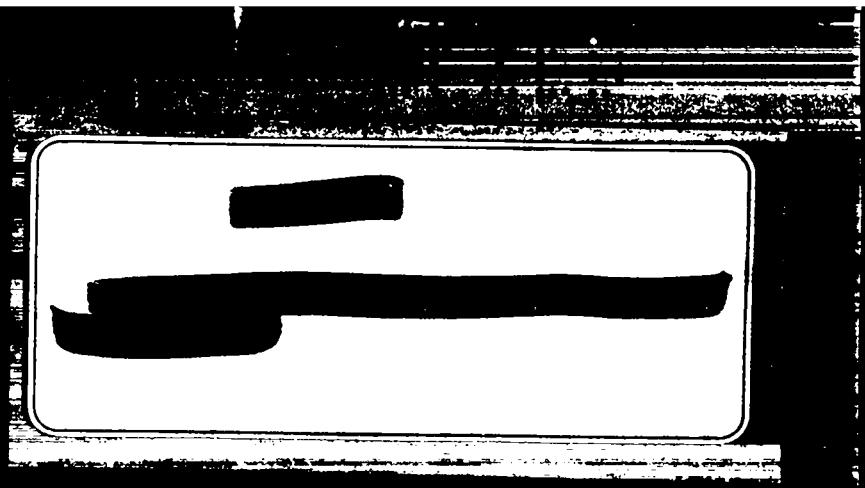

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PLUTONIUM HYDRIDE AND DEUTERIDE

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ABSTRACT

Data are presented showing the relationship between pressure, temperature, and composition of the hydride and of the deuteride of plutonium. The hydride is shown to have the composition represented by the formula PuH_2 at room temperature when the hydrogen pressure is approximately 350 mm Hg. At 200 mm the atomic ratio is 2.97, at 25 mm 2.925, and at 2.4 mm 2.892.

From the 600°C and 500°C isotherms it is evident that the reaction of the metal with hydrogen proceeds in the following steps:

$$(1)\quad Pu + H_2 \longrightarrow PuH_2 ,$$

the Pu and PuH_2 being separate phases;

$$(2)\quad PuH_2 + \tfrac{1}{2}H_2 \longrightarrow PuH_3 ,$$

the PuH_2 and PuH_3 being in solid solution in one another.

The heat of the first reaction is calculated to be -32500 cal/mole. The heat of the second reaction varies with the composition. When H/Pu = 2.6 the differential heat of reaction is -9550 cal/mole while at the ratio H/Pu = 2.87 it is -6180 cal/mole.

The pressure-composition curves for the deuteride are parallel to those for the hydride at the same temperatures. At corresponding compositions the pressures from the deuteride are about 1.45 to 1.50 times greater than those from the hydride.

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PLUTONIUM HYDRIDE AND DEUTERIDE

It has been shown earlier (LAMS-91) that the hydride of plutonium has a composition near to that indicated by the formula PuH_2. While studying the composition of the hydride by means of a pumping method in which the hydrogen was pumped out of the compound at elevated temperatures by means of a Toepler pump, it was noticed that the pressure of hydrogen over the hydride at a given temperature decreased markedly as hydrogen was removed. It was also noted that at or near saturation the pressure of hydrogen over the hydride seemed to be very unpredictable. In order to clarify these uncertainties a careful study was made of the pressure-temperature-composition relationships for the hydride and also for the deuteride.

I. PLUTONIUM HYDRIDE.

A. Determination of the formula

The ratio H/Pu was determined by measurements of the volume of hydrogen taken up and pumped off several successive times. The apparatus consisted of a reaction tube, a 10 ml gas burette for measuring the hydrogen absorbed, and a Toepler pump with 10 ml gas burette for measuring the hydrogen pumped out. The volumes of all parts of the apparatus were accurately known. The reaction tube was heated by means of a Fisher micro combustion furnace.

