THE HYDROGEN DIFFUSION RATE DISCONTINUITIES OF PALLADIUM

Thesis

by

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ABSTRACT

The structure sensitive properties of palladium metal are found to change discontinuously in such a way that the hydrogen concentration and the rate of hydrogen diffusion alter suddenly at a reproducible geometric series of hydrogen pressures. The data of two low pressure concentration studies and a number of low pressure diffusion rate studies are tabulated and plotted so as to show the discontinuities. The best set of values for the critical pressures, obtained by plotting a curve of "breaks", is: 2.6, 5.3, 10.6, 21.3, 42.5, 85, 170, 340, and 620 microns of mercury. A collection of absorption and diffusion rate data from the literature suggests an extension of this series to complete hydrogen saturation $(Pd_4 H_2)$ at 350 millimeters of mercury.

A tentative statistical theory is proposed of the penetration of ionised atoms into a crystal which has an intrinsic secondary structure. The theory predicts the concentration isotherm in terms of the transmission discontinuities. It describes a secondary structure which has finer spacing for each successive higher concentration step and enables a calculation of the value of each spacing.

Several microphotographs of the palladium surface are shown. Measurements of the photographs are compared with the spacings predicted by the theory.

TABLE OF CONTENTS

I. HISTORICAL RESUME

Evidence has been accumulating during the past three years that gases are absorbed by charcoal and metals discontinuously with the pressure of the absorbed gas. These "breaks" in absorption isotherms have been accounted for in terms of the discontinuous properties of the gas, as the sudden appearance of Van der Waal forces at a critical concentration, or by the construction on a smooth surface of the adsorbent of figures of condensed atoms, whose geometrical properties require that new atoms be added discontinuously. Benton and White[1] suggested that the effect might be explained if all the microcrystals of the adsorbing material were of the same size, and recently evidence has been more and more descriptive of a structure of the adsorbent.

The present paper is believed to be an extension of this work. It shows a regular reproducible series of pressure discontinuities in the passage of hydrogen by hot palladium, and deduces the existence of adsorption discontinuities from the anomalies of the transmission curves.

The phenomenon of discontinuous adsorption was first noticed in 1926 by Allmand and co-workers, and was described fully in 1930.[2] Many adsorption isotherms formerly believed to be smooth curves whose points deviated because of experimental error have since been found upon more careful investigation to exhibit discontinuities. The gas-solid systems for which discontinuous isotherms have been proved are benzene, carbon tetrachloride, water and other condensible vapors on charcoal;[3] carbon tetrachloride and water on silica gel by the retentivity method;[4] nitrogen and hydrogen on various metal adsorbents at -183° C.;[5] and hydrogen on charcoal at 0° C.[6] As will be set forth in the main body of this paper, a collection

of data by Gillespie and co-workers[7] can be used to establish a fair case for the existence of absorption discontinuities of the system hydrogen-palladium at 0° C. These absorption isotherm discontinuities have been accounted for by a theory based on Semenoff's[8] treatment of surface equilibria. As the concentration of adsorbed atoms on a surface reaches a critical pressure they pass from a two-dimensional gaseous phase to a close packed liquid state. If it is assumed that the close packed state begins at certain active points and spreads out in concentric rings about an 'island,' it may follow that the completion of each ring of adsorbed atoms will take place at the same critical pressure for every 'island.' In the absence of a precise formulation of this theory, and in view of the sketchy character of the data, this explanation has been adequate for most of the above cases of discontinuous sorption.

However, the writer agrees with G. H. Piper[9] that this theory should not be used to account for those systems in which the temperature is much higher than the critical temperature of the adsorbed gas. These systems include hydrogen on palladium at 300° C (as described in this paper); hydrogen on charcoal at 0° C.;[6] hydrogen on active copper at -183°C.;[5] and hydrogen on charcoal at -183°C.[12]

In order to account for discontinuous adsorption in these cases one must assume[9] that the adsorbent consists of regions of different adsorptive power, and further, that these regions are not distributed about a mean value, but are of only a limited number of sizes and shapes. This conclusion, reached by Piper,[9] independently of the author and published since the preliminary report of this paper was written, may be offered in support of a similar idea concerning the structure of

crystals which has been set forth at length by F. Zwicky on other grounds.[13]

Discontinuities in other properties of palladium have also been reported. Since Graham's[14] original papers on the diffusion and absorption of hydrogen by palladium, workers have investigated practically all aspects of the metal because the phenomena have interesting theoretical bearings in thermodynamics,[15] chemistry[16] and crystal structure,[17] and because the peculiar non-reproducibility of the metal has provoked controversy. Certain anomalous discontinuities in the increase of volume,[18] electrical resistance,[19] and magnetic susceptibility[20] are of particular interest because they help to establish that the discontinuities of transmission and absorption of hydrogen by palladium are a body rather than a surface effect of the nature of catalysis. The length-resistance studies of Harding and Smith[21] are a demonstration of the proposition that hydrogen absorption discontinuities in palladium have to do with phenomena that take place within the metal. They investigated simultaneously the changes in length and in resistance of a fine palladium wire when subject to hydrogen infiltration during electrolysis. The fluctuations in resistance of the wire were found to occur at the same instant with corresponding changes in length. Harding and Smith could not observe the geometric series of critical hydrogen concentrations at which these changes occurred because they had no way to measure effective hydrogen pressure. These fluctuations were unquestionably due to the same body changes which have to do with the absorption and transmission discontinuities described in the present paper. The writer made an attempt to measure length and resistance changes simultaneously with the transmission discontinuities but the set-up proved inadequate.

Several papers have been published[22] on the passage of hydrogen by palladium in which apparatus very similar to that of the writer was used. The essential differences are probably three. No previous worker has had a) so great a pressure sensitivity of a continuously recording manometer, in conjunction with b) so large a ratio of palladium mass to volume of pressure test chamber, and c) a palladium tube which was kept immaculate on the gauge side, while the outside was thoroughly poisoned.

It further appears that no one has previously worked carefully with transition rates at very low pressures. The greater part of the significant data, namely, nine out of a possible eighteen disconntinuities, occur below one millimeter of mercury (see below, figure XVI, the summary of transmission and absorption discontinuities).

The only previously observed transmission discontinuities of any gas-metal system which have come to the writer's attention are those of Holt.[22] His apparatus consisted of two large chambers separated by a palladium system whose temperature was under control. Each chamber was equipped with a mercury U-tube manometer, and either chamber could be filled with hydrogen or evacuated at will. One may conclude from his paper that no special attempt was made to keep either side of the palladium cleaner than the other. Therefore neither of his manometers can be said to have measured a quantity which was proportional to the hydrogen pressure within the palladium metal. For this reason he was not able to reproduce the pressures at which transitions occurred; he only reported that the curves of pressure against time appeared to consist of two portions in every case. (Holt's data will be discussed further below.)

One of the accepted results of the work on palladium is that the greater part of the resistance to passage of hydrogen occurs at the surface. Tammann and Schneider[23] showed that after palladium charged with hydrogen had been exposed to air the velocity of occlusion decreased. Firth[24] devised an experiment which made it highly probable that a protective film of palladium oxide was responsible for most of the inactivity, of 'dead' palladium. Valentiner[25] established that hydrogen sulphide was a poison for palladium. The effect of mercury vapor as a poison for the surface of palladium has not been definitely confirmed[26] but it is probable that mercury has some effect on the transmission of hydrogen by palladium, because Ramsay[15] found it advisable to keep his palladium tube free of it. All of these vapors are present in most laboratories, so that unless great precautions are taken, the surface will become poisoned.

On the other hand the resistance to movement of hydrogen within the palladium is almost nil. Coehn and Specht[27] showed by delicate measurements of the change of electrical resistance of the parts of a piece of palladium metal that hydrogen can be made to flow by the application of very small potential differences. It follows that if a definite attempt be made to poison one side of a palladium septum, while the other side is kept clean of every contamination but pure hydrogen, a gauge on the clean side of the septum may measure a pressure which is nearly proportional to the concentration of hydrogen within the palladium metal. This was done in the experiment described below.

II. DESCRIPTION OF APPARATUS

The apparatus consists essentially of two chambers separated by palladium foil whose temperature can be controlled by a furnace and measured with an adjacent thermocouple. One of the chambers (which will be called the "outside" chamber) may be connected either to a gas mixing panel or to a diffusion pump. The other chamber (which will be called the "inside" chamber) is equipped with a sensitive pressure gauge, and may be connected through a small mercury valve to a larger chamber, which, in its turn, may be connected through a large mercury U-shut-off to a two stage diffusion pump. A schematic drawing of the apparatus is shown in figure I.
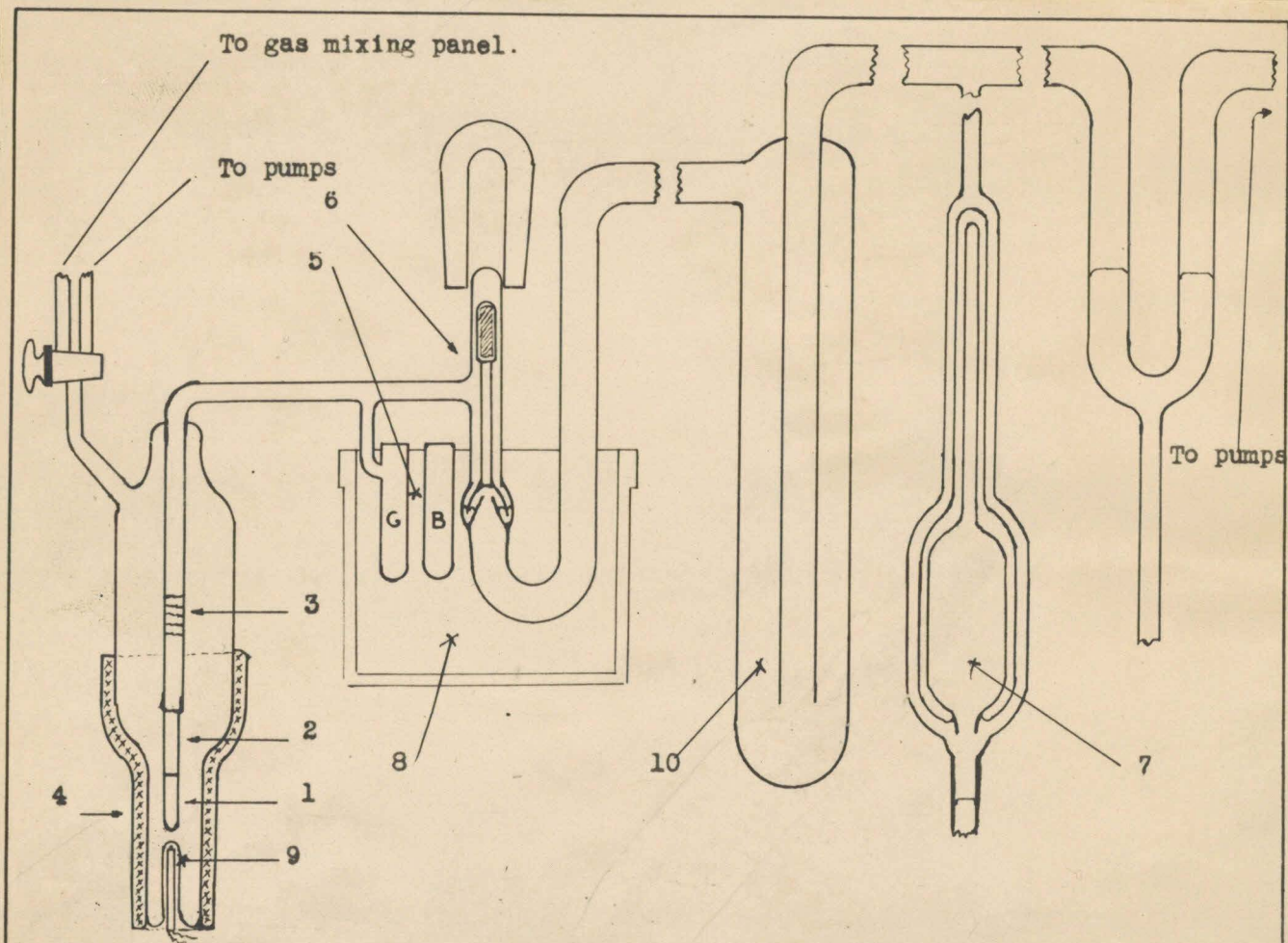

FIGURE I.   SCHEMATIC DIAGRAM OF APPARATUS.

Legend: 1, palladium tip, 2, platinum sleeve, 3, graded seal, 4, furnace 5, Pirani gauge tubes, 6, magnetic shut-off, 7, McCleod gauge, 8, ice bath 9, thermocouple, 10, vapor trap.

A. The gas mixing panel

The gas mixing panel (not shown in figure 1) consists of a battery of four 600 cc. storage pipettes and a burette suitably connected through a capillary manifold. It was used to prepare mixtures of dilute hydrogen with air, inert gases, or poisoning agents. Dilute natural gas was also used in place of hydrogen.

B. The palladium septa

Two duplicate palladium tubes were used. Their dimensions were: outer diameter, 6 mm.; thickness, .15 mm.; length of palladium tip, 3 cm.; length of platinum connection, 4 cm. They were purchased from American Platinum Works on June 27, 1932. No attempt was made to treat the inner surfaces of the tubes, but the external surfaces were activated by the procedure suggested by Ramsay,[15] namely, electrolysis for twenty minutes in .5 N sulphuric acid, using alternating current at 110 volts without a rheostat.

C. The magnetic shut-off

The inside chamber was made as small as possible in order to increase the sensitivity of the gauge to exhalations of hydrogen from the palladium. The miniature mercury shut-off was made of a 3/8" pyrex tube, and the small iron armature was enclosed in an envelope of a 1/4" tube in order to avoid any possibility of error from exhalation of gas from the iron. A small powerful cobalt steel horseshoe was used to hold the valve cup off its mercury seat. This shut-off was immersed with the Pirani tubes in an ice bath in order to prevent variations of pressure due to changes in temperature

of the mercury. At all times the palladium tube was kept warm and the mercury shut-off was kept cold to prevent the mercury from poisoning the inner surface of the palladium tube. All experiments were preceded by a short baking period to drive off any mercury from the inner surface of the palladium.

D. The Pirani gauge

The gauge tubes were made so that the ratio of sensitivity to volume was as large as possible. The glass walls were pulled to egg shell thinness from 3/4" pyrex. Several were pulled, and the two most similar were chosen for balance. Two platinum-iridium resistance wires, ninety centimeters each in length, were mounted in each tube, as shown in figure II, at a distance of one millimeter from the thin walls. These wires were free from all strains and were but forty microns in diameter. One tube was evacuated, baked out and flushed with hydrogen, and sealed off at a pressure of about two microns. The other tube was sealed to the inside chamber as shown in figure I, and the pair were mounted rigidly together in the ice bath.
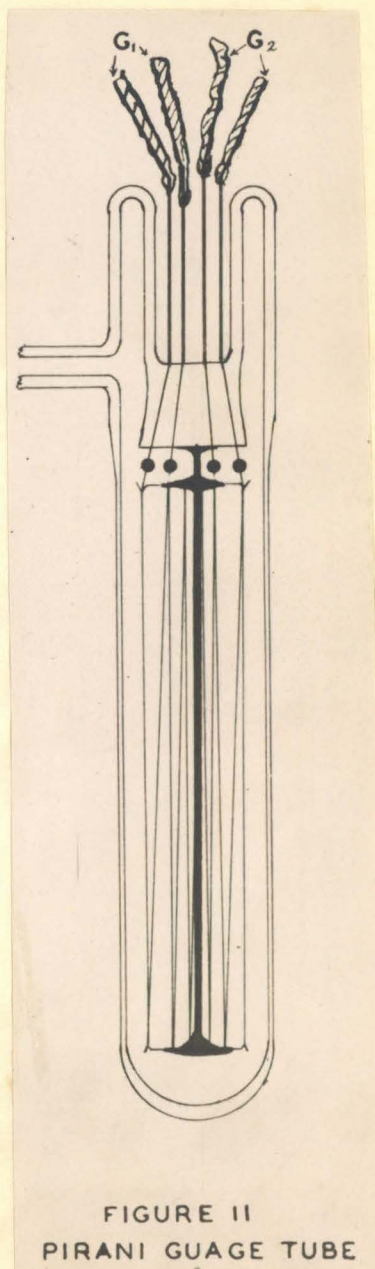
FIGURE II
PIRANI GUAGE TUBE

Using a heating current from a storage battery of seventy milli-
amperes, these gauges were found to have a sensitivity of one ten-
thousandth of a micron (1.2 ohms per micron) and were remarkably well
balanced thermally. They were wired so as to unbalance all four arms
of a Wheatstone bridge as shown in the wiring diagram of figure III.
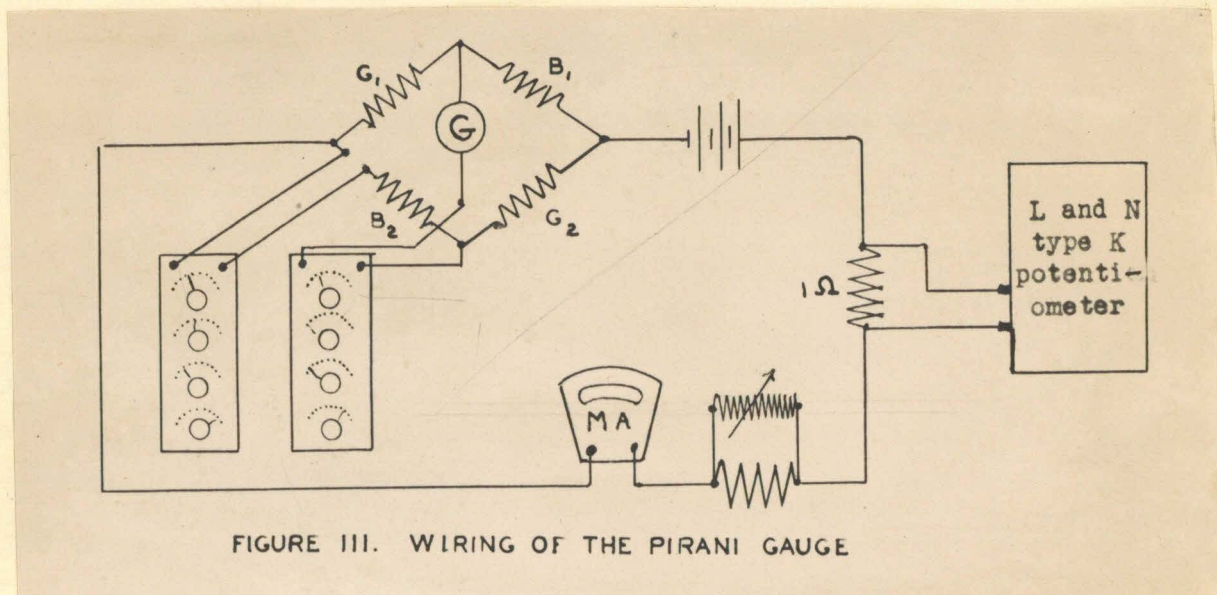
FIGURE III. WIRING OF THE PIRANI GAUGE

The gauges were used with about forty milliamperes heating current,
and the galvanometer was shunted down to give a direct scale reading
of 10 cm. = 1 micron on the galvanometer scale. The current was always
set and checked with the potentiometer at a definite position of the
balance resistance and with the gauge completely evacuated. The current
was not held constant during the reading but was checked at the end of
each run by again evacuating and setting the balance resistance at the
standard position.

