THE HYDROGEN-LEAD, HYDROGEN-PALLADIUM, and DEUTERIUM-PALLADIUM EQUILIBRIA

By

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Department of Chemistry, June 1940

Signature of Professor
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on Graduate Students______________

TABLE OF CONTENTS

SECTION I: THE HYDROGEN—LEAD SYSTEM

SECTION II: THE HYDROGEN—PALLADIUM SYSTEM

Discussion of Results (continued)

SECTION III: THE DEUTERIUM-PALLADIUM SYSTEM

TABLE OF ILLUSTRATIONS

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SECTION I

THE HYDROGEN-LEAD SYSTEM

INTRODUCTION

The investigation of the absorption of hydrogen by lead was undertaken as a result of the work of E. Tarplin (1), whose Master's thesis apparently proved that lead absorbs hydrogen in a manner which obeys Henry's Law: $c = kp$.

This behavior, if it were a fact, should make lead a good medium for a study of the differences in the absorption of the various forms of hydrogen; and in particular, of ortho and para-hydrogen, which are probably so similar that a more complicated absorption curve would show no difference in their behavior.

As a preliminary to such a study, the absorption of normal hydrogen by lead was investigated.

PREPARATION OF MATERIALS

Hydrogen: The preparation and purification of hydrogen are described in Part II of the thesis.

Lead: The first three specimens of lead used in the investigation were prepared according to the directions given in Tarplin's thesis, as follows:

A small sheet of pure lead obtained from the National Bureau of Standards was dissolved in HNO_3, and precipitated as the hydroxide with an excess of NH_4OH. The precipitate was filtered, washed thoroughly with water, and dried at 105°; converted to oxide in a stream of air at 250°-300°; then reduced at the same temperature in a hydrogen stream. The reduction was permitted to continue for more than two hours, although Tarplin states that reduction to free lead is complete in one-half hour. The product is a fine black powder.

Later, when it was found that this treatment was not sufficient for complete reduction, a fourth specimen was subjected to a hydrogen pressure of several atmospheres in a metal bomb, at a temperature of 300°; the process being continued for several days. Even this was found to be insufficient to remove all traces of oxygen, so it became necessary to prepare the finely divided metal by other means.

Investigation of the literature showed no chemical treatment which would yield the desired product in sufficiently pure form, so that the final specimen was prepared as follows:

A sheet of the pure Bureau of Standards lead was washed with 6 N HCl, then rinsed thoroughly with water, alcohol and ether in succession. After this it was heated to 800°-1000° in vacuo for twenty minutes in a graphite crucible, and allowed to cool in vacuo. Upon removal from the furnace it was immediately immersed in benzene to prevent oxidation or formation of the carbonate, then placed in an inert gas chamber containing nitrogen.

The lead was ground to a fine powder with a file, in the inert atmosphere; the outer surface being rejected. The powder, after being sealed into the reaction bulb, was of a lustrous metallic appearance; indicating the absence of oxide or carbonate.

APPARATUS AND TECHNIQUE

These were the same as those described in Part II of this thesis.

RESULTS

The first absorption measurements were made at room temperature, with approximately four gms. of lead.Hydrogen was admitted to the reaction chamber at pressures up to 350 mm. of mercury, and remained in contact with the lead for two days. No absorption was observed.

The experiment was repeated twice more, with pressures up to 600 mm., with the same result.

A new specimen of lead was introduced, of about four grams weight also, and was heated at 200°-230° for three days at a pressure of 600mm. of hydrogen. A substantial decrease of pressure took place, which indicated absorption; but examination showed that water was collecting in the cooler part of the capillary tube. This meant that either the hydrogen contained water or oxygen, or the lead contained oxygen.

It seemed unlikely that the gas contained either impurity. However, the purifying agents were all renewed in order to remove any doubt; and when this did not change the result, an electrolytic generator containind 10% Na OH solution and a small amount of $Ba(OH)_2$ was substituted for the hydrogen tank; without effect.

A third sample of lead was prepared in the same manner as the first two; and after preheating to 200°, and removal of water by evacuation, a run made at 0° disclosed no absorption.

A fourth specimen, part of the third sample, was heated in the vacuum apparatus at temperatures up to 300°, with pressures of hydrogen ranging up to one atmosphere, and with repeated evacuation and replenishment of the hydrogen supply, for a period of about three weeks. At the end of this treatment, small quantities of water were still being formed, apparently from slow reduction of lead oxide by hydrogen. At lower temperatures, there was still no evidence of absorption.

The lead was then placed in a metal bomb connected with a hydrogen tank by steel pressure tubing, and subjected to the full pressure of the tank, at 300°, for a week. CO_2 was permitted to displace the hydrogen, and the bulb containing the lead was sealed into the vacuum apparatus with as little contact with air as possible. Water was still formed when the lead was heated in a hydrogen atmosphere.

At this point the final specimen of lead was prepared as described above. Its weight was approximately ten gms.

When hydrogen was first admitted into the reaction chamber and heated to 300°, a small quantity of water was formed; probably by combination of hydrogen with the oxygen adhering to the walls and to the surface of the lead. Subsequent heating, after removal and renewal of the hydrogen, revealed no further formation of water and no reduction in pressure. No absorption could be detected at any temperature below the melting point of lead, even after several days' standing.

DISCUSSION OF RESULTS

Two principal facts are shown by these results: first, that pure lead does not absorb a measurable quantity of hydrogen; and second, that lead powder prepared as Tarplin prepared it is not pure.

As further evidence that lead does not absorb hydrogen we may cite the results obtained by at least two other sets of observers: namely, Sieverts (2) and Nikitin and Sharkov (3); who have proved that lead does not absorb the gas.

Moreover, all of the metals near lead in the periodic table have been examined for absorption, and a summary of the results made by McBain (4) shows that none of them absorb hydrogen.

The probable explanation of Tarplin's results (i. e., a linear curve, pressure vs. hydrogen concentration) is that he used a value for the volume of the gas burette which was larger than the actual volume. The result of this would be a greater drop in pressure than he calculated when the gas was permitted to expand into the reaction chamber; which would naturally be attributed to absorption. Since the volumes and the temperature are constant, and no absorption takes place, the apparent absorption is proportional to the pressure. Withdrawal of gas would cause the same error in the opposite direction, and the result would be an apparently reversible linear curve.

SECTION II

THE HYDROGEN—PALLADIUM SYSTEM

INTRODUCTION

This part of the investigation was begun as a preliminary to the extension of the work of Gillespie and Downs (1) on the deuterium-palladium system to lower temperatures. Since several workers have measured the sorption of hydrogen by palladium at various temperatures in the range in which we proposed to work, the original plan was to duplicate their work at one or more temperatures as a check on our calibrations and technique.

However, after it was found that our results were apparently better than those previously obtained by the same method, it seemed advisable to extend the scope of the work with hydrogen; so that the majority of the measurements in this research were made on the hydrogen-palladium system.

Three types of attack have been made in general in the study of the equilibria between palladium and various gases: one by varying the temperature and pressure at constant mass; the second by varying the mass of hydrogen and the temperature at constant pressure; and the third by varying the mass and pressure at constant temperature. If a series of constant mass measurements is made at different masses, or a series of isobars or of isotherms, the results of the different types of measurement are equivalent and may be easily correlated.

The first to make careful measurements of the sorption of hydrogen by palladium in the temperature range between 0° and 100° C. were Troost and Hautefeuille (2), in 1874. They saturated the solid metal with hydrogen electrolytically, then measured the quantities of gas given off and the equilibrium pressures when the hydrogen was drawn off at constant temperature by a pump. Their results are shown in the Discussion of Results below, and appear to be fairly good, although the quantities of hydrogen absorbed are not consistent among themselves.

Hoitsema (3), in 1895, made a series of experiments with different masses of gas (constant in each experiment) and obtained results which, translated into isotherms, show apparent lack of equilibrium. This is probably explainable by the fact that in the preparation of his palladium several organic reagents were used, so that the metal may have been impure.

In 1925 Lambert and Gates (4) measured the sorption isothermally, and although their work was undoubtedly very careful and thorough, they evidently came far from attaining equilibrium; due also, probably, to impurities.

Gillespie and Hall (5), in 1926, obtained results which were good, but which received some criticism on the ground that although the measurement was in general isothermal, in order to attain true equilibrium it was found necessary to heat the palladium to a higher temperature and cool it to the equilibrium temperature before measuring each pressure.

In 1931 Gillespie and Ambrose (14) found that it is possible to obtain approximately the same results as those of Gillespie and Hall without the use of heat treatment, if the palladium has been previously heated to the softening point of pyrex to remove the traces of NH_4Cl left by milder heating.

Sieverts and Danz (6), in 1937, made isobaric measurements of the sorption of both hydrogen and deuterium, obtaining quite good results with the former.

The results of these men are shown in the Discussion of Results, in connection with those obtained in the present work.

APPARATUS

The apparatus employed consists of the following: a hydrogen generator, a purification train, a gas burette, a mercury manometer connected with the burette, a reaction bulb containing palladium which is also connected to the burette, a pumping system, and a Mc Leod pressure gage. The entire apparatus is made of pyrex, with all joints fused. In addition to the apparatus proper, an electric furnace and a constant temperature boiling bath were employed.

Hydrogen Generator:

Hydrogen was made by electrolysis of a 10% sodium hydroxide solution containing some barium hydroxide, in a cell with nickel electrodes.

Purification Train:

The hydrogen was led through Desicchlora (anhydrous barium perchlorate) to remove water, then through palladized asbestos at 300° to remove oxygen by the formation of water, and through P_2O_5 to remove any water formed. It was stored in contact with this train before use.

Gas Burette:

The burette is a bulb of 6.7920 $cm.^3$ volume, closed at the top by a double stopcock leading to the hydrogen re-

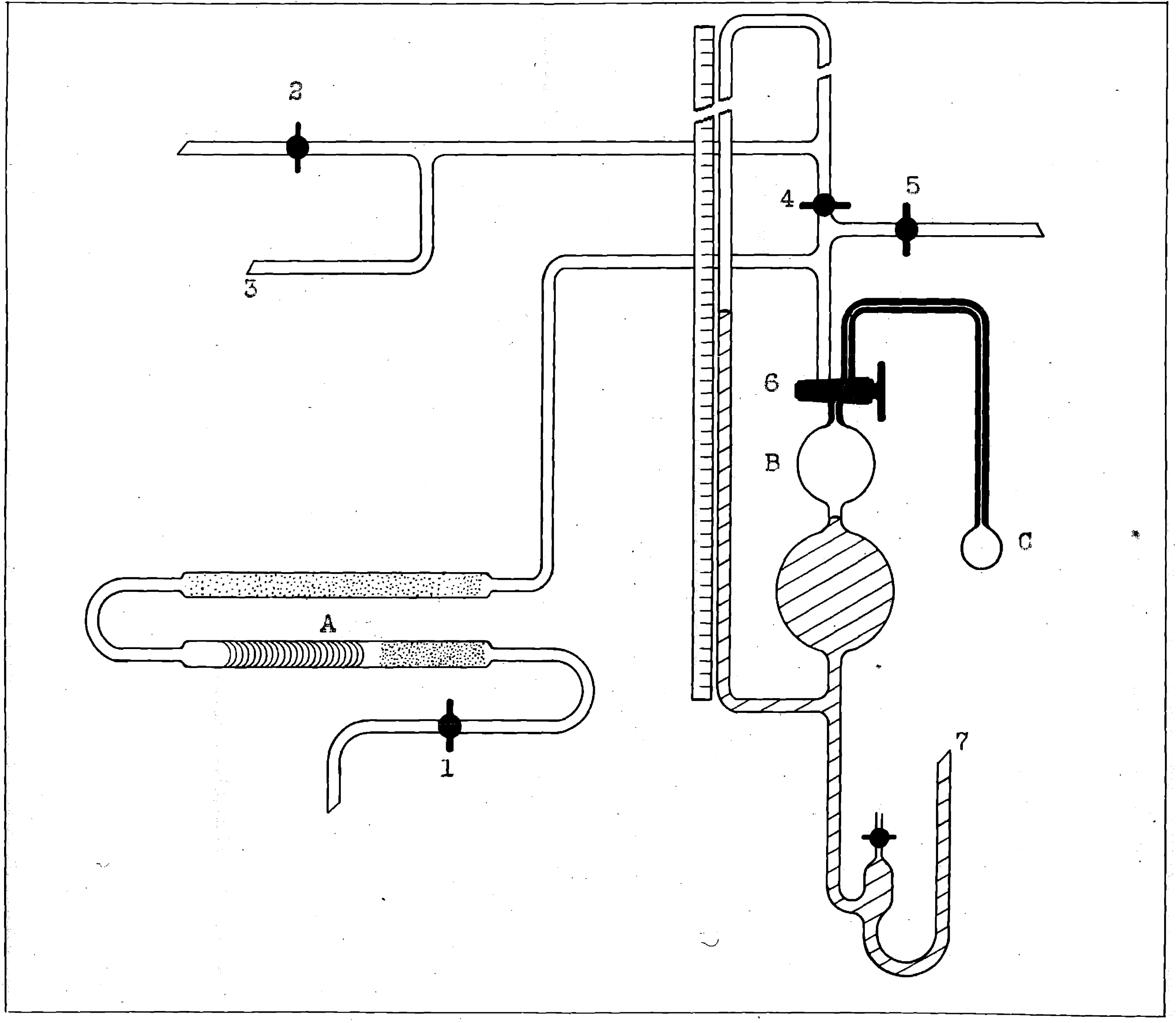
FIGURE 1

A. Hydrogen Purification Train

B. Gas Burette

C. Reaction Bulb

1. To hydrogen generator.
2. To pumping system.
3. To McLeod gage.
4. To evacuated space.
5. To deuterium system.
6. Double stopcock leading from gas reservoir to burette, and from burette to reaction chamber.
7. To mercury bulb.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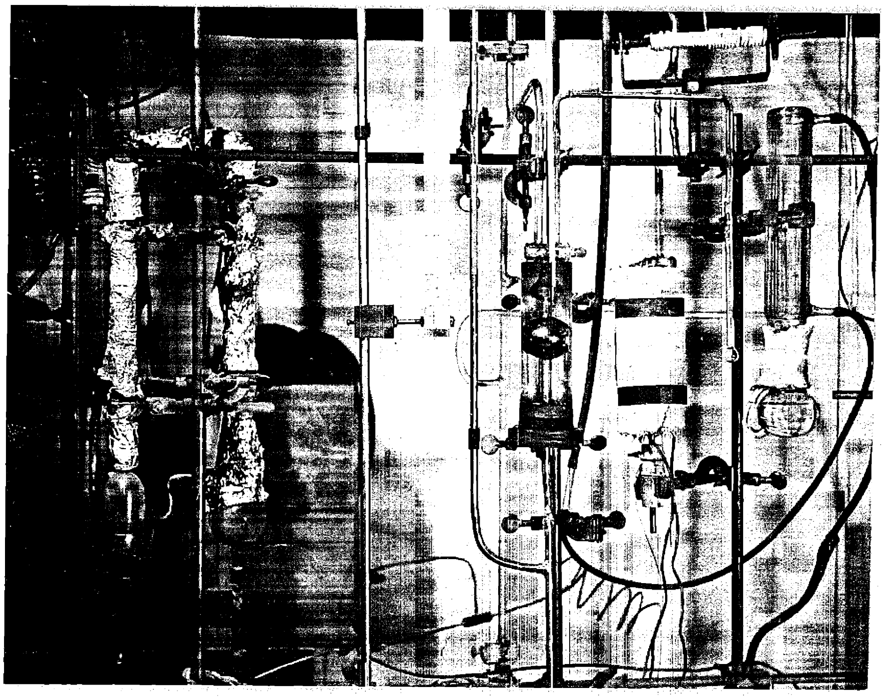


servoir on one side and to the reaction bulb on the other. Pressure readings are made with the mercury level at a mark etched in the lower neck of the bulb. The whole burette is enclosed in a water bath, to eliminate sudden temperature changes.

Mercury Manometer:

The manometer was 100 cm. in height during the first part of the work, but was later increased in height to 200 cm. The mercury level is adjustable by means of a small windlass, and controls the volume of the gas as well as measuring the pressure. Pressures are read with an accuracy of 0.2 mm. of mercury from a meter stick graduated in mm.

Reaction Bulb:

This small bulb, approximately one cm.^{3} in volume, is connected to the burette through a stopcock by means of a capillary tube, in order to keep the dead space volume as small as possible. Several different bulbs have been used, with different specimens of palladium. In changing bulbs, the capillary tube is cut a few cm. above the bulb, and a new bulb with its section of capillary tubing sealed to the old capillary by fusion of the glass.

