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USE OF SORBENT BEDS FOR TRANSFERRING HYDROGEN GASES

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ABSTRACT

The use of uranium or palladium black beds for transferring hydrogen isotopes has been described. Such beds react quantitatively and rapidly with hydrogen and its isotopes, store large volumes of gas as the solid hydride, and can evolve the gas in a controlled manner to give any reasonable pressure. The uranium bed is somewhat simpler to operate since only heat need be supplied to carry out the pumping cycle, while the palladium must be cooled to approximately -100°C to sorb hydrogen and heated to evolve the gas. The palladium bed is very dependable in operation; it is poisoned only by gases like H_2S and CO and, if poisoned, can be easily reactivated. Uranium is rather easily poisoned by small amounts of air; cycling in hydrogen will reactivate the uncombined uranium but the portion reacted with air will be permanently combined.

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USE OF SORBENT BEDS FOR TRANSFERRING HYDROGEN GASES

D. H. Ahmann, P. S. Flint, and O. N. Salmon

INTRODUCTION

The use of uranium or palladium beds for transferring hydrogen gases has been effective in various laboratories and wider application seems probable. Data on the application of uranium for this purpose were collected several years ago for use in design of such beds. Recent developments have indicated that some of these data will be useful for further applications and hence the report was revised and is being given a somewhat wider distribution at this time.

The transfer of hydrogen gases by reacting the gas with a bed and later evolving the sorbed gas in a controlled manner can be referred to as chemical pumping. This method of pumping can be used to advantage in the laboratory to supplement such mechanical transfer pumps as the Toepler or Sprengel types which are usually used to transfer gases. The advantages of a chemical pump are:

a. Greater capacity and pumping speed
b. Rapid and quantitative reaction with pure hydrogen gases
c. Storage of the gas in small volumes
d. Ability to evolve the gas to give any reasonable pressure in a controlled manner

Disadvantages are that the beds may become poisoned or else blanketed by gaseous impurities in the hydrogen gases and, hence, any system should include a mechanical transfer pump to handle gases under such conditions. For this reason it would be desirable to use double ended beds for pumping hydrogen gases, so that gas mixtures containing large amounts of contaminants can be pumped through the bed by mechanical pumps. The effects of various gases on uranium and palladium will be discussed individually.

USE OF URANIUM IN A CHEMICAL PUMP

Preparation and Properties of Powdered Uranium

Uranium metal to be used as an absorbent for hydrogen must first be activated by powdering. This powdering is effected by reacting massive uranium metal with hydrogen at about 300°C to form the hydride (UH_3), a gray-black finely divided compound.[1,2,3] The hydride is then decomposed to the metal by heating at temperatures above 400°C under vacuum. This treatment will remove all but traces of hydrogen (about 0.01 cc H_2/100 g U), leaving a finely powdered, light gray metal. The powdered metal obtained by this process is very reactive; it will react with oxygen and hydrogen at room temperature. Reaction with nitrogen may sometimes occur at room temperature and essentially complete absorption of nitrogen can be obtained at 400°C. The powdered metal has a bulk density of roughly 3 g/cc. The metal is firmly sintered by heating to 600°C, however it is repowdered by another hydriding cycle.

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Properties of Uranium Hydride and Tritide

The compounds of uranium and the isotopes of hydrogen are gray-black ders with a bulk density of approximately three (X-ray density of ~ 11 g/cc). The powder is very finely divided and will completely pass a 400-mesh sieve. The hydride, like the metal, is pyrophoric and quite reactive. It can be calculated from the formula that 140 cc of hydrogen are combined with one gram of uranium.

The dissociation pressures of the compounds have been measured by several investigators[1,3,4] and have been shown to be represented by the equations

$$\text{for } UH_3^{1,3,4} \qquad \log P_{mm} = -\frac{4500}{T} + 9.28$$

$$\text{for } UD_3^{1,3} \qquad \log P_{mm} = -\frac{4500}{T} + 9.43$$

and

$$\text{for } UT_3^{4} \qquad \log P_{mm} = -\frac{4424}{T} + 9.39$$

From these equations the heats of formation are calculated to be -30,800 cal/mole, -30,800 cal/mole, and -30,400 cal/mole, respectively. The dissociation pressures at various temperatures were calculated from these equations and are listed in Table I.

TABLE I

DISSOCIATION PRESSURE OF URANIUM HYDRIDES

Temperature, °C	Dissociation Pressure, mm Hg		
	UH_3	UD_3	UT_3
25	1.54×10^{-6}	2.17×10^{-6}	3.56×10^{-6}
100	0.00166	0.00235	0.00342
200	0.588	0.830	1.10
300	26.9	37.9	46.9
400	394	556	658
407	461	652	760
414	-	760	-
430	760	1070	1260
450	1140	1610	1870

From these data it is apparent that the residual pressure of any of the hydrogen isotopes in equilibrium with uranium at 25°C is negligible. It is also clear that practically complete evolution of hydrogen against one atmosphere pressure can be attained by heating the hydride to 430°C, of deuterium at 414°C, and of tritium at 407°C. A small solid solubility of hydrogen in uranium amounting to about 0.02 cc of hydrogen per gram of uranium at 450°C at one atmosphere hydrogen pressure has been reported.[3] This would cause a 3 cc holdup of hydrogen on a chemical pump containing 150 g of uranium evolving hydrogen at one atmosphere. Since the hydrogen solubility decreases as the square root of the pressure, at pressures of 0.01 mm, the holdup would be about 4×10^{-4} cc/g.