The calibration curve was obtained "on the wing" at approximately
the same speed of exhaustion as in actual operation by recording the
resistance at the instant when mercury trapped off the charge in the
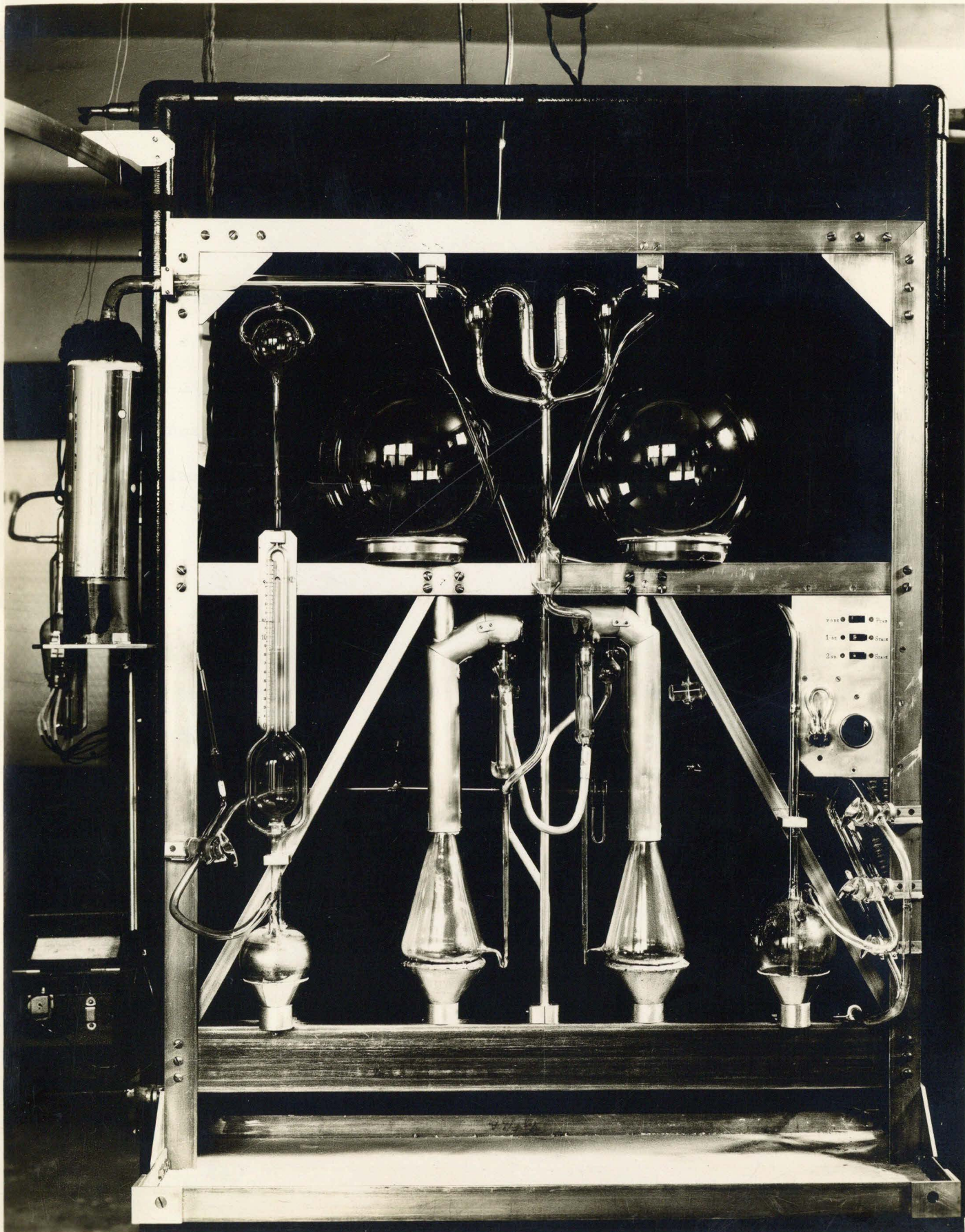
FIGURE IV. DIFFUSION PUMP PANEL.

McCleod gauge chamber. By repeatedly and quickly working the McCleod gauge a fairly reproducible curve was obtained.

The McCleod gauge was made and calibrated by Sperling, a glass blower at the Bureau of Standards.

After the discontinuities of hydrogen transmission were found a test was made of the rate of passage of hydrogen through a capillary in place of the palladium tube in order to verify that the variations were not ascribable to the gauge. No discontinuities were found in the absence of the palladium tube. The calibration curve of the Pirani gauge was a straight line from zero to nine microns, and quite smooth and regular in the upper curved and steep parts. An attempt was made to find discontinuities in the calibration curve by plotting it on semi-logarithmic paper, but no suspicious breaks were found.

E. The pumping system

The pumping system is best described by the photograph of figure IV. The apparatus of figure I (using an ionisation gauge at the time) is at the left. The outside chamber pump connection is made behind - between the first and second stages. It is not visible in the picture. There is no reason to suspect that the pumps could introduce discontinuities of the type found. "Bumping" of the mercury in the pumps occurred very rarely.

III. EXPERIMENTAL PROCEDURE

The evacuated system was kept flushed with hydrogen which was passed through the palladium tube from outside. At all times the inside of the palladium septum was guarded against contamination.

Before making a run of data, the system was prepared by evacuating as completely as possible on both sides of the palladium tube, by repeated torching of all glass and baking of the tube at the temperature at which it was to be operated. The solid CO_2-acetone mixture was applied to the trap to catch any subsequently generated vapors. A hydrogen-air mixture was admitted to the outside chamber and several millimeters pressure of hydrogen was permitted to diffuse into the inside chamber. The outside chamber was then connected to the pumps, flushed with pure air or nitrogen, and pumped hard to keep it clear of hydrogen.

A continuous series of measurements was then taken of the pressure in the inside chamber as the hydrogen diffused outward, using a stop watch and the Pirani gauge. The resulting curves were of two kinds, depending on whether the volume of the inside chamber was large or small. The small volume of the inside chamber was obtained by dropping the magnetic shut-off. The large volume included the dry ice trap, McCleod gauge and the 3/4" tubes connecting with the U mercury shut-off.

The principle difficulty with the procedure was the speed with which the data had to be taken in order to obtain a clear description of the discontinuities in the logarithmic pressure-time curves. If the external surface of the tube was very active, the small volume inside chamber would require a photographic continuous recording device to catch the changes "on the wing". It was found necessary therefore to do most of the work with the large volume inside chamber, using an assistant observer to write the figures while the principal worked the Pirani balance resistance and stop watch. The best safe rate of working was found to be one point every twenty seconds.

The random errors in reading were principally due to the differences in the state of dynamic equilibrium of the Pirani and galvanometer system. The observer read the resistance and time for several positions of the galvanometer beam as it swept across the scale, then switched in more resistance to move the galvanometer beam again to the far end of the scale. This slight sudden change of resistance altered the heating current in the Pirani chamber, and the heat capacity was such that the dynamic equilibrium was disturbed. This trouble was particularly noticeable at the ten ohm changes of the decade resistance box used, but a careful check established that these changes could not possibly be responsible for the discontinuities that were observed in the logarithmic pressure curves. This error had the effect of making the logarithmic curves irregular where they were actually straight lines. There seemed to be no better way to obtain a continuous record of pressure over such a wide range than a Pirani gauge read, perforce, "on the wing."

Wherever possible, auxiliary readings were taken with the McCleod during the high pressure portion of the run.

IV. EXPERIMENTAL RESULTS

The data are plotted in figures V to XV inclusive and are tabulated in the accompanying tables.

A. Diffusion out of a chamber of small volume

Figure V shows the discovery set of data. The points were obtained with the magnetic shut-off in the down position. Fortunately the palladium was in a state which permitted the reading of enough points to establish the steps in the curve. Without these curves the writer would not have been led to plot the logarithims of pressure of the more easily obtained large volume data, and hence would not have discovered the phenomenon.

These data show that a regular series of transition pressure thresholds occur through which the system cannot readily pass. These thresholds are at about the same pressures as in curves VI to XV below. It is evident from curves VI to XV that the diffusion constant does not fall to the low values indicated by the horizontal parts of the curves of figure V. It must therefore be inferred that the steps in the profile are caused by a sudden exhalation of hydrogen which occurs at the same pressures as the change in diffusion rate, this exhalation adding somewhat to the mass of gas in the inside chamber, and delaying the pressure fall as shown by curves of figure V. The fact that the palladium loses its hydrogen in this discontinuous manner suggests that if it were possible to measure the quantity of gas released, isotherms of the previously reported step-like profile would be obtained. This quantitative measurement would require new apparatus and would be difficult to do. However, if the inside volume

is made so large that the exhalations of gas from the palladium septum cannot affect the pressure appreciably, data may be obtained from which transmission rates can be calculated. It is reasonable to expect these diffusion constants to change as the palladium is contracted by its loss of hydrogen.

B. **Diffusion out of a chamber of large volume** (Figures VI to XV)

The logarithm of the pressure is plotted against time producing a series of straight lines, joined at fairly definite angles. It will be seen that the transitions occur in many cases at roughly the same pressures, and that these transition pressures form approximately a regular geometric series.

Along the straight lines it is evident that the diffusion follows the simple law whereby the rate of diffusion through the palladium is proportional to the pressure:

$$\frac{dp}{dt} = \beta P;$$
$$\text{or} \qquad p = e^{-\beta t}$$

At the transitions a change in the diffusion constant β occurs, which may be ascribed to some change in the metal. The bend is not always in the same direction and a few of the transitions are missed on some curves. The cause is probably connected with changes in the catalytic activity of the surface, induced by a change in the secondary structure of the body of the metal.

The magnitude of β varies at the discontinuities in a regular way on some of the curves. For example, an analysis of the slopes of the logarithmic curve of set # 12 (figure XIII) will show that $\beta = kp$. This may be the normal mode of variation which is obliterated by other

variables of the poisoned external surface.

The discontinuities may occur when the hydrogen is passing in either direction. Set # 10 (figure XII) was obtained when hydrogen was passing from a dilute mixture of hydrogen in air into the previously evacuated and shut off small chamber. This curve shows a sudden change in the catalytic nature of the poisoned palladium outside surface which caused it to maintain what was apparently a uniform hydrogen pressure available for diffusion. The rate of passage through the palladium was discontinuous at the same pressures as had been measured before in the opposite direction. It is extremely difficult to produce data of the type of set # 10. When hydrogen is presented to the external poisoned surface it is generally not absorbed or transmitted. It the pressure of external hydrogen be raised, the passage will suddenly occur with a rush; that is, the absorption is autocatalytic. It is impossible to follow the change with a Pirani gauge except in rare instances.

Although the "breaks" in these logarithmic curves are definite in most cases, it is sometimes a little difficult to decide just where the "break" occurs. The fact that the palladium exhales a bit of hydrogen at the same time that the diffusion rate changes causes a slight rounding of the curve, and a displacing of the whole lower part of the curve by a slight unpredictable amount. It is also apparent in some cases that the metal did not assume its new diffusion constant value immediately, but wavered for a few seconds. See, for example, the 100 micron break of set # 5 (figure VII), and the 11 micron break of set # 6 (figure VIII).

The rule by which the discontinuities are chosen is: draw lines through the center of gravity of the segments of the graph. The intersections of these lines mark the critical pressures. There are one or

two cases, however, as in the 39 micron break of set # 9 (figure XI) where the exhalation is so unmistakable that the local anomaly rather than the intersection of the lines is preferred to mark the points.

It is unfortunate that in some runs, as in set # 8 (figure X) the changes in slope are so slight as to be almost indistinguishable. In judging these curves, the critical reader will bear in mind that these data are rigorously and scrupulously free of personal bias. The observer was unaware of any change in rate at the time the data were taken; indeed the calibration curve had to be corrected by McCleod readings taken "on the wing," and the results could not be judged without converting ohms to microns and plotting logarithms. The results of this operation should contain only arithmetic error. The points of sets # 5 to # 14 were plotted by an assistant whose ignorance of the whole matter can be depended upon. It is probable that some of the curves might be improved in appearance by correcting for some highly probable sources of error, as, for example, the correction of the Pirani calibration curve for the various rates of change, the state of disequilibrium induced by the changes in the Pirani balance resistance. None of this has been done. It was thought best to leave the data in their original state, because the essential truth of the existence of a regular geometric series of critical pressures can be seen through the random error by means of a distribution frequency curve (figure XVI).

On the logarithmic chart of figure XVI a short line has been drawn, for every transition observed, on the ordinate corresponding to the temperature of the tube at the time. It is immediately apparent

that these lines are grouped around equidistant zones of pressure. The series fits the formula:

$$\frac{P_{n+1}}{P_n} = 2 \;.$$

The most trustworthy data are in the region between fifteen and one hundred microns, because the Pirani gauge calibration curve is steep and untrustworthy above this range and below it there is confusion with gases other than hydrogen. The distribution of points in the 21.25, 42.5 and 85 micron regions may suggest a variation of transition pressure with temperature, as indicated by the dotted lines. These dotted lines are drawn on a regular geometric series based on the above mentioned reliable part of the data. Their curvature, determined by these more reliable data, is such as to include within the series the absorption curve breaks of Gillespie, Perry and Hall.

All the data obtained below one millimeter are new and are reported for the first time in this paper. An attempt to extend the series by using data previously published is set forth in the points to the right of the one millimeter abscissa.

The transition points shown between one millimeter and twenty centimeters are all from absorption curves which are discussed further below. Their authors either do not recognize them,* as in the case of

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* My justification for picking out absorption curve anomalies which their authors did not recognize is that the authors were in every case concerned with the establishment of so-called "equilibrium" isotherms which they thought should be smooth curves. I have reason for believing that the experimental error which caused those anomalies was a very real thing, attributable to the effect of the exigencies of a secondary structure to which the dissolved hydrogen was forced to conform.

The group of workers which is interested in the thermodynamic properties of palladium have drawn smooth curves wherever possible and as in the case of Gillespie and Hall[7] have also subjected the metal to treatment to eliminate what they regard as "frozen equilibrium."

some of the points from Gillespie and Perry,[7] or they simply point them out as repeatable transition points without an explanation, as in the case of Ubbelohde's[32] 9 cm. pressure transition.

The group of points about the 360 mm. pressure step was obtained by Holt[22] from diffusion curves in substantially the same way as the new points below one millimeter were obtained. The points represent pressures on either side or both sides of a tube which was probably equally poisoned on both sides. The average of Holt's points, which may be expected to be the pressure to which the palladium was subjected in the sense meant in the present experiments, will be seen to lie on the 360 mm. pressure step curve. This may, of course, be fortuitous. It is interesting to note that the same temperature variation is implied by Holt's points as is suggested by these data, and by the relation of Gillespie and Perry's[7] 0°C. steps to the extrapolation of the high temperature series of pressure thresholds.

The experimental results of the palladium hydrogen diffusion study may be summed up as follows. Palladium metal or its hydride undergoes a change at a series of critical hydrogen pressures (most probable values: 2.6, 5.3, 10.6, 21.25, 42.5, 85, 170, 340, 680 microns of mercury if the palladium is at 400° C.). This change involves a discontinuous variation of hydrogen content and of the hydrogen diffusion constant. Each critical pressure seems to decrease somewhat as the temperature of the palladium is lowered.

By combining the results of this study with the results of previous workers we are able to extend the series to atmospheric pressure. It is believed probable that the discontinuous changes in electrical resistance, length, magnetic susceptibility, etc. mentioned in the historical resume have the same hydrogen pressure dependence.

FIGURE V. PRESSURE DURING EVACUATION OF A RELATIVELY SMALL CHAMBER THROUGH HOT PALLADIUM FOIL.

TRANSITIONS IN PALLADIUM INVOLVING EXHALATION OF HYDROGEN OCCUR:

SET #1; 3.8, 5.6, 12, 23, 42, 81, 150, MICRONS.

SET #2; 5.6, 11, 23, 43, 85, 160, MICRONS.
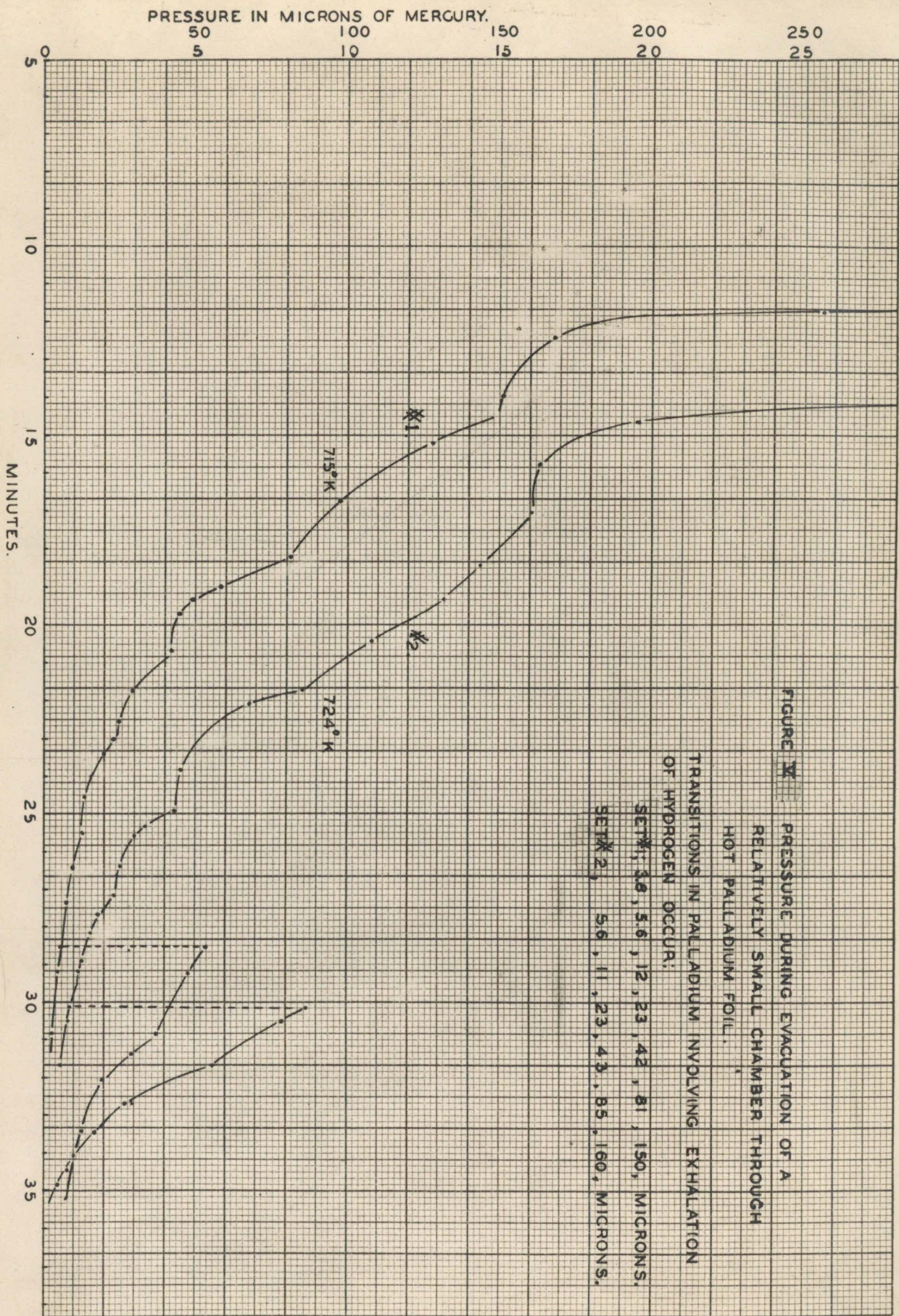
PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 1. Palladium tube A.

