PHYSICAL AND INORGANIC CHEMISTRY

Palladium Hydride.   I.   The Thermodynamic Properties of Pd₂H between 273 and 345°K.[1]

BY DONALD M. NACE AND J. G. ASTON

The 30° absorption isotherm for hydrogen dissolved in a highly active palladium black has been measured and found to agree very closely with an equilibrium desorption isotherm obtained previously by Gillespie and Hall. Partial molar heats of desorption for the system palladium–hydrogen have been calculated from the isotherms. Partial molar heats of absorption and desorption of hydrogen from palladium hydride also have been measured in an adiabatic calorimeter. These values are used to calculate the free energy and the entropy change associated with the formation of Pd₂H from the elements at 30°. Agreement between the calorimetric heats and those calculated from the temperature coefficient of the equilibrium pressure establishes a reasonable criterion of equilibrium for the system.

Introduction

Palladium is a rapid exothermic absorber of large volumes of hydrogen. Although this phenomenon has been the subject of many previous investigations,[2,3] no entirely satisfactory explanation of the nature of the bonding force has been established. The phase equilibria of the hydrogen-palladium system have been extensively investigated for different forms of palladium (wire, foil, sponge and black). Hysteresis effects have been quite evident in all the isotherms, especially those for temperatures below 160°.

By using a special heat treatment technique, Gillespie and Hall[4] obtained, at temperatures as low as 0 and 30°, apparently true equilibrium isotherms which are located between the usually different absorption and desorption curves. The equilibrium isotherm is interpreted as indicating two solid solutions; one is a hydrogen-poor solution (α-phase), the other is a hydrogen-rich solution (β-phase) of approximate composition Pd₂H. For both α- and β-phases X-ray analysis identifies the palladium atom array as being face-centered cubic,

the α-phase having a parameter of 3.886 Å., and the β a parameter of 4.020 Å.[5]

The data presented in this paper were compiled for the purpose of calculating the entropy for the system Pd₂H at near room temperature. Such a value is needed in order to determine the absolute entropy of Pd₂H at 0°K. from a third law study. It is best that this be determined on the sample used for the third law study. Therefore, a series of equilibrium pressure and heat of absorption measurements have been made on a *very active* palladium black between 273 and 345°K.

Materials.—The palladium used is a special grade of palladium black obtained from Baker and Company, Newark, New Jersey. This extremely active palladium is made for their own research purposes, so the method of preparation is not available. The purity is given as 99.9%. Although the density of bulk palladium is 12.0 g./cc., the packed density of this black powder is only 0.6 g./cc. One sample, weighing 34.277 g., was sealed into a gold calorimeter and used for all of the experimental work. The sample was never heated over 100° because the material supposedly sinters at higher temperatures. Any possible oxide of palladium was reduced initially by adding hydrogen to the sample and then degassing at 98°. Following this reduction, the sample was exposed only to very pure helium, nitrogen and hydrogen.

High purity hydrogen made by electrolysis and purified by liquefying and then compressing into a high pressure cylinder was used throughout. All portions of the hydrogen allowed to react with the palladium were first passed through a trap packed with activated charcoal and immersed in a liquid nitrogen-bath.

(2) A complete bibliography of the literature up to 1947 is given by D. P. Smith in the book "Hydrogen in Metals," University of Chicago Press, Chicago, Ill., 1948.

(3) (a) P. Wright, *Proc. Phys. Soc.* (London), **63A**, 727 (1950); (b) R. E. Norbert, *Phys. Revs.*, **86**, 745 (1952).

(4) L. J. Gillespie and F. P. Hall, THIS JOURNAL, **48**, 1207 (1926).

(5) F. Kroger and G. Gehm, *Ann. Physik.* [5] **16**, 171 (1933).

Apparatus.—The container for the palladium black sample is a closed gold cylinder fitted at the top with a gold inlet tube and having an internal volume of 55.6 cc. Connection between the gold calorimeter and a glass vacuum system is made through a platinum–rhodium tube which has an inside diameter of 0.0292 in. and which is gold welded inside the calorimeter inlet tube. The calorimeter contains a 2.5 in. long re-entrant well which is gold welded in the center of the cylinder bottom. The re-entrant well is designed for insertion of a platinum resistance thermometer.