Application of Uranium as a Chemical Pump

Operating Cycle

To prepare uranium as the absorbent in a chemical pump, the metal should be charged into the bed as a massive metal and converted to a powder in situ by means of the hydride cycle. This precaution ensures a highly reactive sorbent and avoids the handling of the pyrophoric powder with its attendant difficulties. No inactive diluent is required for the powdered uranium since, although sintering does occur when the metal is heated above 400°C, the reactivity of the metal is relatively unaffected. It is desirable to prevent entrainment of the uranium particles in the gas stream by containing the powdered metal with fritted metal filters. To avoid partial blocking of the filter a layer of coarse inert material such as Al_2O_3 or MgO between the uranium powder and the filter is recommended.

After obtaining an active bed the uranium can be used as a pump. The pumping cycle can consist of exposing the bed (at room temperature) to the pure hydrogen to be absorbed. The reaction rate at 25°C is high and (as indicated by Table I) is quantitatively complete. For example, the pressure of a system containing 2.5 liters of hydrogen was reduced from 760 mm to 200 μ in five minutes by a 63 g uranium bed (about a threefold excess over the stoichiometric amount). The rate of reaction between hydrogen and uranium has been reported[2] as being at a maximum at 200°C; however, in an experiment similar to that discussed above, heating the bed increased the time of uptake from five minutes at 25°C to 30 minutes at 150°C. This can be explained by considering the heat of reaction between uranium and hydrogen which will raise the bed temperature and hence increase the dissociation pressure of the hydride. Thus, although the higher starting temperature increased the initial reaction rate, the bed temperature was raised to such an extent that the dissociation pressure of the hydride in the bed exceeded the ultimate pressure desired and the bed had to cool before the residual hydrogen could be absorbed.

When the hydrogen is completely reacted with the bed, trace residual gases can be pumped away. For hydrogen containing a large amount of inert gas, it would be necessary to pump the gas through the bed in order to avoid blanketing the bed, a situation which would greatly increase the reaction

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time. The stored gas can then be evolved at a controlled rate by heating the bed. The temperature required for the complete evolution of hydrogen at one atmosphere pressure is 430°C, or above, of deuterium is 414°C, and of tritium 407°C. After evolution the residual gas in the lines could be reabsorbed by cooling the bed. In the case where a mixture of hydrogen isotopes is sorbed on a uranium bed, partial evolution of the gas mixture will give some fractionation of the isotopes[1b] with the heavier isotope tending to concentrate in the gas phase. This fractionation should be taken into account if it is desired to evolve a particular isotopic concentration from a uranium bed containing a mixture of hydrogen isotopes.

To illustrate the use of a uranium bed as a pump, consider pumping four liters of hydrogen. Approximately 30 g of uranium would be necessary, stoichiometrically, to react with this amount of gas. Allowing a fourfold margin of safety, 150 g of uranium, which could be contained in a 150 cc volume, would comprise the reaction bed. If several batches were to be stored, a proportionately larger amount of uranium would be required. Depending on the process used, the "pump" could absorb the four liters of gas in as little as ten minutes. After complete reaction less than a micron of mercury pressure of hydrogen would remain, which would result in a loss of less than 1 ppm. Any trace of impurity not reacted with the uranium could then be removed by pumping. The reacted gases are permanently bound to the uranium and hence would also be removed from the sorbed hydrogen. The hydrogen gas could then be evolved as described previously.

Poisoning

A uranium bed is poisoned by reaction with nitrogen, oxygen, carbon, and most compounds containing these elements. The resulting compounds are stable to hydrogen and are not reduced under any of the conditions encountered during a run. For this reason, if a uranium bed is used as a chemical pump, some provision for replacing the bed must be provided, since slow oxidation due to minor leakage during operation must be expected. If a uranium bed is exposed to a small amount of oxygen or nitrogen, the reactivity of the bed to hydrogen is decreased. Apparently the uranium is coated with a film of oxide or nitride which inhibits and, if thick enough, can completely block reaction of the uranium with hydrogen. An investigation has been carried out to evaluate this effect by experiments which duplicated exposure of the uranium or hydride to large amounts of air and simulated the effect of slow leaks on the reaction characteristics.

The result of air leakage was determined by observing the reaction rates of air contaminated hydrogen (3.2 and 4.6% air) with a 63 g uranium bed. In the case of 3.2% air in hydrogen, the first contacting of the mixture with a fresh uranium bed approximately doubled the reaction time. Further contactings with this mixture, made in each case after evolving the reacted hydrogen from the previous run, resulted in complete poisoning of the bed as was illustrated by the fact that a portion of the unreacted gas remained in contact with the bed with no observable reaction taking place. However, in the two runs made, heating the bed to 250°C and then cooling in the presence of the unreacted

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gases caused the hydrogen to be absorbed. Subsequent tests with pure hydrogen showed the bed to be slightly poisoned after these exposures; however, three cycles with pure hydrogen completely restored the reactivity. Evidently, several cycles of hydride formation and decomposition are required to break up the oxide and nitride coatings and expose fresh uranium surfaces.