Temperature - 715° Absolute.

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
11' 42"	256	30' 50"	3.75
12' 25"	168	31' 23"	2.91
13' 57"	151	32' 6"	1.95
15' 11"	128	32' 31"	1.71
16' 42"	97.5	33' 29"	1.32
18' 11"	80.5	34' 4"	1.00
19'	58	34' 27"	.80
19' 20"	49		
19' 41"	44.8		
20' 50"	42		
21' 42"	29		
22' 34"	25		
23' 1"	23.2		
23' 25"	20		
24' 34"	13.9		
25' 30"	12.1		
26' 25"	9.7		
27' 21"	7.5		
28' 33"	5.4		
29' 11"	4.8		

Set # 2. Palladium tube A.

Temperature - 724° Absolute.

Time	Pressure
14' 40"	195.5
15' 46"	163.4
17' 1"	160.7
18' 22"	144
19' 20"	132
20' 25"	108.1
21' 42"	86
22' 5"	68
23' 50"	45.5

Set # 2 - continued

Time	Pressure
minutes and seconds	microns of mercury
24' 55"	43.2
25' 20"	33.7
25' 35"	30.
26' 22"	25.2
27' 10"	23.6
27' 41"	18
28' 10"	15.9
28' 54"	12.5
29' 10"	11.5
30' 9"	8.65
30' 30"	7.95
31' 41"	5.60
32' 40"	2.71
33' 27"	1.73
34' 4"	1.01
34' 50"	.48

CURVE #4, TIME IN MINUTES.

CURVE 4A TIME IN MINUTES
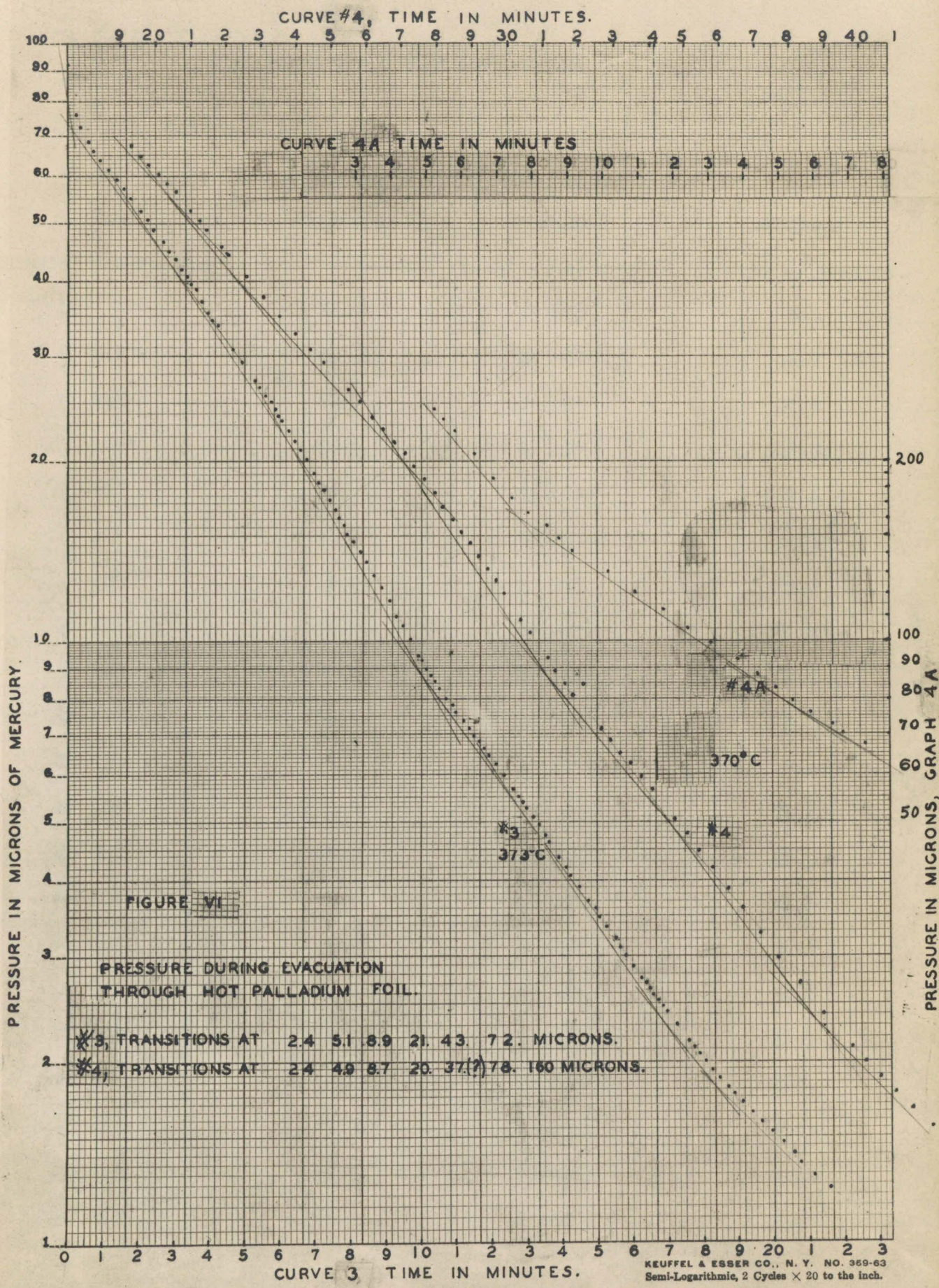
FIGURE VI

PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL.

#3, TRANSITIONS AT   2.4 5.1 8.9 21. 43. 72. MICRONS.
#4, TRANSITIONS AT   2.4 4.9 8.7 20. 37(?) 78. 160 MICRONS.

PRESSURE IN MICRONS OF MERCURY.

PRESSURE IN MICRONS, GRAPH 4 A

#4A
370°C
#4
#3
373°C

CURVE 3 TIME IN MINUTES.

KEUFFEL & ESSER CO., N. Y. NO. 369-63
Semi-Logarithmic, 2 Cycles × 20 to the inch.

PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 3. Palladium tube B.

Temperature - 646° Absolute.

Time minutes and seconds	Pressure microns of mercury	Time minutes and seconds	Pressure microns of mercury
0'	92	3' 59"	35.4
13"	76	4' 6"	34.5
21"	72.3	4' 14"	33.8
34"	68.4	4' 39"	30.85
44"	66	4' 56"	29.2
55"	63.8	5' 19"	27.15
1' 9"	61.4	5' 25"	26.6
1' 22"	59.1	5' 35"	25.8
1' 34"	57	5' 43"	25.1
1' 46"	55.3	5' 51"	24.3
2' 3"	52.4	5' 56"	23.85
2' 15"	50.7	6' 4"	23.4
2' 25"	48.9	6' 14"	22.5
2' 41"	46.4	6' 24"	21.55
2' 50"	44.8	6' 33"	20.9
3' 3"	43.4	6' 43"	20.1
3' 11"	41.9	6' 57"	19.1
3' 21"	40.7	7' 6"	18.4
3' 29"	39.5	7' 13"	17.9
3' 37"	38.9	7' 24"	17.3
3' 48"	37	7' 33"	16.6

Set # 3 - continued

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
7' 39"	16.1	11' 39"	6.8
7' 49"	15.7	11' 47"	6.62
7' 52"	15.1	11' 55"	6.43
8' 4"	14.7	12' 8"	6.07
8' 15"	14.15	12' 20"	5.97
8' 25"	13.6	12' 37"	5.57
8' 39"	12.9	12' 46"	5.50
8' 51"	12.25	12' 52"	5.40
9' 5"	11.65	12' 59"	5.27
9' 18"	10.95	13' 10"	4.98
9' 29"	10.53	13' 21"	4.80
9' 40"	10.03	13' 32"	4.62
9' 51"	9.45	13' 39"	4.50
10'	9.3	13' 55"	4.27
10' 9"	8.95	14' 7"	4.09
10' 16"	8.75	14' 15"	3.97
10' 22"	8.55	14' 30"	3.80
10' 30"	8.30	14' 44"	3.62
10' 41"	8.00	14' 58"	3.50
10' 53"	7.81	15' 3"	3.38
10' 58"	7.6	15' 17"	3.23
11' 11"	7.37	15' 31"	3.08
11' 21"	7.15	15' 40"	3.00
11' 29"	6.95	15' 49"	2.90

Set # 3 - continued

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
16' 1"	2.79	54"	356
16' 15"	2.67	1' 23"	346
16' 22"	2.61	1' 45"	333
16' 29"	2.55	2' 12"	319
16' 35"	2.49	2' 56"	301
16' 43"	2.43	3' 17"	291
16' 51"	2.38	4' 4"	271
16' 59"	2.32	4' 27"	260
17' 15"	2.20	4' 46"	253
17' 35"	2.08	5' 7"	244
17' 45"	2.02	5' 24"	235
17' 56"	1.96	5' 43"	225
18' 5"	1.90	6' 15"	204
18' 16"	1.84	6' 48"	186
18' 29"	1.78	7(20"	174
18' 41"	1.72	7' 46"	164
18' 54"	1.67	8' 18"	156
19' 8"	1.61	8' 39"	148
19' 23"	1.55	9' 1"	142
19' 40"	1.49	10'	130.5
19' 59"	1.43	10' 49"	120.5
		11' 38"	113
		12' 19"	105.2
		12' 59"	99
		13' 45"	93.1

Set # 4. Palladium tube B.

Temperature - 643° Absolute.

0'	383
32"	369

Set # 4 - continued

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
14' 20"	87.9	25' 28"	26.3
14' 49"	83.2	25' 47"	25.05
15' 20"	79.4	26' 6"	23.85
15' 51"	76.	26' 26"	22.7
16' 27"	72.8	26' 43"	21.6
16' 55"	70.	27' 1"	20.55
17' 24"	67.5	27' 18"	19.55
19' 19"	67.1	27' 35"	18.6
19' 34"	64.8	27' 51"	17.65
19' 49"	62.6	28' 7"	16.75
20' 5"	60.2	28' 22"	16.
20' 19"	58.1	28' 38"	15.25
20' 33"	56.2	28' 53"	14.55
20' 59"	52.5	29' 7"	13.85
21' 14"	50.65	29' 22"	13.2
21' 26"	48.9	29' 36"	12.6
21' 50"	45.7	29' 50"	12.
22' 2"	44.15	30' 19"	10.85
22' 33"	40.7	30' 34"	10.35
23' 2"	37.6	31' 5"	9.35
23' 30"	35.	31' 18"	8.9
23' 57"	32.8	31' 34"	8.5
24' 21"	30.85	31' 48"	8.1
24' 45"	29.2	32' 36"	7.12

Set # 4 - continued

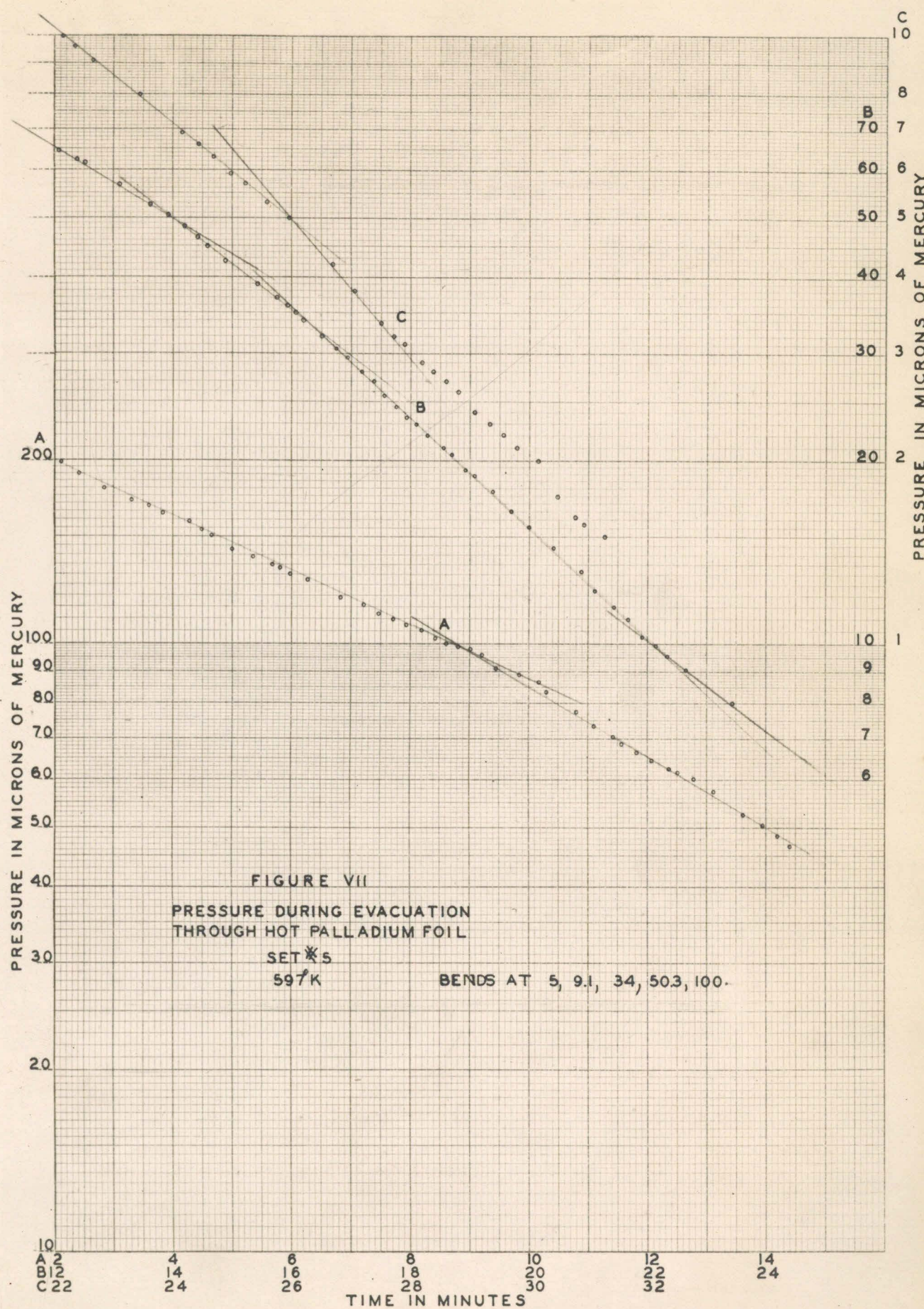| Time	Pressure
minutes and seconds	microns of mercury
32' 52"	6.8
33' 9"	6.5
33' 26"	6.25
33' 44"	5.95
34' 2"	5.65
34' 21"	5.35
34' 40"	5.07
35' 1"	4.78
35' 22"	4.48
35' 47"	4.20
36' 12"	3.88
36' 39"	3.60
37' 9"	3.28
37' 38"	2.99
38' 13"	2.7
38' 54"	2.4
39' 42"	2.11
40' 7"	2.0
40' 30"	1.88
40' 57"	1.77
41' 27"	1.67
42'	1.55

FIGURE VII

PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL
SET 5
597K   BENDS AT 5, 9.1, 34, 50.3, 100.

PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 5. Palladium tube B.

Temperature - 597° Absolute

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
0'	244	6' 15"	127
20"	235	6' 49"	119
40"	227	7' 12"	116
59"	219	7' 27"	112
1' 16"	215	7' 42"	110
1' 45"	207	7' 55"	107
1' 53"	204	8' 11"	105
2' 6"	198	8' 25"	102.5
2' 24"	190	8' 36"	100
2' 51"	180	8' 48"	99
3' 18"	172	9'	98
3' 32"	168	9' 12"	96
3' 50"	164	9' 27"	91
4' 17"	158	9' 50"	89
4' 28"	153	10' 9"	85.4
4' 39"	150	10' 18"	83.2
4' 59"	143	10' 47"	77.6
5' 20"	138	11' 6"	73.3
5' 40"	135	11' 25"	70.5
5' 48"	133	11' 34"	68.9
5' 58"	130	11' 50"	66.6

Set # 5 - continued

Time minutes and seconds	Pressure microns of mercury	Time minutes and seconds	Pressure microns of mercury
12' 5"	64.4	18' 6"	22.85
12' 22"	62.3	18' 17"	22.1
12' 30"	61.2	18' 33"	21.0
12' 46"	60.95	18' 42"	20.3
13' 6"	56.6	18' 56"	19.4
13' 37"	52.6	19' 5"	18.85
13' 56"	50.3	19' 22"	17.8
14' 11"	48.4	19' 42"	16.5
14' 24"	46.7	19' 59"	15.6
14' 35"	45.2	20' 24"	14.3
14' 53"	43.3	20' 46"	13.2
15' 26"	39.2	21' 7"	12.23
15' 46"	37.0	21' 26"	11.5
15' 55"	36.0	21' 40"	11.0
16' 4"	34.9	21' 54"	10.5
16' 12"	34.0	22' 7"	10.0
16' 30"	32.1	22' 21"	9.55
16' 46"	30.4	22' 38"	9.12
16' 55"	29.5	23' 16"	8.72
17' 11"	27.8	23' 25"	8.0
17' 23"	26.7	24' 8"	6.93
17' 34"	25.65	24' 25"	6.58
17' 45"	24.6	24' 41"	6.25
17' 56"	23.7	24' 59"	5.92

Set # 5 - continued

Time	Pressure
minutes and seconds	microns of mercury
25' 13"	5.7
25' 35"	5.3
25' 58"	4.98
26' 41"	4.19
27' 3"	3.8
27' 30"	3.42
27' 43"	3.24
27' 53"	3.12
28' 11"	2.92
28' 23"	2.79
28' 36"	2.68
28' 48"	2.55
29' 4"	2.41
29' 19"	2.3
29' 33"	2.18
29' 47"	2.07
30' 9"	1.97
30' 28"	1.74
30' 46"	1.62
30' 56"	1.57
31' 16"	1.5

FIGURE VIII

PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL
SET #6 , 647° K

BENDS AT 2.2,11.5,20.,47.,96,160,368,600.
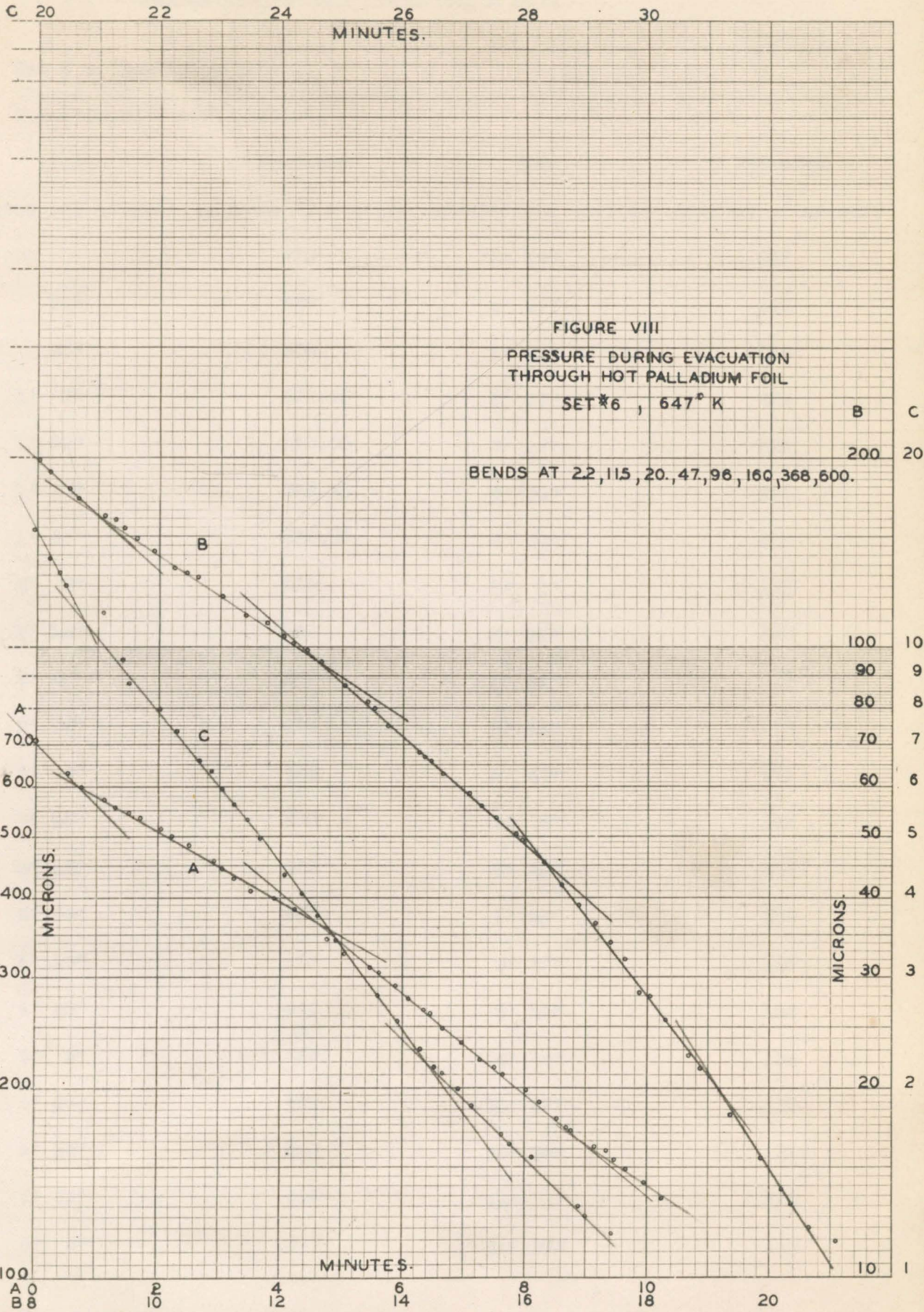
PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 6. Palladium tube B.