Volumes of gas are measured in a calibrated 3-liter Pyrex bulb set up inside a 50-gallon insulated stirred water-bath which is kept at room temperature. Mercury from a storage tank immersed in the water-bath can be raised into or lowered from the 3-liter bulb in order to transfer the gas to the calorimeter. The system is patterned after one described by Giauque and Johnston.[6] The temperature of the water is measured on a mercury thermometer which has been calibrated against a platinum resistance thermometer. The pressure of the gas is measured using a 13 mm. bore, copper cased, mercury manometer. The mercury levels and meniscus heights were referred to a stainless steel, calibrated meter bar by means of a Gaertner Scientific Corporation M901 cathetometer.

The calorimeter vessel was immersed in the inner bath of a double constant temperature bath for the isothermal pressure–composition study and the pressure–temperature studies at fixed composition. The inner bath consists of a 1000-cc. insulated Pyrex beaker equipped with a Transite lid and provided with a stirrer, a calibrated platinum resistance thermometer, an uncalibrated platinum resistance thermometer, and a six-watt light bulb. The uncalibrated resistance thermometer was used to control the temperature by means of a Wheatstone bridge arrangement in which any unbalance of the bridge resulting from a temperature change in the bath of 0.001° or more is detected by a type R galvanometer. A light beam reflected from the galvanometer mirror activates a photocell relay circuit which turns on or off the six-watt bulb. Glycerol was used as the medium in both inner and outer baths. The outer bath was controlled by means of a mercury thermostat at a few tenths of a degree below the temperature of the inner bath. Measured fluctuations of temperature in the inner bath amounted to ±0.002°.

Heats of absorption and desorption were measured in the same gold calorimeter vessel after it had been incorporated in an assembly designed for adiabatic operation with high vacuum insulation. This adiabatic assembly is described in the following paper.[7] Temperatures are measured with a strain-free platinum resistance thermometer, Pt-G-5, based on the International Temperature Scale. The calorimeter was held adiabatic during the addition of gas and until equilibrium was established, or in many cases, until pressure and temperature changes were small enough to allow extrapolation to an approximate equilibrium. The heat of absorption per mole of hydrogen is calculated from the same expression used for heats of adsorption, namely[8]

$$q = \frac{C_p \Delta T}{n} - \frac{V_{cal} \Delta P}{n} \qquad (1)$$

where ΔT is the temperature rise, n is the number of moles of hydrogen absorbed, ΔP is the change in pressure during absorption and V_{cal} is the dead space volume of the calorimeter. The calorimeter was cooled between increments of hydrogen added so that the mean temperature for each rise was about 30°. The mean heat capacity of the system before and after absorption of hydrogen, C_p, was interpolated to the mean temperature for the temperature rise. The measured heat capacities have been corrected for the heat of desorption, which is assumed to be equal in magnitude to the measured heat of absorption but negative in sign, and the heat of

(6) W. F. Giauque and H. L. Johnston, THIS JOURNAL, **51**, 2300 (1929).

(7) Donald M. Nace and J. G. Aston, ibid., **79**, 3623 (1957).

(8) G. L. Kington and J. G. Aston, ibid., **73**, 1929 (1951). In equation 1 a term, due to temperature rise, has been neglected since this term is insignificant. This is the term $n_g R(\partial T/\partial n_a)s$ in eq. 14 of this reference.

compression. The equation for making these corrections to the measured values is

$$C_p = C_m - \frac{(-q)}{\Delta T}(\Delta n) + \frac{V_{cal}\Delta P}{\Delta T} \qquad (2)$$

where C_m is the measured heat capacity and Δn is the increase in the number of moles of gas in the dead space.

After each measurement of heat evolved by a given quantity of gas, the calorimeter was cooled to the initial temperature and one or two heat capacity measurements were made between the initial and final temperatures of the heat of absorption measurement. The heat of absorption was calculated by a series of reiterations of eq. 1 and 2 since q and C_p appear in both equations.