The metal sample was a 52.9 mg pellet designated Solid 5, LAC-32 and was 99.9 per cent pure. It had been twice remelted in vacuo in cerium sulfide crucibles. Its density was 18.35.

In six successive determinations of H/Pu made by measuring alternately the volume of hydrogen absorbed, the volume pumped out, absorbed, etc., the values 3.01, 2.99, 2.91, 2.90, 2.93, 2.96 were obtained.

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The first reaction (solid pellet) showed an incubation period of 8 minutes and was complete in 7 minutes more at 26.4°C. During the reaction some particles of hydride were thrown off the metal piece with sufficient velocity to scatter them a distance of 3 centimeters. In the fifth determination it was noticed that sudden admission of hydrogen to the powdered metal caused it to glow momentarily. That this glowing was not due to oxygen as an accidental impurity in the hydrogen is proved by the results obtained in the sixth determination. This incandescence indicates that the reaction is accompanied by considerable evolution of heat and that the reaction rate is not much hindered by high temperatures.

Using a larger sample (499.3 mg) of metal and measuring the volume of hydrogen pumped off at 550°C, the ratio H/Pu was found to be 2.97 when the initial hydrogen pressure at room temperature was 200 mm, 2.925 when the pressure was 25 mm. and 2.892 at 2.4 mm. Thus when nearly saturated, the metal exhibits a hydrogen pressure that is dependent on its composition. Accordingly the system does not consist simply of two solid phases (metal and hydride) in equilibrium with gaseous hydrogen.

B. Pressure-temperature-composition relationships.

The apparatus is shown in Fig I. The reaction tube was connected to the Toepler pump through a manometer in such a way that when the mercury is drawn down out of the manometer the reaction tube is open to the pump. Hydrogen was admitted to the system through the pump by first drawing the mercury down out of the manometer and out of the mercury seal between the pump and the vacuum line and then filling the vacuum line with hydrogen. With this apparatus and 499.3 mg metal the data in the upper part of Table I were obtained. To measure the lower pressures, at compositions below H/Pu = 2

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a Pirani gauge was substituted for the manometer, necessitating also the use of a new metal sample (65.84 mg).

The experimental procedure was as follows: After forming the hydride the apparatus was evacuated to 200 mm or less and the mercury raised in the Toepler to cutoff. The vacuum line was then evacuated to about 10^{-2} mm so that the measuring burette on the Toepler pump would measure accurately. Then by means of the Toepler pump the reaction tube was pumped down to any convenient working pressure, say 25 mm. Having the manometer set at B to define accurately the volume of the system. The volume of hydrogen obtained in this first pumping (measured in the burette) is always larger than the volume of free hydrogen in the system, the difference being the hydrogen that is evolved from the sample during pumping. The composition of the original hydride is calculated from the total volume of hydrogen pumped out during the whole experiment. The composition at any intermediate time is calculated from the volume pumped out up to that time making correction for the hydrogen present in the system at the temperature and pressure obtaining at that time. The heated part of the system had a volume of 1.757 ml from which is subtracted the volume of the metal, .027 ml. The part of the system at room temperature had a volume of 1.21 ml (to mark A, Fig. I). It would be better to correct for the absolute volume of the hydride rather than the metal, but the density of the hydride is not known. The volume of the hydride is probably less than twice that of the metal. The difference was thought to be so small as to cause no great error in the corrections.

After pumping out a measured quantity of hydrogen the temperature was adjusted to certain fixed values and the pressure read, up to the limit of the manometer. The reaction tube was then cooled so the mercury could be drawn

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down out of both arms of the manometer. Then after heating to a suitable temperature another measured volume of hydrogen was removed. Then after adjusting the manometer another series of pressure and temperature readings was made. The data are presented in Table I. For each pressure the ratio H/Pu has been calculated as mentioned above.