Higher concentrations of air in hydrogen poisoned the uranium bed still more quickly. Thus, on exposure of hydrogen containing 4.6% air to the bed at room temperature the reaction stopped after only a small per cent of the hydrogen was absorbed. Complete absorption was obtained by heating the bed to 250°C. On a second addition of a 4.6% air in hydrogen mixture, a temperature of 285°C was required to complete the reaction. Following this treatment the residual pressure dropped to 400 μ as the bed cooled. For the third run the blocking was more severe and a preliminary heating to 285°C was required to attain an appreciable rate of reaction. On cooling from the maximum temperature of 400°C complete reaction again took place. As a result of the above series of reactions, 10% of the bed was permanently combined as oxide and nitride. Three cycles were then carried out with one volume of pure hydrogen (1/3 the stoichiometric amount of uranium metal present) after which the uptake time was 1.3 times that of the original time for the clean bed.

The effect of exposure of a uranium bed to air was determined by admitting air to a clean bed at 25°C. Of the 76 cm of air added, roughly 15 cm reacted with the uranium (corresponding to about 9% of the free metal present). A single cycling of the bed with hydrogen at 300°C did not completely reactivate the bed, and after four such cycles the time for complete uptake was still 1.5 times that for a clean bed.

As a check of the effect of air exposure on the recovery of hydrogen from a hydrogen-charged uranium bed, air was admitted to a bed containing hydrogen (1/3 of the bed was uranium hydride). Sufficient air to react with 30% of the remaining metal was absorbed; no more air reacted even on heating the bed to 230°C. After this drastic treatment, all the hydrogen was recovered by heating to 500°C. The uptake rate of the bed (now 30% permanently combined) was fair after two cycles with pure hydrogen (uptake time twice that for a clean bed).

From all observed data, it appears that a poisoned bed of powdered uranium will return to its normal reactivity after continued cycling, provided that a reasonable excess of free metal is present. In the above runs, after oxidation, there was always at least twice the stoichiometric amount required to react with the hydrogen present in the next run. In all cases of the uranium poisoning studies, the recovery of the hydrogen from the partially oxidized bed was complete to within the accuracy of analysis ($\pm$ 2%).

In applying a uranium pump for pumping hydrogen isotopes, a manometer should be included in the system. Observation of the reaction time for a known reaction cycle will give an early indication of poisoning of the uranium bed and similarly if poisoning has occurred, will give a measurement

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of the extent of reactivation. If a bed should become temporarily poisoned by air, the recommended procedure for absorbing the remaining hydrogen is to heat the bed to 300°C and allow to cool to room temperature. If the remaining hydrogen is not reacted by this treatment, a heating cycle to 400°C should accomplish partial reaction. If complete poisoning persists, repetition of these heating cycles is required, since this is the only known method for obtaining complete uptake. In the most persistent poisoning observed in the laboratory, one such treatment at 400°C caused complete uptake of the unreacted hydrogen and four or five such treatments almost completely reactivated the bed.

Container

Since the uranium reaction bed will be a finely divided powder unprotected by an oxide coat, the problem of containment in metal without alloying must be considered. The container successfully used in the poisoning studies discussed above was a Type 347 stainless steel crucible capped by sintered Type 304 stainless steel filter crucibles (coarse grade D or E) which served as lids.

Work at this laboratory[5] has shown that there is no alloying of uranium with Type 347 stainless steel below 500°C. In the temperature range from 500 to 650°C there may be some minor alloying of the uranium and iron due to metallic diffusion, and above 650°C alloying can be extensive. Observations of the crucible used for experiments on the chemical pump were in agreement with these results. There was no observable alloying of uranium with stainless steel after three months of operation as a chemical pump where the bed, consisting of uranium powder in the stainless steel crucible, was heated to 500°C (on several occasions to 600°C as a result of maloperation) to evolve hydrogen.

The sintered Type 304 stainless steel lid did show some effect of exposure to uranium. After 30 runs the air flow through the filter was 0.7 as fast as through the clean filter. Boiling the filter in nitric acid (to remove uranium) gave some improvement (0.8 as fast as clean filter). The plugging does not appear to be progressive, since the same extent of blocking is found for a filter used for three runs as for one used for 30 runs. Hence, this portion of the flow reduction is attributed to a surface layer of powder which would tend to plug the larger holes of the filter. The permanent flow reduction through the filter appears to be due to alloying of uranium with the filter. The filter had previously been tested in a hydrogen atmosphere (no uranium metal present) at 600°C for 72 hours with no sign of sintering. This plugging effect has not been fully explained, but does indicate that a layer of coarse powder of some inert material should be used to prevent contact of uranium with the filters.

