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THE PALLADIUM-HYDROGEN EQUILIBRIUM AND PALLADIUM HYDRIDE[1]

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After Graham reported the great absorptive capacity of palladium for hydrogen, the relationship between the two elements became the subject of much experimental study. Besides the interest of the possible compound Pd_2H, the relationship may have bearing on the great catalytic activity of palladium in reduction.

In 1874 Troost and Hautefeuille[2] reported the hydride Pd_2H. They brought more evidence forward than they considered necessary. When the phase rule was announced a few years later, it could be seen that their evidence, though almost complete, was not quite so. A number of workers have since tried to furnish a complete proof, but without success.

Pressure-composition diagrams, obtained by Roozeboom and by Hoitsema for the system Pd-H, were presented by the latter.[3] Hoitsema concluded that the system was isothermally univariant throughout and that, therefore, the compound Pd_2H was not formed. In coming to this conclusion he was not in a position to explain the possibility of observations such as those of Troost and Hautefeuille. Nevertheless, his conclusion as to the nonexistence of the hydride has been generally accepted; and although many writers show a feeling that all is not right, we have learned of only one writer[4] (up to 1925) who regards the existence of Pd_2H as an open question.

Sieverts[5] obtained curves very similar to those of Hoitsema. The curves show no nonvariant portions and the "breaks" are not sharp.

Holt, Edgar and Firth[6] postulate the presence of an amorphous and a crystalline variety of palladium but have hardly demonstrated the presence of these two distinct modifications. The work of A. E. Oxley[7] on the determination of the magnetic properties of palladium that has been

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[1] This paper is an abstract of a thesis presented by F. P. Hall in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology. We wish to acknowledge the assistance of Mr. Emanuel Tarplin during part of the experimentation.

[2] Troost and Hautefeuille, *Compt. rend.*, **78**, 686 (1874); *Ann. chim. phys.*, [5] **2**, 273 (1874).

[3] Hoitsema, *Z. physik. chem.*, **17**, 25 (1895).

[4] A. E. Hill, in Taylor's "Treatise on Physical Chemistry," D. van Nostrand Co., NewYork, **1924**, vol. 1, p. 437.

[5] Sieverts, *Z. physik. Chem.*, **88**, 451 (1914). Especial reference to p. **470**.

[6] Holt, Edgar and Firth, *ibid.*, **82**, 513 (1913).

[7] Oxley, *Proc. Roy. Soc.*, **101A**, 264 (1922).

treated with hydrogen seems to indicate some sort of chemical union between the two components. Likewise the work of Wolf[8] on the electrical conductivity of the system seems to indicate some form of chemical union.

X-ray work by Yamada[9] and by McKeehan[10] seems to give evidence of the formation of solid solutions rather than a compound in this system. However, the evidence does not seem conclusive, as the X-ray results are negative in character rather than positive.

We undertook the present work feeling that Hoitsema's diagrams could not represent true equilibrium conditions, even though we were not able to perceive where the difficulty lay.[11] After our work had been brought to a close, the paper of Lambert and Gates[12] appeared, giving pressure-composition diagrams. These diagrams show, for spongy palladium, very marked hysteresis effects. They prove abundantly that an equilibrium truly independent of time cannot be attained by operating isothermally at the usual temperatures on such material. We believe the same is true for every preparation of palladium that has ever been studied, including our own preparations. Lambert and Gates do not claim definite evidence of the hydride, Pd_2H, but they point out that their curves are not what would be expected if two solid solutions exist, since their descending isothermals "show 'breaks'" at approximately the same composition (about 0.53 atom of hydrogen per atom of palladium) at temperatures of 75°, 103° and 120°. It seems certain that these isothermals are not true equilibrium lines.

Preparation of Materials

Palladium chloride was reduced to metallic palladium by the method of Wieland,[13] using sodium formate. The metal was converted into chloride again and purified through several crystallizations of the characteristic yellow salt, palladosammine chloride, by the method of Gutbier[14] used in atomic weight work. Following Gutbier, the metal was prepared by reducing the yellow salt in a stream of dry hydrogen at about 150°. Stronger heating was necessary to remove ammonium chloride, but the temperature was kept as low as possible. The stream of hydrogen was stopped, carbon dioxide was passed through to replace hydrogen and the metal was cooled in carbon dioxide. The metal was black, finely divided. It could be weighed without a special technique.

