

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

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

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

At  $303.16^\circ\text{K.}$ , using the above calculated values for  $\Delta H^\circ$  and  $\Delta F^\circ$ ,  $\Delta S^\circ_{303.16^\circ} = -23.50 \pm 0.19$  e.u.

### Discussion of Results

The change of slope of the straight line obtained from the pressure-temperature relationship after heating to  $75^\circ$  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  $80^\circ$ . Most of the hydrogen in the hydride had been heated to  $80^\circ$  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  $0^\circ$ .<sup>9</sup> The ice calorimeter apparatus used in both investigations is useful only in measuring fairly rapid heats

(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).

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<sup>9a</sup> at  $0^\circ$  is  $-9362$  cal. mole<sup>-1</sup>. Gillespie and Ambrose<sup>9b</sup> found  $-9283$  cal. mole<sup>-1</sup>. 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  $\alpha$ -phase is found to be lower than the constant heat of absorption found in the mixed  $\alpha + \beta$ -phase. Although Gillespie and Ambrose's<sup>9b</sup> 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<sup>-1</sup> in the  $\alpha$ -phase and 8860 cal. mole<sup>-1</sup> 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  $\alpha$ - and  $\beta$ -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<sup>10</sup> because it involves a new mechanism which is postulated for hydrogen mobility through the metal.

**Acknowledgments.**—One of the authors (D. M. N.) wishes to thank the Socony Mobil Oil Company for the generous provisions of the Socony Mobil Incentive Fellowship. Thanks are due to Mr. C. W. Brouse for the construction of the gold calorimeter and to Dr. R. G. Asch for the construction and help in the calibration of the platinum resistance thermometer.

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

UNIVERSITY PARK, PA.

[CONTRIBUTION NO. 93 FROM THE CRYOGENIC LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

## Palladium Hydride. II. The Entropy of Pd<sub>2</sub>H at 0°K.<sup>1</sup>

BY DONALD M. NACE AND J. G. ASTON

RECEIVED FEBRUARY 13, 1957

The heat capacity contribution due to the absorbed hydrogen atoms in palladium hydride at a composition of nearly Pd<sub>2</sub>H was measured in a newly constructed adiabatic calorimeter over small temperature intervals from 16 to 340°K. A residual entropy of  $0.59 \pm 0.18$  e.u. has been calculated from experimental data to exist at 0°K. It is concluded that Pd<sub>2</sub>H 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 Pd<sub>2</sub>H were a true compound, and there were no hydrogen bonding as in ice, the entropy at 0°K.

(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.

should be zero. This principle has been used by Hildenbrand and Giaque<sup>2</sup> to establish that at low temperatures ammonium oxide and ammonium hydroxide are true compounds. By using calori-

(2) D. L. Hildenbrand and W. F. Giaque, *THIS JOURNAL*, **75**, 2811 (1953).

metric heat capacities measured as a function of temperature, they calculated the absolute entropy of a system from

$$S_T = \int_0^T C_p d \ln T + S_0 \quad (1)$$

where  $S_0$  is the entropy at absolute zero. According to the third law of thermodynamics,  $S_0$  of any substance whose atomic arrangement and quantum states correspond to a unique lowest energy state at the absolute zero is zero. In the preceding paper<sup>3</sup> the entropy change for the reaction at 303.16°K.,  $4\text{Pd} + \text{H}_2 = 2\text{Pd}_2\text{H}$ , is determined as

$$\Delta S_{303.16^\circ} = 2S_{\text{Pd}_2\text{H}} - 4S_{\text{Pd}} - S_{\text{H}_2} = -23.50 \pm 0.19 \text{ e.u.} \quad (2)$$

The experimental heat capacities measured in this investigation were those of the gold calorimeter containing pure palladium black before and after absorption of sufficient hydrogen to form about 98%  $\text{Pd}_2\text{H}$ . Since both sets of heat capacities include the heat capacity of the gold calorimeter, only the difference between the heat capacity of the calorimeter with pure palladium and the calorimeter with palladium hydride has any real significance. If this difference in heat capacity is expressed on a molar basis of hydrogen absorbed,  $\Delta C_p'$  per mole of hydrogen added can be stated to be

$$\Delta C_p' = C_p(2\text{Pd}_2\text{H}) - C_p(4\text{Pd}) \quad (3)$$

If the entropy at 0°K. of pure palladium is zero, eq. 2 can be expressed as

$$\Delta S_{303.16^\circ} = \int_0^{303.16^\circ} \Delta C_p' d \ln T - S_{303.16^\circ}(\text{H}_2) + S_0(2\text{Pd}_2\text{H}) \quad (4)$$