Except for the slight plugging which has been observed, the micrometallic filters have been quite satisfactory for containing powdered uranium. No blowing of uranium powder has been observed even under most adverse conditions of operation, e.g., opening of bed at one atmosphere to vacuum. The filters were operated at the temperature of the bed to ensure that all the uranium hydride in the bed was decomposed when the bed was heated.

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Diffusion Losses

In a metal system the chemical pump is a possible source of diffusion losses of hydrogen, since in the postulated pumping cycle the highest hydrogen pressure will be associated with the highest temperature of the bed. In the case of transferring tritium such losses could be serious. For example, a single-walled Type 347 stainless steel container for the chemical pump, 500 cc in volume with 0.6-cm wall of 350 cm^2 area, would lose 0.2 cc of hydrogen or 0.1 cc of tritium in one hour at 410°C where

$$S = 3.4 \times 10^{-3} \text{ cc/cm}^2\text{/hr}$$

through 1 mm of thickness, for a differential pressure of one atmosphere. This loss is not high; but in the case of tritium does constitute a health hazard. However, in a permanent-type installation such as a chemical pump, the expense of a doubled-walled sorption chamber would be justified. By heating only the inner chamber, the diffused tritium could be contained effectively, and could be recovered.

USE OF PALLADIUM IN A CHEMICAL PUMP

Properties of Palladium

Palladium to be used as a sorbent for hydrogen gases should have a high surface-to-volume ratio to permit rapid saturation of the metal with hydrogen. This is particularly important for use in the sorption of tritium where the rate of equilibration at the temperature of sorption (-100°C) is appreciably slower than that of hydrogen. The material adopted as being most suitable for sorbing hydrogen gases was palladium black. After conditioning with hydrogen this material had a surface area of approximately 8 m^2/g.[6] Other palladium powders, like finely divided palladium sponge, have appreciably smaller surface areas[6] (~ 0.4 m^2/g) and, while adequate sorbents for hydrogen, have a definitely longer reaction time with tritium. Precautions concerning heating of palladium, which should be taken to avoid reducing the surface area by sintering, will be discussed later.

Palladium will sorb up to about 60 cc STP of hydrogen gases per gram (corresponding to Pd $H_{0.6}$). At a given temperature the equilibrium dissociation pressure varies with concentration as shown in Figure KH-9A1219, which gives the isotherm for the dissociation pressure of hydrogen on palladium at -78°C.[7] From the isotherm, the hydrogen dissociation pressure is less than ten microns for capacities as high as 60 cc STP of hydrogen sorbed per gram of palladium. The variation of dissociation pressure with temperature is shown in Figure KH-9A1218 for the case of 20 cc STP of hydrogen per gram of palladium black. The corresponding dissociation pressures for deuterium are estimated from the data on deuterium and hydrogen solubility in palladium at elevated temperatures[8] to be about ten times that for hydrogen at -80°C, about four times at 25°C, and about 2.5 times at 200°C. The corresponding dissociation pressures for tritium were measured and found to be about 25 times that for hydrogen at -80°C,[9] about nine times at 25°C,[9] and about 3.7 times at

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200°C.[10] The pressure-composition isotherm of tritium over palladium at -100°C is shown in Figure KS-520.

The rate of sorption of hydrogen isotopes by palladium black is high. At -80°C, the rate for ordinary hydrogen, as obtained for a six inch deep cylindrical bed containing 35 grams of palladium black dispersed in 200 grams of clean silica sand, is shown in Figure KH-9A1499.[7] The same bed material arranged in a bed one inch or less deep will give a definitely faster rate.[11] It is estimated that at -80°C the time of equivalent reaction for deuterium and tritium will be three and five times that for hydrogen.

The evolution of hydrogen isotopes from palladium is rapid at elevated temperatures and hence is limited only by the rate at which heat can be supplied to all of the palladium. Efficient heat transfer from the heater to the bed can be achieved by suitable design; also, as the hydrogen is evolved it will transfer heat to the center of the sorption bed. At 200°C, over 98% of the hydrogen will be evolved from a palladium bed originally containing 50 cc of hydrogen per gram against a back pressure of one atmosphere. To remove essentially all the hydrogen at 200°C, it would be necessary to reduce the back pressure to less than 1 mm mercury because of the equilibrium solubilities of the hydrogen isotopes in palladium as a function of pressure. At 200°C the hydrogen solubility in palladium black is about 2.2 cc STP per gram of palladium at a hydrogen pressure of one atmosphere. The corresponding solubility at 200°C for deuterium would be about 1.4 cc/g and for tritium about 1.1 cc/g. As in the case of uranium, some isotopic fractionation is observed when a mixture of hydrogen isotopes is partially desorbed from a palladium bed. The heavier isotope will tend to be evolved first. For this reason special precautions should be taken if it is necessary to maintain a particular isotopic concentration.