Isotherms for the H/Pu system are plotted in Figs II and III. The constancy of pressure with changing mol ratio below 2 shown in the 400°C and 500°C isotherms of Fig III indicates that when the atomic ratio is below 2 the reaction is

$$Pu + H_2 \longrightarrow PuH_2. \qquad (1)$$

the Pu and PuH_2 being separate phases. In the region from H/Pu = 2 to H/Pu = 3 the reaction is

$$PuH_2 + \tfrac{1}{2}H_2 \longrightarrow PuH_3. \qquad (2)$$

the PuH_2 and PuH_3 being in solid solution in one another. It is also possible that additional hydrogen may be in solid solution in these compounds.

Pressure-temperature curves are shown in Fig IV for three compositions: H/Pu = 1.97, 2.60 and 2.87, plotting log P against $(1/T^{\circ}_K)$. The values used in drawing these curves were taken from the isotherms, Figs II and III. The equations for the best straight lines through the points are

for H/Pu = 1.97 $\quad \log_{10} P_{mm} = -7.13 \times 10^3 \ (1/T) + 8.77$

for H/Pu = 2.60 $\quad \log_{10} P_{mm} = -4.17 \times 10^3 \ (1/T) + 9.9$

for H/Pu = 2.87 $\quad \log_{10} P_{mm} = -2.7 \times 10^3 \ (1/T) + 8.8$

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TABLE I

PRESSURE-TEMPERATURE COMPOSITION DATA FOR PLUTONIUM HYDRIDE

25°C		100°		160°		200°		300°		400°		500°	
H/Pu	P mm	H/Pu	P	H/Pu	P	H/Pu	P	H/Pu	P	H/Pu	P	H/Pu	P
2.97	200	2.90	153	2.87	364	2.79	354	2.60	405	2.45	245	2.29	160
2.93	22	2.88	88.8	2.82	87	2.75	231	2.55	148	2.31	25.4	2.15	19
2.92	9.5	2.83	8.0	2.77	61.5	2.70	126	2.47	39	2.15	2.2	2.04	2.5
2.91	8.8	2.78	4.4	2.71	15	2.64	41.7	2.31	0.8	2.04	1.4		
2.89	2.5	2.71	1.0	2.64	10	2.56	6.0						
2.83	0.4	2.65	< 1.0	2.56	1.4	2.48	1.4						
							*	1.97	0.0003	1.97	0.008	1.97	0.364
										1.27	0.008	1.27	0.362
										0.66	0.008	0.66	0.365
										0.29	0.008	0.29	0.364
												0.006	0.018

* From this point on pressures were measured by means of a McLeod gauge.

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From the slopes of these lines the heats of reaction are found to be

for reaction (1), $\Delta H = -32500$ cal/mole

for reaction (2), $\Delta H = -9550$ cal/mole when H/Pu = 2.6

and $\Delta H = -6180$ cal/mole when H/Pu = 2.87

The shapes of the isotherms, Figs II and III, indicate that at higher pressures of hydrogen atomic ratios greater than 3 may be obtained, though rather large pressures would be required to increase the ratio significantly. At room temperature the ratio reaches 3 at a pressure of about 350 mm as estimated by extrapolation. At a pressure of 10 mm the ratio is reduced only to 2.92.

II. PLUTONIUM DEUTERIDE

The substitution of deuterium (99%) in place of hydrogen in the above experiments yielded nearly identical results. At room temperature, under 9 mm D_2 pressure the atomic ratio D/Pu was found to be 2.8.

At a composition corresponding to a ratio of 1.95, the pressure at 400°C was 0.01 mm and at 500°C was 0.533 mm. These pressures are definitely higher than the pressures of hydrogen over the hydride at the same temperatures. The curve for log P against $(1/T^{\circ}_{K})$ is parallel with that for the hydride within the limits of accuracy of the data. Accordingly the heat of reaction is the same for the deuteride as for the hydride. The 500° isotherm for the deuteride is parallel to that for the hydride, the pressures at corresponding compositions being 1.45 to 1.50 times greater.