A sample of 1.9338 g. (*in vacuo*) of yellow salt treated in this way yielded 0.9746 g.

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[8] Wolf, *Z. physik. Chem.*, **87**, 588 (1914).

[9] Yamada, *Sci. Repts. Tôhoku Imp. Univ.*, [1] **11**, 451–454 (1922); *Phil. Mag.*, **45**, 241 (1923).

[10] McKeehan, *Phys. Rev.*, **21**, 334 (1923). This article contains an excellent bibliography on the system, palladium-hydrogen.

[11] Some preliminary work was done in this Laboratory by Taneichi Yoneda and by J. H. Perry. [Perry, *Thesis*, Massachusetts Institute of Technology, **1922.**]

[12] Lambert and Gates, *Proc. Roy. Soc.*, **108A**, 456–482 (1925).

[13] Wieland, *Ber.*, **45**, 484 (1912).

[14] Gutbier, *J. prakt. chem.*, (N. F.) **79**, 235 (1909).

of palladium. This is 50.398% of palladium. That calculated for $Pd(NH_3)_2Cl_2$ by 1921 atomic weights (Pd = 106.7) is 50.405%.

A portion of this palladium is called palladium A. Another portion was carried through the formate reduction and is called palladium B. Both preparations had thus been put through both separations, but the final mode of reduction was different, and it was thought possible that this would affect our results. Palladium B was not treated with carbon dioxide and was weighed in a vacuum.

The hydrogen was prepared by electrolysis of a 10% solution of sodium hydroxide, using a platinum anode and a nickel cathode. The hydrogen was then passed over heated platinized asbestos to remove oxygen and then over tubes of phosphorus pentoxide. These tubes were carefully exhausted, being well rinsed with hydrogen and well heated during the exhaustion process. We decided not to use a portion of palladium itself for a further purification of the hydrogen. The hydrogen generator was operated continuously to avoid introduction of nitrogen by diffusion.

Even 0.1% of nitrogen would have had an appreciable effect on the isotherms, except for the fact that all hydrogen withdrawn from the palladium during the experiments was discarded, thus largely eliminating any impurities at the same time.

Description of the Apparatus

A simple water-jacketed volume buret with two calibrated marks, one for 4.6 cc. and one for 29 cc., was provided with a barometer column on which the pressure could be read with a meter stick. The buret had a two-way stopcock with large capillary leads. One lead connected with the hydrogen supply, the other with the reaction chamber. Pressures in the reaction chamber were read by means of the same barometer column, with a zero mark in the capillary lead. All zero corrections were determined when the pressure was the same on both columns in question.

The large volume space in the buret was used when it was necessary to remove hydrogen at low pressure. Hydrogen thus removed was pumped away through the barometer column and delivered into the open air.

Two separate apparatuses of this kind were set up and used, at the same time, in order to make use of the long time intervals required for reaching equilibrium. One was limited to work at 0°, using ice in a large Dewar tube. The other was provided with an oil thermostat, well-stirred and regulated.

The temperatures were read with mercury thermometers which were calibrated shortly after the experiments with a platinum resistance thermometer and found to be accurate to about 0.1°.

For work at the higher temperatures, a special manometer was constructed and the levels were read on a steel tape measure affixed close to the manometer column, which could be opened to the atmosphere in order to get another atmosphere of pressure.

All important volumes were determined by weighing mercury. The volume of one reaction chamber was about 4.8 cc.; of the other, which was used for high temperatures, about 7.7 cc.

For low temperatures, the reaction chamber was connected to the buret through a ground-glass joint which was submerged in the bath. For the higher temperatures, a fused joint in the capillary tube was necessary, but it introduced no appreciable volume error. All other joints in the apparatus were fused-glass joints.

Mode of Conducting the Experiments

The general procedure before starting a run was to evacuate the reaction tube and heat it to about 400°, to cool and admit hydrogen and then to evacuate while the tube was at about 400°. This was to remove any traces of oxygen or other gases. The tube while hot was evacuated with a mercury diffusion pump until the McLeod gage showed 0.001 mm. or less. This procedure was repeated several times before a run was started. Hydrogen was then admitted to the volume buret and after its pressure, volume and temperature were measured it was admitted to the reaction tube and the pressure of the palladium-hydrogen system was measured. The volume of the dead space in the reaction tube was known, and the amount of gas absorbed by the palladium could be calculated, since the dead space was at the same temperature as the palladium, except for the very small and known volume of the part of the capillary outside of the bath, which was assumed to be at room temperature.