Calibration of the volume of the capillary was made with mercury, and the volumes of the bulbs were determined by weighing them with water.

Pumping System:

Evacuation was accomplished by a Cenco Hyvac pump backed by two mercury vapor pumps, and the system was capable of maintaining a vacuum of 10^{-5} mm.

Electric Furnace:

A portable furnace, used for heat treatment of the palladium in the reaction bulb, was made by winding resistance wire around an insulated iron tube whose inside diameter was slightly larger than that of the reaction bulb, and whose lower end was closed by an iron plug containing a hole for a thermocouple junction. An iron rod was screwed into the plug as a means of support. Insulation for the furnace was furnished by asbestos tape and asbestos steam-pipe insulation.

Constant Temperature Bath:

The bath, used for all isotherms except those at 0°, is a boiling bath, in which the reaction bulb is held in the condensing vapor of a pure liquid. The bulb is inside a double jacket above which is a condenser. Part of the condensed liquid flows back over the bulb, while the remainder flows down between the inner and the outer jacket and is carried back to the boiling chamber via a side arm. The outer jacket is wrapped with asbestos as insulation.

PREPARATION OF PALLADIUM

The final stages of the preparation were different for several of the specimens used, and the various treatments will be described individually for each specimen; but the initial part of the preparation was the same in all cases. The method is that employed by Gillespie and Hall (5), modified in some details.

Palladous chloride, obtained from the J. T. Baker Chemical Co. in 1937, was dissolved in aqua regia, evaporated to dryness, baked for one-half hour, dissolved in concentrated HCl, and the solution diluted with about fifteen volumes of water. The solution was filtered to dissolve any insoluble impurities.

A slight excess of NH_4OH was added, forming a "meat-colored" precipitate of $Pd(NH_3)_4Cl_2 \cdot PdCl_2$. This precipitate was digested on a steam bath until it dissolved, then the solution was cooled and filtered. Acidification with HCl precipitated palladosammine dichloride – $Pd(NH_3)_2Cl_2$ –, a yellow salt insoluble in water, which was then filtered and washed with water.

The $Pd(NH_3)_2Cl_2$ was redissolved in NH_4OH, filtered and reprecipitated with HCl; washed with water until $AgNO_3$ gave no further chloride test, and dried in an oven at 105°.

The ammine was reduced by a stream of hydrogen at about 150° to palladium powder and ammonium chloride, after which the hydrogen was displaced by CO_2 before the palladium was cooled.

Up until this point the procedure was the same for all specimens. From here on the treatments differ, so each will be discussed separately.

METHOD OF PROCEDURE

Here again several modifications of the method were employed at different times, and these will be described later. The general method was as follows:

The reaction bulb was thoroughly evacuated at a temperature of at least 160°, after having been rinsed repeatedly with hydrogen.

The first quantity of gas was admitted to the measuring burette and the pressure recorded. Then the pressure was decreased, and the gas allowed slowly to enter the reaction chamber. The pressure was permitted to come to equilibrium, and recorded. At this point the stopcock was closed, a new lot of hydrogen introduced into the burette, and the process repeated.

To withdraw hydrogen, the stopcock was again closed after the equilibrium pressure had been measured. A quantity of gas was rejected from the burette through the other opening of the stopcock, the cock closed and the pressure measured. Then the reaction chamber was opened to the burette, and equilibrium reestablished.

The temperature of the burette was recorded at each pressure measurement.

In general, a run consisted of a series of additions of gas until the pressure-concentration curve was well past the second break, and the equilibrium pressure was two or three times as great as that of the horizontal portion of the curve. We may explain here that the nature of all the curves is as follows: As hydrogen is added to pure palladium the pressure at first rises sharply, then becomes constant and remains so for a long concentration range, whereafter a second sharp rise is encountered.

After addition of the gas was completed a series of withdrawals was made, until at least enough hydrogen was removed so that the pressure again became constant.

Many of the runs included several successive additions and withdrawals.

METHOD OF CALCULATION

The calculation of the quantity of gas sorbed is based on the ideal gas relationship, which is accurate to within 0.1% for hydrogen at the pressures here considered.

The total quantity of gas in the system is determined from the known volume of the burette and the pressure and temperature.

Knowing the quantity of gas in the system, the volume of the dead space, the temperatures of the burette and the reaction chamber, and the equilibrium pressure, we can calculate the quantity of gas which has been sorbed as follows:

Let

P_1, V_1 = pressure and volume of the gas in the burette.

P_2 = pressure at equilibrium, gas in reaction chamber.

$V_{2(r)}$ = volume of the part of the system (burette + stopcock bore + capillary) which is at room temperature (T_r).

$V°$ = volume of the dead space which is at the temperature of the palladium ($T°$).

Then the number of mols of gas added to the system in a single operation is

$$(1) \qquad N_{added} = \frac{V_1}{82.07 x 760 x T_r} \left[P_{1(n)} - P_{2(n-1)} \right] ,$$

where n represents the latest measurement and (n − 1) the one preceding. For the first addition n = 1 and (n − 1) = 0.

The total number of mols in the system is

(2) $$N_{total} = \sum N_{added} \; .$$

The number of mols left unabsorbed at equilibrium is

(3) $$N_{not\ absorbed} = \frac{P_{2(n)}}{82.07x760}\left[\frac{V_{2(r)}}{T_r} + \frac{V°}{T°}\right],$$

$P_{2(n)}$ being the equilibrium pressure.

The total number of mols absorbed at the time of the nth measurement is (2) – (3).

In withdrawal, the number of mols removed in a given operation is

(4) $$N_{withdrawn} = \frac{V_1}{82.07x760xT_r}\left[P_{1(n)} - P'_{(n)}\right] ,$$

where $P'_{(n)}$ is the pressure in the burette after the gas has been rejected.

The number of mols left in the system is the same as (3) above, at equilibrium.

The total quantity of gas, absorbed and unabsorbed, is

(5) $$N_{total} = N_{maximum} - \sum N_{withdrawn} \; .$$

(6) $$N_{absorbed} = (5) - (3).$$

Correction of the pressure for the expansion of mercury was made by multiplying the final result by the appropriate factor, since the nature of the calculations permits this factor to be carried through as a simple multiplier.

It must be noted that a temperature gradient exists between the part of the system which is at room temperature and that at bath temperature. However, the gradient is along a part of the capillary, and includes only a small volume. A determination of this gradient was made at 100°, and it was found that no appreciable error would be made by taking as V° the volume of the bulb and capillary up to the joint made when the bulb was sealed onto the apparatus. The length of the tube below this joint was kept approximately the same for all the bulbs used.

RESULTS

Since many of the results apparently depend upon the pre-treatment of the palladium specimen, and since the procedures differ in some details even during the runs, each run will be dealt with separately in order to avoid confusion.

In general, the results are given in the same chronological order in which they were obtained. Several runs are omitted, either because they prove nothing which is not proved by other runs or because they are known to be in error. For example, a series of hydrogen runs made with a hydrogen tank as source was found to give poor results; later traced to a leak in the connections. Also, a series of deuterium runs is omitted because of a leak in the palladium thimble used for purification.

Run I, Pd 1, 0°:

Pretreatment: Immediately after reduction, the palladium was heated slowly to 460°-480° in a stream of hydrogen, and maintained at that temperature for two hours. Then a stream of CO_2 displaced the hydrogen, and the furnace was cooled slowly in CO_2.

The $Pd(NH_3)_2Cl_2$ had been weighed before the reduction and the palladium was weighed after. The apparent atomic weight of the metal as calculated from these weights was 106.4; the actual atomic weight being 106.7.

The palladium powder, which was light gray in color, was washed in boiling water until no further traces of chloride were detectable with $AgNO_3$ solution; then dried at 105° in an oven.

After being introduced into the reaction bulb, and on the same day as Run I was begun, the specimen was heated to 460° in hydrogen, and was evacuated at that temperature for two hours.

The weight of the specimen was 0.9955 gm.

Procedure: In adding hydrogen the mercury level was kept adjusted so that the pressure was maintained a few millimeters above the expected equilibrium value until the steady state was reached. In withdrawal, the pressure was decreased slowly to the equilibrium pressure.

Results: The equilibrium pressure rose to 4 mm. at 0.0125 a (let "a" be the abbreviation for "atoms of hydrogen per atom of palladium"), remained perfectly constant until the concentration reached 0.54 a where it began to rise very gradually to 8 mm. at 0.60, then with increasing acclivity to 250 mm. at 0.69 a.

Equilibrium was attained within a few minutes at all points except those in the vicinity of the second break in the curve, where periods of time up to an hour were required.

Upon withdrawal of hydrogen, the curve was coincident with the addition curve down to a pressure of 25 mm. and a concentration of 0.645 a, where it began to diverge slightly in the direction of greater hydrogen concentration. The divergence was hardly more than 0.01 a at the maximum. The curve became horizontal at about 3 mm. and 0.61 a.

Frequent tests were made by allowing the palladium to stand for several hours in contact with the gas, to ascertain that the true steady state had been reached.

The results of Run I are shown in Fig. (2).

Run II, Pd 1, 0°:

Pretreatment, procedure and results were the same as for Run I, except that when the horizontal part of the first withdrawal curve was reached a second addition and withdrawal curve pair were obtained as a check on the second break and the -phase region of the curve. The second addition and withdrawal curves were coincident with each other, with the first withdrawal curve, and with that of Run I.

Run IV, Pd 2, 100°:

Pretreatment: The preparation of Pd 2 was the same as that of Pd 1 in all significant details.

The specimen was heated in the reaction chamber at 450° in vacuo for ten hours. Its weight was 0.6991 gm.

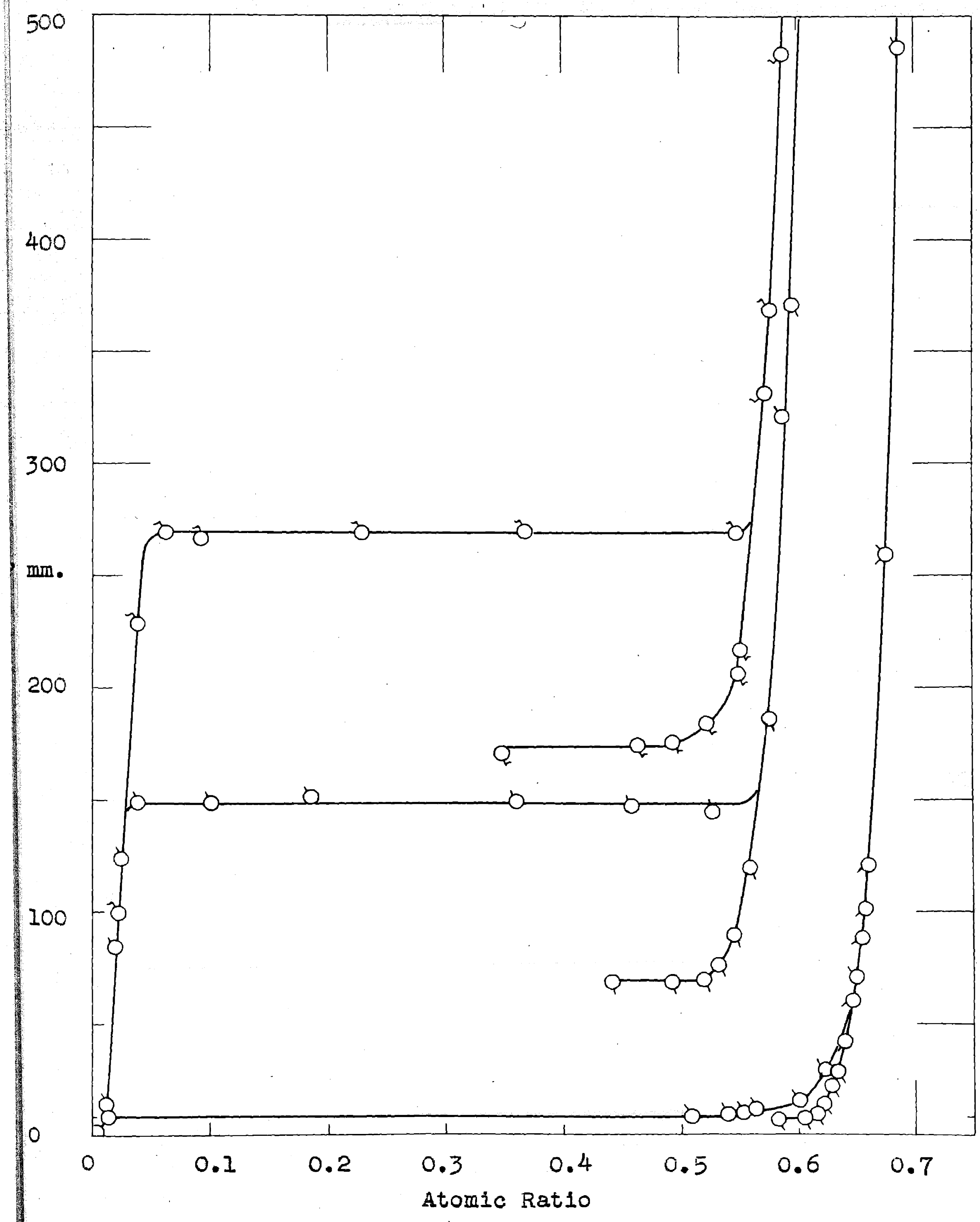
Procedure: In addition of hydrogen, the same procedure was used as in Run I.

A preliminary trial (Run III) had shown that in withdrawal, gradual decrease of pressure to the steady state

FIGURE 2

Runs I, XVII, and XXV; isotherms at 0°, 76.8°, and 100° respectively. Flags directed upward signify addition of hydrogen; downward, withdrawal.

The pressure scale of the 0° isotherm (lowest curve) is half that given by the ordinate numbers. Read 50 mm. instead of 100 mm., etc.


500
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mm.
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0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

value after removal of a quantity of gas led to a pressure well below that of the addition isotherm along the horizontal part of the curve. Therefore an alternative technique was adopted for this run and used in several succeeding runs. The procedure was to allow the pressure to decrease to a value below the expected equilibrium pressure, then increase it slowly to the steady state value. Galstaun had used this technique for part of his measurements, and Downs had also used it for part of his. The method appears liable to suspicion of yielding pressures which are not true equilibrium pressures for withdrawal, since the final operation is an addition of hydrogen; so that in later runs, starting with Run XIV, we reverted to the first method.

Results (Fig. 3): Upon addition, the horizontal part of the curve was reached at about 0.05 a. The pressures along the horizontal varied irregularly from 275 to 290 mm. The second break was not distinct enough to establish its concentration exactly, but was definitely beyond 0.5 a. The curve became almost vertical at about 0.6 a.

The withdrawal curve coincided with the addition curve in the β-phase region. A sharp break occurred at about 0.55 a, and the horizontal was less than five mm. below that of the addition curve.