The absolute entropy of gaseous hydrogen in the standard state has been published<sup>4</sup> and is 31.34 e.u. at 303.16°K. Rearranging eq. 4 and inserting the known values, the entropy of  $\text{Pd}_2\text{H}$  at 0°K. is

$$S_0(\text{Pd}_2\text{H}) = \frac{1}{2}(-23.50 \pm 0.19 + 31.34 - \int_0^{303.16^\circ} \Delta C_p' d \ln T) \quad (5)$$

The zero point entropy of  $\text{Pd}_2\text{H}$  can thus be calculated from the results of a study of the heat capacity contribution of a mole of hydrogen to the heat capacity of palladium when palladium hydride is formed.

If the hydrogen atoms in  $\text{Pd}_2\text{H}$  are randomly distributed at room temperature, the system on cooling under equilibrium conditions will approach a unique lowest energy state corresponding to the most ordered arrangement of the atoms. Frequently the lowest energy state is degenerate, in which case a residual entropy  $k \ln O$  is retained in which  $O$  is the number of equal energy orientations possible and  $k$  is the Boltzmann constant. If the energy differences between possible arrangements are small, a residual entropy of  $\delta$  will be found at the absolute zero when the temperature is lowered to a point where thermal motions are unable to orient atoms into the completely ordered arrangement. Such a situation exists for carbon monoxide, nitrous oxide and nitric oxide.

(3) Donald M. Nace and J. G. Aston, *THIS JOURNAL*, **79**, 3619 (1957).

(4) H. W. Wooley, R. B. Scott and F. G. Brickwedde, *J. Natl. Bur. Standards*, **41**, 379 (1948).

The shape of the heat capacity *vs.* temperature curve necessary for the third law entropy study also serves as a clue to the origin of thermal energies in the solid. The energy content of a solid at low temperatures arises from vibrations of the atoms in the crystal, but molecules have the opportunity to increase their energy in other degrees of freedom, such as rotation of a molecular unit or vibration of atoms within a molecule, as the temperature is increased.

**Apparatus.**—The heat capacity measurements were carried out in a newly constructed adiabatic calorimeter designated as Calorimeter J. The gold calorimeter and the sample of palladium black which it contains are described in the preceding paper.<sup>3</sup> A strain-free platinum resistance thermometer inserted into this calorimeter carries the designation Pt-G-5. It was calibrated between 11.5 and 92.6°K. by comparison under adiabatic conditions with two platinum resistance thermometers which are primary standards of The Pennsylvania State University temperature scale. The two primary standards, Pt-G-8 and Pt-G-12, had been calibrated against the helium gas thermometer.<sup>5</sup> A total of 20 resistance measurements were made in this comparison calibration. Thermometer Pt-G-5 was calibrated on the International Scale by a similar comparison against the two primary standards involving 13 resistance measurements from 92.6 to 300°K. in addition to a precise determination of the ice point resistance. The value of such a calibration on the International Scale made by comparison measurements against a primary standard is that the chance need not be taken of thermally affecting the platinum wire during calibration at the boiling point of sulfur, one of the fixed points on the International Temperature Scale. The scale below 90°K. corresponds to 90.154°K. for the boiling point of oxygen,<sup>6</sup> whereas the value chosen to establish the International Temperature Scale was originally 90.19°K. In this case the value 90.154°K. was used for the boiling point of oxygen and proper adjustments made.

The low temperature cryostat and adiabatic shield arrangement were designed basically like those previously described.<sup>7-9</sup> Details are given in a thesis.<sup>10</sup> Above the shield, inside the cryostat the entering gas is passed through a temperature controlled heat exchanger to bring it to the same temperature as the calorimeter. This was for use in heat of absorption measurements.

**Materials.**—The palladium sample and hydrogen have been described in the preceding paper.<sup>3</sup>

## Results

It was possible to maintain perfectly adiabatic conditions for Calorimeter J above 18°K. The average time necessary for thermal equilibrium was five minutes in the liquid hydrogen region, 15 minutes in liquid nitrogen, and 20 to 30 minutes above 200°K. For 55 experimental heat capacities of the calorimeter containing pure palladium, the average deviation of the points from a smooth curve is shown in Table I.