Temperature - 647° Absolute

Time minutes and seconds	Pressure microns of mercury	Time minutes and seconds	Pressure microns of mercury
0'	710	6' 19"	267
31"	630	6' 27"	262
45"	600	6' 41"	248
1' 8"	571.65	6' 57"	236
1' 20"	559.05	7' 17"	221
1' 32"	546.45	7' 30"	216
1' 43"	536.85	7' 39"	210
2' 3"	514	8' 1"	198
2' 14"	500	8' 12"	190
2' 30"	485	8' 32"	178
2' 54"	458	8' 41"	173
3' 3"	445	8' 47"	171
3' 14"	430	9' 8"	162
3' 42"	410	9' 18"	159
3' 54"	400	9' 26"	154
4' 15"	381	9' 39"	148
4' 48"	345	9' 55"	142
5' 3"	325	10' 15"	134
5' 27"	310	10' 27"	132
5' 36"	303	10' 37"	129
5' 52"	290	11' 1"	120
6' 5"	277	11' 24"	112

Set # 6 - continued

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
11' 47"	109	18' 5"	28
12' 2"	103	18' 13"	25.65
12' 11"	101	18' 41"	22.65
12' 26"	99	18' 53"	21.3
12' 39"	95	19' 23"	18.2
13' 4"	87	19' 53"	15.42
13' 24"	81.9	20' 12"	13.85
13' 31"	80.3	20' 21"	13.2
13' 45"	74.8	20' 39"	12
14' 16"	67.8	21' 6"	11.45
14' 22"	66.7	21' 24"	9.55
14' 29"	65.6	21' 42"	8.73
14' 38"	63.4	22' 1"	7.98
15' 5"	58.5	22' 20"	7.3
15' 19"	55.9	22' 41"	6.6
15' 32"	53.4	22' 52"	6.35
15' 50"	50.4	23' 3"	5.94
15' 55"	49.6	23' 14"	5.62
16' 17"	45.3	23' 27"	5.31
16' 36"	42	23' 39"	4.97
16' 52"	39.2	24' 5"	4.35
17' 9"	36.45	24' 20"	4.05
17' 24"	34	24' 36"	3.75
17' 39"	31.7	24' 55"	3.42
17' 52"	28.2	25' 36"	2.8

Set # 6 -- continued

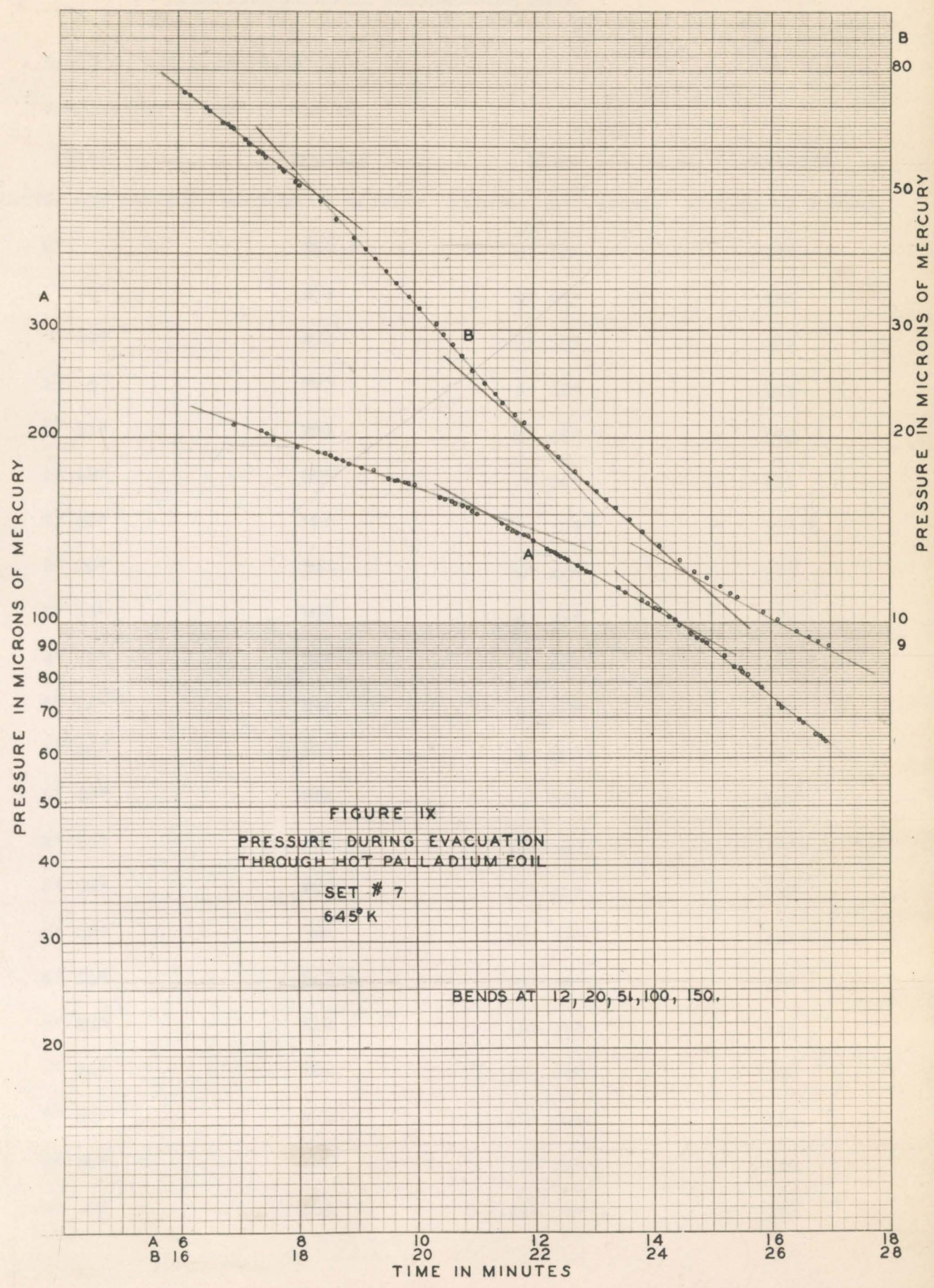| Time	Pressure
minutes and seconds	microns of mercury
25' 55"	2.55
26' 18"	2.3
26' 31"	2.18
26' 39"	2.12
26' 54"	2.00
27' 9"	1.87
27' 37"	1.68
27' 46"	1.63
28' 8"	1.56
28' 51"	1.3
29'	1.25
29' 25"	1.18
29' 32"	1.15
29' 41"	1.11
29' 48"	1.1
30' 11"	1.03
30' 20"	1.01
30' 29"	.99
30' 37"	.96

FIGURE IX

PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL

SET # 7
645° K

BENDS AT 12, 20, 51, 100, 150.

PALLADIUM-HYDROGEN TRANSMISSION DATA

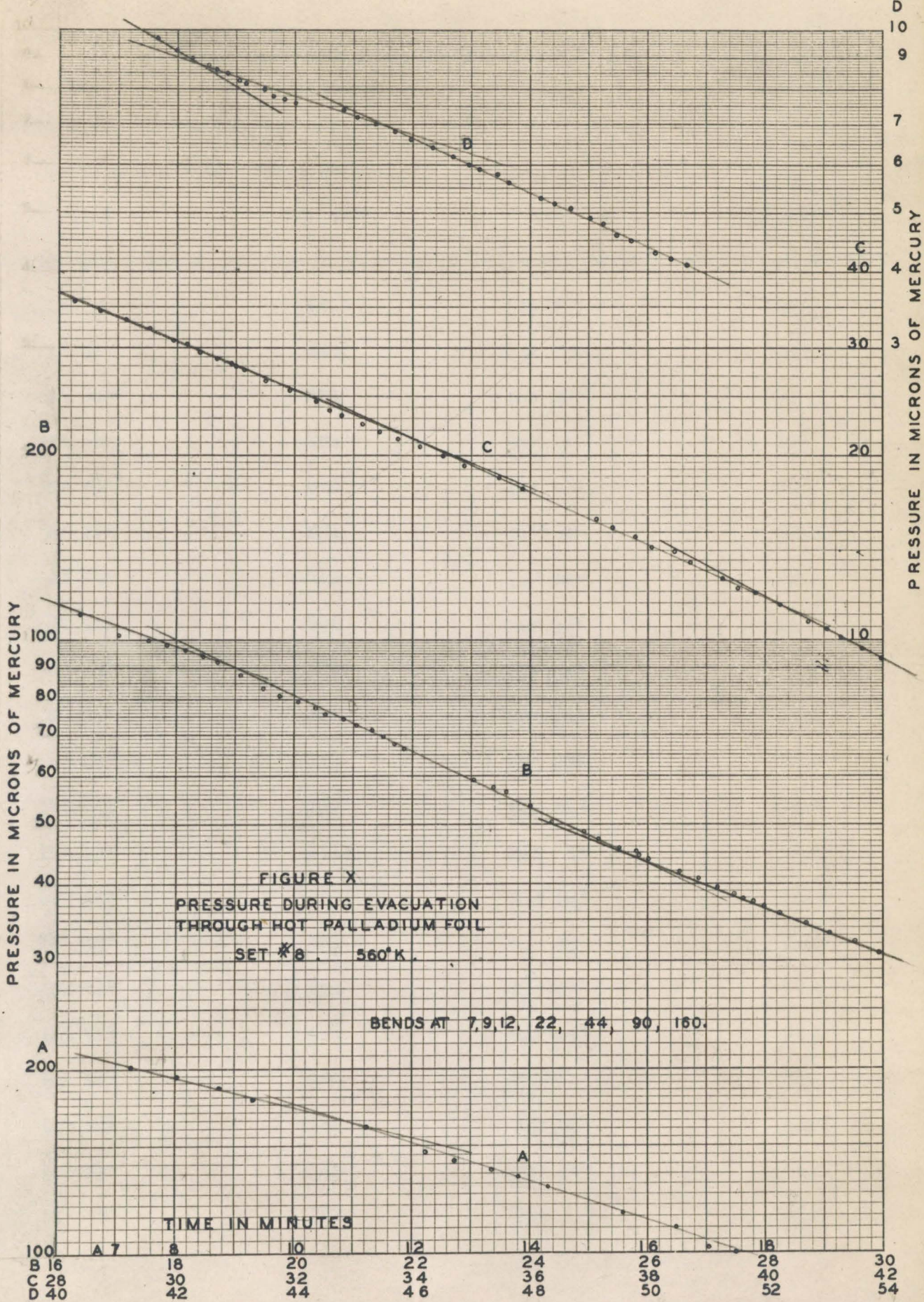Set # 7. Palladium tube A.

Temperature - 645° Absolute.

Time minutes and seconds	Pressure microns of mercury	Time minutes and seconds	Pressure microns of mercury
0'	280.5	8' 23"	189
35"	277	8' 29"	188
50"	275	8' 35"	187
1' 4"	273	8' 42"	185
1' 27"	268	8' 46"	183
1' 48"	266	8' 54"	181
2' 28"	262	9' 8"	178.5
3' 30"	253	9' 20"	177
3' 54"	246	9' 35"	172
4' 1"	244	9' 42"	171
4' 11"	241	9' 45"	170
4' 26"	237	9' 50"	169
4' 49"	234	9' 55"	168
5' 10"	232	10' 1"	167
5' 30"	229	10' 27"	160
5' 59"	224	10' 32"	159
6' 31"	213.5	10' 38"	157
6' 58"	210	10' 43"	156
7' 26"	204	10' 49"	155
7' 33"	202	10' 54"	154
7' 38"	199	10' 59"	152
8' 2"	194	11' 4"	151

Set # 7 - continued

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
11' 28"	145	14' 17"	102
11' 33"	142	14' 22"	101
11' 39"	141	14' 27"	99
11' 44"	140	14' 39"	96
11' 50"	139	14' 45"	94.5
11' 55"	138	14' 50"	93.5
12'	136	14' 54"	92.5
12' 13"	132	15' 13"	88
12' 17"	131	15' 23"	85
12' 20"	130	15' 28"	84
12' 24"	129	15' 32"	83
12' 28"	128.5	15' 36"	82
12' 31"	127.5	15' 47"	79.5
12' 34"	127	15' 51"	78.2
12' 44"	123	16' 8"	73.5
12' 49"	122	16' 12"	72.8
12' 53"	121.5	16' 29"	69.3
12' 57"	121	16' 32"	68.5
13' 27"	114	16' 45"	65.5
13' 33"	112.5	16' 50"	65.1
13' 49"	108	16' 52"	64.6
13' 55"	107	16' 55"	64
14' 1"	106	17' 8"	61.3
14' 7"	105	17' 11"	60.6

Set # 7 - continued

Time minutes and seconds	Pressure microns of mercury	Time minutes and seconds	Pressure microns of mercury
17' 21"	58.8	21' 29"	22.9
17' 25"	58.4	21' 42"	21.9
17' 28"	57.85	21' 50"	21.2
17' 42"	55.4	22' 15"	19.4
17' 45"	54.9	22' 27"	18.6
17' 47"	54.6	22' 43"	17.6
17' 59"	52.6	22' 55"	16.9
18' 3"	51.75	23' 5"	16.35
18' 24"	48.8	23' 15"	15.8
18' 40"	45.25	23' 24"	15.25
18' 58"	42.6	23' 37"	14.65
19' 9"	40.8	23' 50"	14.
19' 20"	39.1	24' 6"	13.3
19' 32"	37.5	24' 27"	12.55
19' 41"	35.9	24' 42"	12.1
19' 55"	34.	24' 56"	11.8
20' 7"	32.6	25' 7"	11.4
20' 20"	30.8	25' 19"	11.15
20' 28"	29.5	25' 26"	11.
20' 39"	28.2	25' 53"	10.4
20' 48"	27.1	26' 6"	10.1
20' 59"	25.8	26' 25"	9.72
21' 11"	24.6	26' 38"	9.45
21' 20"	23.7	26' 47"	9.3
		26' 58"	9.15

FIGURE X

PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL
SET #8 . 560°K .

BENDS AT 7, 9, 12, 22, 44, 90, 160.

PRESSURE IN MICRONS OF MERCURY

PRESSURE IN MICRONS OF MERCURY

TIME IN MINUTES

100	A 7	8	10	12	14	16	18	30
B 16		18	20	22	24	26	28	42
C 28		30	32	34	36	38	40	54
D 40		42	44	46	48	50	52	

PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 8. Palladium tube A.

Temperature - 560° Absolute.

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
0'	280	17' 31"	100
1' 28"	262	17' 51"	98
3' 9"	252	18' 10"	96
3' 39"	248	18' 27"	94
4' 34"	240	18' 42"	92
5' 27"	223	19' 6"	87.6
6' 44"	219	19' 28"	83.2
7' 15"	202	19' 45"	81
8' 2"	195	20' 4"	79.3
8' 45"	187	20' 20"	77.5
9' 19"	179	20' 33"	75.8
10'	170	20' 51"	74.3
11' 13"	161	21' 4"	72.7
12' 14"	147	21' 18"	71.1
12' 47"	142	21' 30"	69.5
13' 22"	137	21' 43"	67.8
13' 51"	133	21' 52"	64.8
14' 19"	128	23' 11"	59
15' 36"	116	23' 23"	57.6
16' 22"	110	23' 36"	56.3
17' 2"	102	24'	53.6

Set # 8 - continued

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
24' 22"	50.3	31' 8"	27.65
24' 48"	48.6	31' 30"	26.7
25' 10"	47.2	31' 54"	25.6
25' 32"	45.9	32' 21"	24.5
25' 42"	45.2	32' 35"	23.7
25' 51"	44.65	32' 48"	23.2
26'	44	33' 8"	22.5
26' 33"	42	33' 25"	21.85
26' 51"	40.85	33' 45"	21.2
27' 11"	39.6	34' 7"	20.65
27' 29"	38.5	34' 32"	19.95
27' 37"	37.9	34' 52"	19.25
27' 47"	37.35	35' 28"	18.4
27' 58"	36.8	35' 53"	17.6
28' 16"	35.8	37' 7"	15.7
28' 42"	34.45	37' 25"	15.25
29' 6"	33.2	37' 47"	14.7
29' 31"	32.1	38' 5"	14.15
29' 55"	30.9	38' 27"	13.75
30' 10"	30.3	38' 42"	13.35
30' 23"	29.6	39'	13
30' 40"	28.9	39' 16"	12.6
30' 55"	28.3	39' 31"	12.2
31'	28	39' 49"	11.9

Set # 8 - continued

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
40' 15"	11.35	47' 9"	5.9
40' 49"	10.65	47' 26"	5.75
41' 3"	10.35	47' 38"	5.6
41' 18"	10.05	48' 11"	5.29
41' 39"	9.65	48' 24"	5.18
41' 59"	9.3	48' 41"	5.06
42' 13"	9.0	49' 1"	4.87
42' 30"	8.75	49' 16"	4.74
42' 39"	8.6	49' 29"	4.62
42' 50"	8.45	49' 44"	4.51
43' 1"	8.3	50' 7"	4.33
43' 10"	8.15	50' 24"	4.21
43' 28"	7.95	50' 41"	4.10
43' 37"	7.8	50' 57"	3.99
43' 49"	7.68	51' 14"	3.86
44'	7.57	51' 33"	3.72
44' 48"	7.4	52'	3.54
45' 3"	7.2	52' 35"	3.31
45' 22"	6.96	52' 53"	3.19
45' 42"	6.8	53' 13"	3.01
45' 58"	6.6	53' 34"	2.78
46' 20"	6.36	54' 2"	2.65
46' 40"	6.18	54' 14"	2.59
46' 57"	6.0	54' 29"	2.50

BENDS AT 5.8, 10.5, 39, 88.