Run V, Pd 1', 100°:

Pretreatment: Since the results obtained with a

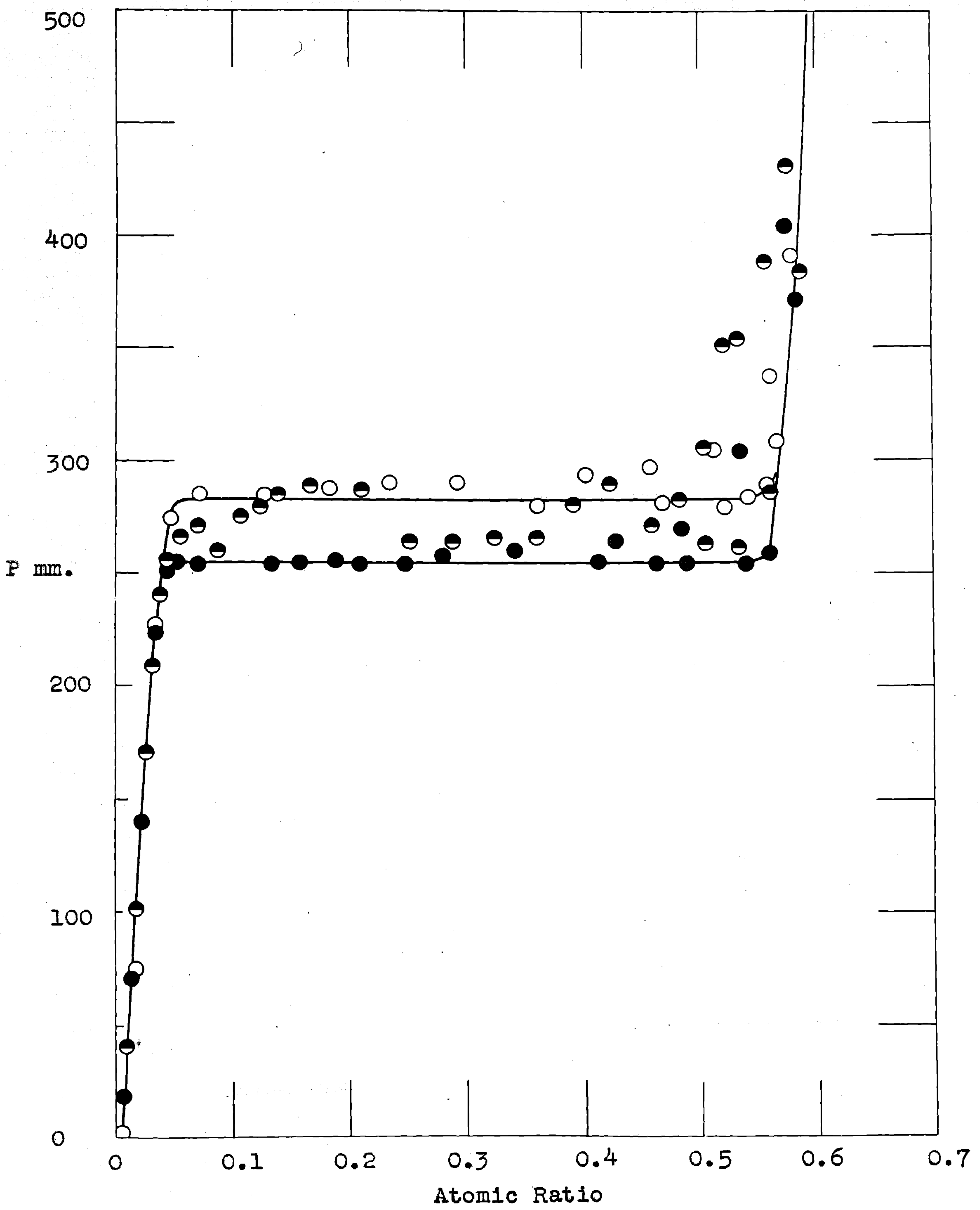
FIGURE 3

Runs IV, VI and VIII: 100° isotherms showing the effect of different preheating treatments, and the effect of withdrawing gas in such a manner that the final operation is addition of gas.

Open circles (Run VIII) represent palladium which has never been heated above 180°. The lower points near the second break represent withdrawal of hydrogen such that the final operation is addition.

Closed circles (Run VI) represent palladium which has been heated above 500°.

Half-filled circles (Run IV) represent palladium which has been heated to 450°.


500
400
300
200
100
0
P mm.
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

new specimen, Pd 2, agreed quite well with those obtained using a specimen which had been used repeatedly (Pd 1), and which had been in frequent contact with mercury vapor, it was concluded that mercury either had not distilled over to the palladium in appreciable quantity, or had no effect on the hydrogen-palladium equilibrium; so a part of Pd 1 was used again.

The new specimen, Pd 1', was heated in hydrogen immediately before the run, for two hours at 525°-550°. Its weight was 0.7394 gm.

Procedure: Same as that used in Run IV.

Results: The first break appears at 0.05 a and 260 mm.; and along the horizontal portion of the curve the pressures vary between 260 and 290 mm., the majority of the points indicating a constant pressure of 260 mm. The β-phase part of the curve coincides with those previously obtained at 100°.

Upon withdrawal, the horizontal occurs again at 260 mm., with a comparatively sharp break at 0.55 a. A second addition and withdrawal give the same results.

Run VI, Pd 1', 100°:

Pretreatment: The specimen was heated to 525°-550° for five hours in hydrogen before the run.

Procedure: Same as for Run IV.

Results: The first break is at 0.05 a and 255 mm. A good horizontal curve is obtained; the pressure remaining below 265 mm. up to a concentration of 0.45 a. The second break is not distinct, but is between 0.5 a and 0.6 a.

The same pressure is obtained in the horizontal part of the withdrawal isotherm; the break occurring at 0.55 a. A second addition and withdrawal yield the same results.

The β-phase part of the curve coincides with previous curves.

Run VII, Pd 3, 100°:

Pretreatment: The preparation method was the same as that by which previous specimens were prepared except for the following:

The palladium was never heated above 175° at any time. It was freed of NH_4Cl by thorough washing with boiling water; powdering, drying, and more washing with boiling water until no further trace of chloride could be detected; then dried at 105°.

The powder, which was black except for a few light gray particles, weighed 0.5095 gm.

Procedure: Same as for Run IV.

Results: The steep α-phase part of the curve differs from those of previous runs in that more hydrogen was sorbed at the lower pressures. The first break is at about 0.065 a and 275 mm.

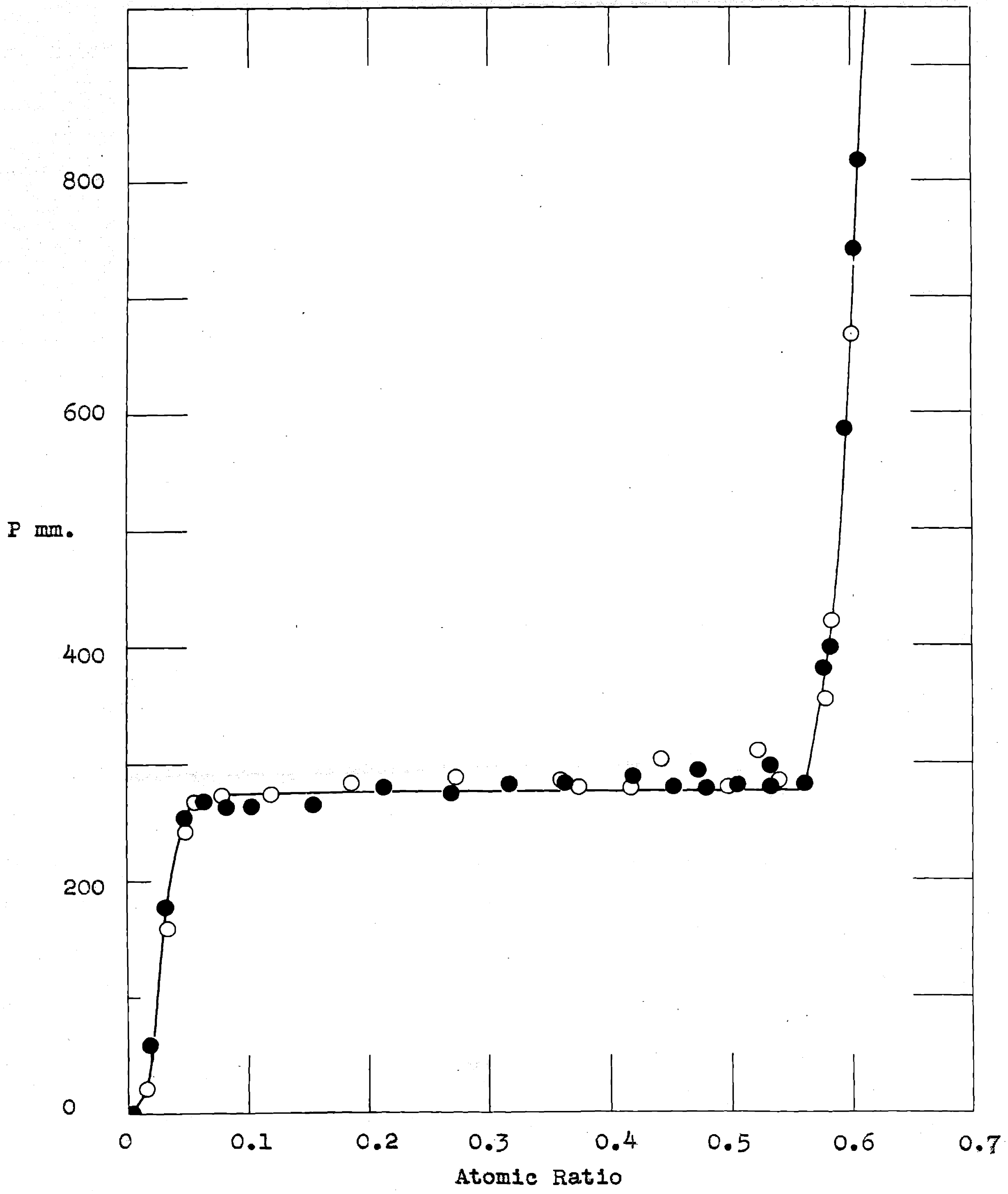
The second break in the addition isotherm is at approximately 0.55 a, as is that of the withdrawal curve. The horizontal, both for addition and withdrawal, is at 275-280 mm.

Cf. Fig. (4) for curve.

FIGURE 4

Runs VII and IX: showing reproducibility of results with different specimens which have undergone the same pretreatment; and showing the effect of withdrawing gas in such a manner that the final operation is addition.

Both runs were made at 100° with palladium which had never been heated above 180°.


800
600
P mm.
400
200
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

Run VIII, Pd 4, 100°:

Pretreatment and procedure were the same as for Pd 3. Weight of the specimen was 0.4482 gm.

Results(Fig. 3): The addition horizontal was at 285 ± 5 mm; withdrawal, 275 ± 5 mm. Breaks and α- and β-phase portions of the curve were the same as for the preceding run.

Run IX, Pd 4, 100°:

Pretreatment, procedure and results were practically identical with those of Runs VII and VIII.

Cf. Fig. (4).

Run XV, Pd 5, 76.8°:

Pretreatment: Same as for Pd 3 and Pd 4. The specimen was never heated above 180°. Weight, 0.5167 gm.

Procedure: The procedure differed from that employed in previous runs (except Runs I and II) in that the withdrawal curve was obtained by permitting the pressure to decrease slowly to the steady state value. It was never allowed to be more than a few mm. below the equilibrium value.

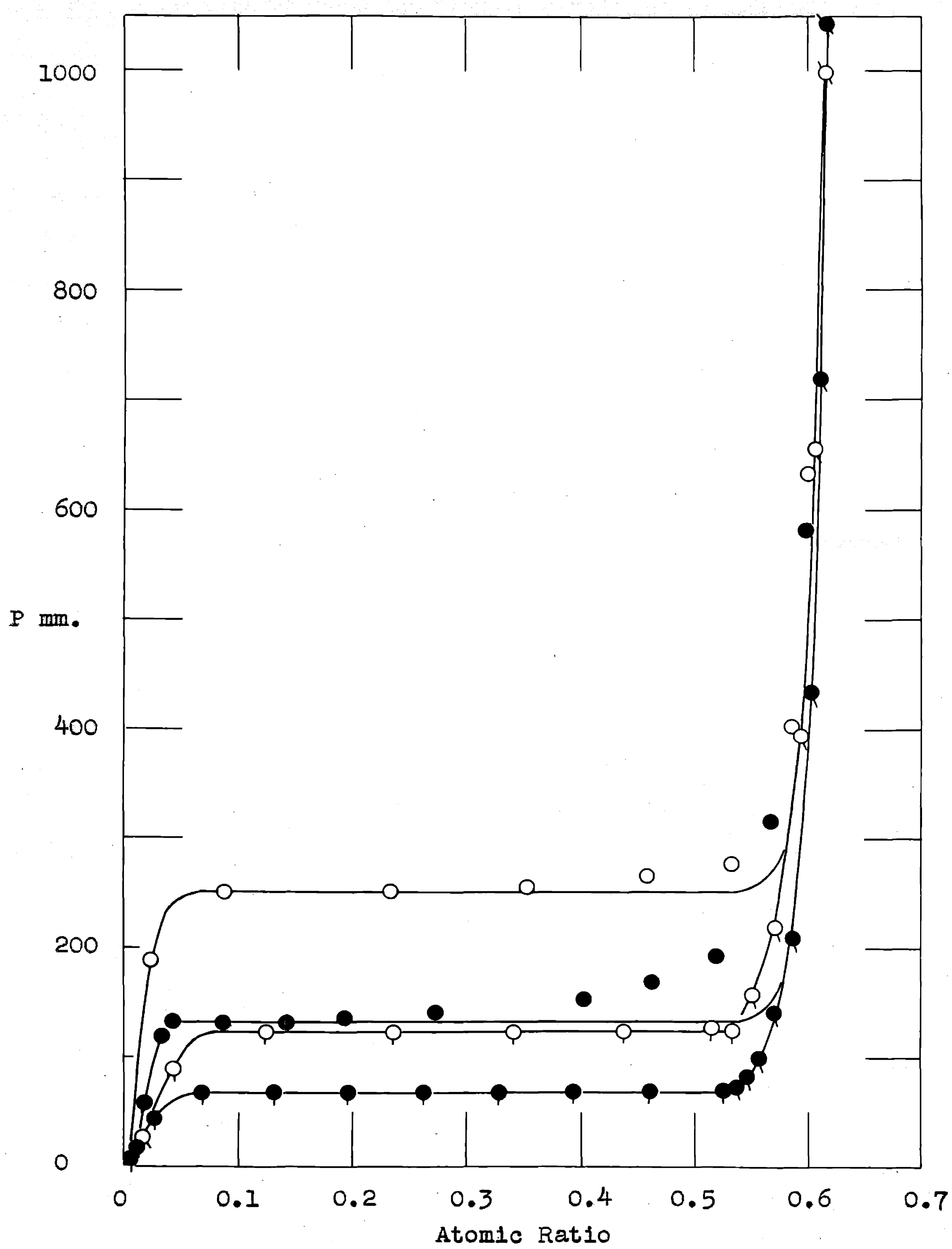
The constant temperature bath contained boiling carbon tetrachloride.

Results: Fig. (5). The first break in the addition isotherm occurs between 0.04 and 0.05 a, and the constant pressure level is at 133 ± 5 mm. The second break,

FIGURE 5

Runs XV and XVI: complete absorption isotherms at 76.8° and 100°, showing that the withdrawal curve is distinct from the addition curve in the univariant region.

Open circles represent the 100° isotherm, closed circles 76.8°. Flags directed downward represent withdrawal of gas.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P mm.
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0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

although not definite, is well beyond 0.5 a.

The withdrawal isotherm shows no tendency to break at the same level as the addition isotherm, but breaks quite sharply at a concentration of 0.54-0.55 a and 68 mm. The curve extends all the way back to the origin. The pressure along the horizontal is remarkably constant, varying less than a mm. at all concentrations from 0.53 a down to 0.06 a. The pressure then drops fairly sharply, approaching the origin in coincidence with the addition curve.

Run XVI, Pd 5, 100°:

Pretreatment: The specimen was heated to 500°-550° for five hours in hydrogen before evacuation.

Procedure: Same as that in Run XV.

Results: The first break in the addition isotherm occurs at 0.05 a and 255 ± 5 mm. The second break is between 0.54 and 0.56 a.

Upon withdrawal, the first break appears at 0.535 a and 124 mm., and the pressure remains constant within two mm. down to a concentration of 0.06-0.07 a before starting to drop. This curve also coincides with the addition curve near the origin; coming in asymptotically to the concentration axis. Cf. Fig. (5) for the curve.

Run XVII, Pd 6, 76.8°:

Preparation: Preparation of Pd 6 was the same as that of Pd 5. Its weight, 0.4165 gm. The specimen was heated to 550° for sixteen hours in hydrogen before evacuation.

Procedure: Same as in Run XV.

Results: Same as in Run XV, except that the addition isotherm becomes horizontal at 148 ± 2 mm.

Run XIX, Pd 6, 100°:

Pretreatment: The specimen was heated at 400° for several hours.

Procedure: This run was intended as a test of temperature effects produced while the run was in process. Two different effects were investigated.

The first was that produced by the procedure of Hall (5), who found that his points fell on a horizontal curve only if the palladium had been heated to 360° and cooled to the equilibrium temperature (100° in this case) before each pressure measurement. Several points were tested in this manner.

The second effect tested was that produced by cooling the metal to room temperature or below, then heating it to the equilibrium temperature before each addition or withdrawal of gas.

