H. Additional hydrogen absorption must form β-phase expanded lattices on the surface of the metal. The process of forming an internal β-phase expanded lattice

(14) H. Brüning and A. Sieverts, Z. *physik. Chem.*, **163A**, 409 (1933).

(15) L. J. Gillespie and F. P. Hall, THIS JOURNAL, **48**, 1206 (1926).

cannot occur spontaneously by diffusion of hydrogen atoms from the surface β-phase lattices into an unexpanded α-phase cube because energy must be absorbed in order to expand the lattice. The mechanism for the formation of internal expanded β-phase lattice must involve an unstable active state and probably one in which three hydrogen atoms are present in one of the already expanded external lattices. Such a process is then followed by the rapid release of the third hydrogen atom into a neighboring α-phase lattice. Obviously the farther from the surface this process must proceed, the slower will be the approach to equilibrium.

The proposed mechanism presupposes that the condition of the surface lattices determines the hydrogen pressure over the hydride. If this is so, desorption of hydrogen from surface β-phase lattices should produce α-phase surface lattices over which the equilibrium pressure of hydrogen is abnormally low. Experimentally this is always observed, even in the case of the two true equilibrium isotherms in Fig. 1 of the first paper[2] in this series. The rapid drop in pressure on desorbing hydrogen implies that surface β-phase lattices have been depleted of hydrogen and become α-lattices. A pressure is soon reached at which a steady state is established in which hydrogen can be desorbed without further lowering of pressure. Since internal lattices must also be undergoing desorption, hydrogen atoms from internal β-phase lattices pass to β-phase lattices near the surface at a rate depending on the hydrogen concentration gradient in the internal lattice. During this rapid flow of hydrogen, the β-lattices near the surface must of necessity have an excess of hydrogen atoms in order that they may pass hydrogen on to α-lattices in the surface. When the pumping of hydrogen from the palladium hydride sample is stopped, the rate of desorption of hydrogen from surface lattices to the gas phase falls to zero. The external hydrogen pressure in equilibrium with the surface lattices will remain fixed at a value depending on the hydrogen concentration which lies entirely in α-phase surface lattices. No sort of β-lattice is possible on the surface unless the pressure is raised to that of the flat part of the isotherm, or as Gillespie and Hall have done, the temperature of the system is raised to a high enough temperature (360°) to equilibrate the system internally.

By the addition of hydrogen, partially desorbed palladium hydride can be brought back to an equilibrium condition with a pressure of hydrogen in contact with it which is again on the true equilibrium isotherm. This is in accord with the theory. Not even the total amount desorbed need be added in order to return the pressure to the equilibrium value of the two-phase region because the pressure is established by the surface lattices. This fact is a striking confirmation.

The model has been shown to be consistent with the two isotherm breaks which occur at the compositions Pd$_8$H and Pd$_2$H. The initial break in the isotherm of Gillespie and Hall[15] occurs at Pd$_8$H in the range 160 to 250°. The fact that the break occurs at somewhat lower hydrogen concentrations at lower temperatures can only be due to lack of

internal equilibrium. Gillespie and Perry[16] have in fact observed several abnormal 0° isotherms for which no break at all occurs.

The second isotherm break occurs at Pd$_2$H from 80 to 200°. The break occurs at higher hydrogen concentrations at lower temperatures possibly because of hydrogen adsorption in structural rifts and defects caused by the independent expansion of each lattice cube.

Significance of the Entropy of Pd$_2$H at 0°K.— In the preceding paper[2] a residual entropy of 0.59 e.u. at 0°K. was compared to the residual entropy of 0.82 e.u. for ice on the basis that random hydrogen bonding can occur in both. In ice, each oxygen atom is surrounded by four tetrahedrally arranged hydrogen atoms. In PdH$_4$·7Pd, only some of the palladium atoms are surrounded by four tetrahedrally arranged hydrogen atoms. For ice, however, only two hydrogen atoms are covalently bound at one time to an oxygen atom while all four hydrogen atoms can be covalently bound to the central palladium atom. Just as random distribution of hydrogen atoms in ice is frozen into a false equilibrium at low temperatures, the arrangement in Pd$_2$H is subject to a similar circumstance. In building a model of PdH$_4$·7Pd, many different arrangements of the PdH$_4$ molecules on corner lattice sites can be constructed. Actually there are five possible arrangements for the distribution in an independent lattice cube, but the cubes are not independent in the metal. The arrangement of PdH$_4$ molecules in one cube partially determines the arrangement in the neighboring cubes. The system is too complex to lend itself to a numerical calculation of the total number of arrangements as can be done in the case of ice. However, since each cube is equivalent to two Pd$_2$H molecules, the

experimental value of 0.59 e.u. allows the choice of two arrangements for the PdH$_4$ molecules in each cubic lattice because

$$S_0 = k \ln 2^{N/2} = {}^1\!/_2 R \ln 2 = 0.69 \text{ e.u.} \qquad (2)$$

Comparison with Free Proton Theory.—It must be remembered that the degree of hydrogen bonding in palladium hydride is changing with temperature as indicated by the heat capacity curve. It is apparent that the covalently bonded hydrogen model at high temperatures becomes a model of interstitial hydrogen atoms vibrating and rotating relative to the palladium lattice. This assembly of hydrogen atoms, even though the hydrogen atoms share electrons with individual palladium atoms, would be indistinguishable from the model of free protons assembled in regular monolayers as considered by Lacher.[17] The straight line relation in the α-phase between hydrogen concentration and the square root of hydrogen pressure applies equally to a PdH covalently bound hydrogen model or to a free proton model. In other words, much that has been explained in the past on the basis of free protons can also be explained by the covalently bound hydrogen. Additional investigations, particularly of neutron diffractions, will have to be conducted at temperatures well below room temperature in order that the covalently bound hydrogen model be further verified.

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Magnesium–Cadmium Alloys. VIII. Heat Capacities of Mg$_3$Cd and MgCd$_3$ between 20 and 290°. The Standard Heats, Free Energies and Entropies of Formation and the Residual Entropies[1,2]

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Heat capacities of MgCd$_3$ and Mg$_3$Cd have been measured between 25 and 270° using a new adiabatic calorimeter permitting a precision of 0.1 to 0.2% in the measurements. Experiments were performed using an intermittent heating technique in order that equilibrium heat capacities might be obtained. The data reveal a specific heat anomaly of the customary type for alloys undergoing order–disorder transitions, with peak values at 83.8 and 150.6° for MgCd$_3$ and Mg$_3$Cd, respectively. With the aid of the heat capacity data, the standard heats, free energies and entropies of formation of the alloys at 270°, which were reported earlier, have been corrected to 25°. The residual entropy of Mg$_3$Cd has been found to be 0.03 ± 0.04 e.u./g. atom and the corresponding quantity for MgCd$_3$ has been found to be 0.16 ± 0.04. The latter is in good agreement with the quantity 0.17 ± 0.01 e.u. computed statistically under the assumption that there is a random distribution of the observed number of Schottky defects over the lattice sites. Attention is directed to the large errors which can occur when the conventional continuous heating technique is used with systems undergoing configurational changes.

In Paper VII of this series heat capacity data for Mg$_3$Cd and MgCd$_3$ between 12 and 320°K.

were presented.[3] Entropies of formation of these two substances at 270° had been determined[4] earlier by the electrochemical cell method and in

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