B

A

A

B

PRESSURE IN MICRONS

PRESSURE IN MICRONS.
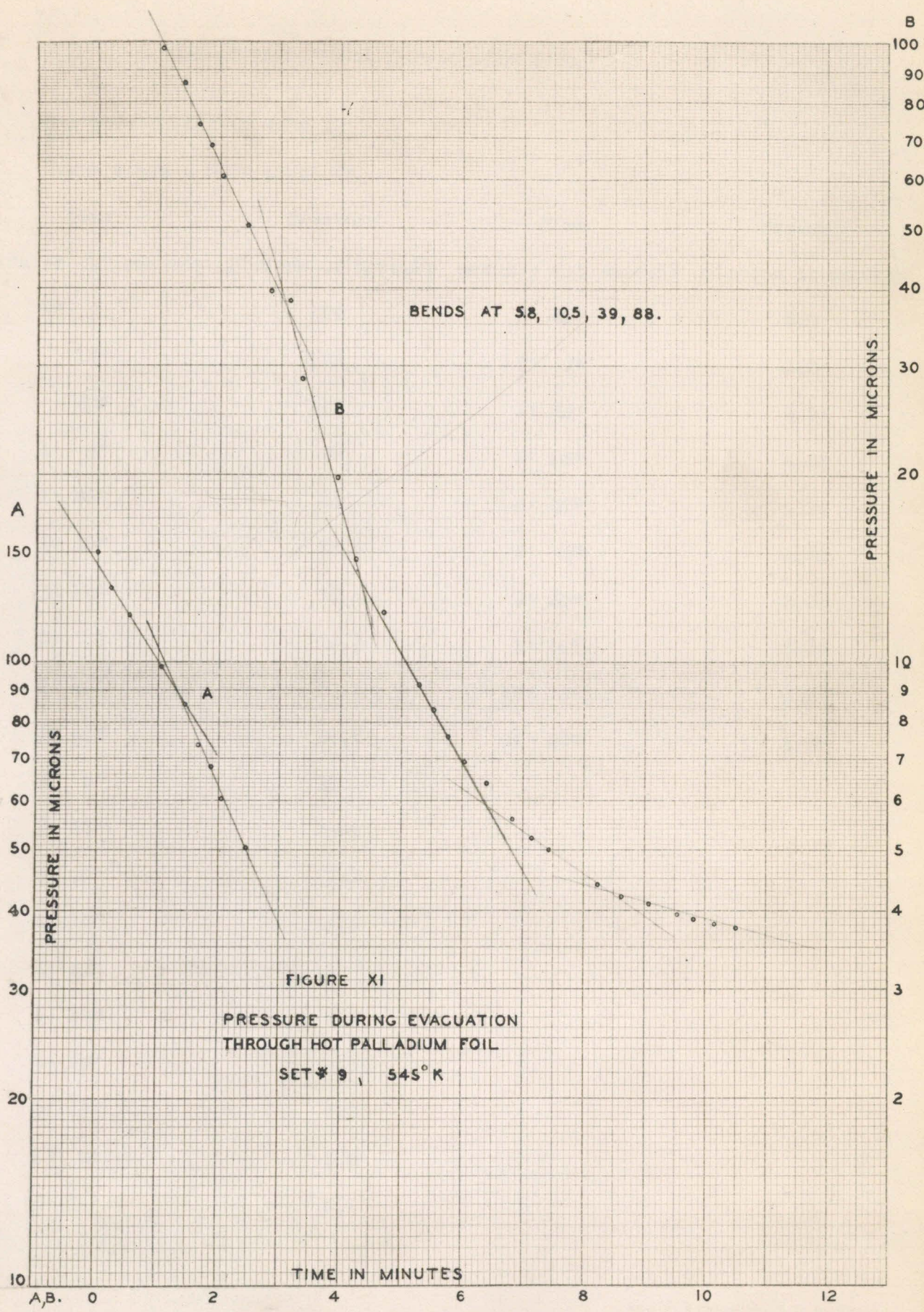
FIGURE XI

PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL

SET # 9, 545° K

TIME IN MINUTES

A,B.

PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 9. Palladium tube A.

Temperature = 545° Absolute

Time minutes and seconds	Pressure microns of mercury	Time minutes and seconds	Pressure microns of mercury
0'	150	6' 49"	5.6
13"	132	7' 9"	5.2
32"	119	7' 25"	4.95
1' 4"	98	8' 13"	4.42
1' 25"	86	8' 37"	4.24
1' 39"	73.5	9' 5"	4.05
1' 50"	68	9' 33"	3.94
2' 3"	60.3	9' 48"	3.88
2' 27"	50.3	10' 9"	3.8
2' 50"	39.7	10' 30"	3.75
3' 9"	38		
3' 21"	28.6		
3' 56"	19.9		
4' 14"	14.6		
4' 42"	12		
5' 18"	9.2		
5' 32"	8.35		
5' 47"	7.6		
6' 3"	6.9		
6' 24"	6.4		

FIGURE XII
PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL

SET ✳ 10, 601°K
SET ✳ 11, 601°K

✳ 10 BENDS AT 9.5, 21, 30, 40.
✳ 11 BENDS AT 12.5, 22.

PRESSURE IN MICRONS OF MERCURY

TIME IN MINUTES

10 B

11

10 A
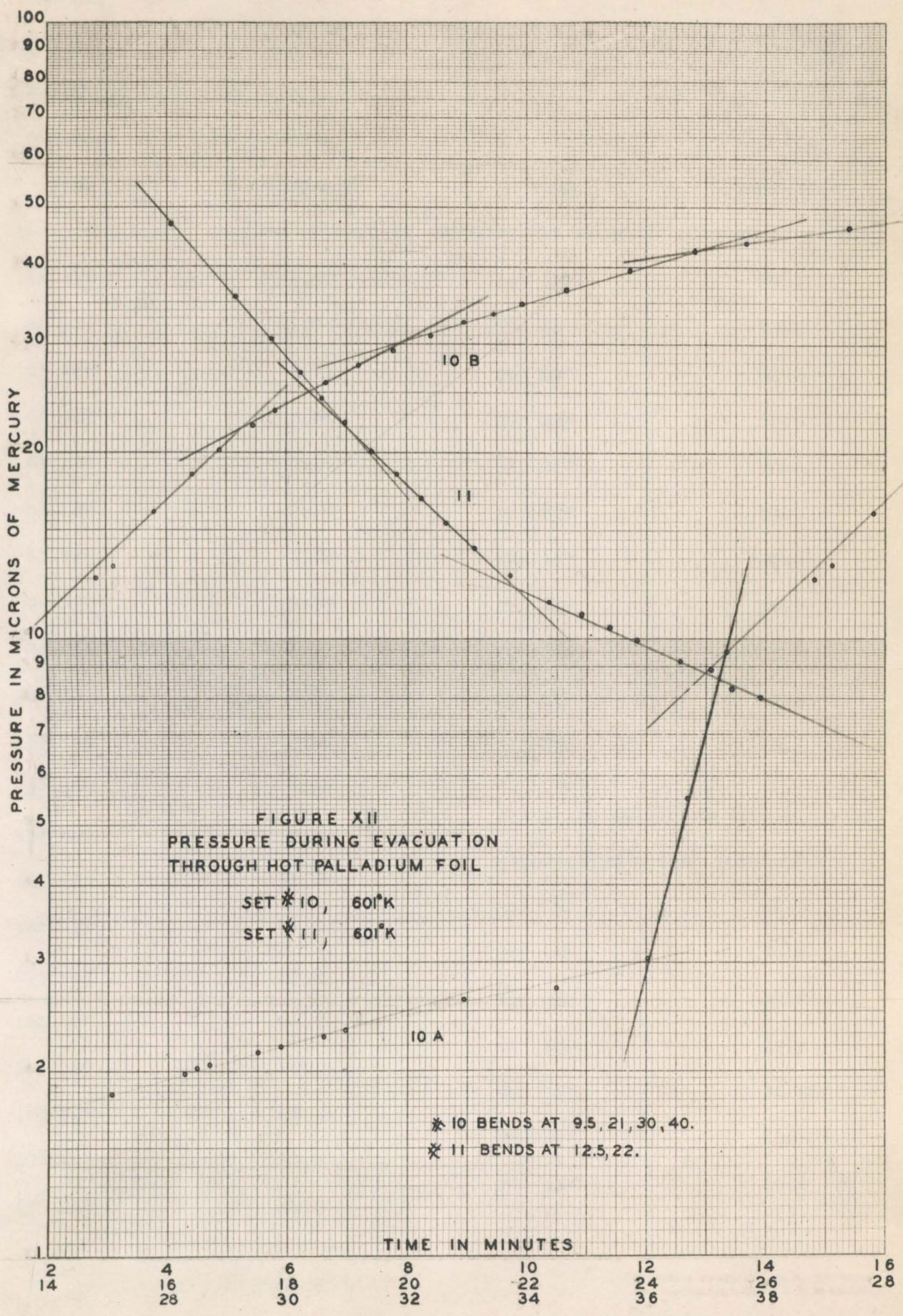
PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 10. Palladium tube A.

Temperature - 601° Absolute.

Time minutes and seconds	Pressure microns of mercury	Time minutes and seconds	Pressure microns of mercury
3' 4"	1.83	19' 12"	27.7
4' 17"	1.98	19' 46"	29.2
4' 29"	2.01	20' 24"	31.0
4' 42"	2.04	20' 57"	32.4
5' 31"	2.14	21' 27"	33.6
5' 53"	2.19	21' 56"	34.9
6' 36"	2.28	22' 40"	36.8
6' 57"	2.33	23' 44"	39.7
8' 57"	2.61	24' 50"	42.3
10' 30"	2.73	25' 41"	43.8
12' 2"	3.03	27' 23"	46.4
12' 40"	5.53		
13' 20"	9.53		
14' 50"	12.53		
15' 7"	13.2		
15' 48"	16.0		
16' 26"	18.4		
16' 53"	20.1		
17' 27"	22.1		
17' 49"	23.2		
18' 39"	25.8		

Set # 11. Palladium tube A.

Temperature - 601° Absolute.

Time	Pressure
28' 4"	47.0
29' 8"	35.8
29' 45"	30.6
30' 13"	27.0
30' 35"	24.45
30' 59"	22.3
31' 26"	20.1

Set # 11 - continued

Time	Pressure
minutes and seconds	microns of mercury
31' 50"	18.4
32' 13"	16.9
32' 39"	15.4
33' 6"	14.0
33' 42"	12.7
34' 23"	11.55
34' 54"	10.88
35' 22"	10.4
35' 50"	9.95
36' 34"	9.2
37' 5"	8.68
37' 26"	8.29
37' 55"	8.0

FIGURE XIII
PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL.
SET#12 , 720°K.

BENDS AT 806 102 128 15 245 76 (?)
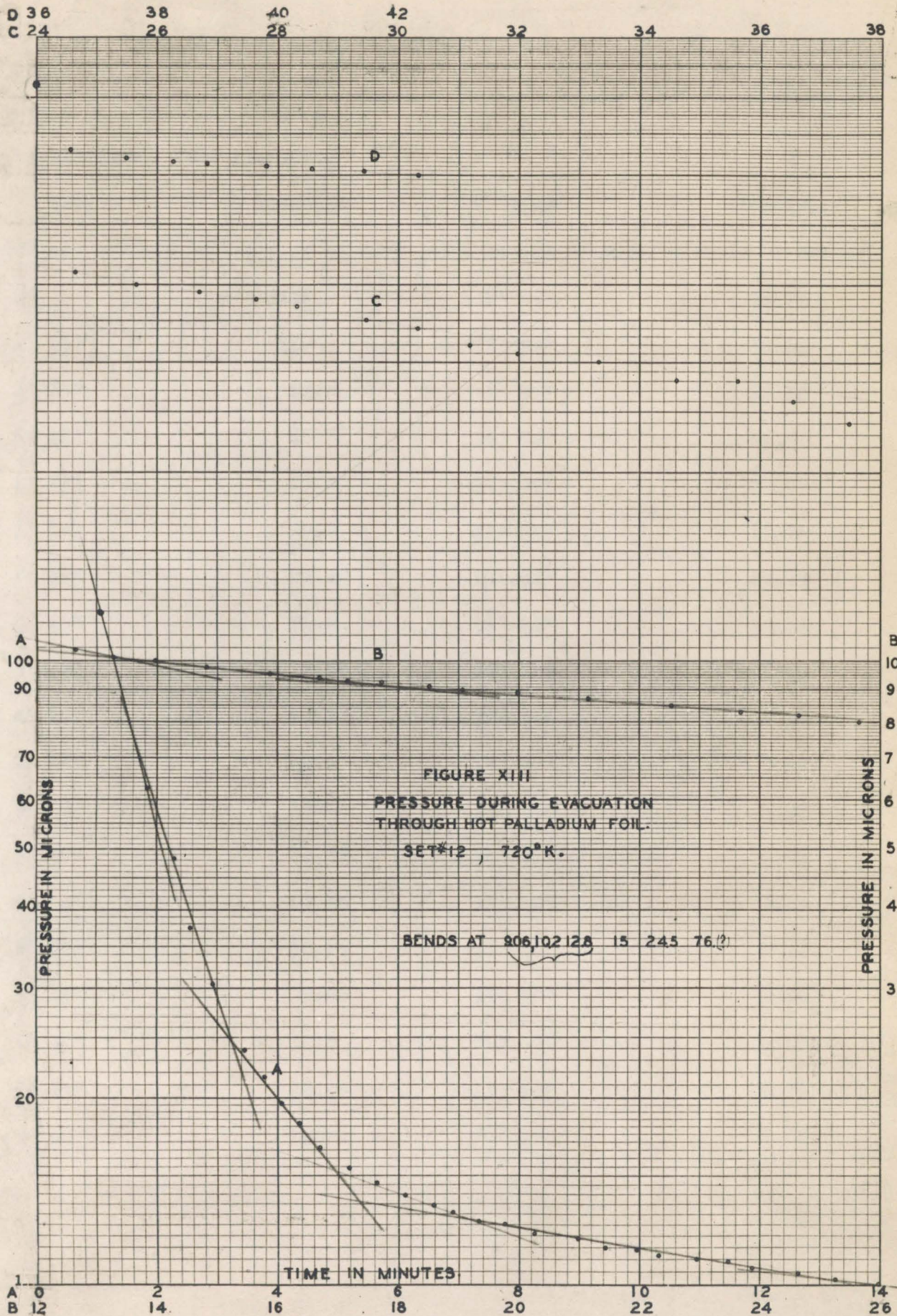
PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 12. Palladium tube A.

Temperature - 720° Absolute.

Time minutes and seconds	Pressure microns of mercury	Time minutes and seconds	Pressure microns of mercury
0'	832	9'	11.78
1' 33"	110	9' 27"	11.54
1' 50"	62.5	9' 57"	11.41
2' 17"	48	10' 19"	11.2
2' 32"	37.5	10' 57"	10.97
2' 55"	30.3	11' 29"	10.75
3' 27"	23.85	11' 53"	10.64
3' 41"	21.6	12' 37"	10.42
4' 3"	19.55	13' 15"	10.22
4' 21"	18.2	13' 58"	10.02
4' 42"	16.6	14' 48"	9.83
5' 10"	15.39	15' 52"	9.63
5' 39"	14.55	16' 41"	9.44
6' 6"	13.86	17' 8"	9.34
6' 35"	13.35	17' 42"	9.25
6' 54"	13.08	18' 30"	9.08
7' 20"	12.7	19' 4"	9.00
7' 46"	12.48	19' 58"	8.85
8' 16"	12.13	21' 10"	8.66

Set # 12 - continued

Time	Pressure
minutes and seconds	microns of mercury
22' 31"	8.48
23' 41"	8.32
24' 38"	8.17
25' 39"	8.02
26' 42"	7.9
27' 37"	7.8
28' 18"	7.69
29' 27"	7.5
30' 20"	7.37
31' 11"	7.24
31' 59"	7.12
33' 20"	6.95
34' 38"	6.76
35' 37"	6.65
36' 34"	6.55
37' 29"	6.41
38' 16"	6.31
38' 51"	6.27
39' 48"	6.20
40' 33"	6.15
41' 25"	6.08
42' 20"	6.00
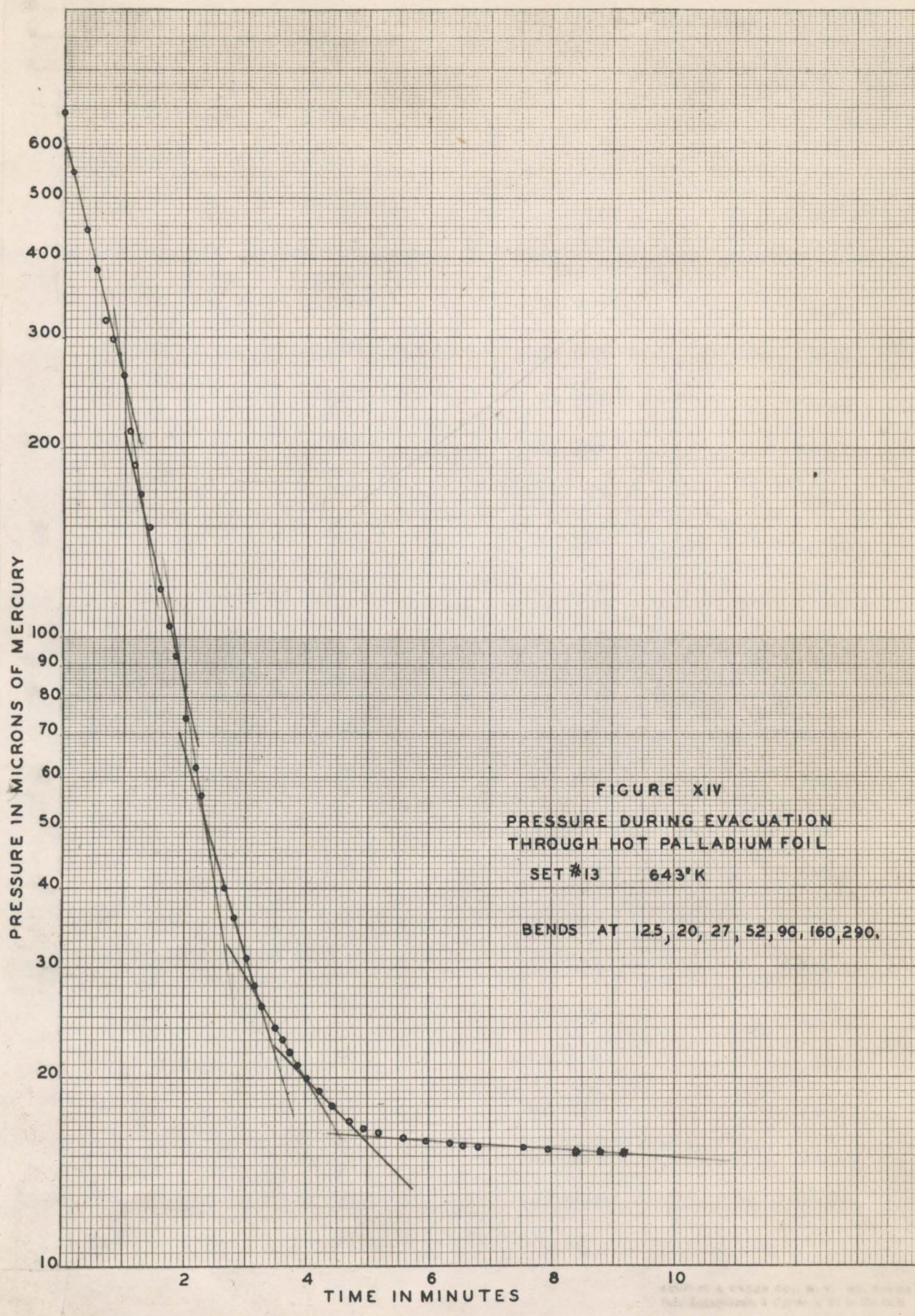
FIGURE XIV

PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL

SET #13   643°K

BENDS   AT 12.5, 20, 27, 52, 90, 160, 290,

PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 13. Palladium tube A.