TABLE I

15 to 50°K.	$\pm 0.13\%$
50 to 100	.08
100 to 250	.05
250 to 300	.08
300 to 350	.15

(5) G. W. Moessen, J. G. Aston and R. G. Asch, *J. Chem. Phys.*, **22**, 2096 (1954).

(6) J. G. Aston and G. W. Moessen, *ibid.*, **21**, 1948 (1953).

(7) J. G. Aston and G. J. Szasz, *THIS JOURNAL*, **69**, 3108 (1947).

(8) J. A. Morrison and G. J. Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

(9) J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, *THIS JOURNAL*, **73**, 1939 (1951).

(10) D. M. Nace, Ph.D. dissertation, Penn. State Univ., University Park, Penna., 1956.

At the conclusion of all the experimental heat capacity measurements for palladium and palladium hydride, the heat capacity of the degassed calorimeter was again determined in the region from 35 to 95°K. These ten heat capacity determinations have an average deviation of  $\pm 0.05\%$  from the new curve but on the average are  $0.06\%$  below the original heat capacity smoothed curve.

The heat capacities of the calorimeter containing first palladium black and later palladium hydride at the composition at which the atomic ratio H/Pd is 0.487 were measured from 16 to 303°K. The experimental data are given in Tables II and III. The heat capacity contribution of one mole of hydrogen to four moles of palladium,  $\Delta C_p$ , is plotted against temperature in Fig. 1. The heat capacity anomaly which occurs between 30 and 100°K. is illustrated on an enlarged scale in Fig. 2. The repeated heat capacity determinations of the degassed calorimeter are also plotted on Fig. 2 as deviations from the original empty calorimeter heat capacity curve, and the deviations have been multiplied by the same factor used to convert the palladium hydride experimental heat capacity difference to a molar basis of hydrogen. The purpose of showing these remeasured heat capacities is to illustrate that the hump cannot be due to any permanent change undergone by the palladium.

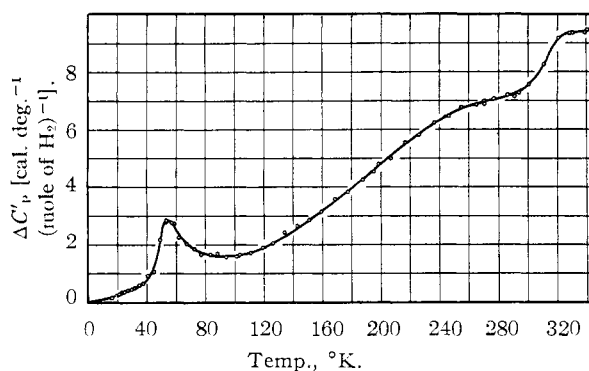


Fig. 1.—Heat capacity due to 1 mole  $H_2$  in  $Pd_2H$ .

The heat capacities in all the temperature regions are quite reproducible for palladium hydride. The agreement among several overlapping series of runs is demonstrated in both Figs. 1 and 2. Obviously, any rearrangement of structure on change of temperature, if such occurs, proceeds rapidly since the heat capacities are reproducible regardless of the initial temperature to which the calorimeter is cooled. Based on the average deviations of the experimental heat capacities, the probable error of the  $\Delta C_p$  is about  $10\%$  at  $15^\circ K.$ , and about  $3\%$  between 25 and  $50^\circ K.$ , decreasing to  $2\%$  above  $200^\circ K.$  On integration to give entropies, the percentage error probably is decreased.

The heat capacity curve for palladium hydride above  $290^\circ K.$  shows a sudden rise. Heat capacities in this range are corrected for the heat of desorption of hydrogen evolved into the dead space of the calorimeter and filling line, the heat of compression of gas in the calorimeter dead space, and the change in concentration of hydrogen in the palladium. The heat of desorption for the quanti-

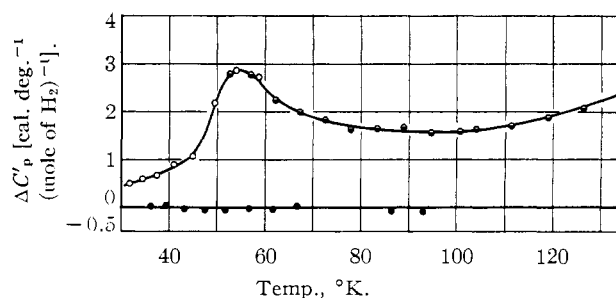


Fig. 2.—Heat capacity due to hydrogen in palladium (4 atoms): open circle, system cooled to  $14^\circ K.$ ; half-filled circle, system cooled to  $50^\circ K.$  only; completely filled circles, after long pumping to remove the absorbed  $H_2$ .

ties of hydrogen desorbed was assumed to be equal, but negative in sign, to the calorimetrically measured heat of absorption,  $-9605$  cal./mole of hydrogen.