The Absorption Isotherm.—A 30° isotherm for the absorption of hydrogen in palladium black was determined in the isothermal apparatus. The isotherm is shown as the solid curve in Fig. 1 where it is compared with the 30° isotherm obtained by Gillespie and Hall.[4] Since the Gillespie and Hall isotherm is a desorption isotherm brought to equilibrium by the use of a 360° heat treatment prior to each pressure measurement, the similarity between these isotherms indicates that true equilibrium has also been reached in the absorption isotherm of this paper. Equilibrium, as revealed by the constant pressure portion of the isotherm, has never reportedly been obtained for the absorption of hydrogen in palladium below 160° without a heat treatment. The reason for the lack of hysteresis in the present investigation is undoubtedly inherent in the extremely finely divided state of the palladium black used. Pressure equilibrium for the isotherm was obtained in two to six hours after addition of a hydrogen increment. Three of the experimental points of the isotherm were obtained after allowing the pressure to come to equilibrium overnight, but the pressure increased only 0.02 mm. after the second hour. The pressure during the horizontal portion of the isotherm varies only ±0.20 mm. from an average of 17.35 mm. This value is 1.45 mm. ($\Delta F = 51$ cal.) below the value obtained by Gillespie and Hall.

After sufficient hydrogen had been absorbed in the palladium to pass the second break in the isotherm, about 12% of the hydrogen was desorbed. The pressure fell to a low value quite rapidly, and the calorimeter had to be heated to 80° in order to desorb such a large quantity of hydrogen. This desorption curve, as shown in Fig. 1, is identical with that obtained by Gillespie and Hall on desorption of hydrogen where the 360° heat treatment was not previously applied.[4] No increase in pressure occurred over a period of four days after desorption of hydrogen. By heating the system again and holding it at 80° for 24 hours, the pressure after the system was cooled to 30° differed from that before the second heat treatment by only 0.10 mm. Reabsorption of hydrogen raises the pressure to a point where it coincides with the original absorption isotherm. A second set of desorption and reabsorption isotherms is shown in Fig. 1.

Isosteric Heats of Desorption.—The palladium hydride at a composition of about 0.40 atom of hydrogen per atom of palladium was heated to 45° and pressures were measured at a series of temperatures from 45 to 75°. The temperature was controlled with an accuracy of ±0.002° and
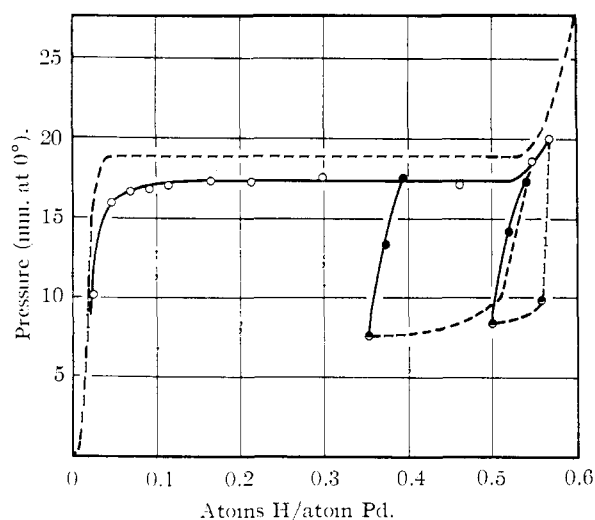
Fig. 1.—Isotherm at 30° for hydrogen in palladium: solid curves, data of present investigation; open circles, absorption; half-filled circles, desorption; filled circles, absorption following desorption; dashed curve, data of Gillespie and Hall.