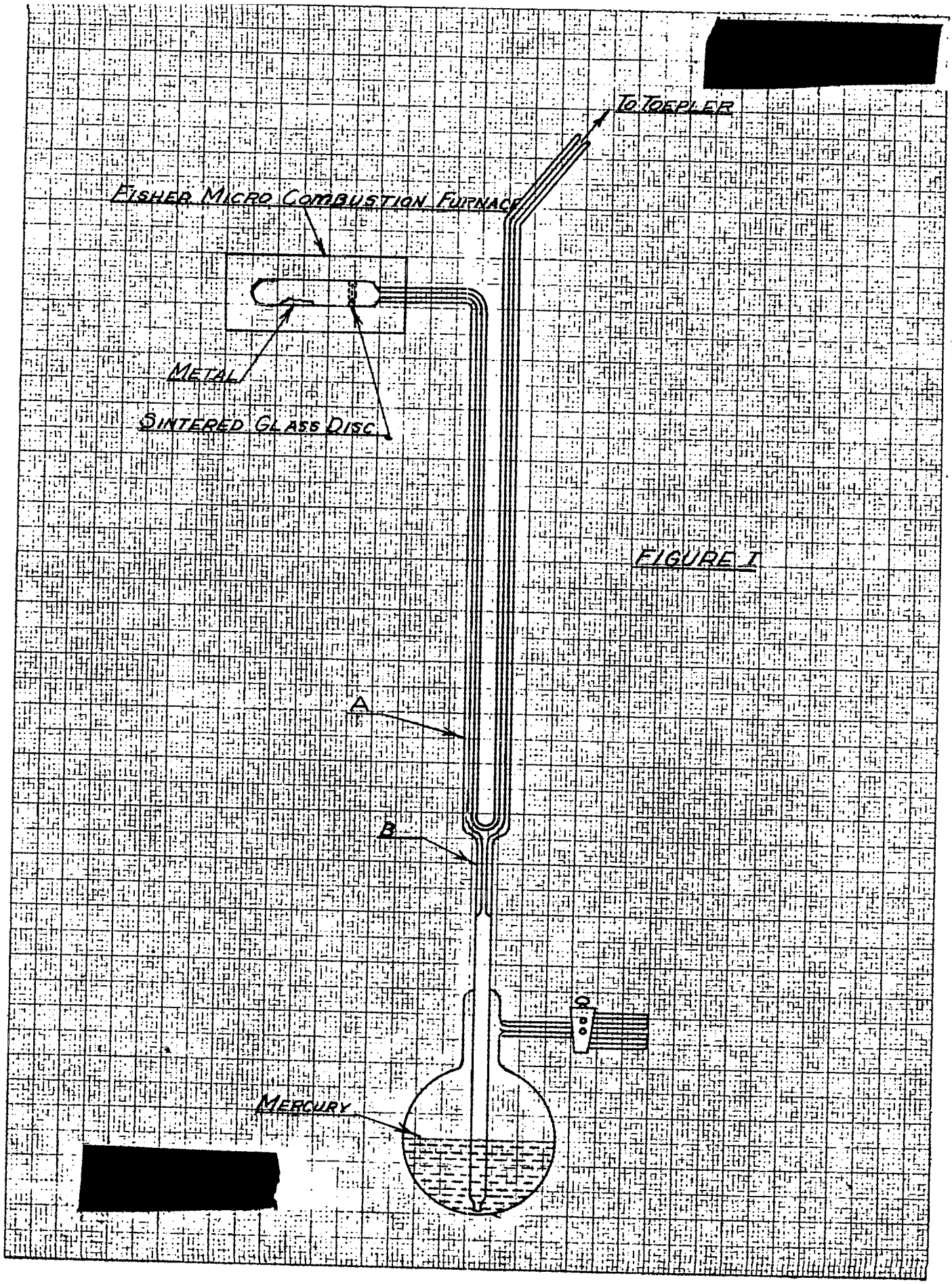

FIGURE I