About 0.2 g. of palladium, weighed accurately, was used in each experiment.

Summary of the Experiments at Zero Degrees

Referring to Fig. 1-A, a zero-degree isotherm, OABCD, was determined by adding hydrogen in small quantities, keeping the system constantly at 0°. The pressures from O to B quickly came to equilibrium, as a rule, but after a little progress along AB, the pressure equilibration became more and more sluggish until it soon became evident that it is impossible in this way to realize a state of equilibrium truly independent of the time over any large range of composition. Points from B to C were therefore plotted as soon as the pressure had become reasonably constant. The system was permitted to remain for a day or two at the point C. From C to D, hydrogen was then withdrawn, until at D the pressure was so low that it became impracticable with the given apparatus to withdraw significant masses of hydrogen.

Faced with this impasse, we finally heated the system to about 200°, for a few minutes. On cooling, the pressure soon arrived at the value E, to our gratification. A second heating did not further displace the pressure from the value E. In like manner, withdrawal of hydrogen brought the system to point F, and a brief heating as before caused the system to arrive at point G after the lapse of a reasonable time. By this means as many points could be obtained as we chose, all points on the line EA.

Such heat treatment is evidently of great value in permitting equilibrium to be established after removal of hydrogen from the system; for it will be observed that the points E, G lie at the same pressure level (within 0.1 or 0.2 mm.) as the point A, which was secured without the aid of any variations of temperature. It is, therefore, impossible that an equilibrium at high temperatures is being "frozen."

We have determined the section OA and AB many times. The angle A was generally quite sharp, although sometimes it was rounded, in which case the section AB was not quite horizontal. Twice it has happened that no change of curvature at all was found at A, the isotherm rising as a continuous adsorption curve. After one such occurrence the palladium A was treated in an electric furnace at 200° with hydrogen, then with carbon dioxide. After being cooled in carbon dioxide the metal was introduced again into the apparatus, exhausted and treated with hydrogen, re-exhausted in the usual way and made the subject of a new experiment. In this new experiment the angle A was obtained. We think that such continuous isotherms are more likely to occur when the metal is produced by reduction with sodium formate.

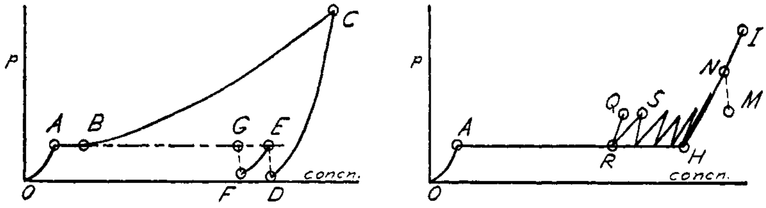

Fig. 1-A. Fig. 1-B.

Illustrating experiments at 0°.

Ordinarily, one heat treatment gave the full effect, but other treatments were usually given to make sure that the maximal effect was in fact reached. The precise temperature did not seem to matter, and after the first few treatments a bath of boiling mercury was always used.

Such heat treatment appears not to have been tried by any previous investigators. It has permitted us for the first time to trace rational phase diagrams for the Pd-H equilibrium.

We have, therefore, used the heat treatment with confidence in the determination of the end H of the horizontal isotherm and the rising isotherm HI. See Fig. 1-B. If the system was in the state Q and hydrogen was withdrawn, on heating the system each time before beginning the pressure measurements, various points on the line QR could be observed. (Further withdrawals would give points along RA.) If from R, hydrogen was added, points along RS could be traced. By alternating series of withdrawals with series of additions of hydrogen, the zigzag lines indicated in Fig. 1-B could be traced. These lines approached a limiting line, IH, which could be traced and retraced up and down, within the experimental error.

The point H was taken as the end of the horizontal part of the isotherm, and the line IH was taken to be the second ascending isotherm. In tracing these lines, the system was heated to 360° before each point was observed. The system was sluggish in this part of the field even after heating, the pressure becoming constant after one to three days, or sometimes longer. The heat treatment appeared of little or no benefit when adding hydrogen, but of great benefit when withdrawing hydrogen. If hydrogen is withdrawn in this region without heating, a point such as M may be observed; after heating the pressure rises in a reasonable time to a value N on the line IH.