Temperature – 643° Absolute.

Time	Pressure	Time	Pressure
minutes and seconds	microns of mercury	minutes and seconds	microns of mercury
0'	680	3' 32"	23.8
8"	550	3' 39"	22.6
22"	445	3' 45"	21.6
33"	385	3' 54"	20.5
41"	318	4' 2"	19.55
49"	298	4' 14"	18.55
58"	260	4' 27"	17.65
1' 6"	212	4' 42"	17.1
1' 11"	187	4' 57"	16.6
1' 17"	168	5' 12"	16.28
1' 25"	149	5' 36"	16.00
1' 36"	118	5' 57"	15.8
1' 45"	104	6' 21"	15.69
1' 51"	93	6' 34"	15.6
2' 1"	74	6' 50"	15.53
2' 10"	62	7' 33"	15.4
2' 17"	56	7' 57"	15.31
2' 41"	40	8' 24"	15.24
2' 50"	35.6	8' 49"	15.15
3' 3"	30.8	9' 10"	15.1
3' 11"	28.3		
3' 18"	26.3		

FIGURE XV

PRESSURE DURING EVACUATION
THROUGH HOT PALLADIUM FOIL

SET 14   590°K

BENDS AT 3.75 , 5 , 10.5   33 ,

PRESSURE IN MICRONS OF MERCURY

TIME IN MINUTES
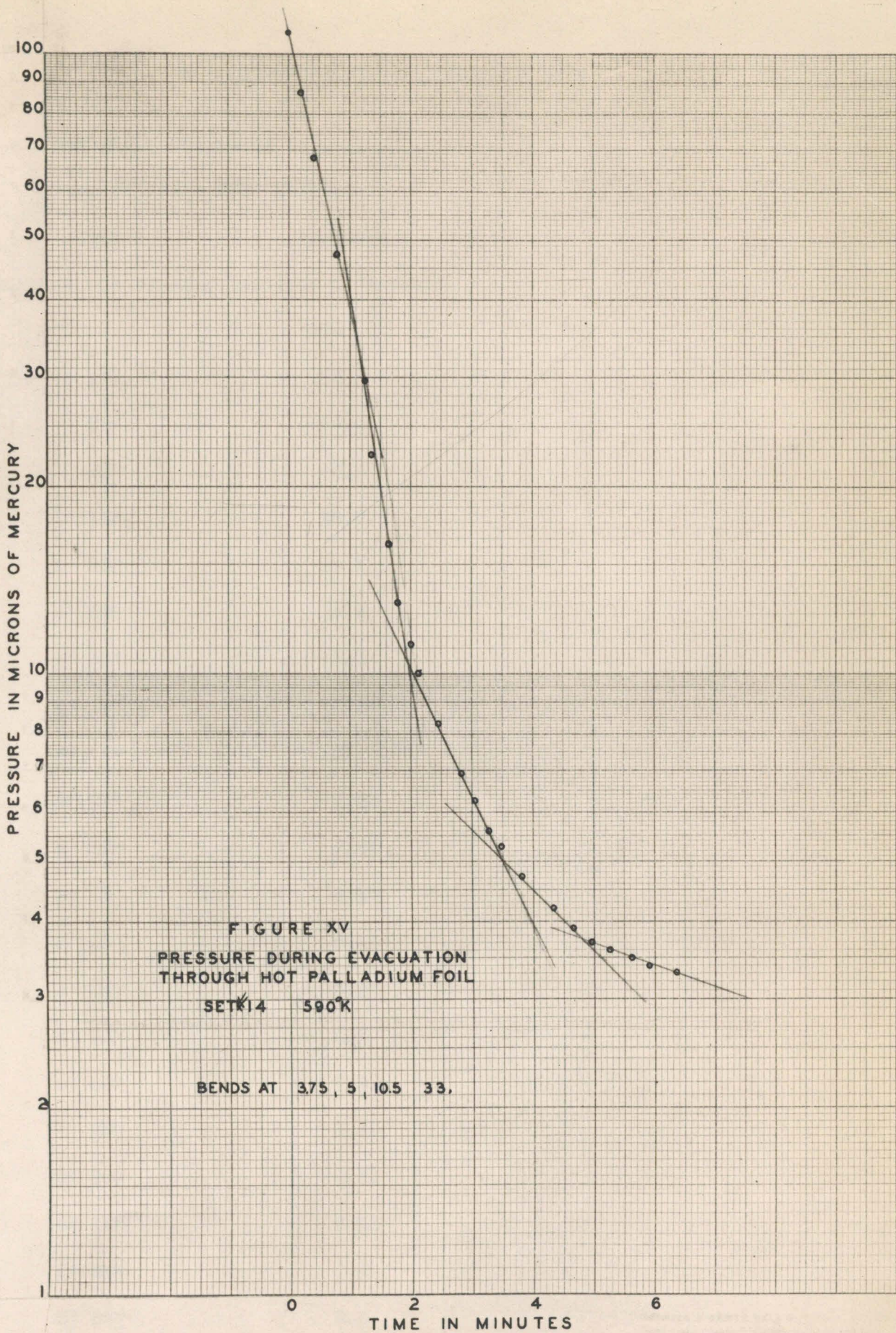
PALLADIUM-HYDROGEN TRANSMISSION DATA

Set # 14. Palladium tube A.

Temperature - 590° Absolute.

Time minutes and seconds	Pressure microns of mercury
0'	108
13"	87
25"	67.9
46"	47.2
1' 16"	29.5
1' 22"	22.6
1' 39"	16.3
1' 50"	13.2
2' 2"	11.05
2' 9"	10.
2' 28"	8.32
2' 50"	6.92
3' 3"	6.25
3' 17"	5.6
3' 28"	5.3
3' 50"	4.7
4' 20"	4.2
4' 39"	3.92
4' 58"	3.74
5' 17"	3.61
5' 38"	3.5
5' 55"	3.4
6' 22"	3.3
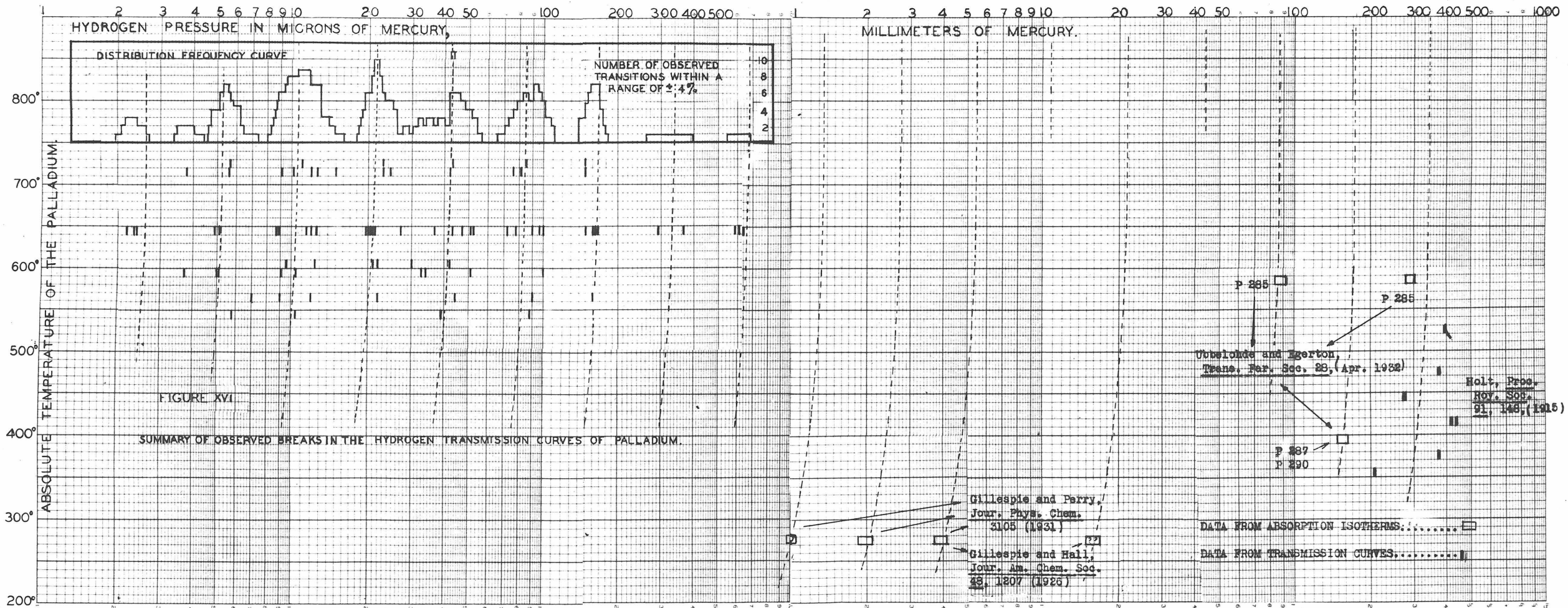
FIGURE XVI

SUMMARY OF OBSERVED BREAKS IN THE HYDROGEN TRANSMISSION CURVES OF PALLADIUM.

V.   A SUGGESTED EXPLANATION FOR THE RESULTS

A.   The relation of hydrogen concentration to secondary lattice spacing

The present section will anticipate the results of the tentative theory somewhat in order to summarize the data more effectively and prepare the concepts to be used in the more formal section below.

When hydrogen is absorbed by palladium the hydrogen is distributed along certain equidistant planes[13] of low potential which are an intrinsic property of the metal.   This peculiar distribution of hydrogen is illustrated by the heavy line lattice of figure XVII.   The possible surface density of hydrogen along these planes is limited.   Most of the hydrogen atoms bear positive charges,[27] so that subsequently absorbed hydrogen is repelled by the first set of planes and must form a new set of planes (indicated by the dotted lines of figure XVII) as remote as possible from the first set.   It is suggested that the repulsion

Figure XVII.
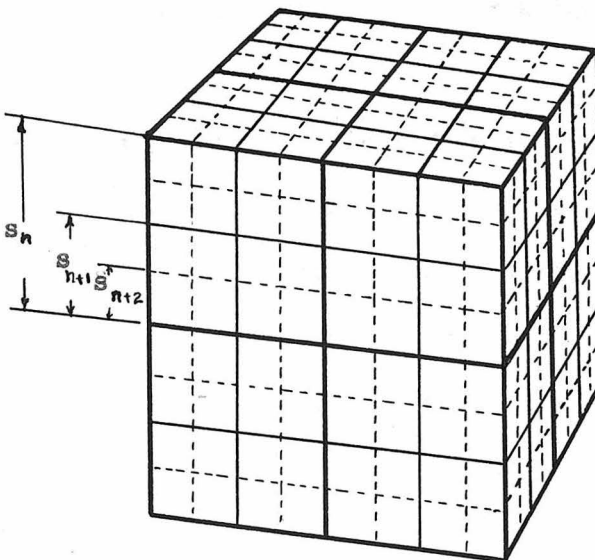
exerted by the first set upon the hydrogen which is entering to form the second set may result in a pressure threshold, which the external hydrogen must exceed before the internal hydrogen concentration can be increased.

It is natural to assume that a plane of hydrogen is combined with a single layer of primary lattice cubes, and it will be shown below that this assumption best fits all the evidence.

Each primary face-centered cube is associated with four atoms of palladium.[7] Those which lie in the hydrogen-rich planes bear either none at all or two atoms of hydrogen, in the form of the partly stable hydride $Pd_4 H_2$.[7] The proportions $Pd_4 H_2$ are established by a study of concentration pressure diagrams of hydrogen in palladium. No evidence has been found for a hydride having proportions $Pd_4 H$.[7]

Having assumed that each hydrogen-rich plane is a plane of primary cubes, and knowing that each cube must bear two hydrogen atoms (at low temperatures), one is in a position to relate any given critical hydrogen palladium concentration to a particular secondary plane spacing. In turn, each critical concentration may be related to a corresponding threshold pressure if one can relate a single concentration to its respective threshold pressure.

Figure XVIII shows a plot of data obtained from the work of Gillespie and collaborators.[7] It will be seen that if these assumptions are valid the set of hydrogen planes which was established at the 2 mm. pressure step was filled when the concentration reached 1.5 cc. per gram, where the pressure begins again to rise. Hence the ratio of empty elementary cubes to hydrogen bearing cubes is 35 to one (52.5 cc. per gram = $Pd_4 H_2$).

If all the hydrogen bearing elements lie on a rectangular secondary
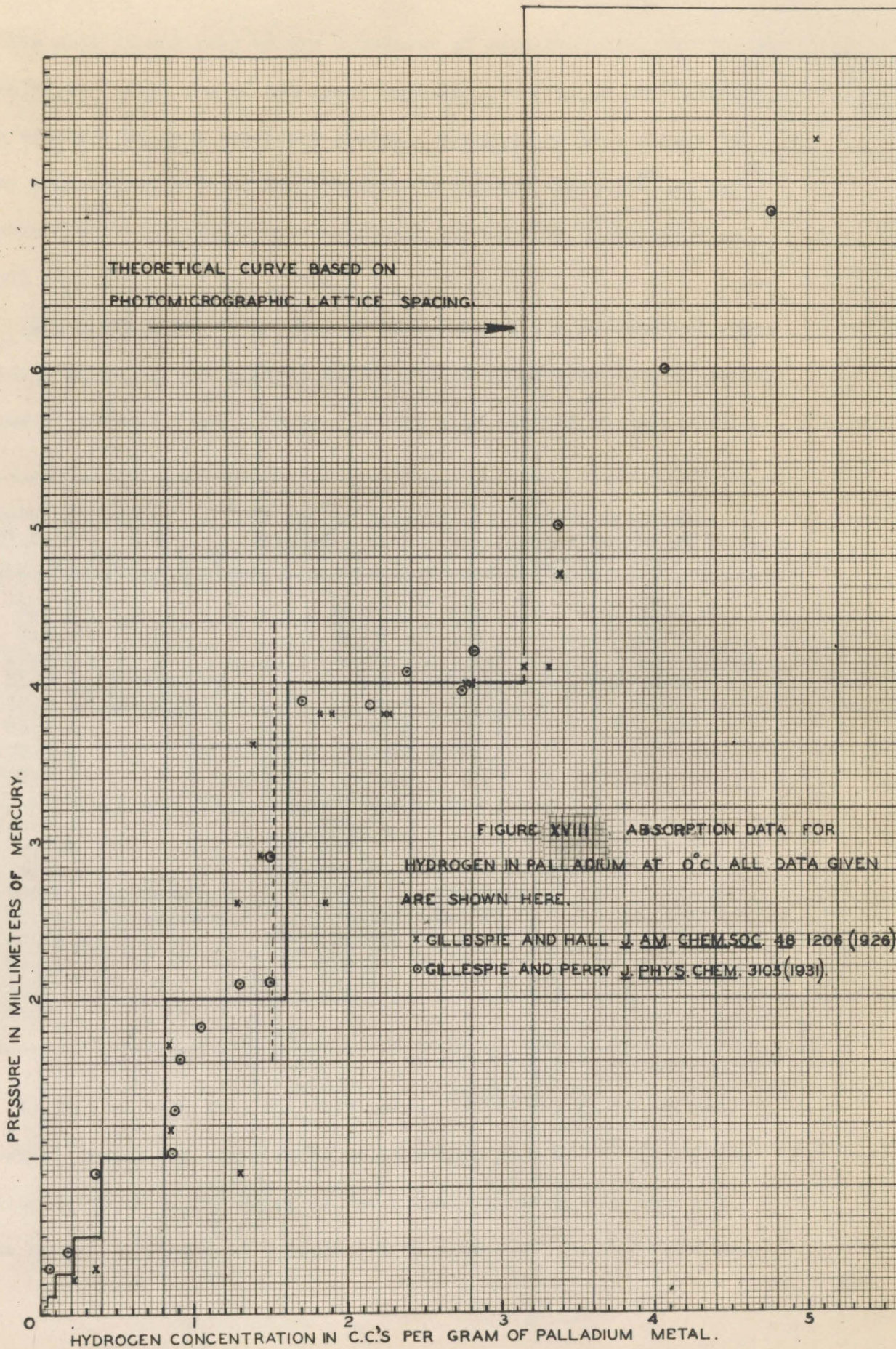
THEORETICAL CURVE BASED ON
PHOTOMICROGRAPHIC LATTICE SPACING.

FIGURE XVIII . ABSORPTION DATA FOR
HYDROGEN IN PALLADIUM AT 0°C. ALL DATA GIVEN
ARE SHOWN HERE.
× GILLESPIE AND HALL J. AM. CHEM.SOC. 48 1206 (1926).
⊙ GILLESPIE AND PERRY J. PHYS. CHEM. 3105 (1931).

PRESSURE IN MILLIMETERS OF MERCURY.

HYDROGEN CONCENTRATION IN C.C.'S PER GRAM OF PALLADIUM METAL.

lattice made up entirely of one thickness of such elements, the spacing demanded by a solution of the cubic equation involved is 104 primary cube elements between secondary planes. Applying to this figure the x-ray measurement 3.95 A° for the primary lattice spacing,[28] it may be seen that the distance between planes at the 2 mm. pressure step is 402 A°.

It follows immediately that if this explanation is accepted, the critical pressures are related to the secondary lattice spacing in the scheme of columns A and B below. Column A is plotted on figure XVI.