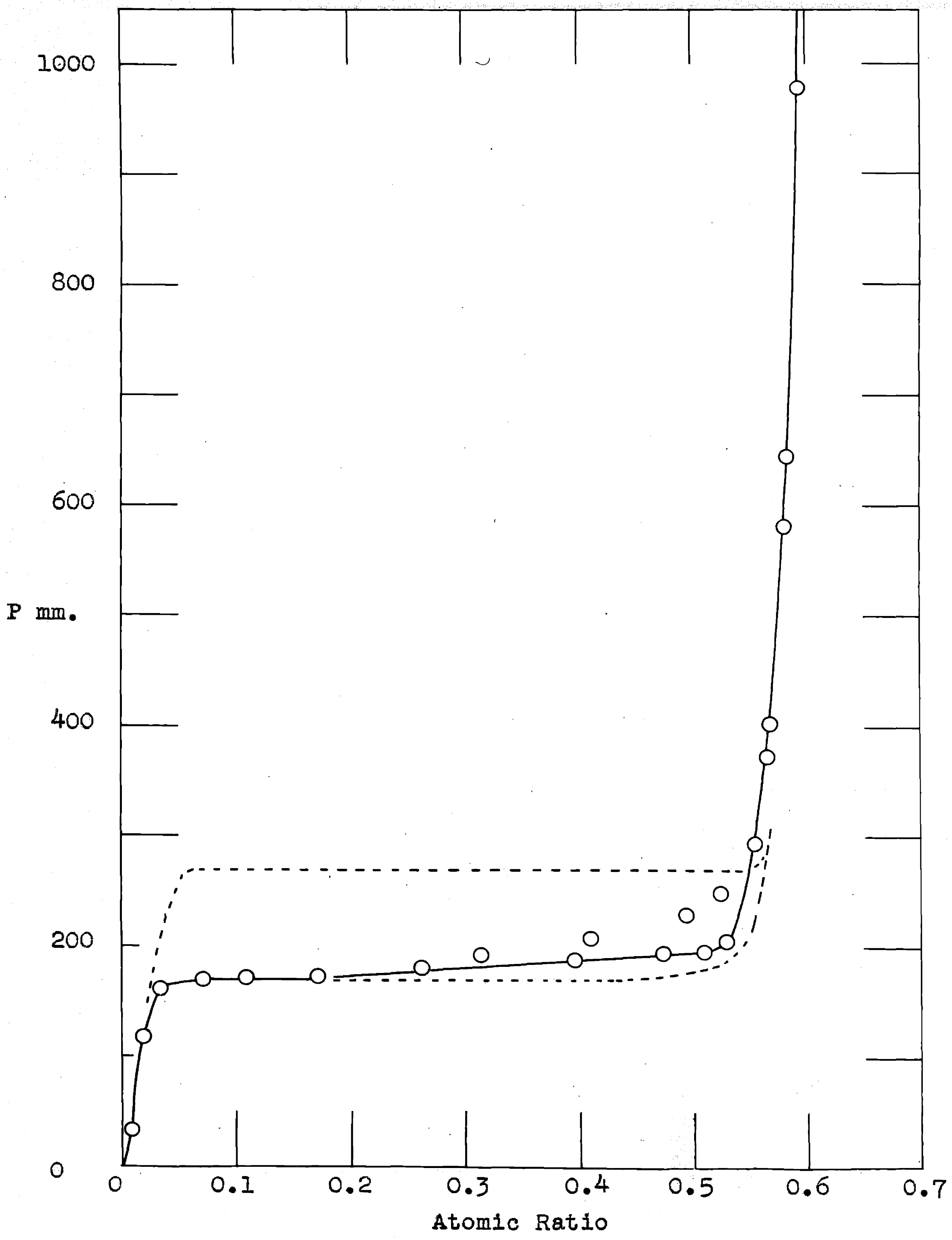
Results: All pressures found by Hall's method of successive heating and cooling were coincident with those obtained in our ordinary isothermal measurements of hydrogen addition.

All pressures resulting from the second method of treatment (i.e., successive cooling and heating) fell on or near the withdrawal curve obtained in our isothermal treatment. Cf. Fig. (6).

FIGURE 6

Run XIX: showing the effect of cooling the palladium and reheating it to the equilibrium temperature (100°) before measurement of each absorption pressure during the run.

The dotted curves represent the usual addition and withdrawal curves at 100°.


1000
800
600
400
200
0
P mm.
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

Run XXIV, Pd 3', 100°:

Pretreatment: This run was made as a test of the effect of time on the activity of palladium which had never been exposed to hydrogen or heated above 200° after its preparation.

Pd 3' is a part of the specimen from which Pd 3 was taken. It was prepared six months before this run, and was stored in contact with air during the intervening period.

After it was introduced into the reaction bulb, Pd 3' was evacuated for several hours at room temperature. Then hydrogen was admitted, still at room temperature. Immediate evolution of heat and the formation of water which condensed on the walls of the chamber, followed by rapid sorption of hydrogen, indicated that the palladium was still very active; also, that a superficial layer of oxide had probably been formed.

The palladium was rinsed repeatedly with hydrogen, both at room temperature and at 180°. It was still in the form of a black powder, weight 0.4556 gm.

Procedure: Same as that of Run XV; gradual decrease to steady state pressure on withdrawal of gas.

Results: Upon addition, the first break appears at 0.05- 0.06 a. The horizontal is at about 270 mm. The pressure remains constant to a concentration of 0.55 a before rising in an almost vertical curve which coincides with the usual β-phase part of the diagram. This sharp break is due, probably, to the fact that in the region of the break the pressure was held at several cm. above the equilibrium pressure for a time, rather than only a few mm., as has been the practice in most of the runs. This does not imply that any withdrawal of gas took place. The mercury was never allowed to rise above the mark at which the equilibrium pressure was measured.

The withdrawal curve became horizontal at about 175 mm. and 0.53 a. Cf. Fig. (7).

Run XXV, Pd 1", 100°:

Pretreatment: In order to ascertain the effect of ageing on the activity of palladium which had been heated repeatedly to 550° and had been frequently in contact with hydrogen, a run was made with a part of Pd 1'.

Pd 1', prepared eight months before this run, was in continual use for two months and then stored in air for six months. Weight of the specimen, which was a light gray powder, was 0.3559 gm.

Procedure: Same as for Run XXIV.

Results: Same as for Run XXIV, except that the horizontal was at 262 mm. on addition of hydrogen and about 165 mm. on withdrawal. These levels are both a few mm. lower than the corresponding levels of the preceding run. Cf. Fig. (7).

Run XXVI, Pd 7, 100°:

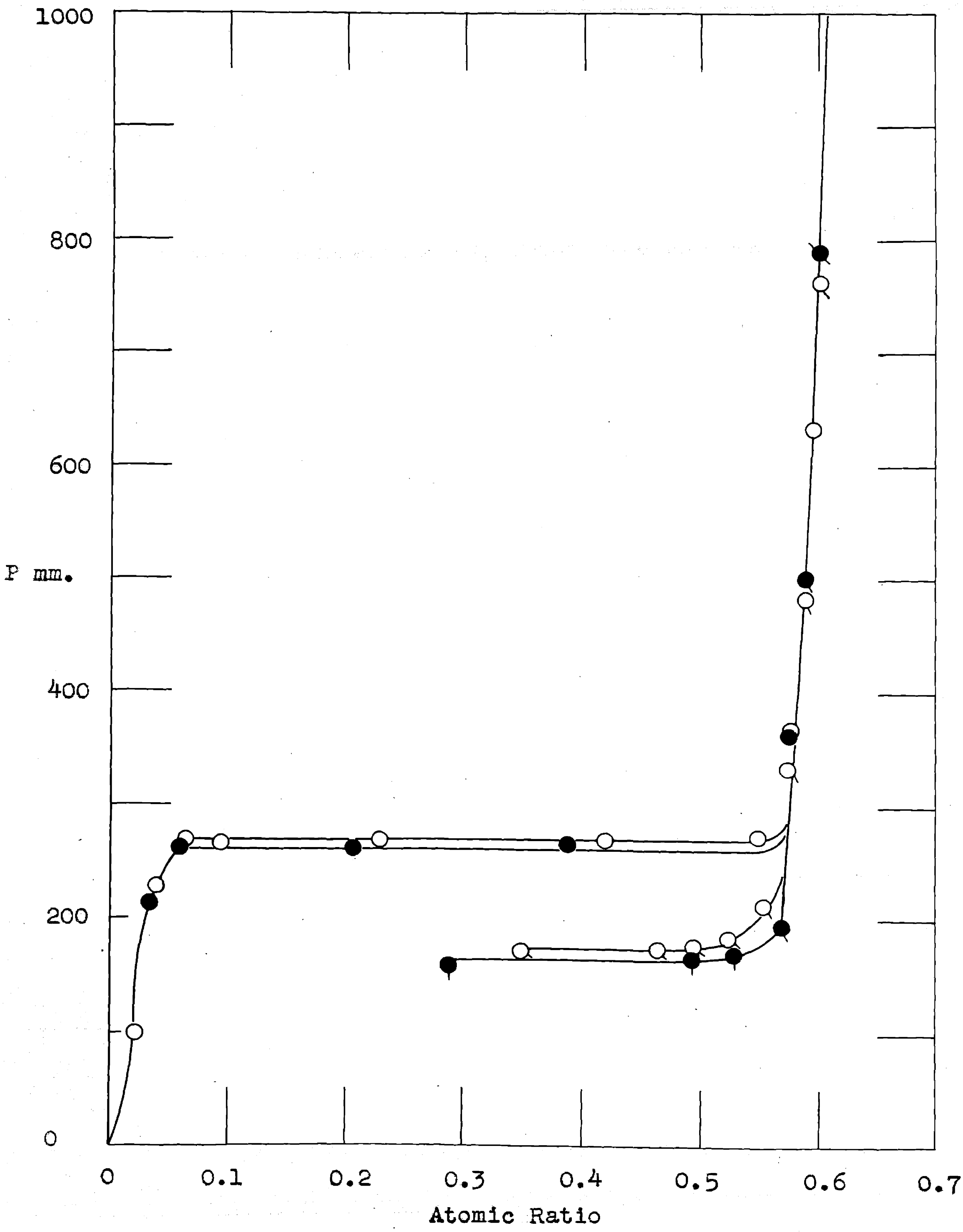
Pretreatment: This run was made for the purpose of determining the effect of impurity on the sorption, in

FIGURE 7

Runs XXIV and XXV, showing that six months' ageing of palladium powder does not decrease its activity.

Open circles represent palladium which has never been heated above 180° and which has not been saturated with hydrogen.

Filled circles represent palladium which has been repeatedly heated above 500° and repeatedly saturated with hydrogen.


1000
800
600
400
200
0
P mm.
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

order to try to explain the discrepancies between the results of various observers.

One of the palladium specimens previously used in this research was dissolved in aqua regia and carried through the same steps of preparation as before, except that after reduction of the ammonium salt the palladium was heated in hydrogen and in CO_2 at temperatures not exceeding 200° for several hours, with no further purification. This left some NH_4Cl still discernible in the metal.

Procedure: Same as that in Run XV.

Results: Upon addition of hydrogen there were no definite breaks in the curve. The curve showed a tendency to flatten out at pressures between 300 and 320 mm., for a short concentration range between 0.1 a and 0.2 a; whereafter the pressure rose sharply to 960 mm. at 0.24 a.

Upon withdrawal, the pressure became constant at 150-160 mm.; which agrees with the corresponding pressure level of pure palladium.

X-RAY CRYSTALLOGRAPHIC STUDY OF PALLADIUM

Introduction: Since sharp and consistent differences had been found to exist between palladium powder which had undergone heat treatment at temperatures above 500° and powder which had not been heated above 200°, it appeared advisable to determine whether any changes had taken place in the crystal structure.

The changes observed are the following: The low temperature form is a black powder, while the high temperature form is a gray powder with lustrous surfaces. The pressure levels at which hydrogen is sorbed are consistently lower along the univariant parts of a given isotherm for the high temperature form; and more hydrogen is sorbed at low pressures (in the α-phase part of the curve) by the low temperature form.

These phenomena could have one of two alternative explanations: either the atomic structure of the crystals is changed (allotropy) or the grain structure changes. Although the latter would appear to be the more probable of the two, the change occurs so far below the melting point(1550°) and is so distinct that allotropy would not be out of the question unless a study were made of the crystal structure.

Several x-ray investigations have been made of the lattice structure of palladium, one of the most accurate and thorough of which is that made by Owen and Jones (7) in 1937. They found that in a given specimen of metal previously heated above 450°, the crystal lattice structure of pure palladium (which is face-centered cubic) has a parameter of 3.8863 Å. at 100°; and this parameter is expanded to 4.025 Å. when the palladium is saturated with hydrogen. It reverts to its original value only after annealing above 450° for two hours, after removal of the gas.

However, they did not examine palladium which had not been preheated.

Procedure: The x-ray measurements were made in collaboration with Mr. B. M. Loring of the Department of Metallurgy, under the supervision of Prof. J. T. Norton.

Two specimens of palladium powder were used. One was Pd 1', which had been used in several runs and had been repeatedly heated above 500°. On the day before the photographs were taken, it had been heated to 500° for two hours and evacuated for one hour at the same temperature. It was a light gray powder.

The other specimen was identical with Pd 4. It had never been heated above 175°, and had not been used for a run. It was a black powder.

The cameras used were two Phragmen cameras covering different ranges of the diffraction spectrum. The radiation employed was chromium radiation, of wave length

2.285 Å. Each of the specimens was photographed by both cameras. The current used for the rays was 0.5 milliamps., and the exposure time thirty minutes.

The lattice parameters were determined by use of the following equation:

$$\sin^2 \theta = \frac{\lambda^2}{4\,a_0^2}\,(h^2 + k^2 + l^2),$$

where θ = angle of diffraction,

λ = wave-length of x-rays,

a_0 = lattice parameter (distance between atomic planes)

h,k,l= indices of atomic planes.

$\sin^2 \theta$ is determined from calibration tables by knowing the distances of the lines on the photographs from a fixed reference point, and the radius of curvature of the cylinder which supported the film in the camera.

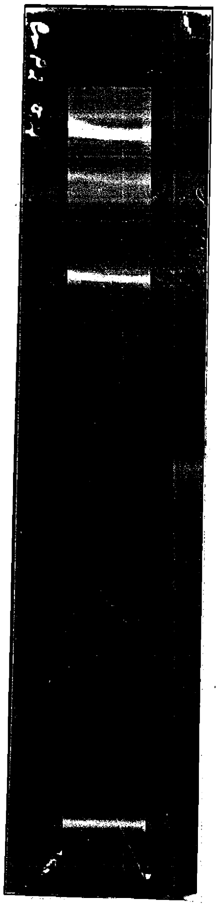
<u>Results</u>: The photographs (see Fig. 8) show that both specimens of palladium have the face-centered cubic structure, and that the lattice parameters are the same, within the accuracy of the cameras. The lattice parameter is 3.9, in agreement with the value of Owen and Jones and others.

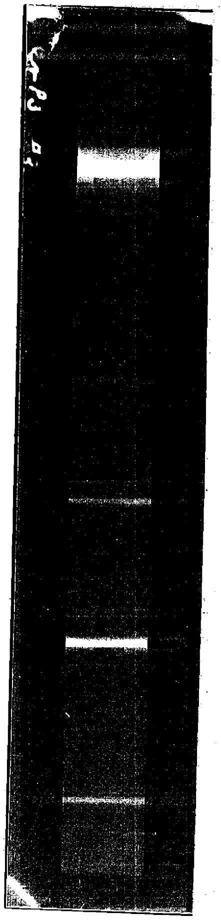
FIGURE 8

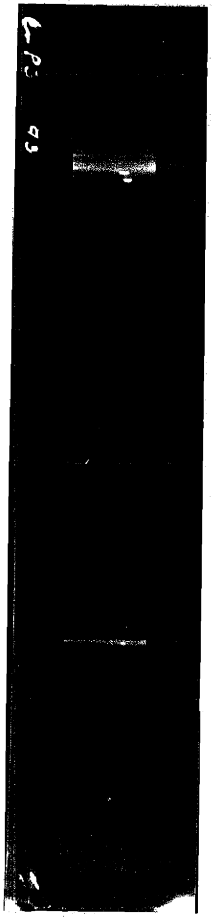
X-ray studies of the high- and low-temperature forms of palladium, proving that both possess the face-centered cubic atomic lattice and have the same lattice parameter.

Photographs 1 and 3 are pictures of Pd 1', a specimen of the high-temperature form which has been saturated with hydrogen.

Photographs 2 and 4 are corresponding pictures of Pd 4, a specimen of the low temperature form which has never been saturated with hydrogen.


L-P2 #2




L-P3 #3

DISCUSSION OF RESULTS

PART A: Comparison With Results of Previous Investigators

0° Isotherms

The first complete 0° isotherms were made by Gillespie and Hall (5) in 1926. They were unable to get good results without the use of the heat treatment described previously, but the curves they obtained with heat treatment coincide almost perfectly with those determined in the present research.