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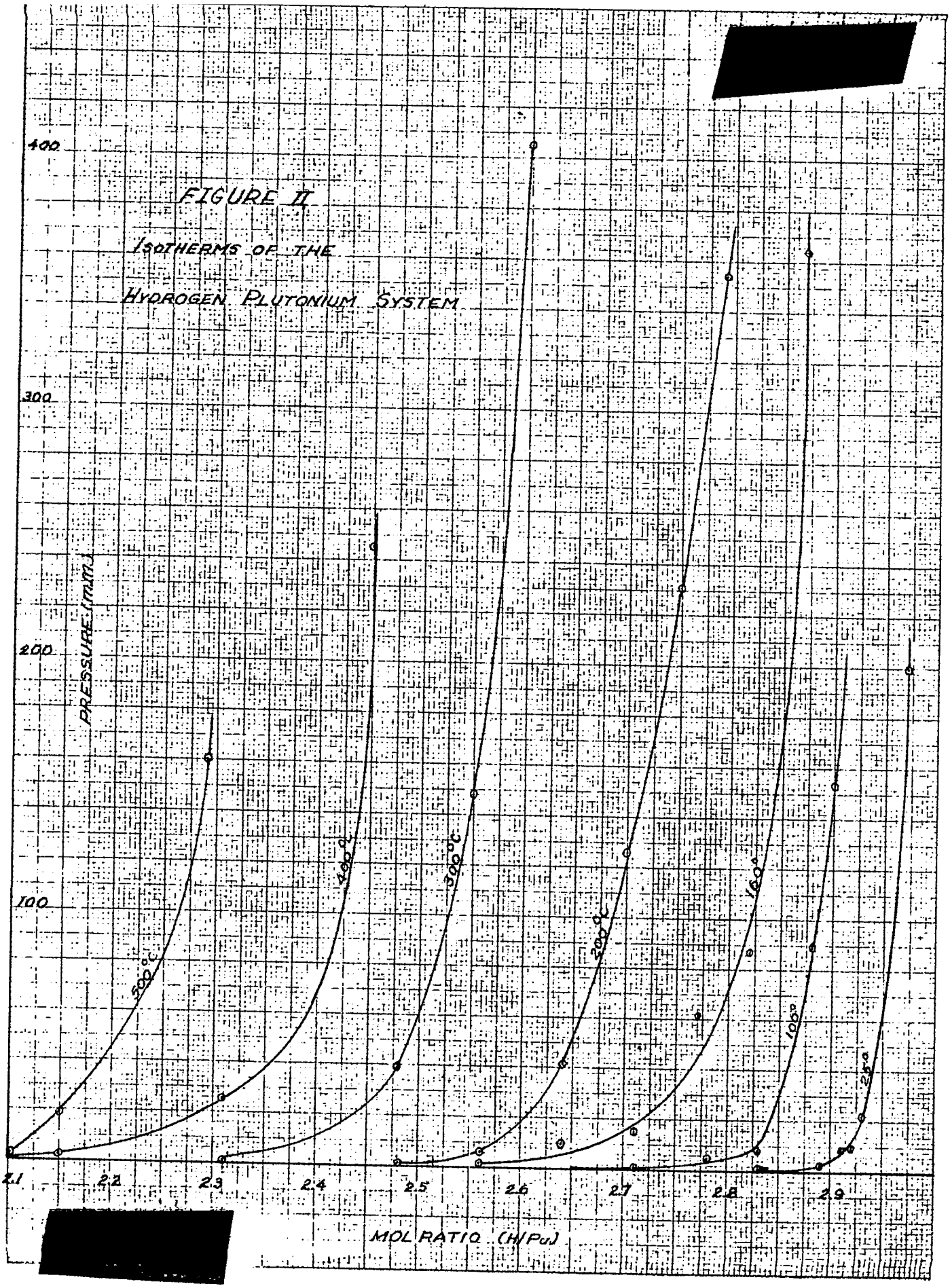