Now it is, of course, possible that the line IH thus found is not quite the true equilibrium line on account of temperature disturbance. The method that gives it is, however, the same method that gives the line AH which is certainly correct (except possibly as to the point H) and we believe that the point H and the line IH are, therefore, substantially correct.

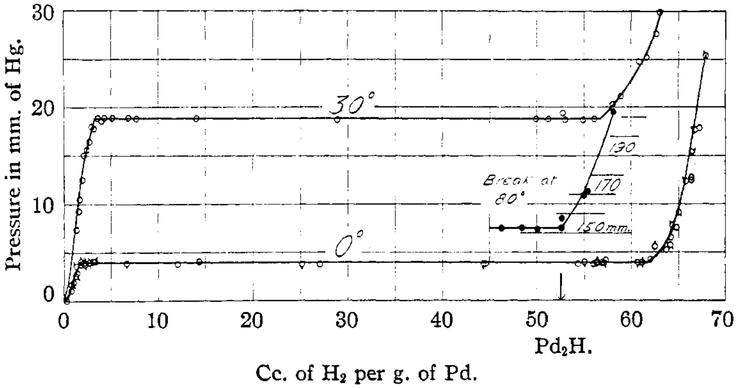

Fig. 2.—0° and 30° isotherms; with inset showing break at 80° with separate pressure but same composition scale. Plain circles on 0° isotherm represent palladium *A*; circles with one mark indicate palladium *B*; circles with two marks indicate the same result with both preparations.

The recent experiments of Lambert and Gates[12] may be taken to suggest the existence of a pure temperature effect, but we do not think such an inference is necessary. We think that the curious temperature effects observed by them after they had cooled their system and restored the temperature are explainable in terms of concentration disturbances. Such concentration disturbances, consisting of a withdrawal and an addition of hydrogen with respect to the solid mass, would be due to the effect of temperature on the gas in the dead space over the solid mass. Examination of their figures shows that, in any given part of the field, the effect of cooling and heating upon the pressure is in the same direction as the effect of adding and subtracting one unit of hydrogen isothermally.

A plot of the results at 0° is given in Fig. 2. Both preparations of palladium were studied, and the curves coincide throughout, as the figure shows. The mode of final reduction to metallic palladium appears to have some influence indeed on the degree of sluggishness with which equilibrium is approached, but no influence on the final equilibrium.

The point H lies at 62 cc. of hydrogen per gram of palladium, representing an excess of 18% of hydrogen over the formula Pd_2H.

Experiments at Other Temperatures

Similar complete isotherms were obtained at 30°, 80°, 160° and 180°, using only palladium finally reduced with hydrogen from the yellow salt.

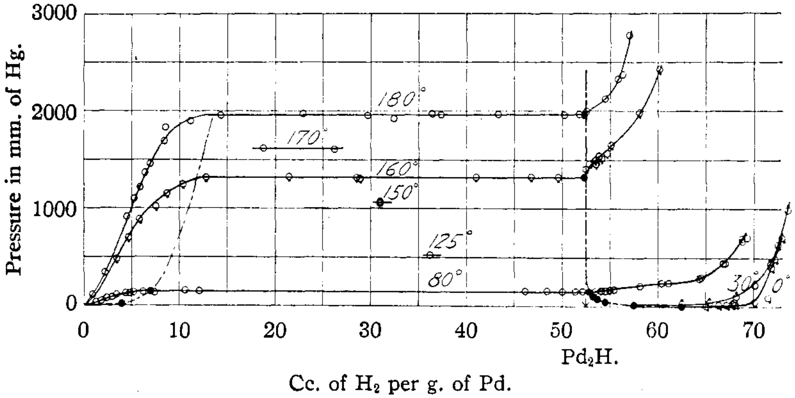

Fig. 3.—Plot of all results at relatively high pressures. The solid circles and the broken lines show the compositions of the coexistent solid phases as functions of the pressure.

Fig. 2 shows the 30° isotherm and also the break in the 80° isotherm on a suitable scale. Fig. 3 shows the isotherms at the three highest temperatures, as well as the high-pressure results on the 0° and 30° isotherms, which curiously appear to intersect.