Critical Pressure (400° C.) A		Secondary Lattice spacing. B		Photomicrographic measurements of lattice spacing. C
2.6		41.0		37.8
5.3		20.56		18.9
10.6		10.28		9.5
21.25	Microns of	5.14	Microns	4.8
42.5	Mercury	2.57		2.4
85.0		1.2864		1.25
170.0		.6432		
340.0		.3216		
.680		1608.0		
1.360		804.0		
2.720		402.0		
5.44		201.0		
10.88	Millimeters	100.5	Angstrom	
21.76	of Mercury	50.25	Units	
43.52		25.125		
87.04		12.56		
174.0		6.25		
348.0		3.12		

It will be seen that the last member of the series of critical pressures (which was observed by Holt) refers to a secondary lattice spacing which is of the order of the primary spacing, but does not agree exactly. It may be concluded from this that the tentative model

of structure agrees with the experimental indications as to the total
number of discontinuities. It is concluded that if hydrogen is led
into palladium at low pressures it will form planes in a regular
spacing which is not an exact multiple of the primary spacing but
instead fits a secondary "verhakung." As more and more sets of planes
of hydrogen grow through the lattice, a situation in which the demands
of the primary spacing are such as to make the secondary spacing
unstable for the hydrogen planes is implied. The only available
primary planes will be too far from the center position of the secondary
lattice. It may be this incommensurateness of the secondary spacing
which makes it difficult to obtain the discontinuous isotherms at the
higher pressures, for there the secondary lattice of foreign atoms
should break down and go into solution chaotically. The only truly
reproducible discontinuities at high pressures (probably) are the ones
described by Holt[22] and perhaps one or two neighboring transitions as
obtained by Ubbelohde.[32] These men began with saturated palladium and
studied the dynamic isotherms as hydrogen was drawn from a saturated
lattice.

The fact that the concentration of hydrogen at the two millimeter
step, as measured by Gillespie and co-workers,[7] can be used by the
theory to relate the threshold pressures to the lattice spacings, in
such a way that the smallest possible secondary spacing fits the
largest measured pressure threshold, is regarded as confirmation of the
theory. On the other end of the series it is observed that the 41
microns predicted is very near the 150 micron thickness of the foil
used.

In all there is room for eighteen pressure thresholds between the photomicrographically observed 37.8 micron spacing and the x-ray (3.95 A°) primary spacing. There is some experimental evidence for the existence of all but two of these. The two which have not been observed are in a region where the theory predicts difficulty because the secondary series and the primary spacing are incommensurate.

B. Quantitative statement of the theory

A homogeneous metal lattice will be everywhere neutral if the volume considered is large enough to include several atoms. Let a plane of ionised foreign atoms be thrust into the lattice. It is evident that as the electrons concerned have a relatively large a priori volume in which to disperse themselves, there will be an excess of positive charge in the neighborhood of the plane of foreign atoms. A surplus foreign atom, being positive, will be repelled from the immediate neighborhood of the plane, and later planes will be spaced therefore at distances apart that are as great as the volume of metal permits, being also restricted by the secondary structure of the metal. From symmetry it may be inferred that such a secondary structure of foreign atoms will comprise three dimensions, particularly in a lattice known to be cubical.

Let it be assumed that a set of such planes of hydrogen or other ionised impurity is formed. What is the distribution of potential ascribable to these planes and how will this potential affect the formation of the succeeding sets of planes?

The laws governing the potential distribution will be those used in treating the distribution of electrons near a hot metal surface:

$$\nabla^2 V = 4\pi\varepsilon\sigma$$

σ = volume density of charge.

$$\frac{\sigma}{\sigma_0} = e^{\frac{\varepsilon(V-V_0)}{KT}}$$

ε = dielectric constant of the palladium lattice when devoid of the valence electrons.

and the differential equations to be solved (in one dimension) are:

$$\frac{d^2V}{dx^2} = 4\pi\varepsilon\sigma \quad ; \quad \overline{\sigma} = \overline{\sigma}_0 e^{\frac{\varepsilon V}{KT}}$$

The boundary conditions used are, (see figure XIX)

$$\text{at } X = 0; \quad \frac{dV}{dX} = 0, \quad V = 0, \quad \sigma = \sigma_0$$

The solution is:[30]

$$V = -\frac{2KT}{\varepsilon} \log \cos\left(\left\{\frac{2\pi\varepsilon^2\sigma_0}{KT}\right\}^{\frac{1}{2}} X\right)$$
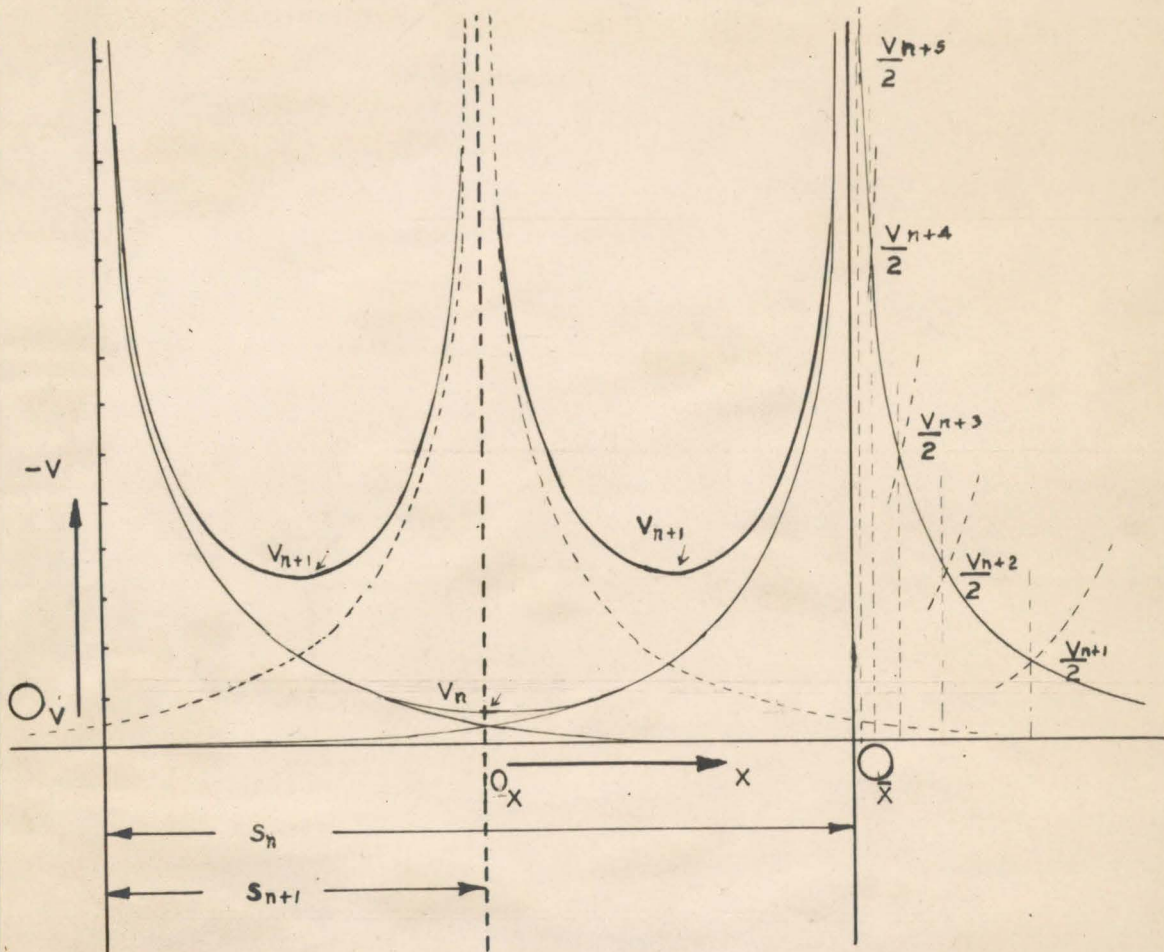
FIGURE XIX.

It is evident that the next set of planes of foreign atoms must form midway between the planes of the previous set, for there the potential is lowest, and the critical concentration of foreign atoms will be built up there first as the external pressure of foreign atoms increases. The only information which might fix σ is the fact that at the plane there are two positive charges for every elementary cube in the plane of cubes. This boundary condition is hard to use because at the plane V approaches infinity.

Consider the effect on the original electron distribution of the formation of the new planes of foreign atoms. There will be no mutual induction effects, for every electron is in equilibrium under the opposing vectors of concentration gradient and potential gradient. Adding directly the solid line potential and the subsequent dotted line potential:

$$V_{n+1} = \frac{-2KT}{\epsilon}\left[\log\cos\left(\left\{\frac{2\pi\epsilon^2\sigma_0}{KT}\right\}^{\frac{1}{2}}X\right) + \log\cos\left(\left\{\frac{2\pi\epsilon^2\sigma_0}{KT}\right\}^{\frac{1}{2}}X + \frac{\pi}{4}\right)\right]$$

$$= -\frac{2KT}{\epsilon}\log\cos 2\left\{\frac{2\pi\epsilon^2\sigma_0}{KT}\right\}^{\frac{1}{2}}X .$$

Hence, the effect of adding two sets of planes at distance S, to get a double set having distance S/2, is the same as would have been obtained if the spacing S/2 had been used in the original calculation.

It is therefore true that the variation of the potential of the space midway between the planes, as the number of planes is successively doubled, may be obtained from the single curve of potential for one spacing and having a fixed σ_0. Namely, the subsequent lowest potentials V_n are given by:

$$V_n = V_s\left(\frac{S-X}{2^n}\right)$$

or if the coordinates are shifted so as to make x = 0 at the plane instead of midway between the planes

$$V_n = V_s\left(\frac{\bar{X}}{2^n}\right) = -\frac{2KT}{\varepsilon}\log\sin\left(\left\{\frac{2\pi\varepsilon^2\sigma_o}{KT}\right\}^{1/2}\frac{\bar{X}}{2^n}\right)$$

As most members of this series are close to the plane

$$V_n = -\frac{2KT}{\varepsilon}\log\left\{\frac{2\pi\varepsilon^2\sigma_o}{KT}\right\}^{1/2}\frac{\bar{X}}{2^n} \qquad (1).$$

This formula fixes the height of the potential barrier which the ionised foreign atoms must pass in order to get into the palladium at the place where the successive planes form. The successive values of the potential are indicated on figure XIX, being at the intersections of the potential graph with abscissae, each of which is half as far from the boundary as the previous abscissa.

In the process of passing into the interior of the metal, the hydrogen molecule must be adsorbed to the surface, atomised, ionised and probably distorted by the forces of the metal. In the case of hydrogen in palladium all this results in the release of energy as:

$$H_2 + 4\ Pd = 2\ Pd_2\ H_1 + 9280 \text{ at } 0° \text{ C., 1 atm.}[29]$$
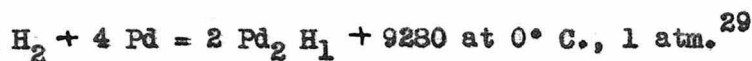
It is assumed that these things remain constant with pressure and their effect is lumped into the constant $\propto$. Thus, if N is the number of molecules per cc. at the surface of the palladium, the number per cc. penetrating the potential minimum depends on the potential in this way

$$\rho = N\propto e^{-\frac{V}{KT}}$$

It has been shown that the potential takes a series of discrete values V_n. Substituting from (1)

$$\rho_n = N_n\propto e^{-\frac{1}{KT}\left(-\frac{2KT}{\varepsilon}\log\left(\left\{\frac{2\pi\varepsilon^2\sigma_o}{KT}\right\}^{1/2}\frac{\bar{X}}{2^n}\right)\right)} \equiv N_n\propto\left\{\left(\frac{2\pi\varepsilon^2\sigma_o}{KT}\right)^{1/2}\frac{\bar{X}}{2^n}\right\}^{2/\varepsilon}$$

$$= N_n\frac{C}{T^{1/2}}\left(\frac{\bar{X}}{2^n}\right)^{2/\varepsilon} \cdots \cdots \cdots \qquad (2).$$

$$\left\lceil C = \left(\frac{2\pi\varepsilon^2\sigma_o}{K}\right)^{1/2}\right.$$

At a critical value of ρ , the same for every n, a new set of planes is formed. By equating ρ_n to ρ_{n+1}, the ratio of the successive N_s

$$\frac{N_n + 1}{N_n} \quad \left(= \frac{P_{n+1}}{P_n}\right) = \left[\frac{\frac{\overline{X}}{2^n}}{\frac{\overline{X}}{2^{n+1}}}\right] = 2^{2/\varepsilon} \ - - - - - \ (3).$$

$\lceil P = pressure.$

is obtained.

At a fixed temperature, then, each successive critical pressure is $2^{2/\varepsilon}$ times as great as the preceding pressure. This prediction is fulfilled by the experimental evidence given above and is in agrmement with many other discontinuous absorption isotherms in metals.*

---

* The pressure steps which Benton[5] finds in the absorption isotherms of copper, nickel and iron are generally in a series which is not quite geometric. It is apparent that in the case of copper, ε , in the formula

$$\frac{P_{n+1}}{P_n} = 2^{2/\varepsilon}$$

is a larger number than 2 and may vary as the polarizability of the atoms varies with the field strength. It is probable that the atoms have different polarizabilities in different directions, so that in the case of magnetic materials in which the orientation varies systematically with the secondary structure, the symbol ε will have to be written as a function of n.

If the temperature is permitted to vary, it would be expected from formula (2) that each critical pressure would vary with the square root of the absolute temperature. There is an indication in the above summary (figure XVI) of a decrease in p_n with temperature which is greater for low temperatures.*

---

* In order to obtain a competent theory of temperature variation it is probable that one must treat the intermediate processes lumped in the above constant α .

The pressure thresholds of the above suggested theory have been

calculated in one dimension. The superposition of two other sets of orthogonal planes of bound atoms with associated electrons may be accomplished by direct addition of the potentials, since all positive charges are assumed to be bound.

It would be expected from this explanation that critical values of the hydrogen pressure might be found separately for the planes perpendicular to each axis. The critical pressure of every completed cubical secondary lattice would be double the completed cubical lattice of the next larger spacing, but the possibility of the existence of two intermediate smaller discontinuities is not excluded by the theory. This is seen in some of the recent adsorption isotherms of Burrage.[31] There are intermediate bends in some of the logarithmic curves of the present paper which may be so interpreted. The data are as yet incompetent to establish a "fine structure."

C. Test of the theory from the general shape of absorption isotherms

The above theory states that a new set of planes of hydrogen atoms strikes through the metal at every one of the critical pressures listed. This definitely fixes the concentration as a function of the pressure. Having related a particular spacing of the above geometric series to its respective pressure discontinuity (by an absorption measurement) one is in a position to calculate the concentration to be expected at all other pressures.

This law is derived on the assumption that the temperature is such that every cube element of a plane of palladium cubes has its full complement of hydrogen (each cube $Pd_4 H_2$).

Let the primary lattice be a, and let the distance between planes of hydrogen atoms be s (see figure XVII). By a plane of hydrogen atoms is meant the atoms which are contained in a slab of elementary cubes of thickness a, in which each cube holds two hydrogen atoms. The number of hydrogen atoms per unit area of such a plane is $2 (1/a)^2$. Counting all the atoms on all the planes of a unit cube independently the figure N_p is arrived at for the number of atoms on the planes.

$$N_{planes} = 3 \cdot 1/s \cdot 2 (1/a)^2$$

Along the intersections of such planes there are lines of common atoms which have been counted twice and corner atoms which have been included three times in the figure N_p. Correcting for these duplications

$$N_t = 3 \cdot \frac{1}{s} \cdot \frac{2}{a^2} - 3 \cdot \frac{1}{s^2} \cdot \frac{2}{a} + 2 \frac{1}{s^3}.$$

There are four palladium atoms to every elementary face-centered cube, making a total of :

$$N_{Pd} = 4 \cdot \frac{1}{a^3}.$$

The ration of number of hydrogen to number of palladium atoms is thus:

$$\text{Concentration} = N_t = \frac{3 \cdot \frac{1}{s} \cdot \frac{2}{a^2} - 3 \cdot \frac{1}{s^2} \cdot \frac{2}{a} + 2 \frac{1}{s^3}}{\frac{4}{a^3}}$$

$$= 1.5 \frac{a}{s} - 1.5 \left(\frac{a}{s}\right)^2 + .5 \left(\frac{a}{s}\right)^3.$$

s may take a geometric series of values based on a secondary spacing π which is a fundamental property of the metal, namely:

$$s = \pi \cdot 2^{\frac{n\varepsilon}{2}}$$

where n takes a series of integral values, each of which refers to a particular number of a geometric series of critical pressures as well as to the spacing involved. Thus,

$$\frac{P_o}{P_n} = 2^{\frac{n\varepsilon}{2}}$$

where p_o is a pressure depending on the degree of ionisation, etc. of the hydrogen or other impurity involved. This theory is as yet not competent to decide which pressure threshold refers to which spacing, but if one pair can be related experimentally, the relations of all the others will be known. The data of figure XVIII is used to relate the two millimeter pressure step at 0° C. to a lattice spacing of 402 A°. Because the microphotographs (described in the next section) are probably more accurate than the position of the dotted line of figure XVIII this figure is corrected to 379 microns, which is the corresponding value in the series extrapolated from 39.5 microns as a convenient microscopically determined base. Also for convenience, 19.5 microns is chosen as the corresponding pressure base ($19.5 = 2$ mm. $\times \frac{1}{210}$).

This results in the following formula for the highest concentrations C_{p_n} at each pressure threshold:

$$C_{p_n} = 1.5 \times \frac{3.95 \times 10^{-8}}{3.95 \times 10^{-3}} \times \frac{P_n}{1.95 \times 10^{-3}} - 1.5 \times \left(\frac{3.95 \times 10^{-8}}{3.95 \times 10^{-3}} \times \frac{P_n}{1.95 \times 10^{-3}}\right)^2$$

$$+ .5 \times \left(\frac{3.95 \times 10^{-8}}{3.95 \times 10^{-3}} \times \frac{P_n}{1.95 \times 10^{-3}}\right)^3.$$
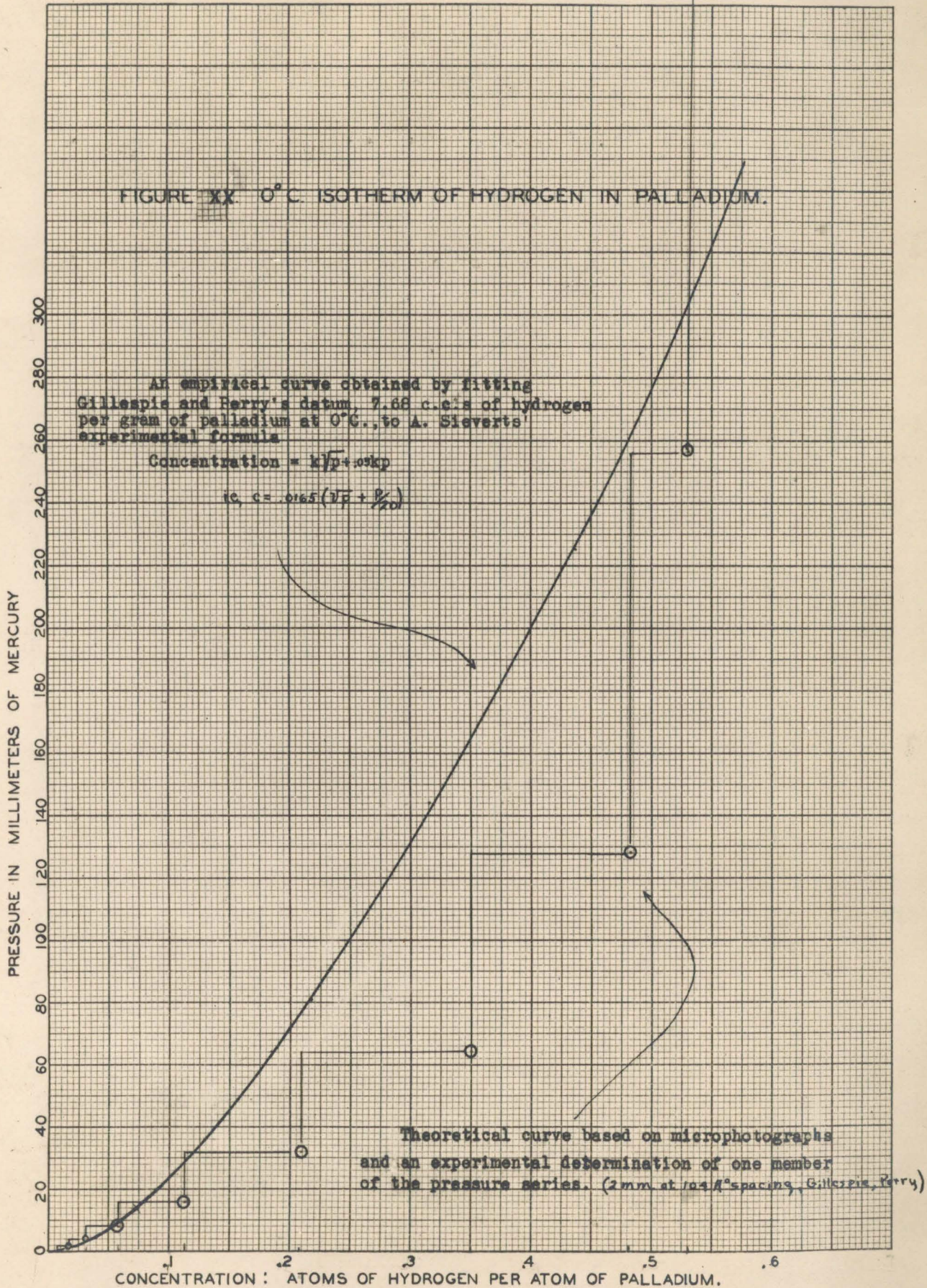
$$= 1.5 \times \frac{P_n}{195} - 1.5 \left(\frac{P_n}{195}\right)^2 + .5 \left(\frac{P_n}{195}\right)^3. \tag{4}$$

P in cms. Hg

C in $\dfrac{\text{Atoms of H}}{\text{Atoms of Pd}}$.