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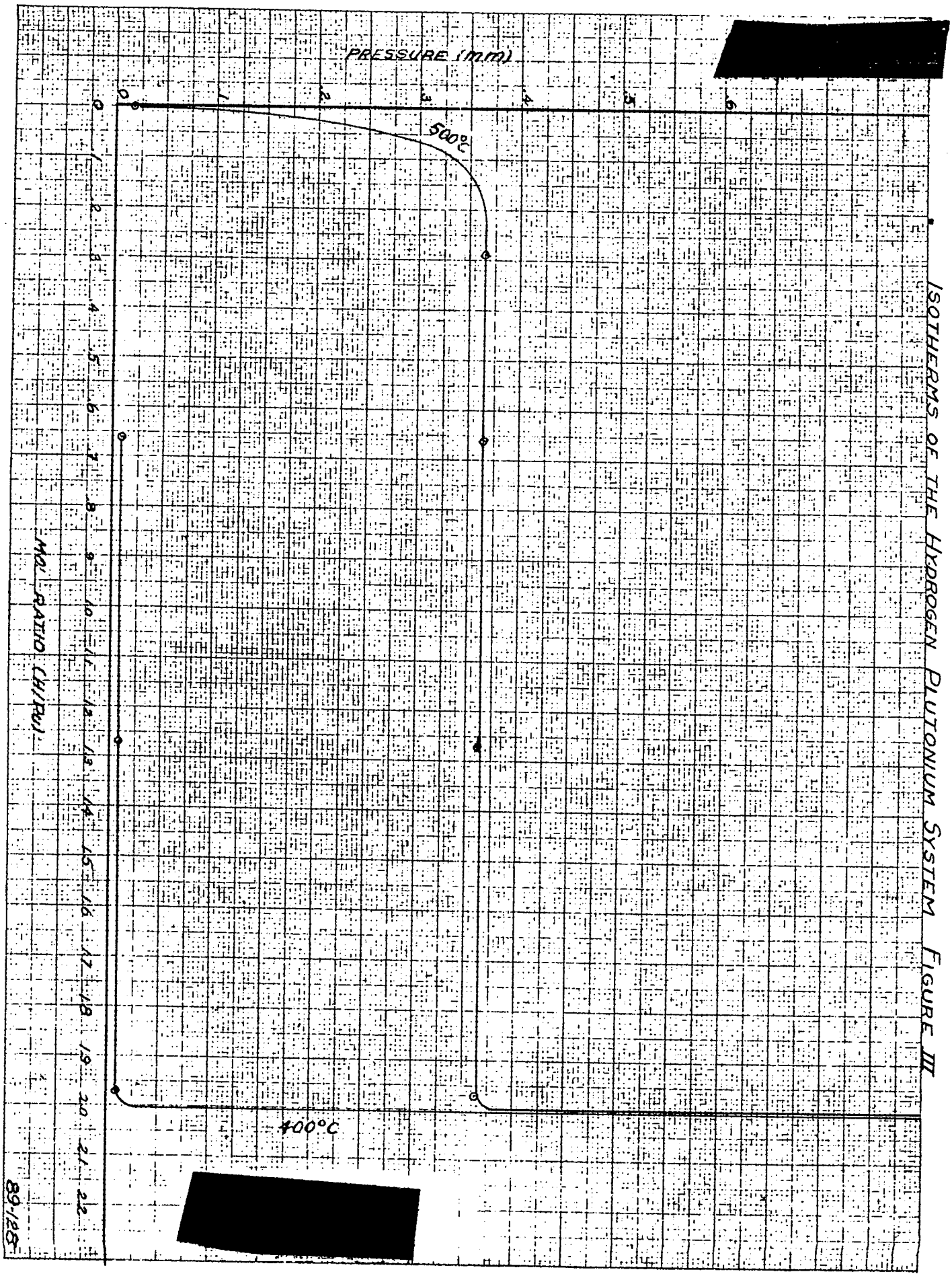
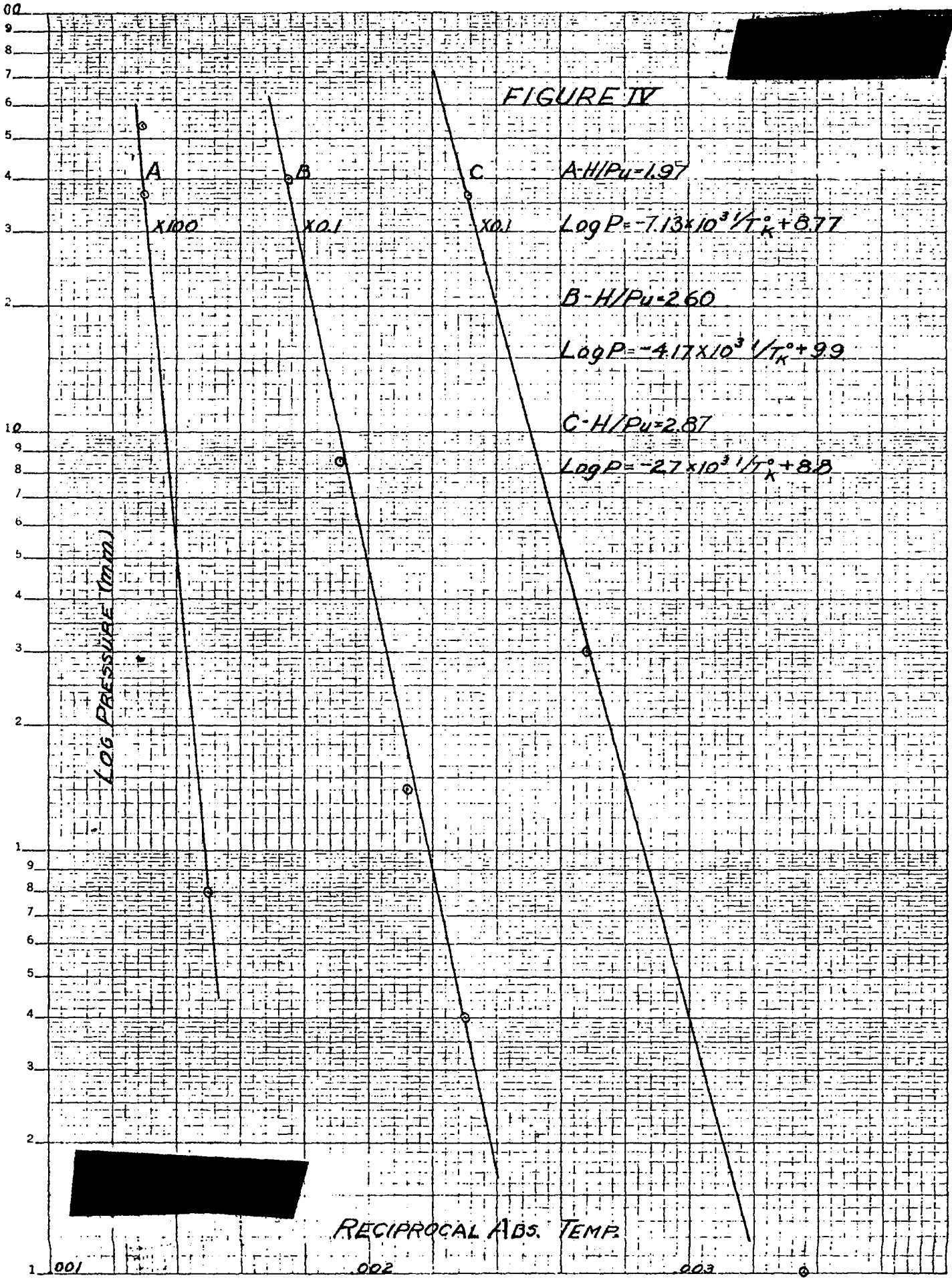


ISOTHERMS OF THE HYDROGEN PLUTONIUM SYSTEM FIGURE III



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