Fig. 3 shows that the isotherms indicate the compound Pd_2H at high temperatures. The break at 80° is located at a composition only 0.2 or 0.3% in excess of this compound, and at higher temperatures, at least up to and including 180°, the breaks occur at exactly the Pd_2H composition, 52.5 cc. of hydrogen per gram of palladium, within the experimental error.

Certain of the discrepancies are due to the accumulation of volume errors in withdrawing and adding hydrogen many times before reloading. Points are also included which were obtained by variation of the temperature over part of the experimental range, such as the high point over the horizontal part of the 30° isotherm. Such points generally gave nearly correct values, although the system was not always heated to 360° after the variation of temperature.

Comparison of the Pressure Data with Those of Previous Investigators

Our pressures along the horizontal isotherms differ from those of Troost and Hautefeuille and those of Hoitsema by 100 or 200 mm. of mercury at high temperatures.

Table I gives the pressure in millimeters of mercury, calculated from a smoothed graph for rounded temperatures, and for a few odd temperatures of interest in view of previous work. A plot was drawn, Fig. 4, representing the deviations: log p (observed) $- [(a/T) + b]$ as a function of $1/T$. In smoothing the observations it was assumed that a log p, $1/T$ plot is nearly straight at low temperatures but shows curvature at higher temperatures. If such smoothing is justified, our measurements are consistent either within 0.7% on the pressures or, at the lowest pressures, with discrepancies not exceeding 0.2 mm. The values calculated for temperatures from 100° to 120° are uncertain by 3%, due to arbitrariness in determining the curvature of the deviation plot. Our calculated pressures are much higher than the descending horizontal isotherms of Lambert and Gates. We infer that Troost and Hautefeuille and that Hoitsema did not obtain equilibrium, and in such an event a few hundred millimeters mean little, as is shown in the diagrams of Lambert and Gates working with one preparation of palladium.

TABLE I

PRESSURES IN MILLIMETERS OF MERCURY OVER HORIZONTAL ISOTHERMS, OBSERVED AND CALCULATED BY MEANS OF DEVIATION CURVE OF FIG. 4

Temp., °C.	0	30	75	80	100	103	120	160	180
p calcd.	3.75	18.9	126.5	151.6	292	321	518	1327	1970
p obs.	3.95	18.7	...	152.6	...	...	...	1326	1961

Table I is based on the experimental values given in Table II for the temperatures at which complete isotherms were determined. The corresponding deviations are shown by solid black circles in Fig. 4. Data

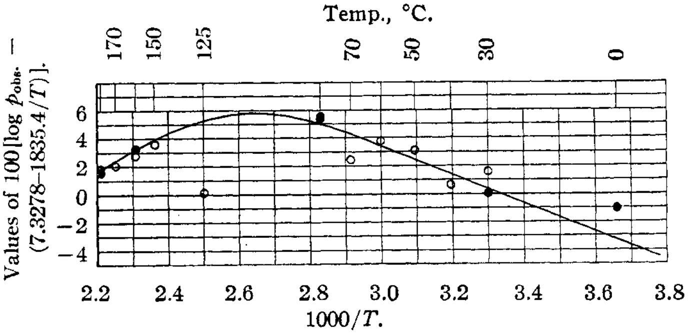

Fig. 4.—Deviation plot representing the effect of temperature on pressure over horizontal isotherms. Solid circles are from complete isotherms (Table II).

TABLE II

EQUILIBRIUM PRESSURES OF HYDROGEN OVER PALLADIUM AT VARIOUS TEMPERATURES AND COMPOSITIONS

Composition c in cc. of hydrogen (standard conditions) per gram of palladium. Pressure p in mm. of ice-cold mercury. Dotted lines indicate a complete removal of hydrogen.