The sorption and evolution of hydrogen isotopes by palladium black is reproducible after long and continuous use provided the palladium bed is properly prepared. There is no permanent poisoning of palladium black by any of the ordinary gaseous constituents found in hydrogen or air.[7] Some permanent poisoning of palladium takes place at the sorption temperature of -78 to -100°C when hydrogen contains hydrogen sulfide or carbon monoxide. In each case the palladium can be reactivated by thermal cycling in a hydrogen atmosphere between -80 and 300°C although the capacity decreases somewhat for the case of the hydrogen sulfide poisoning. Poisoning by hydrogen sulfide results from the formation of a palladium sulfide film and by carbon monoxide probably is caused by formation of a carbon film on the palladium. Both the sulfur and carbon can be completely removed by heating the palladium in an atmosphere of oxygen to 300 or 400°C followed by reduction in hydrogen at 300 or 400°C after the oxygen gas has all been pumped away. At the temperatures required for the complete sorption of hydrogen isotopes (i.e. -78 to -100°C), palladium adsorbs small amounts of nitrogen and helium and later evolves these gases as impurities in the hydrogen isotopes. By such operations as pumping off the first fraction of the evolved gas which will contain all the adsorbed gases, the remainder of the sorbed gas can be evolved as pure hydrogen gases.[6]

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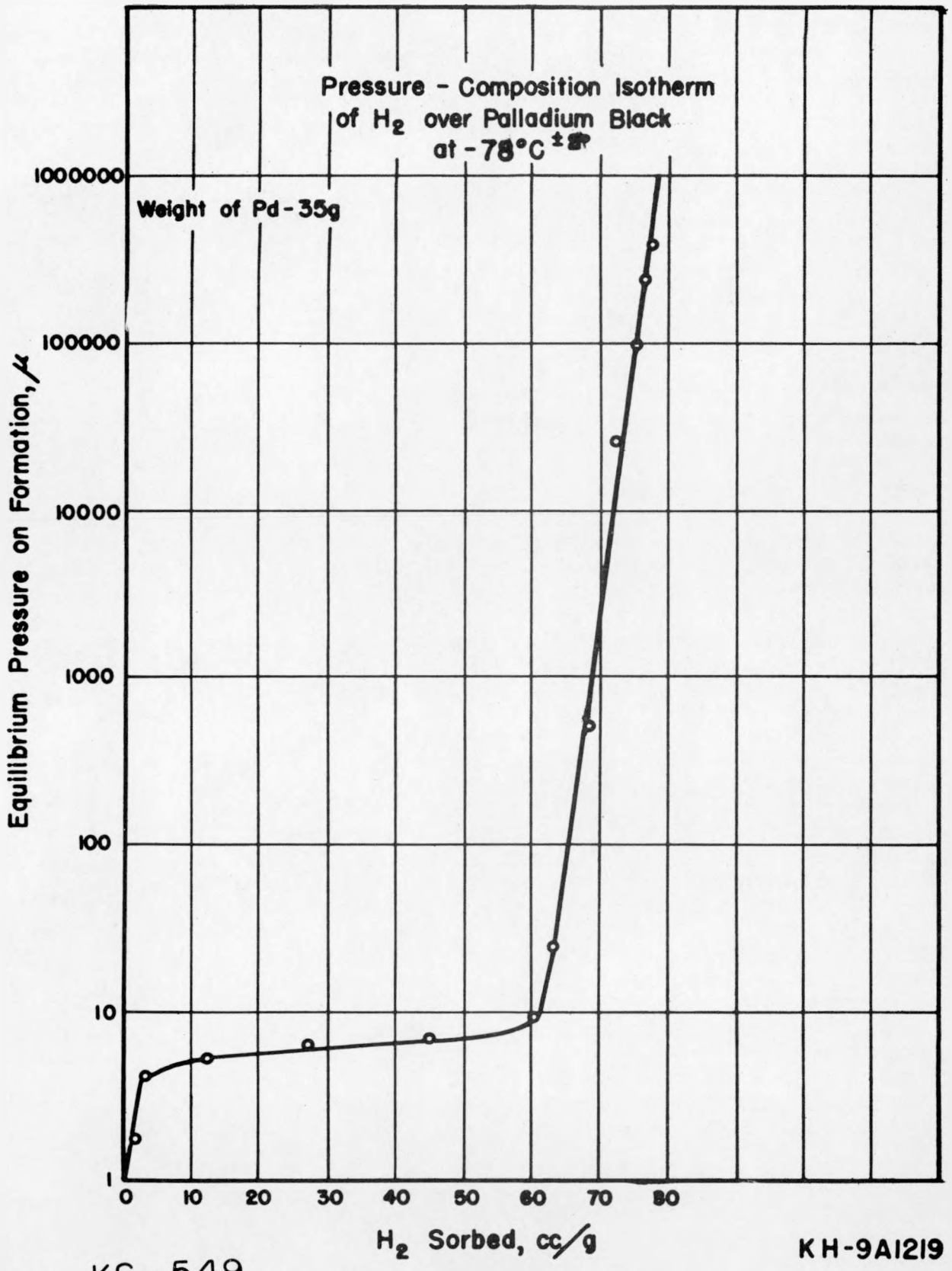