TABLE II  
HEAT CAPACITY OF CALORIMETER J CONTAINING 0.3212 MOLE PALLADIUM AT ROUNDED TEMPERATURES  
 $0^\circ C. = 273.16^\circ K., 1 \text{ cal.} = 4.1833 \text{ int. joules}$

$T$ (°K.)	$C_p$ (cal./deg.)	$T$ (°K.)	$C_p$ (cal./deg.)	$T$ (°K.)	$C_p$ (cal./deg.)	$T$ (°K.)	$C_p$ (cal./deg.)
15	0.444	68	6.569	185	10.52	305	11.71
16	.516	71	6.802	190	10.58	300 <sup>a</sup>	11.68
17	.604	75	7.104	195	10.65	305	11.70
18	.703	80	7.440	200	10.71	310	11.73
19	.808	85	7.745	205	10.78	315	11.75
20	.919	90	8.024	210	10.83	320	11.78
22	1.165	95	8.260	215	10.88	325	11.81
24	1.426	100	8.476	220	10.93	330	11.84
26	1.691	105	8.674	225	10.98	335	11.87
28	1.967	110	8.866	230	11.03	340	11.90
30	2.241	115	9.038	235	11.08	345	11.93
32	2.521	120	9.202	240	11.13		
34	2.799	125	9.346	245	11.17		
36	3.078	130	9.483	250	11.22	36.203 <sup>a</sup>	3.110
38	3.349	135	9.609	255	11.27	39.413	3.540
41	3.743	140	9.780	260	11.32	43.157	4.017
44	4.128	145	9.848	265	11.38	47.316	4.524
47	4.494	150	9.952	270	11.43	51.760	5.029
50	4.840	155	10.05	275	11.48	56.662	5.539
53	5.166	160	10.14	280	11.53	61.638	6.016
56	5.477	165	10.22	285	11.58	66.639	6.453
59	5.775	170	10.30	290	11.62	86.418	7.819
62	6.052	175	10.37	295	11.65	92.865	8.150
65	6.316	180	10.45	300	11.68		

<sup>a</sup> Heat capacities at this and the following temperatures were measured after degassing of the calorimeter following all heat capacity measurements on  $Pd_2H$ .

Table IV contains a summary of the entropy change found by evaluating the integral in eq. 5.

The zero point entropy can now be stated to be  $S_0(Pd_2H) = \frac{1}{2}(-23.50 \pm 0.19 + 31.34 - 6.66 \pm 0.16) = +0.59 \pm 0.18$  e.u.

The entropy of  $Pd_2H$  thus approaches a value of  $0.59 \pm 0.18$  e.u. at the absolute zero of temperature. This discrepancy from an entropy of zero must be due to some degree of randomness in the arrangement of hydrogen atoms in the metal.

### Discussion

The combination of bonding potentialities of unfilled inner shells of palladium and the observed exothermic release of energy when hydrogen is absorbed in palladium would certainly lead one to consider chemical bonding of some sort between

TABLE III  
EXPERIMENTAL HEAT CAPACITY INCREASE DUE TO PRESENCE OF 0.07819 MOLE H<sub>2</sub>

H/Pd = 0.4869  
0°C. = 273.16°K., 1 cal. = 4.1833 int. joules:

T (°K.)	$\Delta C_p$ (cal./deg.)	T (°K.)	$\Delta C_p$ (cal./deg.)	T (°K.)	$\Delta C_p$ (cal./deg.)
16.178	.012	67.110	.157	206.972	0.391
17.661	.015	72.353	.145	216.515	.435
19.153	.017	77.702	.128	226.277	.454
20.613	.020	83.135	.130	236.387	.487
22.218	.025	88.674	.132	246.783	.506
24.318	.029	94.315	.123	254.982	.531
26.637	.032	100.385	.125	265.553	.537
28.997	.036	103.758	.128	270.130	.545 <sup>a</sup>
31.619	.039	111.187	.133	271.201	.535
34.376	.047	118.784	.148	277.257	.549
37.385	.052	126.149	.162	286.208	.561
40.847	.072	134.105	.189	294.254	.568
44.896	.084	142.658	.206	291.877	.557
49.312	.171	151.002	.223	301.383	.592
53.849	.224	159.665	.246	311.302	.647
58.472	.214	168.646	.281	321.318	.717
52.478 <sup>b</sup>	.220	177.938	.309	331.269	.731
56.870	.217	187.552	.333	340.930	.742
61.946	.217	195.721	.354	328.407	.731
		198.271	.376	339.544	.732

<sup>a</sup> Cooled to 50.5°K. <sup>b</sup> This and following data corrected for heat of desorption and heat of compression.

TABLE IV  
CALORIMETRIC ENTROPY CHANGE

0-15.85°K.	Debye extrapolation = 0.05 ± 0.01 e.u.
15.85-28.19	$\int \Delta C_p d \ln T = 0.16$ .01
28.19-118.85 (hump)	.83 .02
28.19-118.85 (without hump)	1.38 .04
118.85-303.16	4.24 .08
0-303.16°K.	$\int_0^{303.16} \Delta C_p d \ln T = 6.66 \pm 0.16$ e.u.

palladium and hydrogen atoms as the probable explanation for the absorption process. If such bonding does occur, the character of the metallic bond between palladium atoms is undoubtedly involved in a resonating system probably involving hydrogen bridge bonds as suggested by Rundle.<sup>11</sup>

The heat capacity curves of Figs. 1 and 2, in general, rise rapidly with temperature. In addition, an anomaly exists at 55°K. which is of the type commonly attributed to the beginning of molecular rotation in a covalent molecule. The 55°K. anom-

(11) R. E. Rundle, *THIS JOURNAL*, **69**, 1719 (1947).

aly is similar to that of (NH<sub>4</sub>)<sub>2</sub>O at about the same temperature as recently reported,<sup>2</sup> NH<sub>4</sub>Cl, NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and CH<sub>4</sub> (references given in ref. 2). Rotation of the tetrahedral NH<sub>4</sub><sup>+</sup> ion and CH<sub>4</sub> molecule is commonly regarded as responsible for the increased energy absorption in the neighborhood of the anomaly. In the case of pure compounds, the anomaly is of the  $\lambda$  type, indicating that the potential barrier to rotation depends on the degree to which neighboring molecules are rotating. In cases where the cooperative interaction between neighboring molecules is not very great, the anomaly becomes less sharp. The effect of reducing the cooperation between neighboring molecules of methane is shown when methane is diluted with krypton. The  $\lambda$ -type anomaly<sup>12</sup> for pure methane is converted to a broad rounded hump for the methane in dilute solid solution with krypton.<sup>13</sup>

At temperatures above 55°K., the heat capacity contribution of hydrogen rises continuously at a rapid rate up to room temperature. The absence of a leveling off of the heat capacity indicates vibrational degrees of freedom present in the hydride which could be associated with molecular vibrations of covalently bound atoms. The heat capacity of pure palladium and of molecular hydrogen, or even of free protons if such could be present in the palladium lattice, would reach a constant classical limit at temperatures much lower than room temperature.

The residual entropy of 0.59 e.u. at the absolute zero of temperature suggests that on cooling palladium hydride to very low temperatures the hydrogen atoms are frozen in one of several possible configurations. Pauling<sup>14</sup> has explained the 0.82 e.u. residual entropy of ice at 0°K. by assuming random hydrogen bonding. A somewhat similar situation may exist in palladium hydride and will be discussed in the following paper.<sup>15</sup>

**Acknowledgments.**—One of the authors (D. M. N.) wishes to thank the Socony Mobil Oil Company for the generous provisions of the Socony Mobil Incentive Fellowship. The help of Mr. L. F. Shultz, who produced all of the refrigerants and aided in the assembly of the apparatus, was invaluable.

UNIVERSITY PARK, PA.

(12) A. Eucken and H. Veith, *Z. physik. Chem.*, **B34**, 275 (1936).

(13) K. Clausius, L. Popp and A. Frank, *Physica*, **4**, 1105 (1937).

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1945, p. 301.

(15) D. M. Nace and J. G. Aston, *THIS JOURNAL*, **79**, 3627 (1957).