c	p	c	p	c	p	c	p	c	p
Palladium A at 0°									
1.43	2.90	56.65	3.80	14.34	4.10	66.40	12.60	70.18	51.90
1.87	3.80	56.35	3.90	...	...	64.80	7.60	71.51	95.70
2.26	3.80	56.00	3.80	0.21	0.20	64.20	6.60	71.85	407.0
2.77	4.00	54.35	3.80	0.85	1.10	63.70	5.30	72.16	496.6
3.13	4.10	44.59	3.80	1.07	1.90	62.00	4.30	72.55	640.0
57.30	4.20	27.06	3.80	...	...	61.14	4.00		
56.90	4.00	12.04	3.80	67.20	17.9	66.40	12.80		
Palladium B at 0°									
68.00	43.8	66.7	17.7	57.00	4.00	...	...	1.83	4.08
60.70	4.0	67.9	25.4	56.36	4.00	0.36	0.30	2.11	4.02
61.20	4.0	66.4	15.4	44.37	3.80	0.83	1.70	3.30	4.10
62.5	5.6	64.15	5.8	25.14	3.80	1.27	2.60	65.02	9.13
64.4	7.8	...	...	6.63	3.90	2.21	3.80		
65.8	12.4	55.02	4.0	1.38	3.60	2.76	4.00		
Palladium A at 30°									
62.65	27.7	2.44	15.6	2.70	16.4	58.9	21.2	0.92	1.58
54.90	18.7	3.15	17.8	2.97	18.0	57.0	18.8	2.10	15.04
53.00	18.7	3.55	18.9	5.10	18.9	56.1	18.8	4.00	18.60
51.20	18.8	4.28	18.9	6.80	18.9	58.0	20.3	66.0	52.50
49.40	18.8	...	...	68.2	109.3	...	...	63.1	29.60
28.90	18.7	0.98	4.0	65.4	43.0	1.69	10.5	61.6	25.30
...	...	1.31	7.4	63.0	29.9	7.65	18.8	14.0	18.15
1.59	9.3	1.97	12.5	60.8	24.8	...	...		
Palladium A at 80°									
1.75	46.2	4.79	127.9	1.31	30.1	55.0	169.6	52.6	152.6
3.48	105.8	5.23	135.6	2.43	78.6	52.6	157.8	48.4	152.6
10.62	153.6	6.15	140.1	3.41	115.4	50.0	151.9		
12.09	152.1	7.43	131.6	68.81	670.1	46.3	152.6		
2.98	85.2	...	...	58.10	212.6	55.4	171.6		
Palladium A at 160°									
3.43	488	10.39	1244	53.51	1508	49.55	1325	58.10	2000
4.65	700	12.82	1313	52.43	1403	46.77	1331	53.50	1460
5.87	888	53.84	1541	60.11	2434	41.03	1327		
7.56	1016	52.82	1463	55.08	1657	21.48	1324		
8.69	1153	54.67	1577	54.10	1527	52.30	1321		
Palladium A at 180°									
8.53	1733	43.29	1970	52.53	2006	4.52	919	8.49	1695
36.42	1979	37.35	1963	50.20	1966	5.28	1097	11.15	1896
32.39	1929	29.61	1960	54.50	2130	5.82	1219	14.31	1955
56.30	2380	56.95	2788	0.97	101	6.42	1363		
51.78	1970	55.70	2333	2.15	336	6.98	1458		

from Table III are not taken into account, the deviations for which are shown in Fig. 4 by rings.

Table III presents miscellaneous points determined by varying the temperature after having obtained equilibrium. Occasionally hydrogen was withdrawn, in which case (and not otherwise) the system was heated to 360° before taking pressure readings. In some cases, the change of composition due to temperature effect was enough to cause inaccuracy, but usually such a disturbing effect was not great. Some of these points refer to horizontal portions of the isotherms. When these points were plotted with respect to temperature, it was found that the value for 125° was quite bad, suggesting a mistake rather than an ordinary error. The other points are consistent only to about 3%. We have not been able to account for this poor consistency to our entire satisfaction. It is, therefore, possible that the consistency shown in Table I is illusory and that these figures also are uncertain to about 3%, especially from 80° to 150°. Excluding the value for 125°, these miscellaneous points confirm a curvature in the log p, $1/T$ plot.

Table III

Miscellaneous Equilibrium Measurements

C and *p* are as in Table II. *R* or *L* after a temperature value indicates that the temperature was raised or lowered to that value. H after a temperature figure indicates that hydrogen was withdrawn and the system heated to 360°. The experiments start with equilibrium at 160°.