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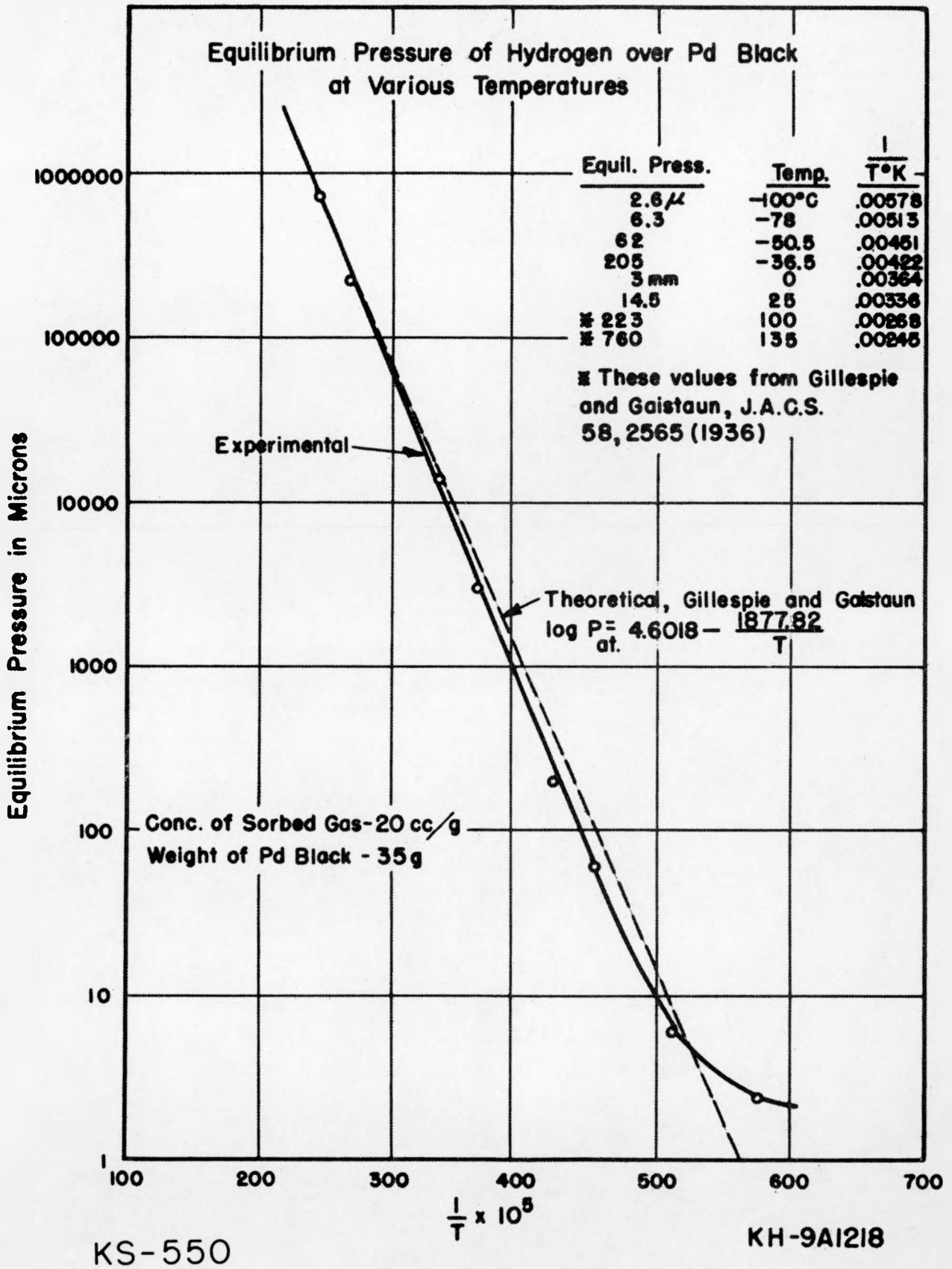