The reason for the necessity of heat treatment in their work lies, apparently, in the fact that their method of removing NH_4Cl from the palladium after reduction was not sufficiently drastic. They believed that the impurity was sufficiently removed by prolonged heating below 300°, without further treatment. However, Gillespie and Galstaun (8) found later that such mild heating leaves appreciable quantities of NH_4Cl in the metal.

Run XXVI, which will be discussed below, shows that the presence of this impurity has distinct effect on the sorption.

76.8° Isotherms:

Several investigators have measured the sorption of hydrogen at 75° and 80°. Fig. (9) compares their results with ours.

FIGURE 9

Comparison of results of four observers at 76.8°.

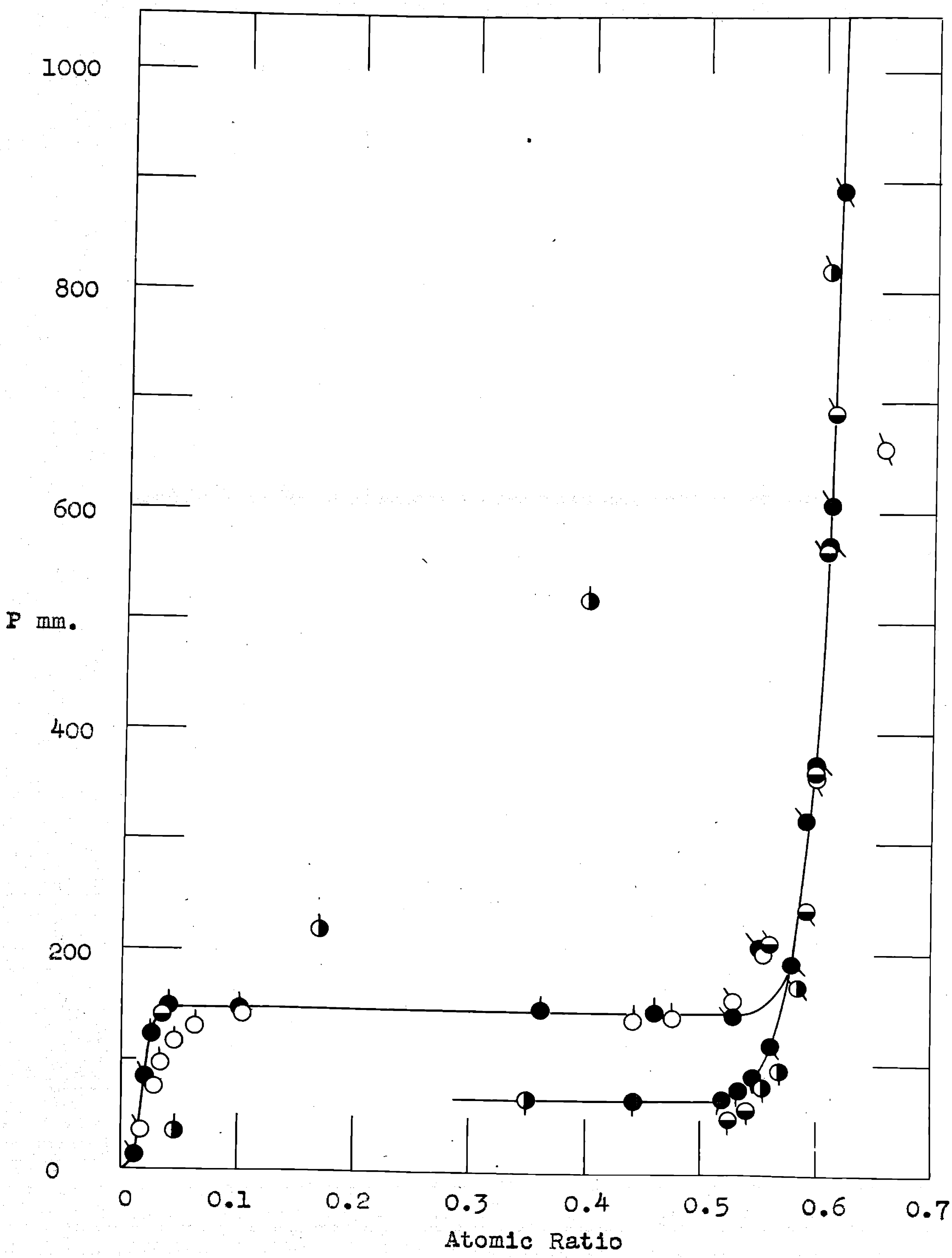
Filled circles represent our results (Run XVII).

Open circles, Gillespie and Hall.

Circles with vertical diameters, Lambert and Gates.

Circles with horizontal diameters, Sieverts and Danz.

Flags directed upward represent addition; downward, withdrawal of hydrogen.


1000
800
600
400
200
0
P mm.
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

Lambert and Gates (4), in 1925, made a series of isotherms with palladium granules whose method of preparation was not given. In all of their isotherms long periods of time, ranging from a lower limit of one day, were required for each addition point to come to a steady state. The addition curves show no sign of a univariant portion. Their withdrawal curve, however, which was obtained at 75°, coincides almost exactly with ours both in the β-phase region and as to the pressure of the horizontal, when the isotherm is translated to 76.8° by use of a log P vs. 1/T plot. Their withdrawal curve breaks sharply and maintains a constant pressure whose value is the same as ours.

Gillespie and Hall obtained results with their heat treatment which agree very well with our addition curve, except that their breaks are not sharp; which caused them to conclude that the first break is at a slightly greater concentration than ours, and the second break at a smaller (0.5 a).

Sieverts and Danz (6) measured a series of isobars at different pressures. Translating their results into a 76.8° isotherm shows that they agree almost perfectly with ours in all respects.

100° Isotherms

Fig.(10) compares our results with those of four other sets of investigators.

Troost and Hautefeuille, with the electrolytic method described in the introduction, obtained two curves at 100° which agree with ours except that the pressure of

FIGURE 10

Comparison of the results of five observers.

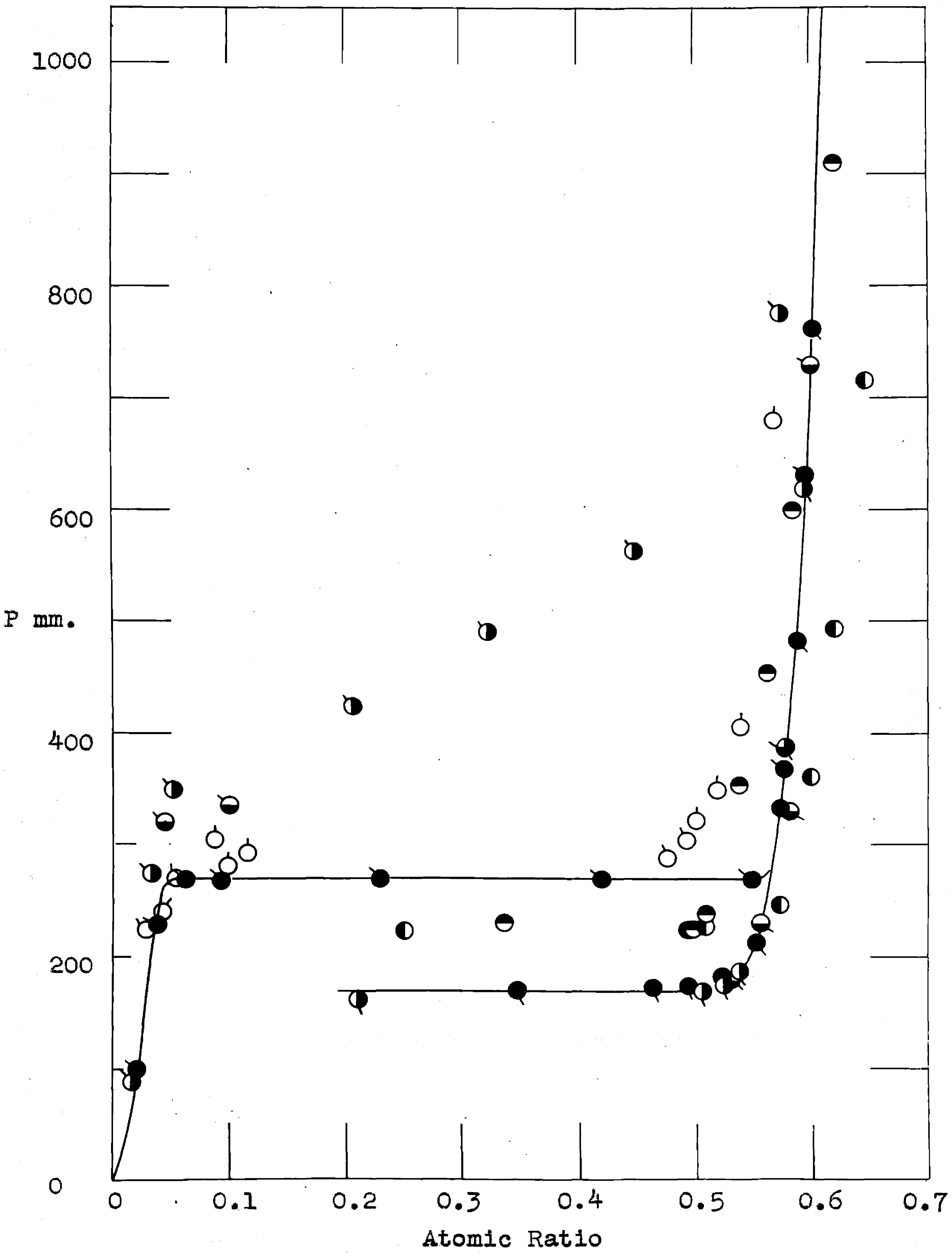
Filled circles represent our results (Run XXV).

Open circles, Hoitsema (constant mass, solid sheet metal).

Circles with right side filled, Lambert and Gates.

Circles with lower half filled, Sieverts and Danz (isobars).

Circles with upper half filled, and with left half filled, two runs made by Troost and Hautefeuille (electrolytic saturation of metal plate).


1000
800
600
P mm.
400
200
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

the horizontal is slightly lower than ours (225 mm.). The β-phase region beyond the second break is at a slightly smaller hydrogen concentration than ours in one of their curves, and slightly greater in the other.

Their palladium was in the form of a plate of massive metal.

Hoitsema in 1895 made a series of constant mass measurements at various masses, with both sheet and spongy palladium. His results with spongy palladium demonstrate failure to reach equilibrium. With plate metal, however, he obtained a good horizontal which agrees with our addition curve, except that the second break is at a slightly lower concentration.

Lambert and Gates (4) made a 103° isotherm which bears the same relation to ours as did their 75° isotherm to ours (allowing for the slight temperature differences), except that they went to sufficiently high pressures in the 103° run so that their last two addition points agree with ours, as well as the withdrawal points.

The measurements of Sieverts and Danz have also been translated into a 100° isotherm whose addition horizontal exceeds ours by from 50 to 100 mm., but whose -phase region and withdrawal curve coincide almost exactly with ours.

PART B: Effects of Heating Palladium

I. Preheating

In these sorption measurements several definite and consistent effects of heating have been observed. The nature of these effects and the temperatures at which they come into existence appear to confirm the observations of other workers in different fields.

We have found that palladium powder which has not been heated above 200° is a black powder; that between 300° and 500° there is a transition interval; and that palladium heated to 500°-550° becomes a light gray powder with lustrous surfaces.

The same three stages appear in the sorption curves. Upon examination of the isotherms obtained at 100° from different specimens of palladium treated the same in all respects except the preheating, it is evident (see for example Runs IV, VI and VIII) that the pressure along the horizontal is about 30 mm. higher for the low temperature form than for the high; and that there is a transition state between these two extremes, in which the pressures vary irregularly between the upper and lower levels.

A third difference is shown in Fig. (12), which demonstrates clearly that palladium which has not been heated above 200° sorbs more gas at very low pressures and concentrations than the high temperature form. Also, the quantity of gas taken up at a given low pressure is much more constant for different specimens of the high temperature form than for the low.

Our x-ray analysis has shown that the effect of heat is not to change the atomic structure of the metal, but rather to modify the grain structure. The change in color from black to gray indicates that the surfaces become more regular, and that if any change in crystalline form appears it is toward a form which has more reflecting surfaces. The same reasoning leads to the conclusion that there is less total surface in the gray form than in the black.

The fact that the high temperature and low temperature forms of the metal take up the gas at two distinct, reproducible levels indicates that the temperature effect is not a random annealing effect, but a distinct transition from one crystalline form to another; both forms having the face-centered cubic atomic lattice, as proved by the x-ray results.

The greater initial sorption by the low temperature form indicates that it has greater surface area.

Additional evidence that the effect is not ordinary annealing is found that it takes place so far below the melting point. Also, the low temperature form is presumably in an unstrained condition, since it was made by simple reduction of the salt; so that ordinary annealing, which is a conversion of a strained to an unstrained condition, does not explain the results.

Tammann and Schneider (8) have conducted an investigation of the effect of heating on the crystalline form in palladium plate. They determined that at room temperature the crystals on the surface of the metal are dodecahedral, and that heating to 300° does not change the structure. Beginning at 400° a new, very small grain appears, which is so small that the crystal form cannot be determined by the reflection method (in which the shape of the crystals is found by the angles at which light is reflected). These crystallites grow to a maximum in size at 550°, and their structure is found to be icositetrahedral. An icositetrahedron, as well as the more common dodecahedron, is characteristic of the face-centered cubic lattice; and has twenty-four faces rather than the twelve faces of the low temperature form.

A further discovery by Tammann and Schneider is that if the metal is heated still higher the number of icositetrahedral crystallites decreases sharply, and at 1200° they have entirely disappeared.

The x-ray work of Owen and Jones, previously discussed, affords further confirmation of the above results. They found that the lattice of palladium which had been distorted by occlusion of hydrogen was restored to the unstrained condition after heating above 450°, which is easily explained by the change in crystalline form.

These temperature effects probably account for at least a part of the discrepancies between the results of different observers whose sorption measurements show apparent equilibrium but do not agree exactly.

II. Heat Treatment During Run

The results of Run XIX, Fig. 6, prove that with pure palladium, heating the palladium-hydrogen system for a short time has the effect of a mere withdrawal of gas from the metal, while cooling results in an addition of gas. The results may be taken as confirmation of the existence of two distinct pressure levels for addition and withdrawal of hydrogen, since successive heating and cooling yields a point on the usual addition curve, while the reverse procedure results in a point on the ordinary isothermal withdrawal curve.

PART C: Effects of Ageing Palladium Powder

Runs XXIV and XXV demonstrate that the activity of palladium powder does not diminish with time, at least within six months. Both its catalytic action on the combination of hydrogen with oxygen, and its sorption of hydrogen, remain unimpaired. Cf. Fig.(7).

The work of Holt, Edgar and Firth (9) apparently proves that cold-rolled palladium plate diminishes in activity with time. Our results indicate that the phenomenon is a result of the strain, rather than being a normal property of the metal.