pressures determined within ±0.04 mm. A plot of log p vs. $1/T$ for the equilibrium pressure data over this 30° temperature range is shown in Fig. 2 (open circles). On a large scale plot no curvature is evident. The slope of this line corresponds to a heat of desorption of 8870 cal./mole of hydrogen, which agrees very closely with the value of 8860 cal./mole obtained by Gillespie and Hall[4] from their 30 and 80° equilibrium values (line with no points in Fig. 2). However, it was found that on decreasing the temperature from 75 to 45°, the pressure values did not fall on the same straight line but established a new straight line (filled circles). The palladium hydride was heated again, and the equilibrium pressure was measured at several temperatures between 45 and 75° (half-filled circles). Pressures also were measured at several temperatures on cooling to 50°. All points obtained after the first 75° heating lay on the second straight line. The 14 experimental points from 55 to 75° were least squared to fit a straight line. The heat of desorption calculated is 9440.8 cal./mole of hydrogen The most probable error in the experimental data corresponds to ±0.1 mm. pressure at 75° or ±0.5 mm. at 55°. The probable error in the heat of desorption is ±0.9 cal./mole of hydrogen if equilibrium could be assumed.

In the process of measuring heats of absorption and heat capacities in the adiabatic calorimeter, additional pressure-temperature data were observed. Log p vs. $1/T$ plots of the data obtained are shown in Fig. 3. The sample of palladium hydride had been completely degassed prior to these measurements and hydrogen added until the final composition corresponded to 0.487 atom H per atom Pd (open circles). It was during this addition of hydrogen that calorimetric heats of absorption also were measured. The isosteric heat calculated on the basis of the slope of this line is 9330 cal./mole. After a period of two months
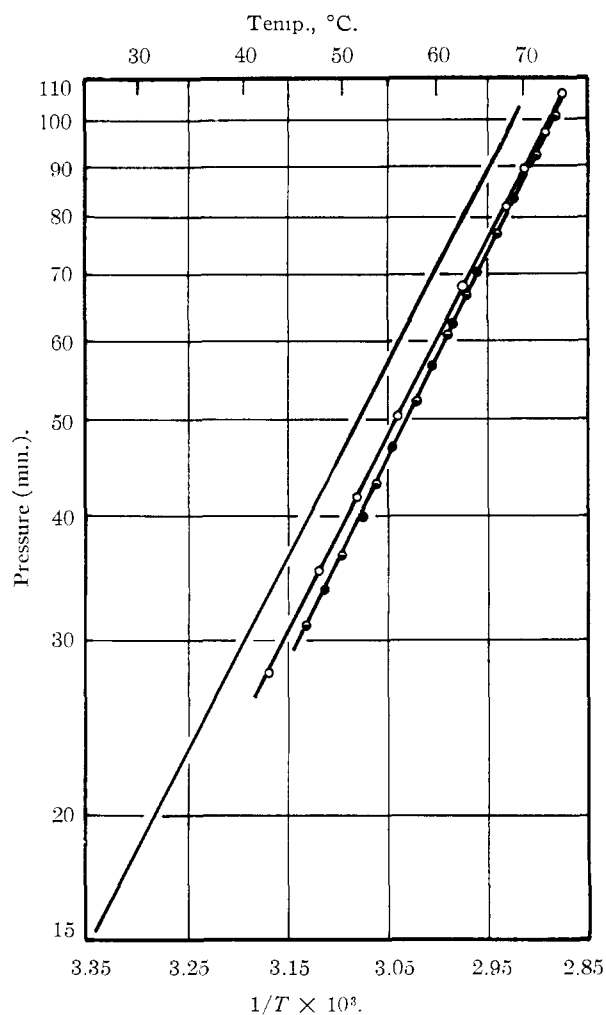

Fig. 2.—Pressure-temperature data for Pd + 0.2 H_2: open circles, preheated to 35° only; filled circles, preheated to 75° and temperature lowered to point; half-filled circles, preheated to 75°, cooled to 45°, and then raised to point; line without points, data of Gillespie and Hall.

during which time the sample was subjected to temperatures from 15 to 300°K., pressures were again measured from 12 to 73° (half-filled circles). The plot of these data gives an isosteric heat of 9640 cal./mole. However, after heating to 73° and cooling to room temperature (filled circles), the corresponding isosteric heat is 10,300 cal./mole.