T	*c*	*p*	*T*	*c*	*p*	*T*	*c*	*p*	*T*	*c*	*p*
170 R	18.87	1613	80 H	66.83	446	60 L	54.25	72.6	80 H	51.40	152.8
180 R	22.91	1975	80 H	64.43	289	50 L	54.51	47.6	70 L	51.80	100.0
170 L	26.24	1603	80 H	61.11	241	80 R	52.91	153.6	60 L	52.15	71.4
160 L	28.88	1314	80 H	54.55	161	70 L	53.41	102.0	50 L	52.33	47.7
150 L	31.02	1059	70 L	55.05	110	60 L	53.70	71.6	40 L	52.58	29.8
160 R	28.92	1308	60 L	55.38	75.6	50 L	54.10	47.6	30 L	52.70	19.4
125 L	36.20	525	50 L	55.65	49.7	40 L	54.30	29.6	30 H	73.50	998
125 R	36.22	522	40 L	55.85	31.0	50 R	53.10	48.1	30 H	72.94	705
150 R	31.00	1062	40 H	54.71	29.5	60 R	52.76	71.7	30 H	71.68	441
...	...	..	80 R	53.44	155	70 R	52.60	100.7	30 H	70.10	222
80 H	68.70	707	70 L	53.94	104	80 R	52.03	152.6	30 H	68.21	108

On plotting for the first rising isotherms log p against log composition, straight lines were not obtained. Thus Henry's law cannot be applied to show that hydrogen dissolves as atomic hydrogen or as any other fixed species. This was noted by Sieverts,[15] who equated the composition to the expression $k_1\sqrt{p} + k_2p$. We found that as the pressure approached zero the tangents on our plots approached 0.5, as if the first portions of hydrogen dissolve as atoms. This is in accord with the form of Sieverts' expression.

Remarks on the Heat Treatment

Abundant evidence was obtained to show that hydrogen, expelled by heat, returns to the solids on cooling providing no excess of hydrogen is

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[15] Ref. 5, p. 446.

present. In the case of the data presented in Table II, upon which our diagrams and conclusions are based, the heat treatment was repeated to proved constancy of final pressure in about 80% of the points. Proof that constancy had been attained was occasionally omitted along the horizontal isotherm after four or five points along the isotherm had been determined by heating to constancy. It was also omitted after small *additions* of hydrogen along the second rising isotherms. In brief, evidence was secured for each part of each isotherm.

The heating at 360° was for a period of two to four minutes. About one-half of the dead space was under the boiling mercury during the heating.

Our results refer, of course, to palladium which has recently been heated, but this is ordinarily the case in any event, because of the necessity of freeing the original palladium from oxygen and hydrogen.

The Heat of Condensation of Hydrogen in Palladium

The heat effect, $-\Delta H$, for the reaction,

$$\mathrm{H_2,\ gas,\ 1\ atm.} + \mathrm{4Pd,\ 1\ atm.} = \mathrm{2(Pd_2H),\ 1\ atm.\ (decomposed)} \qquad (1)$$

can be calculated from our measurements, in simple fashion, by assuming that hydrogen is an ideal gas and that the energy effects due to changes of volume or pressure of the solids are negligible. The result refers to palladium hydride decomposed into two saturated solid solutions, but at 80° (and higher) one of these solutions is nearly pure $(\mathrm{Pd_2H})_x$ and comprises nearly all the mass of the system.

Where the pressure is independent of the composition the ordinary Clapeyron equation can be used. Where the pressure varies along the isotherm, we can integrate the partial molal heat content of hydrogen at constant mass of palladium, thus obtaining the total heat.

Whether the pressure varies or not we shall have as final result:

$$-\Delta H = -2.3\ R \int_0^1 \left(\frac{\partial \log p}{\partial\, 1/T}\right)_e \mathrm{d}n_1 \qquad (2)$$

where n_1 is the number of moles of hydrogen dissolved in the four gram atoms of palladium under an equilibrium pressure p at a constant equilibrium temperature T. The quantity $-\Delta H$ is the heat evolved in the change of state written above[16] in Equation 1.

To obtain the above equation we start with one mole of hydrogen and imagine its pressure reduced to an infinitely low value at the constant temperature in question. The change in H $(= U + PV)$ is zero for the perfect gas.