PART D: Correlation of Pressures Along Horizontals With Previous Data From This Laboratory

Gillespie and Galstaun have correlated the pressures of the horizontals of their isotherms between 200° and 300° with those of Gillespie and Hall at lower temperatures, and have obtained the equation

$$\log_{10}p = 4.6018 - 1877.82/T$$

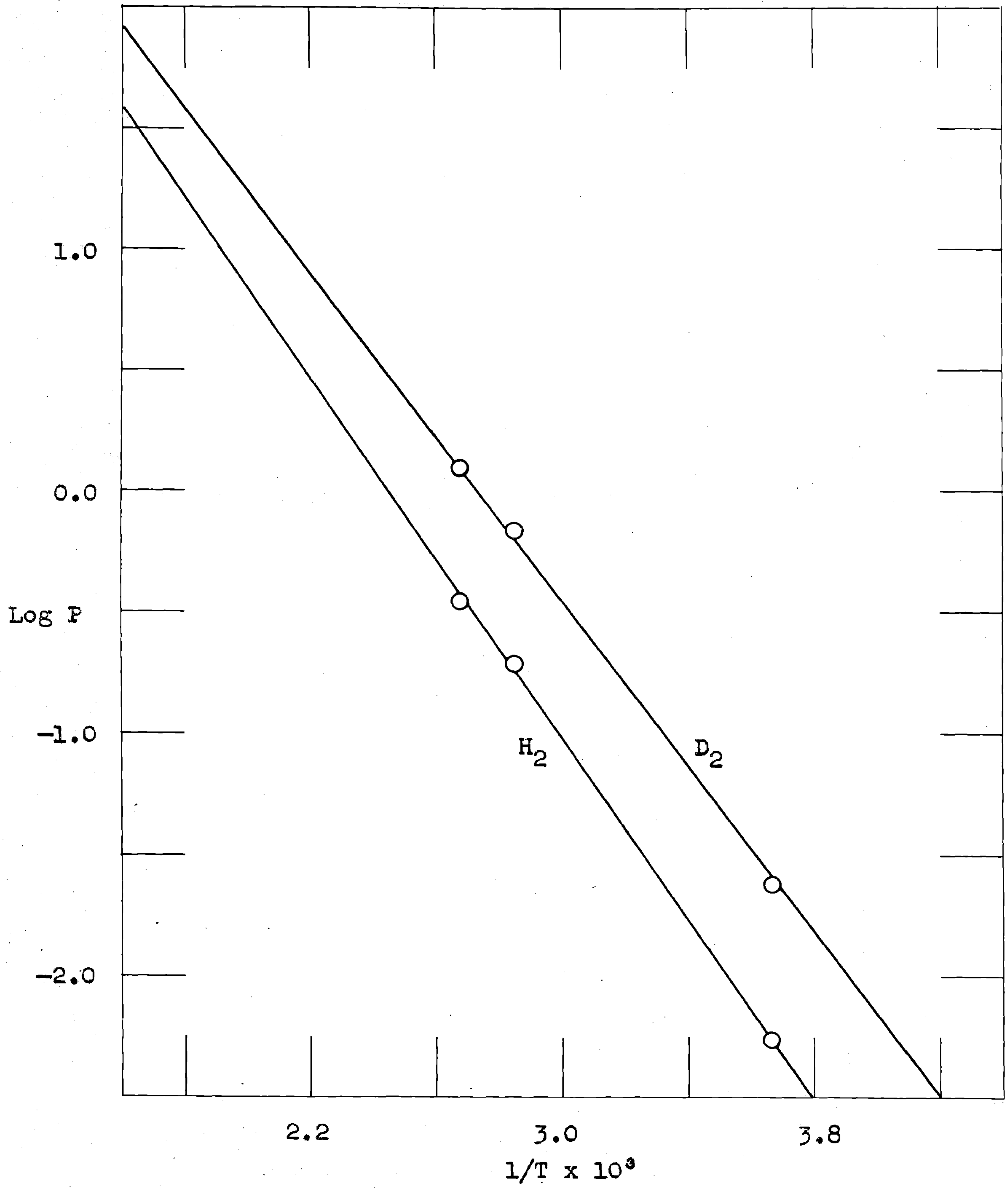
to fit the data.

The pressures calculated from this equation at 0°, 76.8° and 100° respectively are 4 mm.,131 mm., and 282 mm. Our values, taken from Runs I, XV, and VIII, are respectively 4 mm., 133±5 mm., and 285 ± 5 mm. These figures are taken from the addition isotherms of the low temperature form of palladium.

It will be remembered, however, that the pressure level at a given temperature varies somewhat with the pretreatment. Fig. (11) shows that even our pressures which deviate most from the equation agree quite well.

FIGURE 11

Circles represent pressures of our addition horizontals at 0°, 76.8° and 100°. The straight lines are those given by the equations determined by Gillespie and Galstaun for hydrogen at higher temperatures, and by Gillespie and Downs for deuterium.


1.0
0.0
Log P
-1.0
-2.0
H_2
D_2
2.2
3.0
3.8
1/T x 10^3

PART E: Absorption Versus Adsorption

It is evident from the following consideration that adsorption accounts for very little, if any, of the hydrogen taken up by palladium:

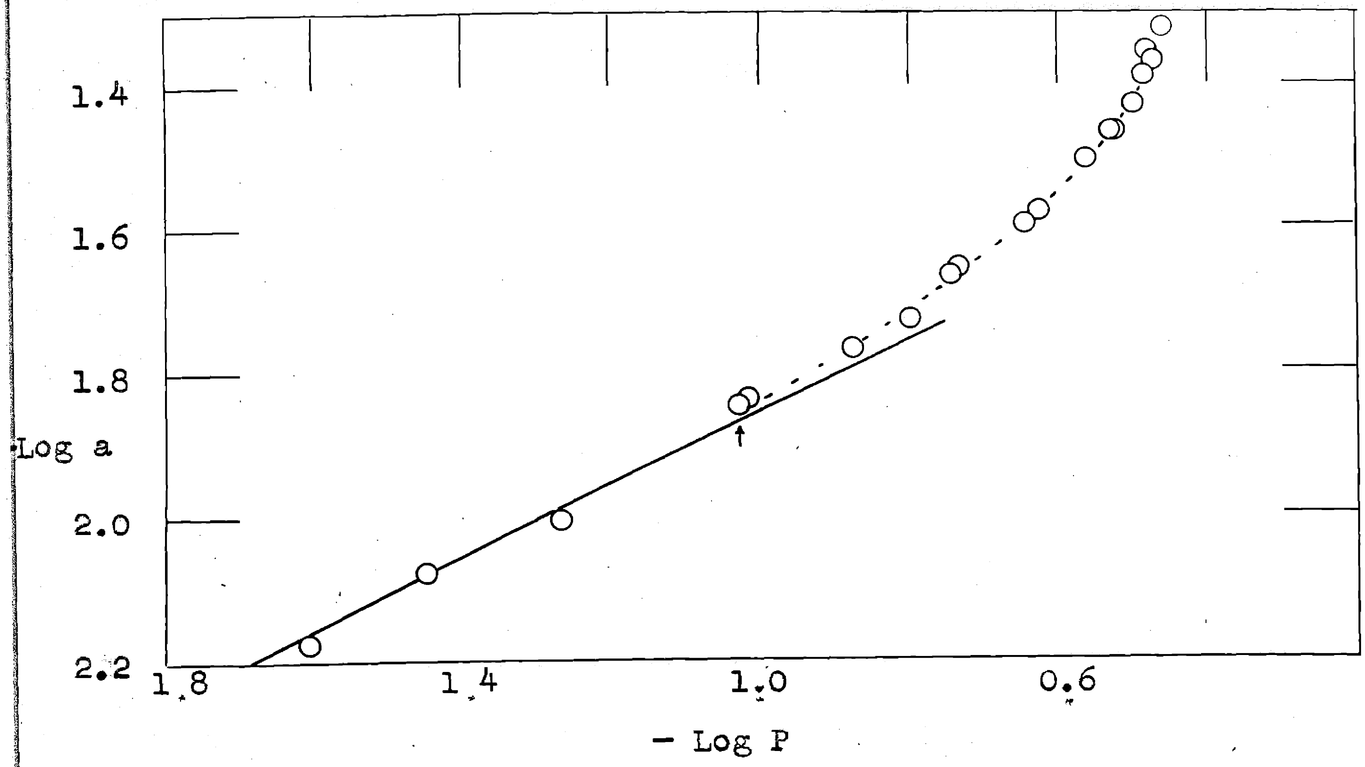
Adsorption is by definition a purely surface phenomenon, and as such its extent depends upon the surface area of the adsorbing medium. We have seen that the quantity of hydrogen sorbed by palladium is the same within a maximum difference of five or ten per cent, whether the metal is in the form of a plate or consists of a powder, whose surface area is thousands of times greater. As a matter of fact, there is probably no difference at all in the extent of sorption between the powder and the plate metal at true equilibrium; the smaller sorption reported by Hoitsema being very likely due to impurity or to the difficulty of attaining equilibrium in the plate metal. One of the two isotherms obtained by Troost and Hautefeuille with plate metal (see PART A) shows even more apparent sorption than we have found in powder.

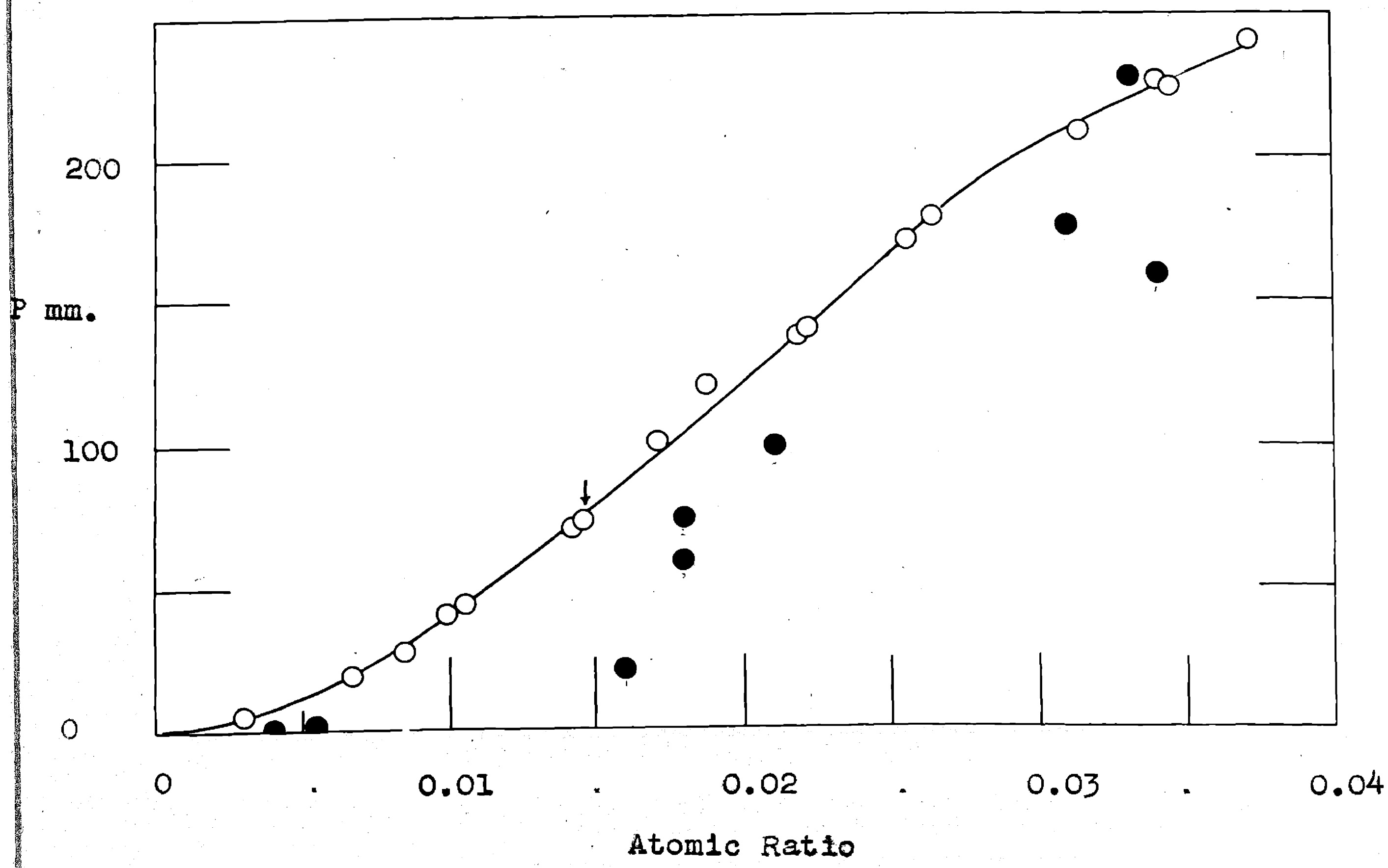
Additional evidence that we are dealing with absorption rather than adsorption lies in the fact that deuterium (see PART III) is found to be taken up in slightly smaller quantities than hydrogen. It is well known that in true adsorption the heavier isotope is taken up in grea-

FIGURE 12

In the lower graph, filled circles represent four runs made with palladium which had never been heated above 180°. Open circles represent the same number of runs made with palladium specimens which had been heated above 450°. The points are all taken from 100° isotherms.

In the upper graph a logarithmic plot is shown in which the points are the same as the open circles in the lower graph. The arrows point to a pair of corresponding circles. The straight line to which the curve becomes tangent has a slope of 1/2; evidence that in dilute solution the hydrogen is absorbed in atomic form, and according to Henry's Law.


1.4
1.6
1.8
Log a
2.0
2.2
1.8
1.4
1.0
0.6
- Log P


200
P mm.
100
0
0
0.01
0.02
0.03
0.04
Atomic Ratio

ter amount, rather than in smaller.

We have seen (Fig. (12)) that the low temperature form of palladium powder, which presumably has the greater surface area, initially sorbs more hydrogen than the high temperature form. At first sight, this seems to prove that some adsorption takes place. However, if we examine the sorption curves as a whole, we find that the β-phase region of the low temperature form coincides with that of the high temperature form; or, in other words, that the total quantity sorbed is the same for both forms. This could not be the case if the low temperature metal initially adsorbed more gas than the high temperature form and absorbed the same quantity.

It appears more logical to suppose that the greater surface of the low temperature form makes the initial absorption easier because less energy is required for absorption of gas near the surface than deep in the metal.

PART F: Mechanism of Absorption

We may consider the first part of the absorption curve as representing a simple solution of hydrogen in palladium, without the complication which arises when a new phase is formed.

The theoretical form of this curve may be determined quite simply by applying the Mass Action Law and Henry's Law.

If we assume that the gas is absorbed in the molecular state we have, by Henry's Law,

(1) $C_{H_2} = k\ p_{H_2}$.

If we assume that the gas is absorbed in the form of atoms,

(2) $p_{H_2}^{1/2} = k_1\ p_H$, and $C_H = k_2\ p_H = k_3\ p_{H_2}^{1/2}$.

By the same line of reasoning, if the gas were absorbed in the form of H_3 molecules the equation would be

(3) $C_{H_3} = k\ p_{H_2}^{3/2}$.

Each of these equations conforms to the expression

(4) $C = k\ p_{H_2}^{x}$.

Taking the logarithms of both sides,

(5) $\log C = \log k + x \log p_{H_2}$.

If we plot our experimental data as log C vs. log p_{H_2}, at low concentrations, "x" is the slope of the line; so that we can determine in which form the hydrogen enters the palladium.

Such a curve is plotted in Fig. (12), using as data the results of four 100° isotherms obtained from specimens which had been heated above 450°.

The points are shown to fall very well on a line whose slope is 1/2, which means that the concentration of hydrogen is proportional to the square root of the pressure; and that hydrogen is absorbed in the atomic state by palladium.

This conclusion agrees with the findings of Harris, Jost and Pearse (11), who determined that in the same region of the curve the rate of diffusion of hydrogen through palladium is proportional to the square root of the pressure.

PART G: "Hysteresis"

All investigators who have made true addition and withdrawal isotherms, or measurements which can be translated into such isotherms, have found that the horizontal part of the withdrawal curve is at a pressure well below that of the addition curve. Most of these investigators have had trouble in attaining a steady state, so the natural assumption has been that the discrepancy is due entirely to hysteresis resulting from a failure to reach equilibrium; or, in other words, that there is a single equilibrium curve lying between the upper and lower levels.

There is strong evidence, however, that this is not the case. In the present work, the steady state was reached rapidly and without difficulty. Both the addition and the withdrawal curves have been shown to be exactly reproducible with specimens which have undergone the same kind of preliminary treatment, and identical in character for all specimens. Either curve can be traced and retraced for its entire length in both directions, by two different methods; mechanical manipulation of the pressure so that the final operation is addition or withdrawal as desired, or corresponding heat treatment to achieve the same effect.

Furthermore, the pressure levels of the horizontal parts of the addition and the withdrawal isotherms have proved to be perfectly constant over long concentration ranges, although they are very different from one another.

Comparison of the results of other investigators with ours confirms our observations. All reliable data agree in these respects with ours, in spite of the fact that the methods of preparation of the palladium differ.

It is of interest to note the fact that the addition curves of Lambert and Gates show obvious failure to obtain equilibrium, but their withdrawal curves agree with ours and with those of Sieverts and Danz. This appears to indicate that impurity in their palladium retarded the absorption, but not the withdrawal of hydrogen.

These facts lead to the conclusion that there are two true steady state levels, one for addition and the other for withdrawal of gas.

This conclusion does not appear to agree with ordinary phase rule concepts, which do not allow two equilibrium pressures to exist in a system whose state is otherwise the same. It becomes necessary, from the thermodynamic point of view, to infer from the experimental results that the two curves mark the upper and lower boundaries of a region in which "passive resistance" to absorption or withdrawal of hydrogen, or both, exists. Since the thermodynamic laws of equilibrium do not apply to such a case, any explanation of the phenomenon will doubtless come from physical reasoning.