This variation of the isosteric heats must be due to lack of internal equilibrium.

Calorimetric Heats of Absorption and Desorption.—Heats of absorption were measured calorimetrically at 30° at various concentrations of hydrogen. Heats of desorption of hydrogen from palladium hydride were measured at 68°. The heat determinations are listed in Table I.

The heat of absorption of hydrogen remained constant over the entire mixed phase region of palladium hydride. The average value of the heat is −9605 cal./mole at an average temperature of 30.195°. The average deviation of the heat of absorption is ±45 cal./mole and of the temperature is ±0.146°.
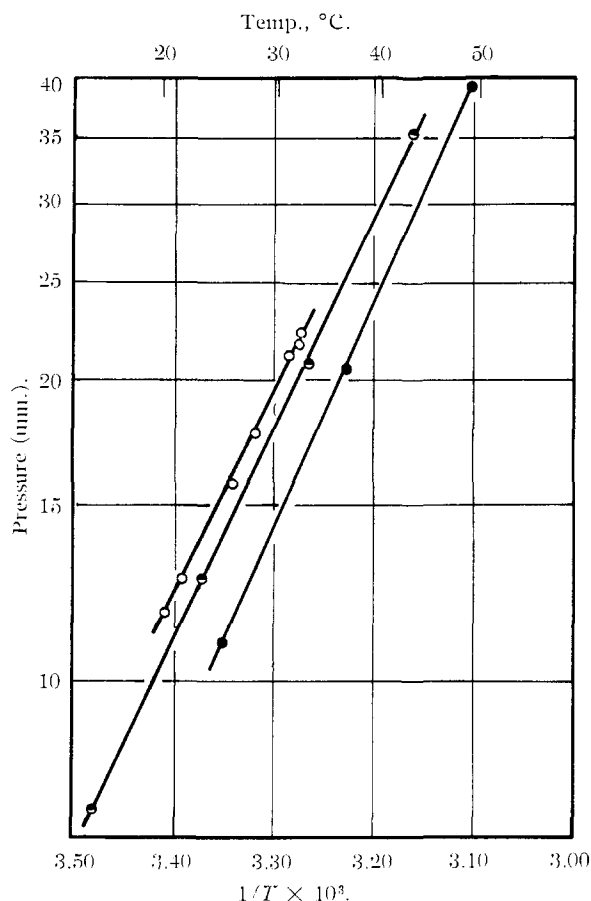
Temp., °C.

Fig. 3.—Pressure–temperature data for Pd + 0.2435 H₂: open circles, immediately after addition; half-filled circles, after two months; filled circles, after subsequently heating to 73° and cooling to room temperature.

The heats of desorption do not agree well with those of absorption or with each other; this is due undoubtedly to a great lack of equilibrium during desorption, whereas there is good equilibrium for the absorption.

The heat of the reaction

$$4Pd + H_2 \,(1 \text{ atm.}) = 2Pd_2H \tag{3}$$
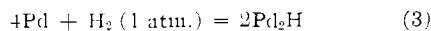
is the total heat of absorption of hydrogen from pure palladium to the composition of Pd_2H based on a mole of hydrogen. The one determination of the α-phase heat evolution resulted in a value of 8948 cal./mole; the average heat evolution during formation of β-phase Pd_2H is 9605 cal./mole. Since the α-phase heat evolution, which occurs up to the atomic ratio 0.125, corresponds to one-quarter of the over-all reaction to form Pd_2H, the value of $\Delta H°$ corresponding to equation 3 is given by

$$\Delta H° = \tfrac{1}{4}(-8948) + \tfrac{3}{4}(-9605) = -9440 \pm 45 \text{ cal./mole} \tag{4}$$

Since the heats of absorption are measured directly, lack of thermodynamic equilibrium should not greatly affect them, particularly when the equilibrium during absorption is as good as it was in these measurements. The fact that the isosteric heats are even close to the measured values is an indication of relatively good equilibrium in