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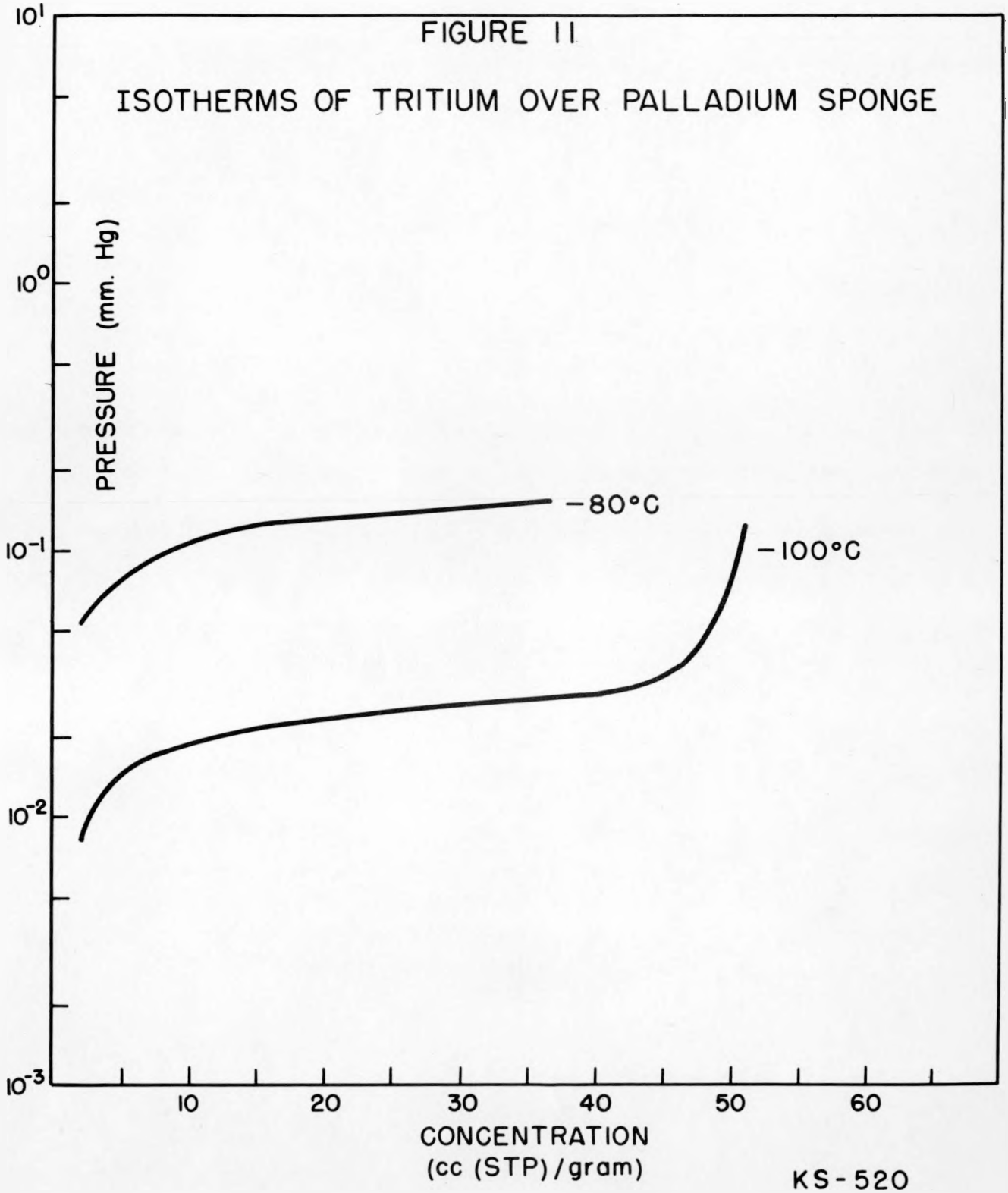
FIGURE 11

ISOTHERMS OF TRITIUM OVER PALLADIUM SPONGE



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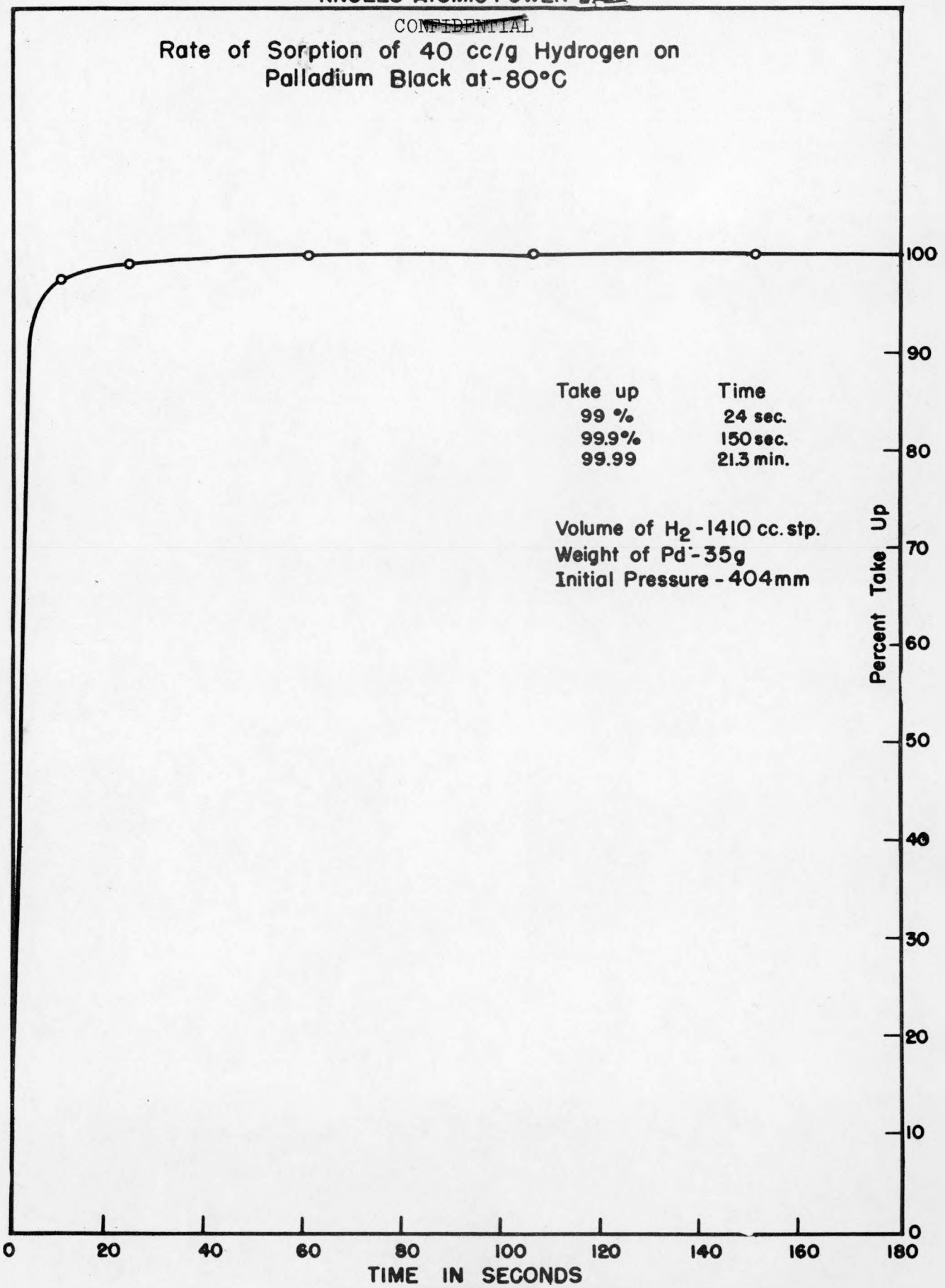
Rate of Sorption of 40 cc/g Hydrogen on Palladium Black at -80°C