H
1

PART H: Compound Formation

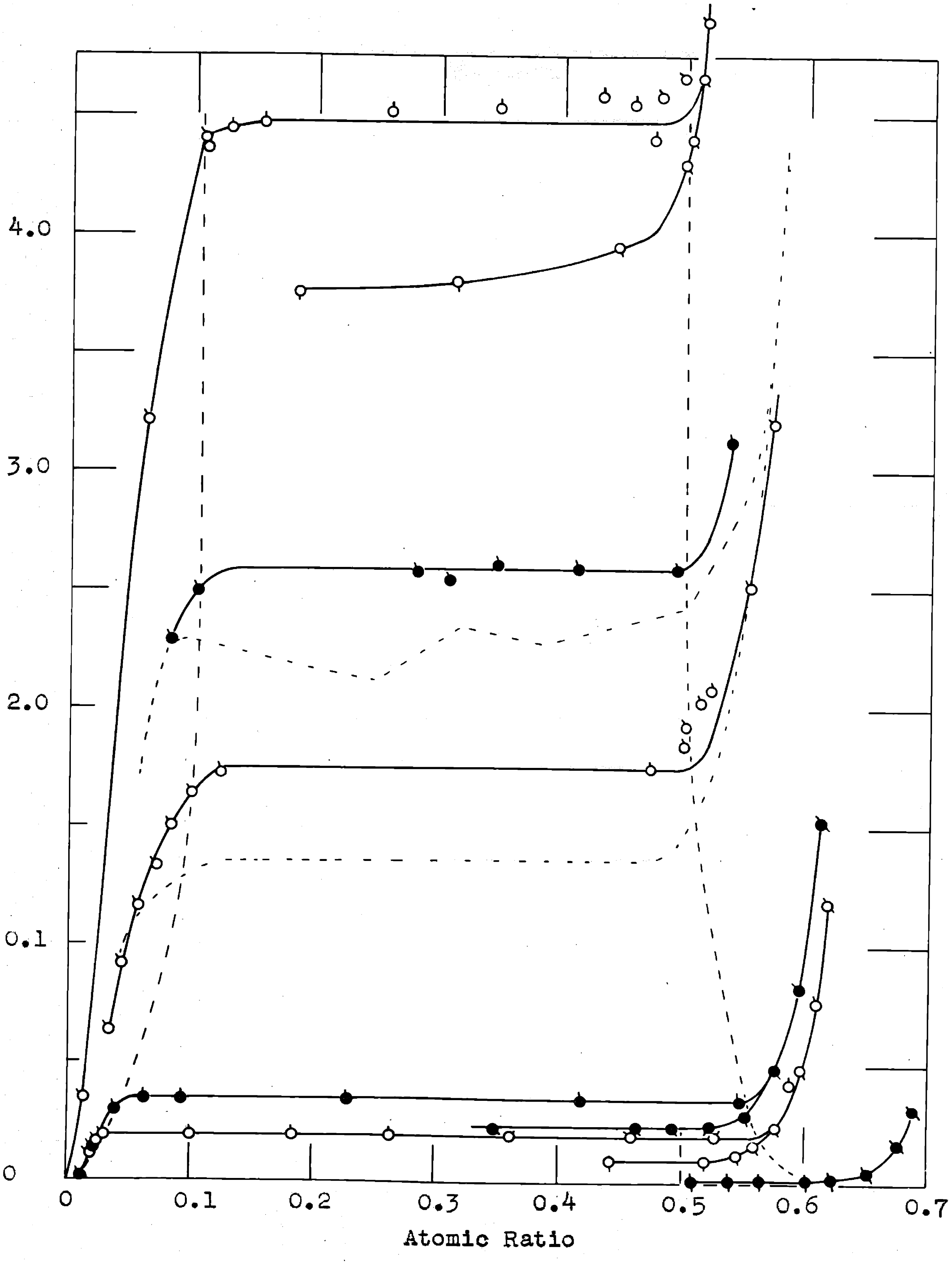
Our results (see Fig. 13) show that no compound exists in the temperature interval between 0° and 100°. The second break in the pressure-concentration curve, which denotes formation of the β-phase, is definitely beyond 0.5 a (Pd_2H) at all temperatures in this interval, and is at a different concentration for each temperature.

The previous opinion in this laboratory, based mainly on the work of Hall, has been that the compound Pd_2H is formed at all temperatures between 80° and 200°; but the new evidence obtained in the present research appears to prove that the slope of the tangent to the phase envelope is infinite for a temperature range of not more than 40° (160° to 200°), and is probably not exactly vertical at any point on the envelope.

The steepness of the tangents in the neighborhood of 0.1 a and 0.5 a remains unquestioned, however, and indicates that the corresponding atomic configurations are significant in the absorption phenomenon, although perhaps definite compound formation cannot be claimed.

FIGURE 13

Partial phase diagram of the hydrogen-palladium system; isotherms at 0°, 76.8° and 100° (our results); 160° and 180° (Gillespie and Hall); and 200° (Gillespie and Galstaun). The dotted curves above and below the curve at 160° are the addition and withdrawal isotherm of Bruning and Sieverts, at 160°.


4.0
3.0
2.0
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

SECTION III

THE DEUTERIUM-PALLADIUM SYSTEM

INTRODUCTION

This part of the investigation was undertaken for the purpose of completing the phase diagram of the deuterium-palladium system by extending the measurements of Gillespie and Downs (1) to lower temperatures. They obtained a series of isotherms in the region 200°-300° and extending to fifty atmospheres' pressure. This region includes the critical solution point.

The present work covers the region between 0° and 100°, and consists of isotherms at three temperatures: 0°, 76.8°, and 100°.

APPARATUS

The apparatus, except the part employed in generation and purification of deuterium, was the same as that used in the hydrogen experiments.

PREPARATION AND PURIFICATION OF DEUTERIUM

Deuterium was made by electrolyzing heavy water in the vacuum-tight apparatus used and described by Downs. The deuterium oxide had been obtained from the California Isotope Co., and possessed a guaranteed purity of 99.9%.

The gas was freed of water by means of a liquid nitrogen trap, and of oxygen by diffusion through a palladium thimble maintained at 300° by a heating coil.

PROCEDURE

The technique employed in all three of the deuterium runs was the same as that used in the last few of the hydrogen runs: i.e., gradual increase of pressure to a few mm. above equilibrium pressure on addition, with somewhat higher pressures near the second break; and gradual decrease of pressure to a few mm. below equilibrium pressure on withdrawal.

RESULTS

Run XXI, Pd 6, 100°:

Pretreatment: Pd 6 was heated to 500° for 18 hours in hydrogen, evacuated at the same temperature, and rinsed repeatedly with deuterium both at room temperature and at 200°.

Results: The first break in the addition isotherm appears at 0.035 a and 950 ± 5 mm. The pressure remains constant up to a concentration of 0.45 a, and the rise is not steep until the concentration is 0.5 a.

Although the highest pressure recorded is 1200 mm., the pressure was increased to 1800 mm. to insure complete formation of the β-phase before withdrawal of deuterium. That this object was attained is proved by the fact that the last point of the addition curve falls on the curve representing withdrawal of gas.

The break in the withdrawal isotherm occurs at 0.5 a and 600 mm.

Run XXII, Pd 6, 76.8°:

Pretreatment: The palladium was heated at 500° for twelve hours in D_2, immediately after the preceding run and before the present one.

Results: Upon addition, the first break appears at about 0.035 a and 525 ± 5 mm. The pressure remains below 530 mm. up to a concentration of 0.5 a, and begins rising steeply at approximately 0.53 a.

The highest pressure recorded was 1130 mm. at 0.58 a, but the pressure was increased to above two atmospheres.

The withdrawal curve breaks at about 0.52 a and 275 ± 5 mm.

Run XXIII, Pd 6, 0°.

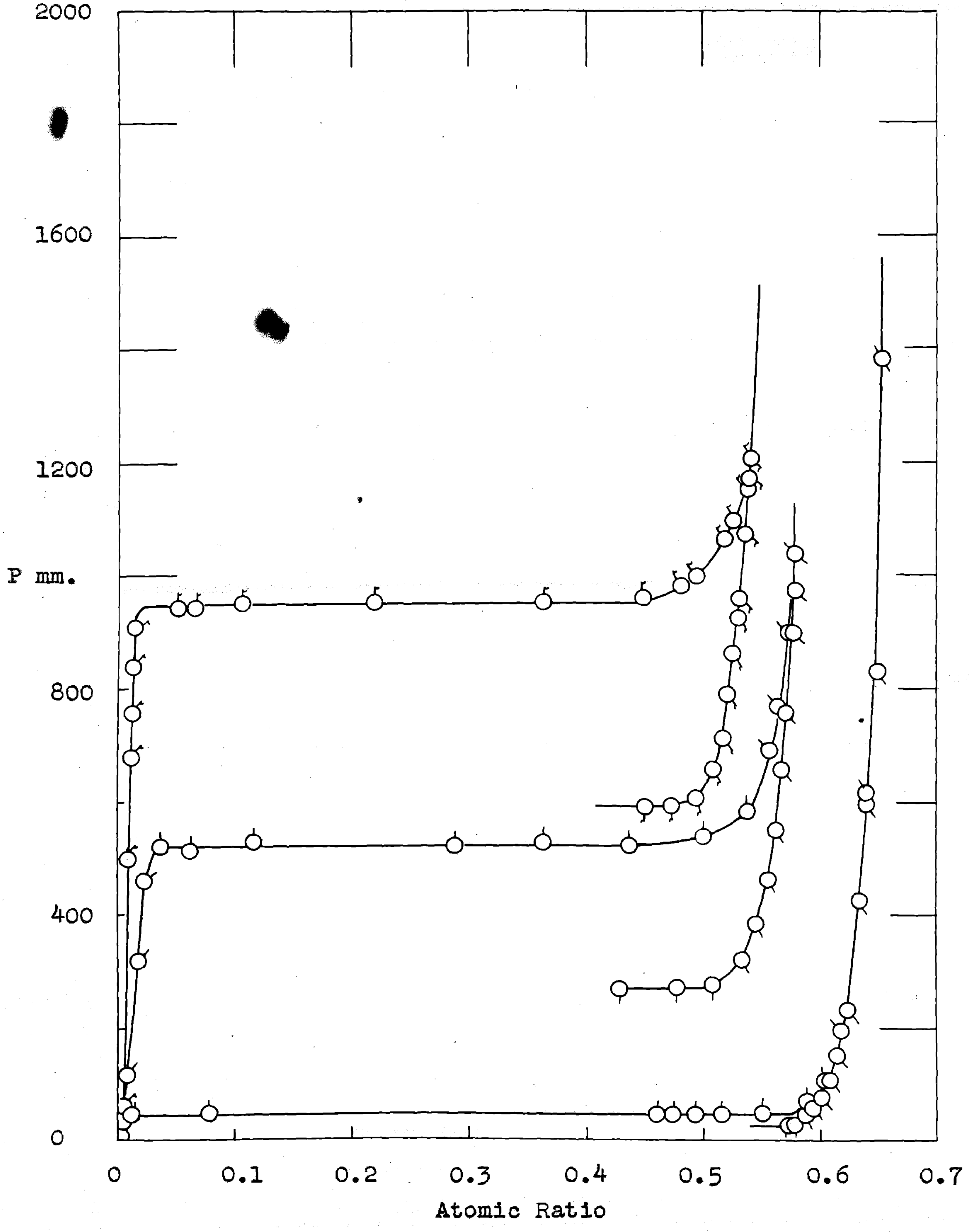
Pretreatment: The part of the curve in the region of the β-phase was obtained at the conclusion of Run XXII, leaving the same deuterium in the system and cooling it to 0° to obtain the first point in the addition curve.

After the β-phase region had been investigated, the system was evacuated at 200° and the α-phase end of the curve determined.

Results: The first break is at about 0.012 a, and the pressure of the horizontal is 17 ± 1 mm., for the addition isotherm. The second break occurs at 0.58-0.59 a both on addition and on withdrawal. The horizontal of the withdrawal curve is at approximately 10 mm.

FIGURE 14

Deuterium isotherms at 0°, 76.8° and 100°. The scale of the 0° pressures is half as great as that given by the figures.


2000
1600
1200
P mm.
800
400
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

DISCUSSION OF RESULTS

PART A: Comparison

Comparison of the deuterium isotherms with the corresponding hydrogen isotherms shows a striking parallelism in the quantities absorbed. At each temperature the deuterium absorbed is very slightly less than the hydrogen, although the absorption pressure of deuterium is almost five times as great as that of hydrogen at low temperatures.

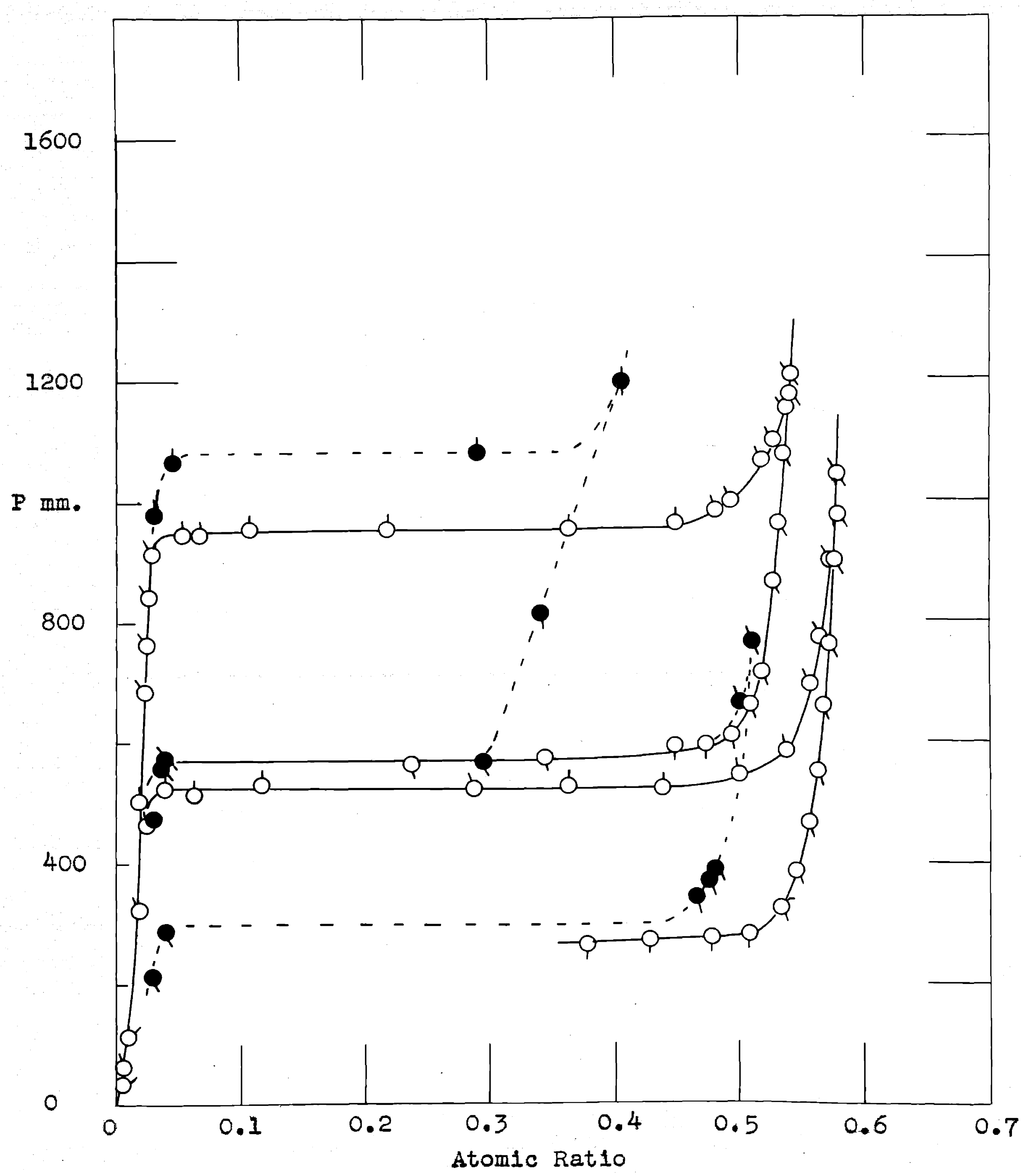
Sieverts and Danz have made the only measurements with which we can directly compare our results. Fig. (15) shows the comparison of the curves at 76.8° and 100°.