A. HEAT OF ABSORPTION OF HYDROGEN AT 30°

1 cal. = 4.1833 int. joules

Phase	Change in moles of H_2	Mean ratio H/Pd	Mean temp. T_m, °K.	ΔH, cal. mole⁻¹
α	0.01653	0.052	305.685	-8948
$\alpha + \beta$	.01198	.140	303.638	-9643
$\alpha + \beta$	.01134	.212	303.335	-9554
$\alpha + \beta$	.01273	.287	303.519	-9562
$\alpha + \beta$	.009905	.358	303.664	-9564
$\alpha + \beta$	.007176	.412	303.223	-9665
$\alpha + \beta$	.005464	.451	303.617	-9583
$\alpha + \beta$	.002800	.477	303.382	-9665
Av. of all $\alpha + \beta$			303.355	-9605 ± 45

B. HEAT OF DESORPTION OF HYDROGEN AT 68°

| $\alpha + \beta$ | 0.007878 | 0.460 | 341.270 | 10280 |
| $\alpha + \beta$ | .007851 | .412 | 341.753 | 9304 |

the absorption measurements. Thus we emphasize that the calorimetric heats of absorption are the only ones that need be considered. Their internal consistency is an excellent confirmation of the estimated accuracy.

Free Energy and Entropy for Formation of Pd₂H.—The change in the standard free energy for reaction 3 can be calculated from the pressure–composition relation during the course of the reaction in which

$$\Delta F° = 2F°_{Pd_2H} - F_{H_2}° - 4F°_{Pd} = 2F°_{Pd_2H} \tag{5}$$

Since reaction 3 represents a solution of hydrogen in palladium with the two limits being pure palladium and pure Pd_2H, the entire process can be treated thermodynamically using the conventional method for handling solutions; that is, the partial molar free energies of the components are considered

$$F°_{Pd_2H} = 2(\bar{F}_{Pd})_{Pd_2H} - 1(\bar{F}_H)_{Pd_2H} \tag{6}$$

The free energy in the standard state of Pd_2H (which is, of course, pure Pd_2H) is thus relative to those of pure palladium and hydrogen in the ideal gas state at 1 atm. pressure. Since the hydrogen in Pd_2H is in equilibrium with hydrogen gas at the equilibrium pressure, P_{H_2}, the partial molar free energy of hydrogen in palladium hydride is given by

$$(\bar{F}_H)_{Pd_2H} = \tfrac{1}{2}\bar{F}_{H_2(H)} = 0.5RT \ln p_{H_2(Pd_2H)} \tag{7}$$

Using the Gibbs-Duhem equation, one obtains

$$(\bar{F}_{Pd})_{Pd_2H} = -0.5RT \int_{x=0}^{x=0.5} x \, d \ln p_{H_2(Pd_2H/x)} \tag{8}$$

where x stands for n_H/n_{Pd}. Since the square root of the pressure follows a straight line relationship with composition at the very low concentrations of hydrogen, the integral is best evaluated in two parts: the integral of $x \, dp^{1/2}/p^{1/2}$ at low concentrations, i.e., an upper limit of $x = 0.04$, and the integral $x \, d \ln p$ for the higher hydrogen concentrations. The experimental pressure–composition data used in the evaluation of the integral are taken from the isotherm of Fig. 1 which is extrapolated at low concentrations of hydrogen to coincide with the isotherm of Gillespie and Hall. Graphical integration of eq. 8 produced a value of $(\bar{F}_{Pd})_{Pd_2H} = -18.7$ cal./mole. The standard molar free energy of Pd_2H is then evaluated from eq. 6 and 7 to be $F°_{Pd_2H} = -1153 \pm 6$ cal./mole. The hydrogen pressure in equilibrium with Pd_2H for this calcu

lation was taken as the average equilibrium pressure for the seven heat of absorption measurements in the mixed phase region. This average pressure is 18.78 ± 0.91 mm. From eq. 5, $\Delta F^\circ_{303.16^\circ}$ = −2306 ± 12 cal./mole.

According to the second law of thermodynamics, the entropy change for reaction 1 is

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} \qquad (9)$$

At 303.16°K., using the above calculated values for ΔH° and ΔF°, $\Delta S^\circ_{303.16^\circ}$ = −23.50 ± 0.19 e.u.