We now imagine the hydrogen put in contact with four atoms of palladium at the infinitely low equilibrium pressure. We then increase the pressure at constant temperature, reversibly, when n_1 will increase from zero

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[16] The heat evolved in the reversible addition of hydrogen equals $-\Delta H$ only when the isotherm is horizontal.

to one. At the same time the pressure rises along the isothermal, becoming constant along the horizontal portion. When the gas phase has disappeared we raise the pressure to one atmosphere without any further appreciable change in H. We have to find $\int dH$ for the addition of hydrogen (n_1) to the constant mass (n_2) of palladium at constant temperature.

$$dH = (\partial H/\partial n_1)_p\, dn_1 + (\partial H/\partial p)_{n_1}\, dp = T(\partial S/\partial n_1)_p\, dn_1 = T(\partial S/\partial n_1)_{pTn_2} dn_1 \quad (3)$$

We have noted that $(\partial H/\partial p)_{n_1} = 0 = dn_2 = dT$ and at constant pressure $dH = TdS$. S is the entropy of the whole system. The mass of this system is constant, in the sense that no matter crosses its boundaries, therefore, $dH = TdS + Vdp$ and it would be incorrect to add a term μdn. Planck[17] has evaluated $T(\partial S/\partial n_1)_{pTn_2}$. It is equal to $-L = -RT^2(\partial \ln p/\partial T)_c$, where subscript c refers to constant composition and the minus sign is due to an opposite meaning of dn_1. This gives Equation 2 when integrated.

The slope $(\partial \log p/\partial 1/T)_c$, multiplied by -4.58, gives the (differential) heat evolved in calories per mole at any particular composition. At low temperatures, 0–80°, this heat rises slowly with the hydrogen content from an initial value of 6000 at small content of hydrogen, to a value of about 8860 along the horizontal isotherms and reaches values about 9740 for dilution of the second unsaturated solution. The integrated values for $-\Delta H$, in calories per mole of hydrogen, are 8780 at 0°, 8700 at 30° and 8450 at 80°. Mond, Ramsay and Shields[18] measured the heat evolved when hydrogen at about 22° and one atmosphere was run into an ice calorimeter containing palladium. The heat effect per gram of hydrogen increased only very slightly with hydrogen content, was assumed to be constant and the best average value was given as 4644 calories. Per mole this would be 9362. The corresponding $-\Delta H$ for the reaction at one atmosphere and 0° we find to be 9210 calories per mole.[19]

The change of state, however, is indefinite as regards the number and masses (possibly the kinds) of the phases present, since they appear not to have been in equilibrium. Doubtless some of the second unsaturated solution was formed, so that the mean heat per mole should lie between our figures 8860 and 9740, as in fact it does.

Our calculated heats depend on the smoothing used for calculating values in Table I. When the pressures are smoothed, using the improbable assumption that log p is linear with $1/T$, the final result 8780 will be about 5% lower.

Summary and Conclusions

The equilibrium between palladium and hydrogen has been reinvestigated. It was found possible to bring the system into equilibrium by re-

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[17] Planck, "Thermodynamics," trans. by Ogg. Longmans, Green and Co., New York, 1917, p. 197.

[18] Mond, Ramsay and Shields, *Phil. Trans. Roy. Soc.*, **191A**, 105 (1898).

[19] By subtracting 22, $C_p = 151$. The pressure correction is negligible.

moving an excess of hydrogen from the gas phase, producing a deficit, thereafter heating the system a short time to about 360° and finally restoring the original temperature. Once the system has been brought to equilibrium in this way, hydrogen can be driven off by short heating to about 360° and be returned to the solids reversibly, although it was not found possible by isothermal operation to remove hydrogen and to replace it with fresh hydrogen.

The pressure along the horizontal isotherm at 0° measured in this way was the same as that determined without heating along the first part of the horizontal isotherm.

The conclusion was drawn that this method of securing equilibrium is legitimate and the method was used to determine isotherms at 0°, 30°, 80°, 160° and 180°. Two palladium preparations, reduced to the black metallic state in different ways, were found to give identical isotherms at 0°.

The data are presented in tables and graphs. The graphs show two solid solutions. The saturated solution richer in hydrogen has practically the composition of Pd_2H at 80°, 160° and 180°, but at lower temperatures contains a progressively greater excess of hydrogen.

It is concluded that a hydride, probably best written Pd_4H_2, exists which separates practically pure at high temperatures.

Planck's formula for the differential heat of evaporation is used to calculate the decrease in heat content for the formation of (decomposed) hydride. Applied at 0°, 30° and 80°, we find, respectively, 8780, 8700 and 8450 calories per mole of hydrogen. No close check with direct calorimetric data can be obtained, probably because of uncertainty as to the changes of state in the direct calorimetry.

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