Their curves show considerably less absorption than we obtained, especially at 100°. The pressures of their horizontals are somewhat higher than ours, except that the withdrawal curve of their 100° isotherm coincides with ours. Their results confirm the presence of two levels,, one for addition and the other for withdrawal, of the same order of magnitude as ours, at each temperature.

Sieverts and Danz calculated that their palladium contained about 1.5 % of impurity. Their smaller absorptions may mean that deuterium absorption is more sensitive to impurity than is hydrogen absorption.

FIGURE 15

Comparison of our deuterium isotherms at 76.8° and 100° with those of Sieverts and Danz. Open circles represent our results.



1600
1200
P mm.
800
400
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

PART B: Correlation of Pressures Along Horizontals With Downs' Data

Fig. (11) shows the fit of our addition pressures in the univariant parts of the curves with the linear equation determined by Gillespie and Downs. The equation is: $\log_{10}P_{atm.} = 4.6330 - 1696.11/T.$

The pressures calculated from the equation at 0°, 76.8° and 100° are respectively 20 mm., 464 mm. and 930 mm. Those obtained from our data are 17 ± 1 mm., 525 ± 5 mm., and 950 ± 5 mm.

The graph shows that the equation fits our data as well as any linear equation can.

PART C: Compound Formation

Fig. (16) is a partial phase diagram. All the pressures of each deuterium isotherm are multiplied by a factor (the ratio of the pressures of the hydrogen and the deuterium horizontals) which brings the pressure of the deuterium horizontal down to that of the hydrogen, in order to simplify the comparison. Cf. Fig. (13).

The envelope is almost vertical between 100° and 200° at about 0.5 a, showing that deuterium has at least as great a tendency toward compound formation as hydrogen.

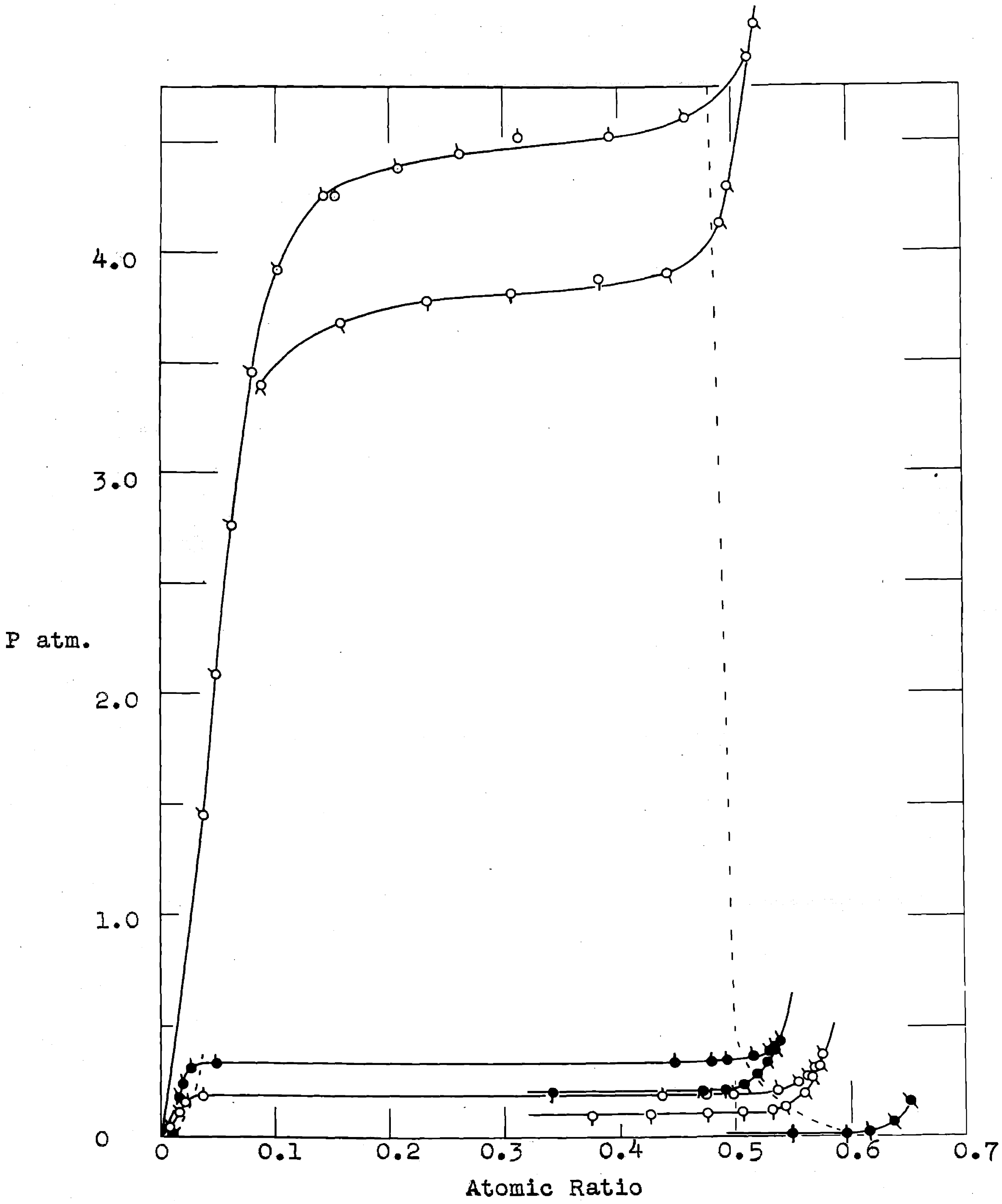
FIGURE 16

Partial phase diagram of the deuterium-palladium system. Isotherms at 0°, 76.8° and 100° (our results); and at 200° (Gillespie and Downs).

In order to simplify comparison with the phase diagram of the hydrogen-palladium system (see Fig. 13) all the pressures in each deuterium isotherm are multiplied by the ratio of the pressure of the corresponding hydrogen horizontal to the pressure of the deuterium horizontal; which makes the curves practically coincident.

The ratios, pH_2/pD_2, were obtained by making use of the equation given by Gillespie and Downs:

$$\mathrm{Log}_{10} pD/pH = 0.0312 + 181.71/T.$$



4.0
3.0
P atm.
2.0
1.0
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic Ratio

PART D: Isotope Separation

It is evident that the magnitude of the difference in absorption pressures between hydrogen and deuterium at a given temperature should afford an effective means of separation of a mixture of the isotopes.

One possible complication must be considered which might cause difficulty in an attempt to obtain complete separation; the complication being that palladium catalyzes the reaction between hydrogen and deuterium to form HD. It is quite possible, however, that since absorption takes place only after dissociation any intermediate formation of HD molecules would have no great effect on the absorption pressures. If we may assume this to be true, it is quite simple to formulate a method for virtually complete separation starting with a mixture containing any amount of deuterium above one mol per cent.

Sieverts and Danz (6) made some absorption measurements with hydrogen-deuterium mixtures in which the horizontals are slightly below those of pure deuterium; but even with a fifty per cent mixture (richest in hydrogen of the mixtures they used) the separation factor was still almost as great as the factor we obtain from the phase diagrams of the pure gases. Part or all of the difference observed may be due to impurity or to different condition of the palladium.

At 100°, the pressure of the deuterium horizontal is 3.65 times as great as that of the hydrogen horizontal. At 0°, the ratio is 4.25.

A possible method of separation is as follows: Let a small bulb containing palladium be connected through stopcocks to a large bulb confining the gas mixture on one side, and to a pumping system on the other. Adjust the quantity of gas so that the amount of hydrogen absorbed by the palladium does not exceed the concentration of the second break in the isotherm at the temperature of the separation, and so that the partial pressure of deuterium is below that of the deuterium horizontal so that only slight absorption of deuterium can take place.

Open the stopcock connecting the gas with the palladium and allow equilibrium to take place. Then close the stopcock, and pump the hydrogen from the palladium chamber. Repetition of the process two or three times should result in very nearly pure deuterium. A small quantity of deuterium will always remain in the hydrogen; however, proper choice of temperatures and pressures can make this quantity negligible.

PART E: Discussion of Downs' Abnormal Absorption Curves Obtained With Deuterium

Downs obtained results which led him to conclude that deuterium is not absorbed in the normal manner unless the palladium lattice has been previously expanded by absorption of hydrogen.

In this research we made no experiments with the absorption of deuterium by new palladium such as that with which he obtained his abnormal results; but our measurements were made with metal which had been thoroughly annealed at 500°-550° after the removal of hydrogen.

The x-ray work of Owen and Jones proves that annealing above 450° completely restores the lattice to its undistorted condition after saturation with hydrogen; so it appears that Downs' results cannot be attributed to this cause.

It is possible that deuterium is even more sensitive to traces of impurity than is hydrogen. Evidence supporting this hypothesis is found in the results of Sieverts and Danz, which show that with the same palladium they obtained much poorer absorption curves using deuterium than using hydrogen (see Figs. 10 and 15). Perhaps Downs' abnormal results with new palladium are attributable to traces of impurity which were later removed by heating in vacuum , so that following runs gave normal results.

SUMMARY

PART I: The Hydrogen-Lead System

1. The absorption of hydrogen by lead was investigated at temperatures between 0°C. and 100°C.

PART II: The Hydrogen-Palladium System

1. A number of isothermal measurements was made of the absorption of hydrogen by palladium at 0°, 76.8°, and 100°C.
2. Investigation was made of the effects on absorption produced by
   (a) Impurity in the palladium.
   (b) Preheating the palladium at different temperatures.
   (c) Different techniques of adding hydrogen to and withdrawing it from palladium.
   (d) Different heat treatments during a run.
   (e) Ageing the palladium powder.
3. Our results were correlated with those of other investigators, to explain discrepancies between their observations.
4. An x-ray investigation was made of the atomic structure of unheated and of heated palladium.

PART III: The Deuterium-Palladium System

1. An absorption isotherm was obtained at each of the temperatures 0°, 76.8° and 100° C.

CONCLUSIONS

PART I: The Hydrogen-Lead System

1. Lead does not absorb an appreciable quantity of hydrogen.

2. Pure lead powder is apparently not obtainable by reduction of lead oxides with hydrogen.

PART II: The Hydrogen-Palladium System

1. Purity of the palladium is of extreme importance in obtaining equilibrium, as regards both the rate of attaining the steady state and the determination of correct values of the equilibrium conditions. Impurity is the probable cause of the majority of the discrepancies between the results reported by various investigators.

2. The technique of adding hydrogen to and withdrawing it from palladium determines whether the pressure-concentration curve obtained is an "addition" or a "withdrawal" curve. If the final operation in obtaining a given point is an addition of hydrogen, the point falls on the higher of two possible steady state curves, even though the resultant of the operations has been a withdrawal of gas; and conversely, if the final operation is withdrawal of hydrogen the point falls on the lower curve. Each curve is reproducible; and is retraceable for its entire length, by

manipulation of either temperature or pressure.

3. The temperature to which the palladium has been preheated

(1) varies the absorption pressure as much as ten %;

(2) varies the quantity of hydrogen absorbed at low pressures and concentrations;

(3) changes the appearance and color of the palladium.

Correlation of our results with others appears to prove that the phenomenon is a result of a change in the crystal form of the palladium from dodecahedral to icositetrahedral; both forms being characteristic of the face-centered cubic atomic lattice.

4. Palladium powder does not decrease in activity with time; at least not within six months.

5. The pressures of our addition horizontals agree very well with the extrapolated log P vs. 1/T curve determined by Galstaun; insofar verifying thermodynamic reasoning.

6. Absorption, rather than adsorption, is the cause of the taking up of hydrogen by palladium.

7. Hydrogen is taken up by palladium either as atoms or as protons.

8. A hypothesis is suggested explaining the experimental results on the basis of an irreversible, rather than a reversible, process.

9. The phase envelope of the hydrogen-palladium system is vertical for only an extremely short range, if at all; although it is nearly so from 100° to 200° in the vicinity of the concentration corresponding to the compound Pd_2H.

PART III: The Deuterium-Palladium System

1. The quantity of deuterium absorbed by palladium at a given temperature is very slightly less than the hydrogen. The form of the absorption curve is the same, but the absorption pressure of deuterium exceeds that of hydrogen by a factor ranging from 3.65 at 100° to 4.25 at 0°.

2. The pressures of our addition horizontals agree with the extrapolated log P vs. 1/T curves of Downs.

3. The phase envelope is steeper than that of hydrogen, but not quite vertical, between 100° and 200° and in the immediate vicinity of the concentration Pd_2D.

4. Separation of pure deuterium from a hydrogen-deuterium mixture may be accomplished comparatively rapidly and efficiently by use of the different absorption pressures.

BIBLIOGRAPHY—PART I

(1). Tarplin, E., "Lead-Hydrogen System"; Master's Thesis, Part II, 1925, M.I.T.

(2). Sieverts, A.,"Solutions of Gases in Metals"; Z. Elektrochem. 16, 707 (1910).

(3). Nikitin, N.I. and Sharkov, V.I., "Absorption of Gases by Finely Divided Metals"; J. Russ. Phys.-Chem. Soc. 58, 1095 (1928).

(4). McBain, J.W., "The Sorption of Gases and Vapors by Solids"; 262. J. Routledge and Sons, Ltd., 1928.

BIBLIOGRAPHY-PARTS II AND III

(1). Gillespie, L.J. and Downs, W.R., "The Palladium-Deuterium Equilibrium"; J.A.C.S. 61, 2496 (1939).

(2). Troost, L. and Hautefeuille, P., "Sur les Alliages de l'Hydrogene Avec les Metaux"; Ann. Chim. Phys. (5) 2, 273 (1874).

(3). Hoitsema, C., "Palladium und Wasserstoff"; Z. Phys. Chem. 17, 1-42 (1895).

(4). Lambert, B. and Gates, S.F., "Investigation of the Relationships Existing Between Hydrogen and Palladium"; Proc. Roy. Soc. A-108, 456 (1925).

(5). Gillespie, L.J. and Hall, F.P., "Palladium-Hydrogen System and Palladium Hydride"; J.A.C.S. 48, 1207 (1926).

(6). Sieverts, A. and Danz, W., "Loslichkeit von Deuterium und von Wasserstoff in festem Palladium, III"; Z. Phys. Chem. B-38, 46 (1937).

(7). Owen, E.A. and Jones, J.I., "The Effect of Pressure and Temperature on the Occlusion of Hydrogen by Palladium"; Proc. Phys. Soc. 49, 587 (1937).

(8). Tammann, G. and Schneider, J., "Zur Kenntnis der Abhangigkeit der Absorptiongeschwindigkeit des Wasserstoffes durch Palladium, Eisen und Nickel von der Kristallitenorientierung"; Z. anorg. u. allgem. Chem. 172, 43-64, (1928).

(9). Holt, A., Edgar, E.C. and Firth, J.B., "Sorption of Hydrogen by Palladium Foil"; Z. Physik. Chem. 82, 513-40 (1913).

(10). Gillespie, L.J. and Galstaun, L.S., "The Palladium-Hydrogen Equilibrium and New Palladium Hydrides"; J.A.C.S. 58, 2565 (1936).

(11). Harris, L., Jost, W., and Pearse, R.W.B., "Separation of Hydrogen Isotopes by Diffusion Through Palladium"; Proc. Nat. Acad. Sci. (19) 12, 991-94 (1933).

(12). Bruning, H. and Sieverts, A., "Der elektrische Widerstand wasserstoff-beladener Palladiumdrahte zwischen 160° and 310°"; Z. Phys. Chem. 163-A, 409 (1933).

(13). Lacher, J.R., "A Theoretical Formula for the Solubility of Hydrogen in Palladium"; Proc. Roy. Soc. A-161, 525 (1937).

(14). Gillespie, L.J. and Ambrose, O., "The Heat of Absorption of Hydrogen by Palladium Black at 0°"; J. Phys. Chem. 35, 3105 (1931).

Biog.

BIOGRAPHICAL NOTE

The writer, Stanley Donald Stookey, was born in Hay Springs, Nebraska, on May 23, 1915. In 1921 his family moved to Cedar Rapids, Iowa, where he resided until he received the B.A. degree at Coe College, in 1936. He was awarded the Edward Hart Research Fellowship at Lafayette College, Easton, Pa.; and received the M.S. degree from that institution in 1937. He was appointed a Teaching Fellow in Chemistry at M.I.T. in 1937, and held that position for three years '37-'38, '38-'39, and '39-'40. His Major was physical chemistry, Minor physics, in the course of study leading to the Ph.D. degree.