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The catalytic conversion of hydrogen-oxygen mixtures to water at a palladium surface will occur.[7] However use of a water decomposer bed of heated uranium, magnesium, or others in conjunction with a palladium bed will serve to recover the hydrogen gases when necessary.

Maintenance of the surface area of palladium black and hence its activity is not difficult. Palladium particles will sinter somewhat at the temperatures required for evolution. According to the work of W. R. DeHollander and his associates at Hanford,[6] temperatures of 200°C and below do not have much effect on the surface area of palladium after it has been conditioned. DeHollander did find[6] that conditioning reduces the surface area by about one half (i.e. from 14.5 m^2/g to 8.4 m^2/g). To reduce the rate of sintering the finely divided palladium has been dispersed in an inert powder such as silica sand (50-150 mesh). Sorption beds of this mixture have been in continuous operation for months with no sign of decreased activity.

Preparation of a Palladium Bed for Sorption of Hydrogen Isotopes

The palladium used for sorption of hydrogen has been catalytic grade palladium black. The bulk density of this material, which is available commercially (e.g., American Platinum Works and others), is about 0.6 g/cc. During the purification of palladium black (dispersed in silica sand) the bulk density increases to about 1 g/cc. Palladium supported on a number of inert materials, such as asbestos, alumina, etc., appears to offer an advantage over palladium black by maintaining the surface area but increasing the dispersal and giving a more massive sorbent. Since the beds are sometimes used to transfer tritium, the supported palladium has been avoided because of the absorbed or chemically bound water in the supporting medium which could exchange with sorbed tritium; however, the importance of this effect has not been investigated and may be negligible.

The sorption bed was prepared by mixing the palladium black with two to four parts by weight of clean sand. The bed was then degassed at room temperature. Following this, hydrogen was added to remove absorbed oxygen and was then pumped off at room temperature. The bed was heated to 100°C with continuous pumping to remove the less volatile materials that might be present. The cycle was repeated, but the bed was heated to 350 to 400°C before pumping off the hydrogen. Two such treatments should give a clean, active palladium bed; however, the cycle can be repeated to ensure absolute freedom from oxygen. After such a treatment a 1000 g palladium bed at -78°C should sorb 99% of 50 liters of hydrogen in ten minutes starting with an initial pressure of about 500 mm of mercury.

Design and Operation of a Palladium Sorption Pump for Hydrogen Isotopes

Suitable container materials for a palladium bed are fused quartz for use in a glass vacuum system and stainless steel for use in a metal vacuum system. Provision for pumping the reaction gases through the bed if necessary will improve the versatility of the sorption bed for removing and evolving hydrogen from various gas mixtures. The sorption bed should be

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kept as shallow as possible, consistent with limits of design and avoiding possible channeling, to permit rapid uptake and evolution of the sorbed hydrogen gases. The sorption bed can be held in place by fritted filters which will prevent blowing of the fine palladium particles. A layer of sand placed between the filter and the bed will prevent possible plugging of the filter by the palladium particles.

The recommended operation is to sorb the hydrogen isotopes on the palladium bed at -78 to -100°C. For protium, bed temperatures of -78°C are sufficient to reduce the protium pressure to less than 10 μ of mercury. For tritium, it is necessary to cool the bed to -100°C or below to obtain residual tritium pressures of less than 30 μ. Sorption of hydrogen on palladium will occur at lower temperatures of course, but any large amount of contaminating gas like nitrogen (at ~ -100°C) or even helium (at ~ -150°C) will block sorption of hydrogen by adsorbing on the surface of the palladium and blocking access of the hydrogen to the palladium. For that reason, sorption on palladium at temperatures much lower than -100°C is not recommended. The hydrogen gases can be desorbed at bed temperatures of 150 to 250°C. Higher desorption temperatures may cause progressive sintering of the palladium.

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