The values of C_{p_n} are shown on figure XX as circles. The solid line represents the manner in which the concentration should vary with the pressure if the secondary lattice persists unbroken into the higher pressures. The low pressure end of the curve is shown on figure XVIII as a solid line. The pressures used there are taken from figure XVI.

FIGURE XX O°C. ISOTHERM OF HYDROGEN IN PALLADIUM.

An empirical curve obtained by fitting
Gillespie and Perry's datum, 7.68 c.c's of hydrogen
per gram of palladium at 0°C., to A. Sieverts'
experimental formula

Concentration = $k\sqrt{p} + .05kp$

ie, $c = .0165\left(\sqrt{p} + \frac{p}{20}\right)$

Theoretical curve based on microphotographs
and an experimental determination of one member
of the pressure series. (2 mm at 104A°spacing, Gillespie, Perry)

Because the secondary lattice and the primary lattice are incommensurate at the close spacing, it should be expected that the high pressure range is metastable, and that the "breaks" will be hard to reproduce exactly. Actually the measured points lie all over the region defined by the theoretical curve.

The assumption that every elementary cube of the plane of hydrogen atoms is saturated is relatively true only for temperatures in the neighborhood of 0° C. The check obtained between theory and Gillespie's points in figure XVIII may indicate that at that temperature all parts of the plane of hydrogen not lying on the intersections of the planes are saturated within 5%.

A collection of data on the variation of hydrogen concentration in palladium with temperature is contained in a paper by Sieverts.[33] The curves show that as the temperature is reduced there is a sharp increase in concentration at about 150° C. (atmospheric pressure) where the ratio of hydrogen atoms to palladium atoms changes from about .06 to .4. As the temperature is further reduced to 0° C. the concentration approaches the proportion .5 ($Pd_2 H$) asymptotically.

The work of Gillespie, Perry and Hall[7] at 0° C. shows an interesting check of the theory at low pressures. At the higher pressures the check is tenable. Because the secondary spacing is not commensurate with the primary spacing, the secondary planes cannot penetrate a primary plane exactly halfway between the set produced at the next lowest critical pressure, but must lie in less stable positions on either side. According to this theory then, the higher pressure steps are not as stable as the lower steps, but are of the nature of metastable states which might be obtained by special experimental arrangements such as perfectly pure single crystals, etc. It may be significant that isotherms which do

extend a considerable way into this metastable state have been measured at 0°C.[34]

The usually accepted generalization is that of Sieverts[10] who summarizes all his work, at any temperature, by the equation

$$C = k_1 \sqrt{P} + k_2 P$$

k_2 is negligible at the higher temperatures and is about three percent of k_1 at the lowest temperature tested (138° C.). By using the lower pressure portion of Gillespie, Perry and Hall's [7] data to establish the value of k_1 in the above equation, a series of points has been calculated which represent the curve as Sieverts would have found it; i. e., without the sudden break toward higher concentration (which Gillespie and co-workers were interested in establishing by violent heat treatment) and at the required temperature.

This "generalized experimental curve" is plotted over the calculated curve on figure XX. It will be seen that the resemblance is satisfactory. At the lower pressures some parts of the palladium sample, being less regular in structure than others, immediately absorb their full complement of hydrogen, so that the experimental curve may be too high at low pressures. However, Sievert's law is not valid at these low pressures. The true situation is shown by the data of figure XVIII. The subsequent course of the curve shows too small a rate of absorption of hydrogen with pressure because the proportions are calculated in terms of the total weight of the sample. Actually only a part of the sample was still absorbing hydrogen. If the chaotic grains of the absorbing sample had been separated from the more regular grains the absorption curve would reproduce the theoretically calculated curve more exactly.

Sieverts explained his square root relation by postulating that the hydrogen dissolves as atoms and appealing to the fact that the very small concentration of H atoms in the gas phase is proportional to the square root of the pressure. Tammann[11] objected that Henry's law, used in Sieverts' argument, is valid only for reversible systems, while in the case of hydrogen in palladium marked hysteresis had been observed.

The theory presented above shows that the square root relation is only apparent, being the effect of the changing ratio of atoms on intersections to atoms on planes as the number of planes increases. The presence of discontinuities in the absorption curve of figure XVIII definitely decides the issue in favor of the law of equation (3) above and against Sieverts' law.

VI. SUPPLEMENTARY MICROPHOTOGRAPHIC STUDY

If the theory suggested above is valid the presence of a 2.5 micron pressure threshold in the data of figure XVI demands the existence of a 41 micron secondary structure spacing. Since this spacing is within the range of visibility of the microscope an attempt was made to photograph it. The results obtained are not conclusive, but are presented here for whatever significance may be attached to them.

The tubes used in the transmission experiments have been subjected to a treatment which might be expected to develop a visible secondary structure. In preliminary activation they were electrolysed in $H_2 SO_4$ (.5 N., 60 cycles, 110 volts, without a rheostat) and rubbed with fine emery powder to remove the slime of oxide. They stood for days in the presence of extremely low concentrations of hydrogen at temperatures up

to 400° C., and were repeatedly oxidized and reduced at these low hydrogen
pressures during the course of the experiments. A fine grey powder which
will discolor a handkerchief is released at the surface after such treat-
ment. The action is entirely analogous to the etching of a metal surface
by alternate oxidation and reduction with weak acid. In the absence of a
liquid, however, there is probably a greater tendency for micro-crystals
to flake off completely, revealing the structure in three dimensions, as
the following pictures show.

They were taken with a Leitz-Wetzlar 4 mm. objective using a 6x (H)
eye-piece and a bellows setting of 45 cms. A green filter was used. The
magnification is 500x.

Picture no. 1. Tube A. A view of three sides of a cube (Figure XXI)

The observer was able to prove to himself that this was a true cube
by shifting the focal plane of the objective. This cube is tipped so
that the edges AB, AC, and AD (scratched on the celluloid cover slip)
make angles with the focal plane of about 22°, 30°, and 60°, respectively.
The length of edge AB is measurable on the plate as 17.5 mm. which
converts to a real length of 37.8 microns. The larger dark face shows
a regular pattern which is attributable to component cubes of spacing
just one-eighth of the 37.8 micron spacing. Three dark bands adjacent
to and parallel to AB are clear enough to permit measurement of this
spacing. The distance from the line AB to the third dark band, measured
in the direction of AC (30° with focal plane) is 6.25 mm. The inferred
length of the smaller cube edge is thus 4.82 microns, which compares
well with one-eighth of 37.8.

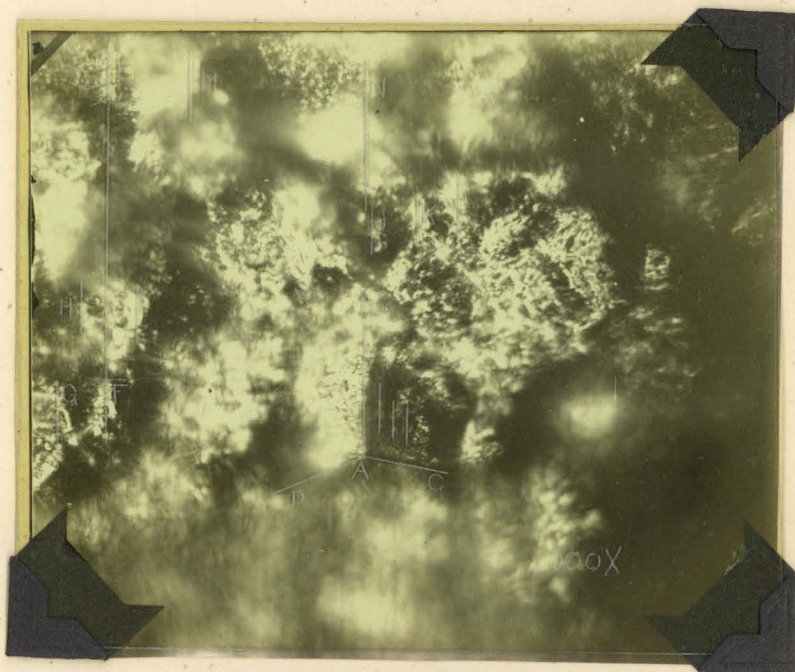Extended study of the figures in focus will lead to the belief that

Figure XXI

Picture # 1

The celluloid cover slip bears letters which
are referred to in the text. It may be removed
for close inspection.

the whole field of lights and shadows is best interpreted by the mind's eye as made up of cubes and fragments of cubes, all having edges parallel to the large cube in the center.

In the extreme upper left there is an illuminated face (E) having a sharp boundary on the right side. This boundary seems to be the upper edge, corresponding to edge AB in the large cube. Two dark lines parallel with AD mark off the band into three cube faces all made up of spots of light. Measurement of the total length along the upper edge yields an apparent length of 6.8 mm. By using the cosine ratio this figure is converted to a true edge length of 4.88 microns, which compares very favorably with the measurement of the size of the components of the large definite cube ABCD.

The visible part of the middle one of these cubes is apparently composed of three rows of light spots having four spots to each row. The fourth row can be seen but is in shadow and not truly distinguishable from the adjoining parts. An obvious conclusion is that this 4.88 micron cube is made up of cubes having an edge of 1.22 microns, and that these are just visible because they are at the limit of resolution of the microscope. On many of the pictures taken the texture is determined by these 1.22 micron cubes which seem to be broken apart everywhere so that they scatter light as units.

Thus there is fairly clear evidence in this microphotograph of cubes having edges of 37.8, 4.88 (or 4.82), and 1.22 microns.

A series of cubes arranged step-wise in the attitude of cube ABCD and cubes E have definite diagonal distances between top edges (such as AB) which are marked by the edge of a shadow cast by the

cube in light which comes from the left. The following such "projected diagonal" distances can be measured. The letters refer to markings on the celluloid cover slip drawn over possible such shadow edges.

$$F - G = 6.4 \text{ mm.}$$
$$H - I = 7.5 \text{ mm.}$$
$$J - K = 6.1 \text{ mm.}$$
$$K - L = 5.5 \text{ mm.}$$

_____

Average = 6.38 mm. (Implies 4.84 micron cubes.)

In conclusion there is apparent evidence for the existence of cubes of spacing 38.7, 9.7, 4.82, and 1.22 microns. The fact that lines EF and AN extend through colinear shadow edges suggests that the whole area is part of a coherent secondary lattice characterized by the above spacings.

Pictures no. 2 and no. 3. Tube A. End view of cubes showing subdivision in three dimensions (Figure XXII)

The objective was focused on two levels of the same area; picture 2 was taken at 11.6 microns deeper in the tube wall than picture 3. This value is barely within the error of measurement of a possible true 9.7 microns spacing.

The square ABCD is not very definite but has a measured average edge length of 19 microns and is subdivided into four roughly equal parts. Sub-cubes have been knocked off opposite ends of a diagonal to reveal the depth, which may be the same as the width of the small cube.
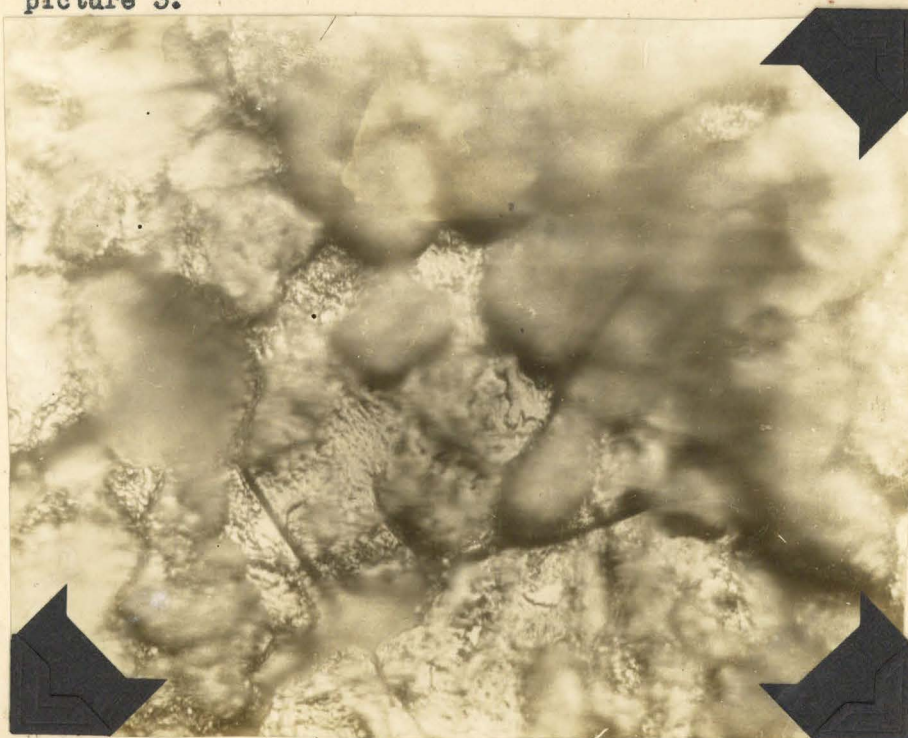
These microphotographs may be interpreted as a verification of the theory. The spacings observed are within eight per cent of the spacings predicted by the theory from absorption measurements.
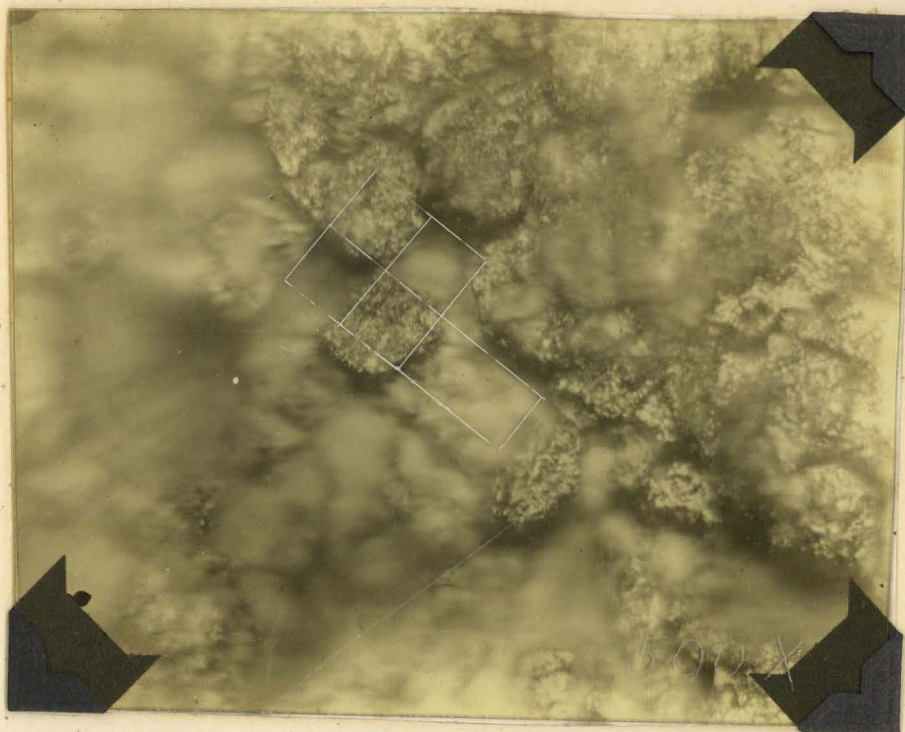
Picture # 2

Figure XXII

Microphotographs of two levels of the same area: picture
2 was taken at 11.5 microns deeper in the tube wall than
picture 3.

Picture # 3

VII. CONCLUSION

A. Experimental results

1. The absorption of hydrogen by clean palladium varies discontinuously with the pressure of hydrogen at temperatures between 250° C. and 500° C.

2. The diffusion constant of the palladium changes discontinuously at about the same instant that the change in hydrogen concentration occurs.

3. The critical pressures have been resolved into a regular geometric series such that each successively higher critical pressure is just twice the last one.

4. A curve of distribution frequency of observed critical pressures has been plotted which gives as the most probable values of the critical pressure series, in microns of mercury: 2.6, 5.3, 10.6, 21.3, 42.5, 85, 170, 340, 620.

5. Several microphotographs of the palladium surface are shown with corresponding measurements of secondary structure spacings.

B. Discussion and theory

1. A study of the literature made, after the experiments were performed, has revealed that palladium has many other properties which are discontinuous with hydrogen concentration. It is probable that these other discontinuities are associated with the same structure changes which are responsible for absorption and diffusion rate anomalies.

2. No previous experiment has measured effective hydrogen pressure closely enough to reveal the reproducibility of the phenomenon or to establish that the changes occur at an orderly series of pressures.

3. A compilation of absorption data from the literature provides considerable support for an extension of the series from 620 microns to complete hydrogen saturation at 350 millimeters of mercury.

4. An attempt has been made to account for the whole group of discontinuous phenomena by a tentative statistical theory of the penetration of an ionised impurity into a metal lattice which has an intrinsic secondary structure.

5. The experimental bases of the tentative theory are certain measured discontinuities of absorption and the existence of the geometric series of critical pressures. From these the theory predicts the whole range of the hydrogen absorption isotherm for low temperatures, the nature of the secondary structure of the palladium hydrogen solution, and the value of the secondary spacings.

6. The first prediction has been compared with such results as are available in the literature.

7. Microphotographs were taken and compared with the second prediction. The results of the comparisons are favorable but not conclusive.

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