Discussion of Results

The change of slope of the straight line obtained from the pressure–temperature relationship after heating to 75° obviously involves some change in the structure of palladium hydride which is brought about by the increase in temperature. The change is apparently permanent since the desorption energy is fixed according to the highest temperature to which the hydride has been heated. The most surprising aspect of this effect is that only 10% of the hydrogen in the palladium had not previously been heated to 80°. Most of the hydrogen in the hydride had been heated to 80° when the two desorption experiments illustrated in Fig. 1 were accomplished. This indicates that the hydrogen pressure is determined by a relatively small quantity of hydrogen which probably is located in the surface lattices of the metal and which is not in all cases in internal equilibrium with the hydrogen in the interior of the metal. This fact is explained in the third paper of this series. The fact that equilibrium pressures are indicative of only the surface hydride concentration invalidates the use of isosteric heats at low temperatures for absolute values of the heat of desorption.

Heats of absorption have been measured twice before calorimetrically, both times at 0°.[9] The ice calorimeter apparatus used in both investigations is useful only in measuring fairly rapid heats

of reaction, certainly not in observing heat effects over long equilibrium times. The average of a set of almost constant values measured by Mond, Ramsay and Shields[9a] at 0° is −9362 cal. mole⁻¹. Gillespie and Ambrose[9b] found −9283 cal. mole⁻¹. The palladium blacks used by both these investigators are known to exhibit hysteresis effects when hydrogen is absorbed at low temperatures so that these values are probably too low on this account.

From the experiments of this paper, the heat of absorption in the α-phase is found to be lower than the constant heat of absorption found in the mixed α- + β-phase. Although Gillespie and Ambrose's[9b] calorimetric investigation detected no difference in the heat of absorption at low and at high concentrations of hydrogen, their isosteric heats were 6000 cal. mole⁻¹ in the α-phase and 8860 cal. mole⁻¹ in the mixed phases.

The fact that the several investigations give better agreement for the calorimetric heats of adsorption than for the isosteric ones must be due to the fact that they are less affected by lack of equilibrium.

As mentioned above, the fact that the calorimetric desorption heats for the mixed α- and β-phases are not constant during desorption must be due to the very great desorption hysteresis evident in the isotherm of Fig. 1. The reason for desorption hysteresis, even though absorption hysteresis does not occur, will be discussed in a following paper[10] because it involves a new mechanism which is postulated for hydrogen mobility through the metal.

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(9) (a) L. Mond, W. Ramsay and J. Shields, *Trans. Roy. Soc. (London)*, **A186**, 657 (1895); (b) L. J. Gillespie and H. A. Ambrose, *J. Phys. Chem.*, **35**, 3105 (1931).

(10) Donald M. Nace and J. G. Aston, This Journal, **79**, 3627 (1957).

UNIVERSITY PARK, PA.

Palladium Hydride. II. The Entropy of Pd₂H at 0°K.[1]

By Donald M. Nace and J. G. Aston

The heat capacity contribution due to the absorbed hydrogen atoms in palladium hydride at a composition of nearly Pd₂H was measured in a newly constructed adiabatic calorimeter over small temperature intervals from 16 to 340°K. A residual entropy of 0.59 ± 0.18 e.u. has been calculated from experimental data to exist at 0°K. It is concluded that Pd₂H does not approach a completely ordered state at low temperatures and so is not a true compound. The shape of the heat capacity curve indicates the probability of covalently bound hydrogen at low temperatures with a dissociation process occurring as the temperature is varied. More evidence for this model is to be given in the succeeding paper.

Introduction

If Pd₂H were a true compound, and there were no hydrogen bonding as in ice, the entropy at 0°K.

should be zero. This principle has been used by Hildenbrand and Giauque[2] to establish that at low temperatures ammonium oxide and ammonium hydroxide are true compounds. By using calori-

(2) D. L. Hildenbrand and W. F. Giauque, This Journal, **75**, 2811 (1953).